The chemistry of manganese enolates

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I. INTRODUCTION

Metal enolates play an important role in modern stereoselective synthetic methods. The chemistry of enolates is profoundly affected by the metal counterion associated to it. While historically most of the research on enolates has focused on alkali metal derivatives, however, more recently, much effort has been expended on studying enolates derived from transition metals. Transition metal enolates are supposed to feature *O*-bonded isomers **I** rather than *C*-bonded structures **II** (Figure 1). In this chapter we will discuss methods of preparation of manganese enolates and their applications in organic synthesis.

This chapter is organized taking into account the synthetic method used to generate the manganese enolates. Each section shows some synthetic applications of these enolates.

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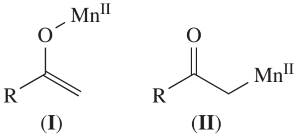
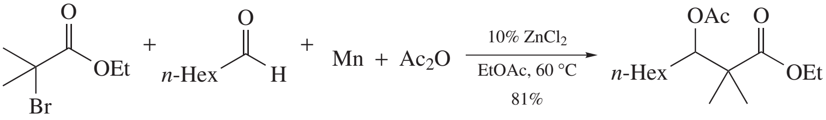


FIGURE 1.

II. GENERATION OF MANGANESE ENOLATES FROM ACTIVE MANGANESE METAL

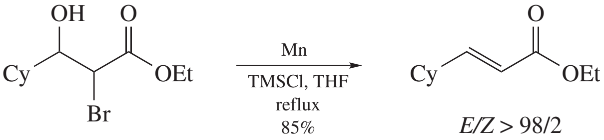
Manganese is a non-toxic[1] and cheap[2] metal. The reduction potential of the Mn^{+2}/Mn^0 system (-1.03 V)[3], adequate to reduce an important number of organic functions, would lead to anticipate an extensive use of Mn^0 in organic synthesis. However, in contrast to other metals such as Li, Mg, Zn or Sm, the applications of this metal in organic synthesis are not fully developed. Among the main reasons is the inability of commercially available manganese to react directly with organic compounds as a consequence of its passivity[4].

Only two papers have been published reporting the use of commercial manganese to generate manganese enolates. In the first one, Cahiez and Chavant carried out a Reformatsky-type reaction of 2-bromoesters with aldehydes promoted by commercial manganese in the presence of catalytic amounts of $ZnCl_2$ and stoichiometric amounts of acetic anhydride[5]. The corresponding *O*-acetyl-3-hydroxyesters were isolated in good yields (equation 1). A lower yield (35%) was obtained when a ketone (nonan-2-one) was employed instead of aldehydes.



(1)

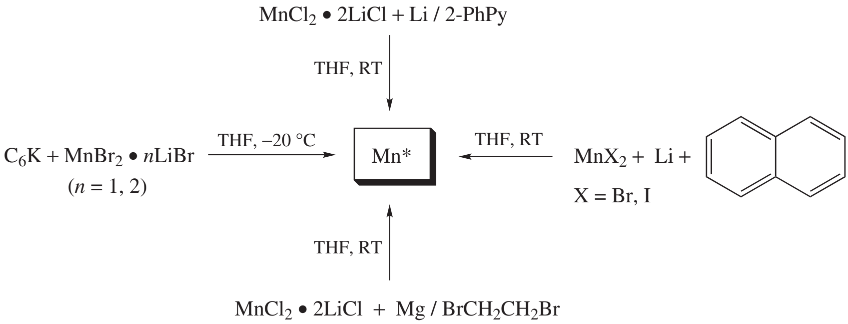
The second publication described the first β-elimination reaction promoted by manganese. This reaction takes place through the generation of a manganese enolate upon treatment of 2-bromo-3-hydroxyester with commercial manganese and a stoichiometric amount of Me_3SiCl, as sole additive. The enolate intermediate experiences a spontaneous β-elimination process affording the corresponding (E)-α,β-unsaturated ester with complete stereoselectivity (equation 2)[6].



(2)

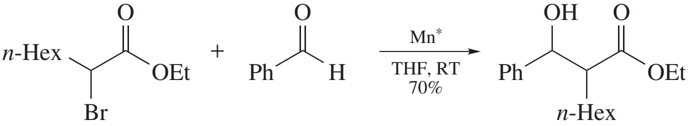
Taking into account this limited number of publications, it can be concluded that the generation of manganese enolates from commercial Mn, activated with different additives, presents important limitations. To overcome the lack of reactivity of manganese metal, different procedures to obtain active manganese were described (Scheme 1). Rieke and coworkers[7] reported the first preparation of active manganese in 1996 by treatment of anhydrous $MnCl_2$ with lithium in the presence of a catalytic amount of naphthalene in THF at room temperature. Although Rieke Manganese (Mn*) can be also obtained from

$MnBr_2$ and MnI_2, Mn* obtained from MnI_2 is less reactive. The same year, Fürstner and Brunner published another preparation of active manganese (Mn-graphite) by reduction of the soluble ate-complex $MnBr_2{\bullet}n\text{LiBr}(n = 1, 2)$ with the potassium-graphite intercalation compound C_8K in THF[8]. Later on, in 1998, Oshima and coworkers[9] described an alternative preparation of active manganese by reduction of $MnCl_2{\bullet}2LiCl$ with magnesium turnings previously activated with 1,2-dibromoethane. Finally, in 1999, Cahiez and coworkers[10] developed an improvement of the Rieke method using 2-phenylpyridine instead of naphthalene for the reduction of $MnCl_2{\bullet}2LiCl$ with lithium. In this last procedure, 2-phenylpyridine can be easily removed by an acidic work-up.

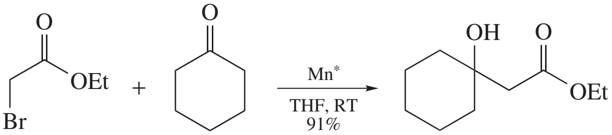


SCHEME 1

With the appearance of the aforementioned methods to prepare active manganese, various contributions reporting new synthetic applications of manganese enolates were published. Suh and Rieke[11] developed a Reformatsky-type reaction of α-haloesters and α-halolactones with aldehydes and ketones promoted by active manganese (Mn*) for the preparation of 3-hydroxyesters in good to high yields[7]. It is noteworthy that this reaction was carried out at room temperature in the absence of $ZnCl_2$ and acetic anhydride (equation 3). Even more, this reaction was successfully applied to sterically hindered ketones (equation 4).

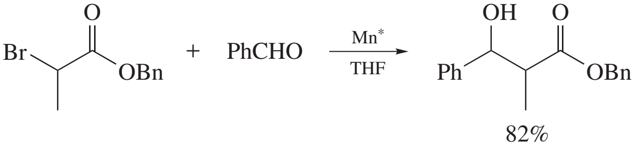


(3)



(4)

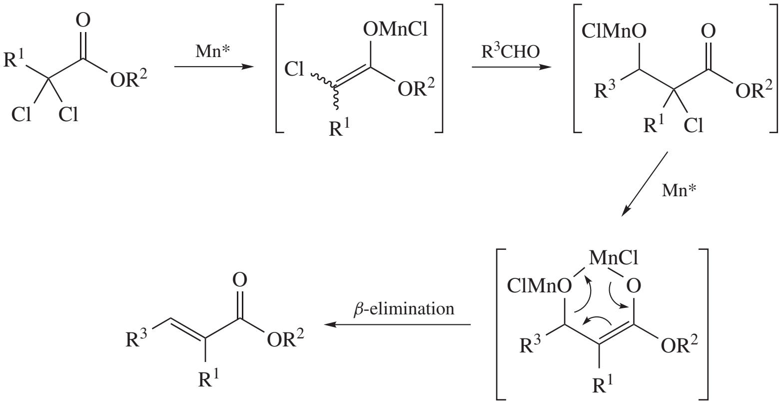
The Oshima manganese was also used to promote the addition of different α-haloesters (equation 5) to electrophiles, mainly aldehydes and ketones, using a Barbier-type methodology[12].



(5)

Sequential reactions are protocols in which the isolation of intermediates is not necessary. These methods held enormous potential in organic synthesis as a consequence of their simplicity, and because considerably less time, effort and material are required to obtain organic compounds when compared with more traditional multistep procedures. In an ideal sequential reaction, each step should be carried out with very high selectivity and in high yield. Consequently, only a limited group of reagents, such as SmI_2[13], are suitable to promote sequential processes.

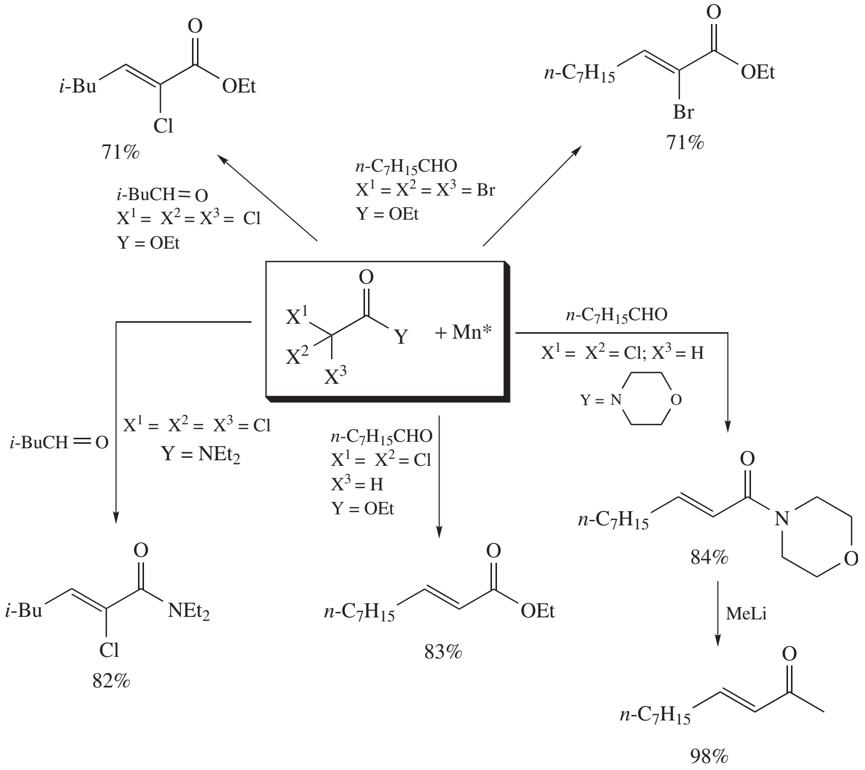
Active Mn (Cahiez method) has been also successfully used to promote sequential reactions involving manganese enolates. In a seminal report of Concellón and coworkers, the synthesis of α,β-unsaturated esters with a total E-stereoselectivity and in high yield was described. For this transformation α,α-dichloroesters were used as starting materials[14]. Upon treatment with Mn*, a manganese enolate was initially generated that reacts with a variety of aldehydes, to afford the expected α-chloro-β-alcoholate. By a further reduction with Mn*, a β-functionalized enolate intermediate was formed and underwent a spontaneous β-elimination reaction to yield the corresponding α,β-unsaturated ester. To explain the total E-stereoselectivity observed in this elimination reaction, a cyclic transition state controlled by chelation of a Mn(II) center by two oxygen atoms was proposed (Scheme 2).



SCHEME 2

This process proved to be general and provided better results than those previously obtained when SmI_2 was used in analogous sequential reactions.

This methodology was later generalized to the preparation of (E)-α,β-unsaturated amides, from α,α-dichloroamides and Mn*, also with a total stereoselectivity. The unsaturated amides obtained could be readily and efficiently transformed into ketones, aldehydes or carboxylic acids without jeopardizing the stereoisomeric integrity of the C−C double bond (Scheme 3)[15].

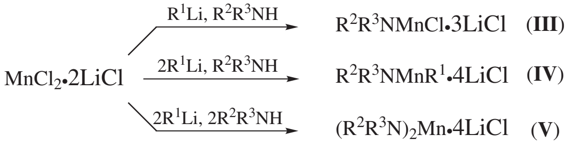


SCHEME 3

Finally, (Z)-α-halo-α,β-unsaturated esters (fluoro, chloro or bromo) and (Z)-α-chloro-α,β-unsaturated amides were also obtained with complete Z-selectivity from trihaloesters or trichloroamides, respectively, through a similar sequential reaction. Again, the unsaturated amides or esters prepared could be readily transformed into ketones, carboxylic acids or haloallylic alcohols[16]. Some representative examples of these sequential reactions are outlined in Scheme 3.

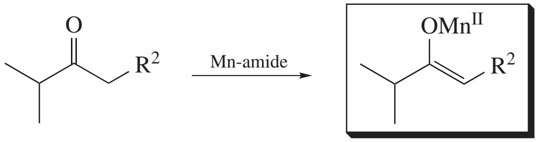
III. GENERATION OF MANGANESE ENOLATES BY DEPROTONATION PROCESSES EMPLOYING MANGANESE AMIDES

Different manganese amides (chloromanganese amides **III**, organomanganese amides **IV** or manganese diamides **V**) can be prepared, in THF at room temperature, by reaction of an organolithium compound with a mixture of the ate-complex $MnCl_2 \cdot 2LiCl$ and a secondary amine. In a seminal paper, Cahiez and coworkers established the conditions necessary to prepare these species depending on the stoichiometry of the organolithium compounds and/or amine used (Scheme 4)[17]. Aromatic Mn-amides, in opposition to lithium amides, can be stored in THF solutions, at room temperature under inert atmosphere for several months.



SCHEME 4

Deprotonation of ketones by Mn-amides **III**–**V** affords kinetic enolates (deprotonation occurs on the less substituted α position) with a preferential Z-geometry (equation 6).

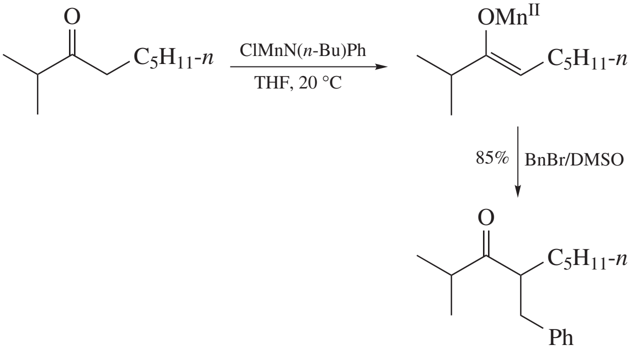


kinetic enolates

(6)

The reactions of manganese enolates generated from manganese amides with different electrophiles, such as alkyl halides[17], trimethylsilyl chloride[18], azodicarboxylates[19] and nitroolefins[20] have been reported.

Mn-enolates prepared from ketones reacted readily with C-electrophiles affording different α-substituted ketones. A comparative study on the monobenzylation of 2-methylcylohexanone was carried out using lithium and manganese enolates. The best regioselectivities and yields were obtained from manganese enolates[17]. Accordingly, the reaction of manganese enolates with alkyl halides, such as MeI, BnBr, n-BuI, allyl bromide and bromoacetates, afforded the corresponding monoalkylated products in high yields and with high regioselectivity (equation 7). The best results were obtained when a mixture of THF and DMSO, or NMP, was used as solvent[17]. On the contrary, in neat THF, this reaction occurs slowly and gives moderate yields.

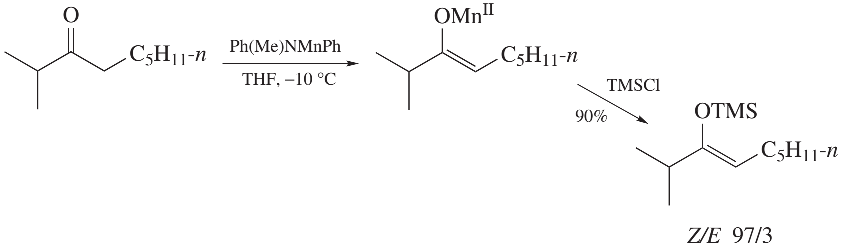


Regioselectivity > 97%

(7)

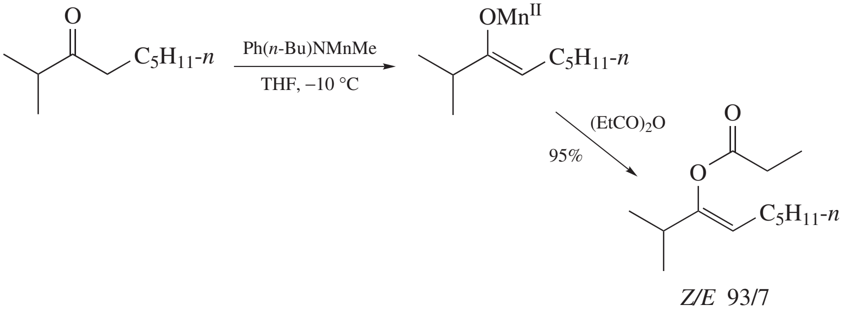
Silyl enol ethers are very versatile intermediates in organic chemistry. Cahiez and coworkers studied the preparation of Z-silyl enol ethers derived from ketones under mild conditions, in high yields and with good stereoselectivities (Z/E 93/7 to 100/0), trapping

Mn-enolates prepared from Mn-amides with TMSCl. When this reaction was carried out on unsymmetrical ketones it demonstrated a good regiocontrol (equation 8)[18].



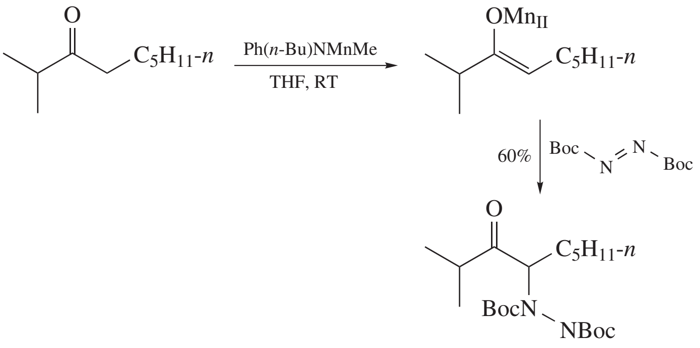
(8)

In the same communication, the acylation of these Mn-enolates in a regio- and stereoselective manner was also reported. The authors employed carboxylic acid anhydrides as electrophiles to yield enol esters in high yields (equation 9).



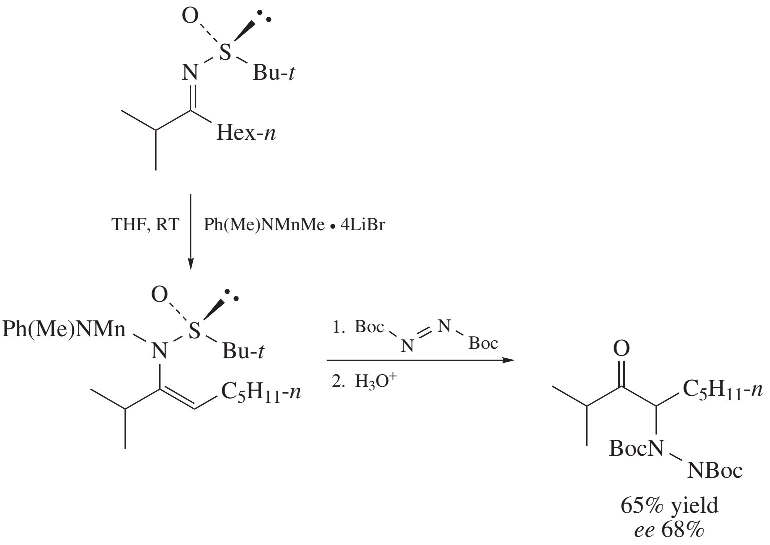
(9)

The synthesis of α-hydrazino ketones (as a precursor of α-aminoketones)[21] via the electrophilic amination of Mn-enolates with azodicarboxylate has been also performed in excellent yields and with very high or total regioselectivity (equation 10)[19].



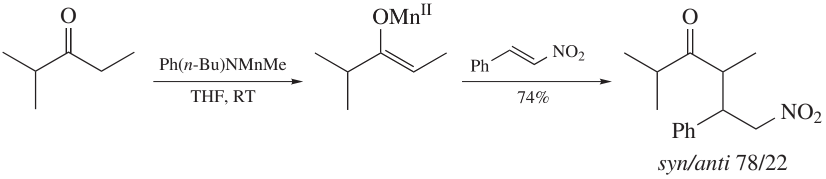
(10)

The chiral version of this reaction was carried out on enantiopure N-sulfinyl manganese enamines. These species, after hydrolysis, afforded α-hydrazino ketones with enantiomeric excess from 40 to 68% in moderate yields (50–65%). No determination of the absolute configuration of the major product has been included in the publication (equation 11)[19].



(11)

Ricci, Cahiez and coworkers reported the Michael addition of Mn-enolates to nitroolefins in high yields and stereoselectivities. When manganese enolates derived from unsymmetrical ketones were used, the process took place in a regioselective manner, the kinetic adduct being isolated as the sole product (equation 12)[20].



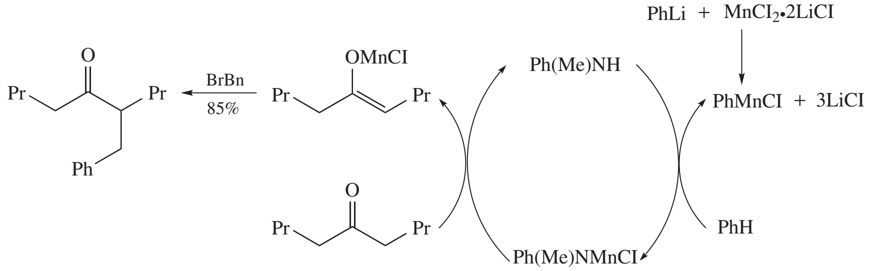
(12)

Finally, Cahiez and coworkers also described the generation of manganese enolates by deprotonation of ketones with PhMnCl in the presence of a catalytic amount (between 7 to 20%) of N-methylaniline using THF/sulfolane as solvent[22]. The proposed catalytic cycle intervening in this reaction is shown in Scheme 5.

The obtained enolates were used in monoalkylation reactions and in the synthesis of silyl enol ethers or enol esters in high yields.

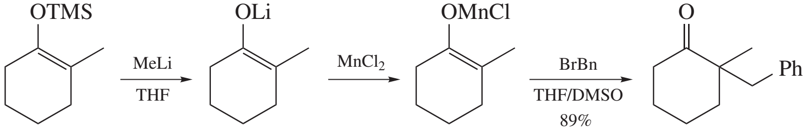
IV. GENERATION OF MANGANESE ENOLATES BY TRANSMETALATION REACTIONS

As discussed before, deprotonation of ketones with manganese amides mainly affords kinetic manganese enolates (equations 7–12). Also, both kinetic and thermodynamic



SCHEME 5

Mn-enolates (equations 13 and 14, respectively) can be readily prepared from the corresponding Li, Na, K or Mg-enolates by a metal–Mn exchange reaction using $MnCl_2$ or $MnBr_2$[17, 23].



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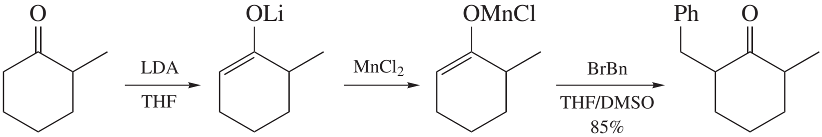
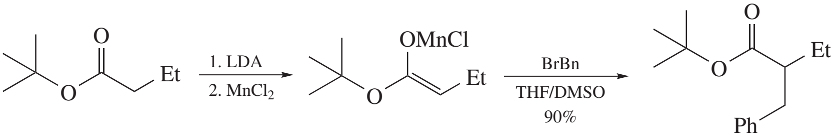


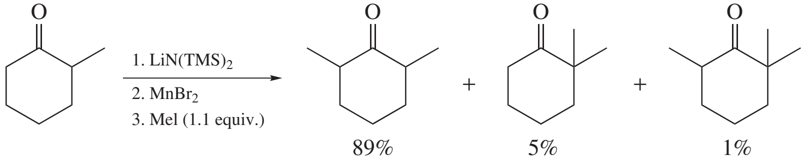
(14)

This process is general and can be applied to esters. Employing similar conditions to those used for the alkylation of esters, it is possible to perform the alkylation of esters as shown in equation 15.



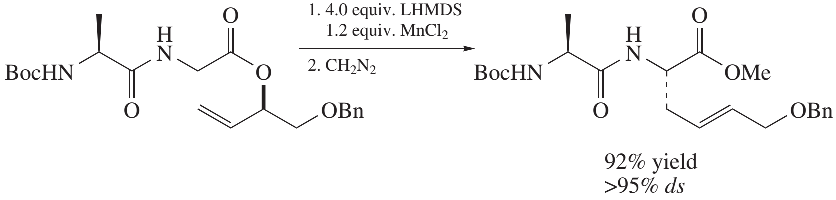
(15)

Reetz and Haning have demonstrated that transmetalation of Li enolates, prepared from ketones, with $MnBr_2$ lead to manganese analogs that reacted fairly with MeI to provide the corresponding α-monomethylated ketone in high yields (equation 16). In this way the formation of polyalkylated products, a typical problem observed in the alkylation of Li-enolates, was avoided[24].



(16)

Kazmaier and Maier carried out the modification of peptides making use of the chelate Claisen rearrangement of a Mn-enolate prepared from a Li−Mn transmetalation reaction (equations 17 and 18)[25]. After testing several metallic enolates, the authors concluded that the best results, in terms of yield of products, were indeed obtained with manganese enolates. It was also proved that this transformation was totally independent of the peptide and of the protecting groups employed. An additional advantage is the possibility of preparing dipeptides in a diastereomerically pure form when chiral esters are used.



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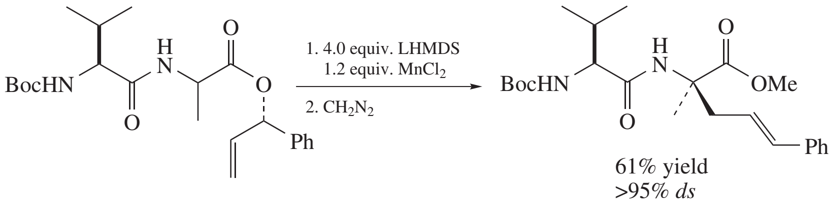
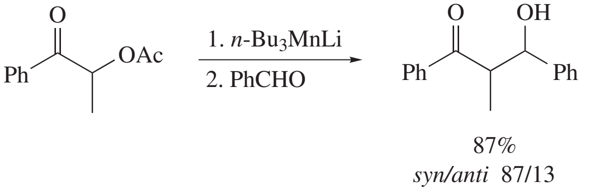


(18)

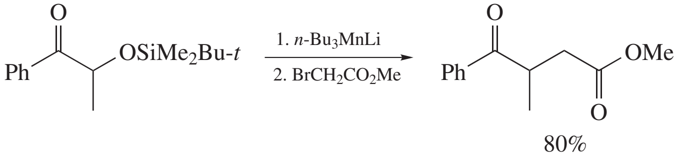
V. GENERATION OF MANGANESE ENOLATES USING TRIALKYLMANGANATES

Finally, manganese enolates can also be prepared employing organomanganate compounds[26, 27]. In a seminal paper, Hosomi and coworkers[28] described the application of organomanganate compounds (n-Bu_3MnLi) in the generation of enolates from α-acetoxypropiophenone through an acetoxy−metal exchange process. For example, the reaction of a Mn-enolate so formed with benzaldehyde afforded the corresponding aldol in 87% yield (equation 19).

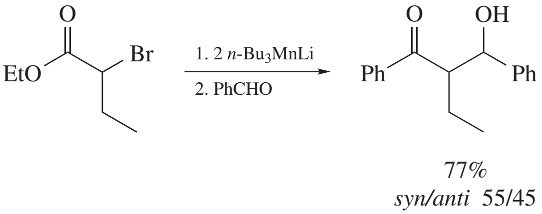


(19)

This transformation was also performed on ketones bearing a silyloxy (equation 20) or a halogen group (equation 21) at the α position. Again, the enolates were formed successfully and byproducts derived from undesired nucleophilic substitution pathways were not observed. These reactions proved to be successful and comparable yields of products were obtained in all cases.



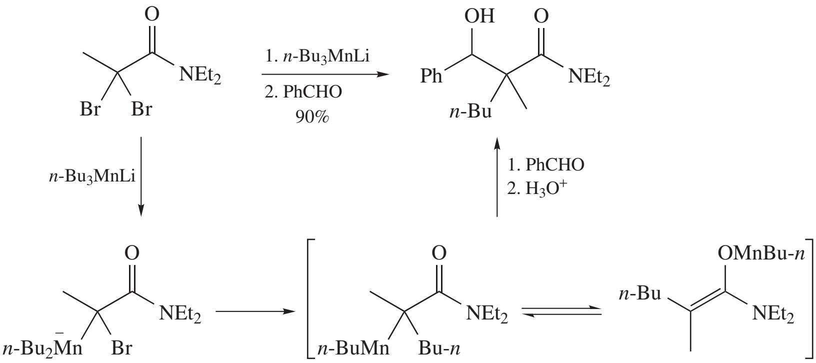
(20)



(21)

Using this method it is important to note that the regioselectivity of the metalation process depends exclusively on the nature of the starting material employed (where the acetoxy, silyloxy or halogen group is present). In this way, either thermodynamic or kinetic enolates can be prepared in the case of unsymmetrical ketones.

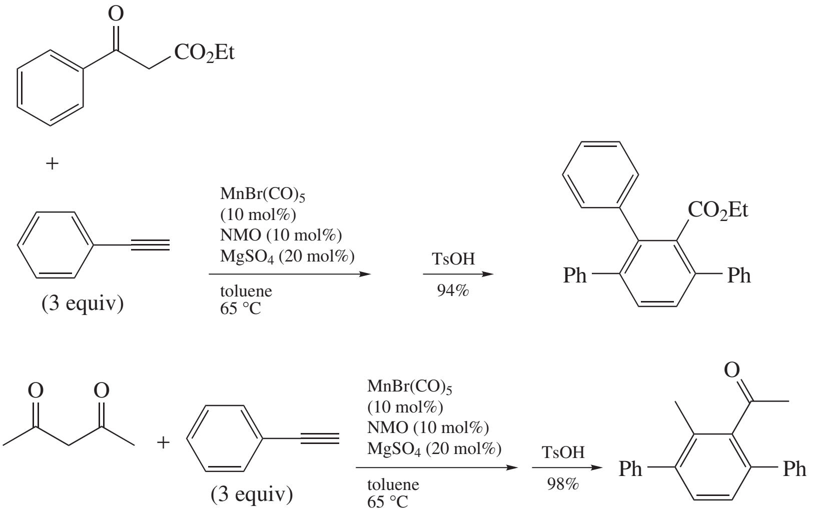
Oshima and coworkers applied a similar process on *tert*-butyl dibromoacetate or *N*,*N*-diethyldibromoacetamide[29]. These substrates lead to the corresponding aldol-type adducts after reaction with tributylmanganate followed by addition of an electrophile, such as benzaldehyde (Scheme 6). Initially, a halogen–manganese exchange reaction took place. On this intermediate, butyl migration and bromide elimination afforded the corresponding α-butyl organomanganese derivative, which finally reacted with the corresponding electrophile.



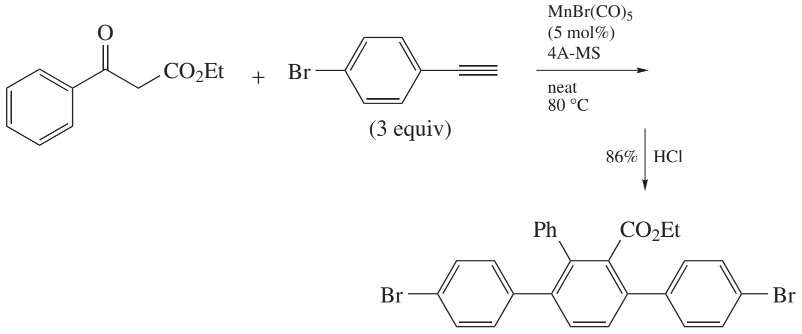
SCHEME 6

VI. OTHER APPLICATIONS OF MANGANESE ENOLATES IN SYNTHESIS

Apart from the classical methods of forming Mn-enolates, described above, there are yet other synthetic procedures where these species are involved. Very recently, in 2008, the groups of Tsuji and Nakamura[30] and Takai[31] and their coworkers reported independently a new manganese-catalyzed [2+2+2] intermolecular cycloaddition coupling of a 1,3-dicarbonyl compound (β-ketoester or diketone) and two terminal acetylenes, to produce synthetically relevant terphenyl derivatives. The products were obtained in good to excellent yields and with a total regioselectivity. Two different sets of conditions proved to be satisfactory: $MnBr(CO)_5$ (10 mol%), *N*-methylmorpholine oxide (10 mol%) and $MgSO_4$ (20 mol%) (Tsuji–Nakamura's procedure, equation 22) or $MnBr(CO)_5$ (5 mol%) and 4 Å molecular sieves (Takai's conditions, equation 23). Interestingly, other transition metal complexes investigated, such as $W(CO)_6$, $ReBr(CO)_5$, $FeI_2(CO)_4$, $[RuCl_2(CO)_3]_2$, $Co_2(CO)_8$, $Rh(acac)(CO)_2$ and $IrCl(CO)(PPh_3)_2$, were ineffective for this transformation.

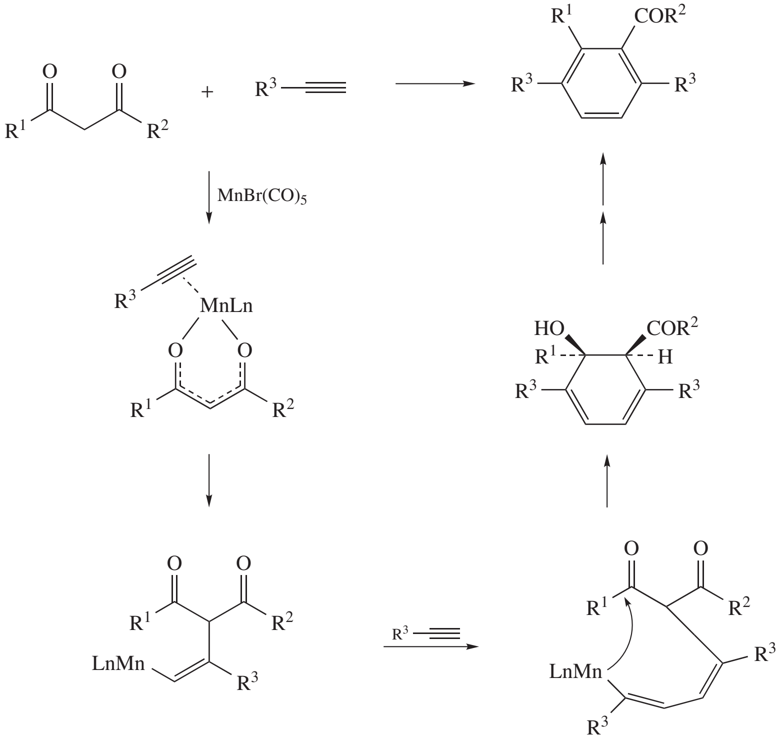


(22)



(23)

In a later report, Nakamura and coworkers[32], aided by Density Functional Theory (DFT) calculations, shed light on the mechanism of this reaction (Scheme 7). According to this study, the experimentally observed reaction takes place through: (1) formation of the manganese enolate of a 1,3-dicarbonyl compound, (2) addition of the manganese enolate to a terminal alkyne to give a vinylmanganese complex where the metal is attached to the terminus of the alkyne, (3) insertion of a second alkyne into the vinyl–Mn bond to give a dienylmanganese complex where the metal becomes attached to the substituted side of the alkyne, and (4) finally, intramolecular nucleophilic addition of the dienylmanganese to the carbonyl group.



SCHEME 7

In summary, this collection of reports shows the enormous potential of manganese enolates in synthetic organic chemistry. Their easy and mild preparation surely leads us to anticipate a bright future for these not-so-much yet used species.

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Structures and reaction mechanisms of manganese oxidants

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I. OXIDATIONS BY PERMANGANATE ION

A. Preparation of Potassium Permanganate ($KMnO_4$)

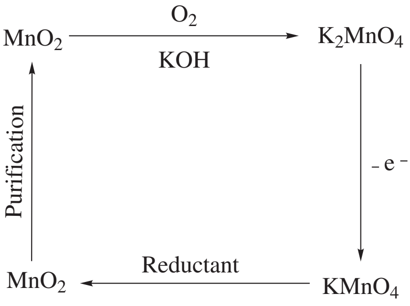
The starting material for the preparation of potassium permanganate is manganese dioxide ($Mn^{IV}O_2$). In the first step, MnO_2 is oxidized to potassium manganate ($K_2Mn^{VI}O_4$) by oxygen under basic conditions (equation 1)[1]:

$$2\,MnO_2 + O_2 + 4\,KOH \longrightarrow 2\,K_2MnO_4 + 2\,H_2O \tag{1}$$

Potassium manganate is then oxidized to potassium permanganate ($KMn^{VII}O_4$) electrochemically (equation 2)[1]:

$$K_2MnO_4 \longrightarrow KMnO_4 + K^+ + e^- \tag{2}$$

Manganese dioxide ore is widely deposited in the earth's crust. It is found in commercially important quantities in several countries, including South Africa, Ukraine, China, Australia, Brazil, Gabon, India and Mexico. Manganese dioxide can also be recovered and recycled from the products obtained when permanganate reacts with various reductants, making the process almost infinitely sustainable as illustrated in equation 3[2].



(3)

Carus Corporation, the world's largest manufacturer of potassium permanganate, has recycled approximately 500 tons of manganese dioxide in this way over the last two decades.

Potassium permanganate is an effective electron accepter or oxygen atom transfer agent. Since its use in selective and nonselective organic syntheses has been thoroughly reviewed[3-10], the discussion herein will focus primarily on the mechanisms of its reactions, including proposed structures for transition states and reactive intermediates.

B. Structure and Solubility of Permanganate Compounds

The structure of the permanganate ion has been studied extensively using spectroscopic and theoretical approaches. The general result emerging from these studies is that permanganate resembles a dipositive manganese cation surrounded by four oxygen atoms over which three negative charges are distributed[11, 12]. As depicted in Figure 1, the molecular geometry of the ion is tetrahedral.

When combined with a cation such as potassium or sodium, permanganate is very soluble in water, but insoluble in nonpolar solvents. However, reasonable solubility in nonpolar solvents can be achieved by replacing the potassium cation with quaternary ammonium or phosphonium cations (Q^+) (equation 4).

$$\mathrm{KMnO_{4(aq)}} + \mathrm{QX_{(org)}} \rightleftharpoons \mathrm{QMnO_{4(org)}} + \mathrm{KX_{(aq)}} \qquad (4)$$

$$Q^+ = NR_4{}^+ \quad \text{or} \quad PR_4{}^+$$

Quaternary ammonium permanganates prepared in this way have been isolated and characterized[13]. Most often, however, they are prepared and used *in situ*. The latter is a preferred approach because most quaternary ammonium permanganates ignite above certain temperatures and some have been reported to explode under reaction conditions[14]. Many useful synthetic processes involving oxidation by permanganate have also been achieved using phase transfer technology[4, 5].

It is the organophilicity of the quaternary cations that increases the solubility of quaternary ammonium permanganates in organic solvents. X-ray crystallographic studies of some of these compounds has suggested that the charges of the ion pair become partially buried under hydrocarbon chains, giving a greasy exterior that more easily dissolves in nonpolar solvents such as methylene chloride or carbon tetrachloride[4]. For example, the compound that exhibits the highest solubility in the largest number of organic solvents is methyltri-*n*-octylammonium permanganate. The superior ability of this quaternary ammonium ion to promote the solubility of permanganate has been attributed to a 'penetration effect' that allows for the formation of an ion pair partly shielded by the three octyl groups[5].

The organophilicity of potassium permanganate can also be increased by complexing the potassium ions with either crown ethers, **1**, or acyclic polyethers, **2**[15–19] (equations 5 and 6).

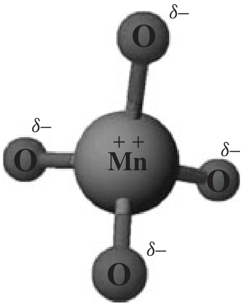
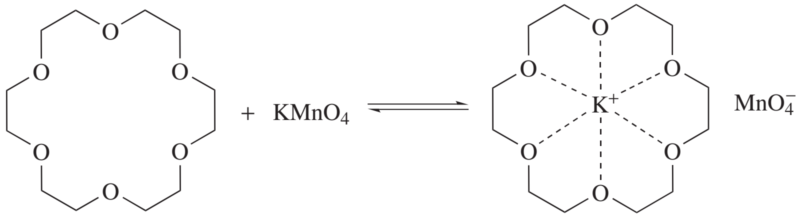
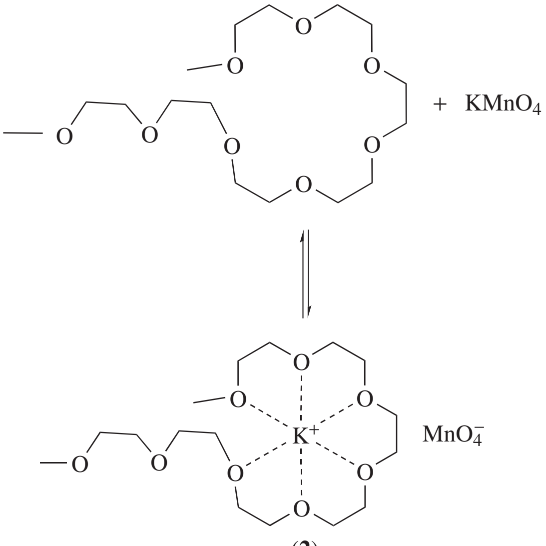


FIGURE 1. Permanganate ion



(**1**)

(5)



(**2**)

(6)

Potassium permanganate adsorbed on a solid support is also an effective oxidant under heterogeneous conditions. If potassium permanganate and a solid support, such as alumina or silica gel, are ground together and added to a well-stirred solution of a reductant in a nonpolar solvent, oxidation occurs with surprising rapidity[20–27].

Even more surprisingly, potassium permanganate can also be used for some oxidative transformations under solvent-free conditions[28–37].

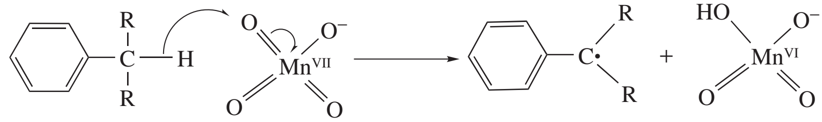
C. The Mechanism of C–H Bond Cleavages by Permanganate

Potassium permanganate has often been used very effectively for oxidations at the benzylic position of aromatic systems (equation 7).

$$\mathrm{Ar-CHR_2} \xrightarrow{\mathrm{KMnO_4}} \mathrm{Ar-C(OH)R_2} \tag{7}$$

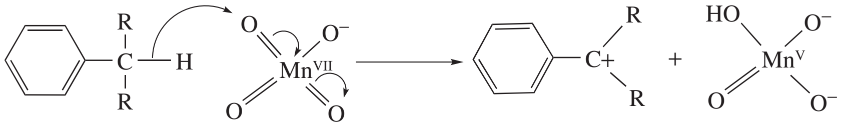
The mechanism of this reaction, cleavage of a single carbon–hydrogen bond, has been studied extensively. Several possible mechanisms that can be considered are outlined in equations 8–12.

Hydrogen atom abstraction with the formation of a free radical:



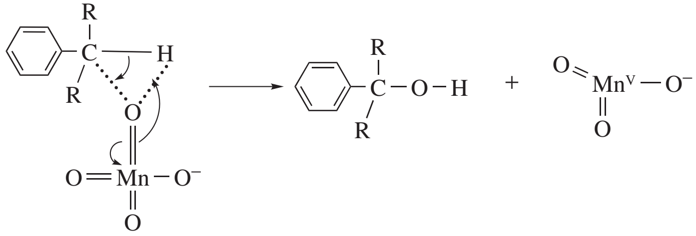
(8)

Hydride ion abstraction with formation of a carbocation:



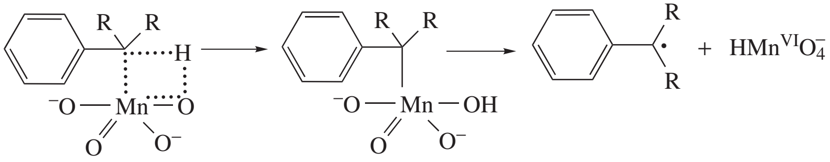
(9)

An oxygen insertion mechanism:



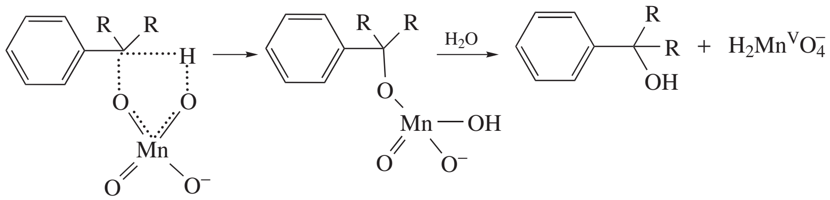
(10)

A [2+2] addition mechanism:



(11)

A [2+3] addition mechanism:



(12)

Experimental evidence which can be used to distinguish between these possibilities includes the following observations:

(i) The reaction rate is first order in both the oxidant and the reductant[38–41], consistent with a bimolecular mechanism.

(ii) The use of oxygen-18 labeled permanganate gives a product (an alcohol) containing oxygen-18[38], indicating that the oxygen atom in the product comes from the oxidant and not the solvent.

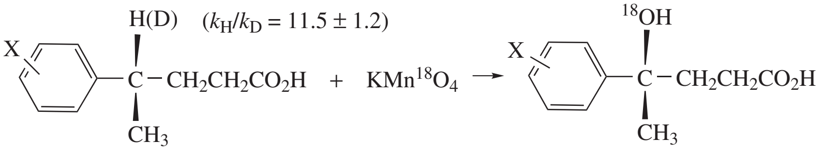
(iii) The reaction proceeds with net retention of configuration[38, 39], demonstrating that the oxygen atom in the product has been incorporated into the molecule from the same side as the departing hydrogen atom.

(iv) A primary kinetic isotope effect is observed when the benzylic hydrogen atom is replaced by deuterium[39–41], establishing that C−H bond cleavage occurs in the rate-determining step of the mechanism.

(v) Enthalpies of activation correlate well with C−H bond strengths as is typical for hydrogen abstraction reactions[40].

(vi) Rates of reaction are not very sensitive to the presence of substituents on the aromatic ring[39, 40], suggesting that excessive charge (positive or negative) is not present on the benzylic carbon atom in the transition state.

The experimental data reported by Brauman and Pandell[39] and Wiberg and Fox[38] for the oxidation of substituted phenylalkyl carboxylic acids, **3**, can be combined (as in equation 13) to help define the most likely mechanism for the cleavage of C−H bonds by permanganate.



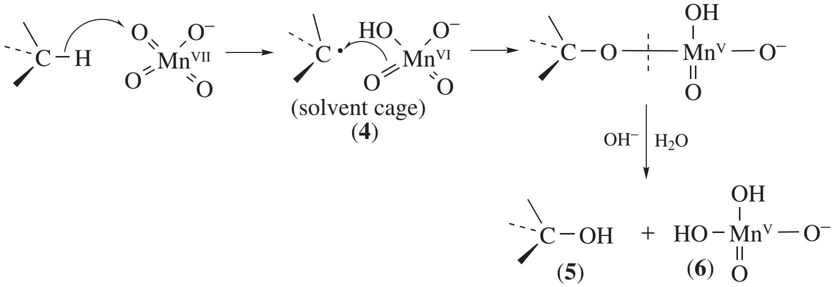
(**3**)

(13)

X	k_X ($M^{-1}s^{-1}$ x 10^3)
p-CH_3	3.5
H	3.8
p-NO_2	1.4

(30–40% retention of configuration)

Most researchers agree that the evidence is consistent with a mechanism initiated by a rate-determining hydrogen atom abstraction (equation 14) followed by recombination of the products, the greater part of it occurring before the intermediates can exit the solvent cage, **4**[38−41]. Hydrolysis then cleaves the O−Mn bond producing an alcohol with retained configuration, **5**, and a manganate(V) species, **6** (equation 14).

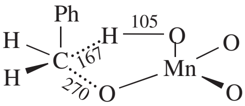


(14)

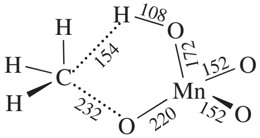
The fate of the manganese species, **6**, produced in these reactions is somewhat uncertain. Its formal oxidation state is 5+, i.e. $KMnO_3$ or KH_2MnO_4. However, manganate(V) compounds are known to be exceedingly reactive oxidants under all but extremely basic conditions[1, 6]. It is believed that disproportionation reactions or hydrogen atom abstractions from the solvent occur with the formation of manganese(IV) compounds (MnO_2 or H_2MnO_3) under neutral or mildly basic conditions.

Since the intermediates have fleeting lifetimes, there is little or no possibility of characterizing them using classical methods. However, the correctness of this mechanism has been verified using theoretical calculations to test possible transition state structures. The calculations clearly indicate that while a hydrogen atom is being transferred to one of the permanganate oxygen atoms, a second oxygen atom assists by interacting with the incipient carbon free radical[42, 43].

Structures **7** and **8** summarize the data reported by Strassner and Houk for the dimensions of the transition states that occur during the initial steps for the oxidation of toluene and methane by permanganate[42]. Although these results refer to reactions in the gas phase, they are likely valid for reactions in solution because the rates of permanganate oxidations are not excessively sensitive to solvent effects.



(**7**)

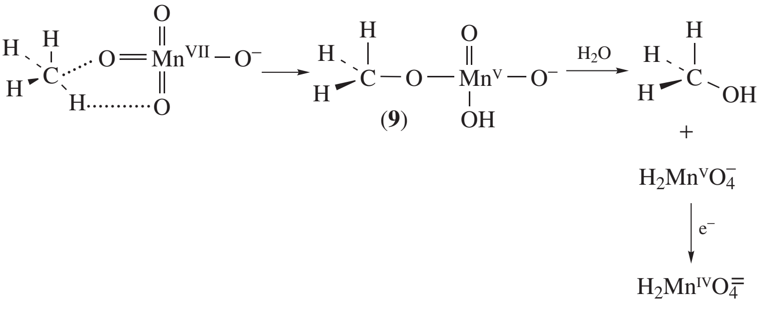


(**8**)

Bond lengths are in picometers

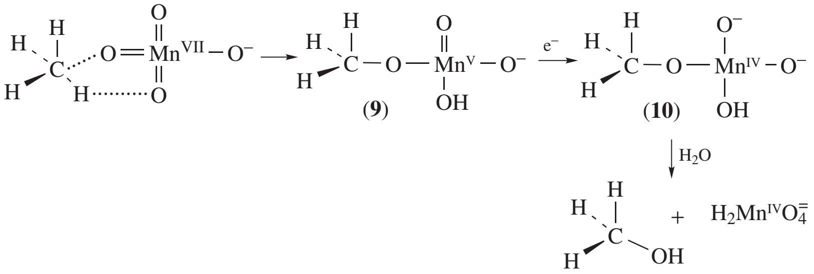
In both structures **7** and **8** it is clear that a second oxygen atom assists by stabilizing the emerging carbon free radical as a hydrogen atom is transferred. The H−O bond lengths in both transition states (105 pm and 108 pm) are very close to the lengths expected for 'normal' hydrogen−oxygen bonds, indicating that hydrogen atom transfer is quite advanced in the transition state and that the free radical is well developed. For comparison purposes it may be noted that H−O bond lengths are usually about 100 pm and that the Mn−O bond lengths in crystalline potassium permanganate are 163 pm[44].

The close proximity of the second oxygen atom to the putative carbon free radical suggests that formation of the proposed manganese(V) intermediate, **9**, may occur in a synchronized mechanism, as illustrated in equation 15.



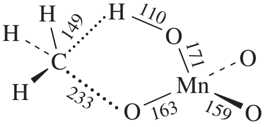
(15)

Whether the reduction of manganese(V) to manganese(IV) occurs before or after hydrolysis is impossible to determine on the basis of currently available experimental evidence. It could occur after hydrolysis, as depicted in equation 15, or before hydrolysis to give intermediate **10**, as in equation 16.



(16)

Lam and coworkers have also reported a theoretical study of the reaction between methane and permanganate[43]. Their study indicates, similarly, that in the transition state, **11**, two oxygen atoms participate in the hydrogen atom transfer step—one oxygen atom accepts the hydrogen while the other oxygen atom helps to stabilize the developing free radical.



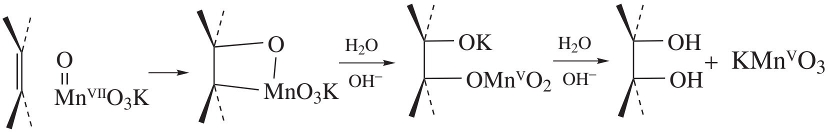
(**11**)

If, however, the reactions were perfectly synchronized, complete retention of configuration would be obtained. The fact that only partial retention is usually observed indicates that other competing processes must also be possible. Inversion of configuration could happen if the free radical was able to rotate within the solvent cage or if it escaped the solvent cage before interacting with an oxidant.

Under strongly acidic conditions, manganese(VII) oxide exists as MnO_3^+[45]. Stewart and Spitzer[46] have studied the oxidation of hydrocarbons by this reagent in concentrated trifluoroacetic acid solutions. They observed a primary kinetic isotope effect of 4.3 when the rates of oxidation of cyclohexane and cyclohexane-d_{12} were compared at 25 °C. The relative rate constants for the oxidation of primary, secondary and tertiary alkanes were found to be 1 : 60 : 2100. These results were interpreted to indicate that the reaction under strongly acidic conditions was also initiated by a hydrogen atom transfer.

D. The Reaction Mechanism for the Oxidation of C=C Bonds by Permanganate

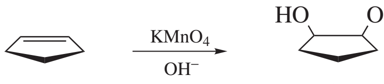
A mechanism for the oxidation of alkenes by permanganate was suggested by Wagner over a century ago[47]. He proposed a [2 + 2] addition between Mn=O and C=C bonds, followed by hydrolysis (equation 17).



(17)

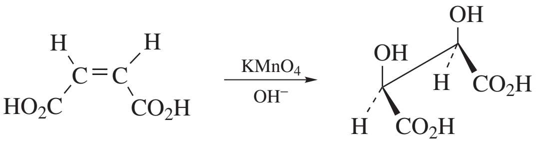
It appears that Wagner based his mechanism primarily, if not entirely, on an analysis of the products obtained from the oxidation of compounds containing carbon–carbon double bonds. He was aware that under basic conditions, oxidation of alkenes by permanganate results in dihydroxylation with the formation of vicinal diols, as indicated in equation 17.

Subsequently, Boeseken[48] studied the stereochemical course of the reaction and found compelling evidence that the reaction proceeded by way of *syn* addition. For example, oxidation of cyclopentene, **12**, gives *cis*-1,2-cyclopentanediol, **13**, whereas maleic acid, **14**, gives (2*S*, 3*R*)-2,3-dihydroxybutanedioic acid, **15**, as illustrated in equations 18 and 19[48b].



(**12**) (**13**)

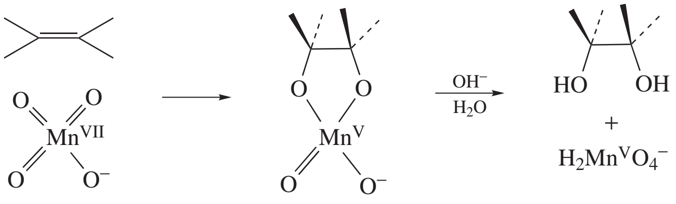
(18)



(**14**) (**15**)

(19)

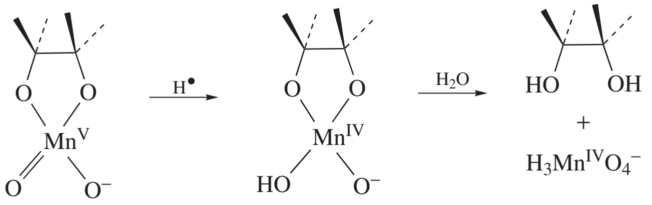
These results can be most easily understood by assuming that permanganate and carbon–carbon double bonds undergo a [2 + 3] addition reaction, giving a cyclic manganese(V) diester, **16**, followed by hydrolysis to the corresponding vicinal diol (equation 20).



(**16**)

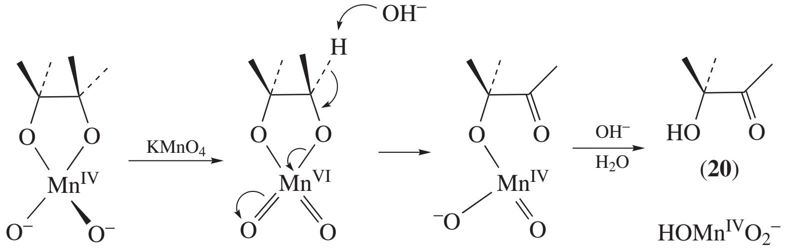
(20)

Manganese(V) oxides are extremely reactive compounds under all but very alkaline conditions[1,6] and it has been observed that the first detectable intermediate in these reactions has an oxidation state of 4+ (not 5+, as implied in equation 20)[49–52]. Therefore, the initially formed manganate(V) cyclic diester, **16**, must be rapidly reduced to the corresponding manganate(IV) diester, **17**, by abstraction of an electron or a hydrogen atom from the solvent before hydrolysis occurs (equation 21).



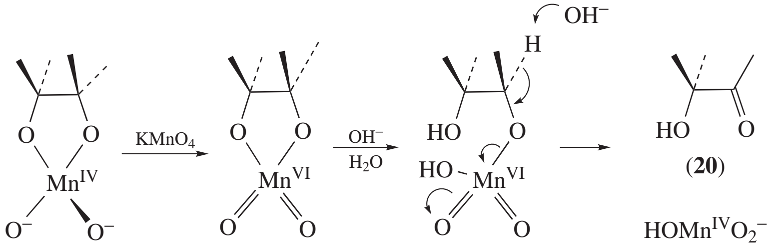
(**16**) (**17**) (21)

Although cyclic manganese(IV) diesters, **17**, appear to be formed under all conditions, the identity of the products obtained is dependent on reaction conditions. As indicated above, diols (**13** and **15**) are formed under basic conditions. If, however, the concentration of base is low and/or the concentration of oxidant is high, **17** is oxidized to a manganate(VI) diester, **18**, before hydrolysis occurs. Base-catalyzed ring opening of **18** to **19** followed by hydrolysis results in the formation of ketols, **20**, plus a manganese(IV) compound, **21** (equation 22).



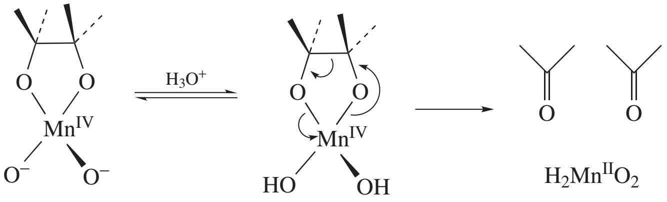
(**17**) (**18**) (**19**) (**21**) (22)

Alternatively, hydrolysis of **18** to **22** could precede the redox step (equation 23). As is true for most fast steps that follow rate-limiting steps, it is impossible to determine the sequence in which they occur—suffice to note that two reactions are required to convert **17** into **20**.



(**17**) (**18**) (**22**) (**21**) (23)

Protonation of oxidants, such as $CrO_4^=$ or MnO_4^-, is known to greatly increase the vigor of their reactions with reductants[46, 53, 54]. Similarly, protonation of the intermediate manganate(IV) diester, **17**, (when acidic conditions are used) gives a more reactive intermediate, **23**, that undergoes a facile cleavage of the carbon–carbon bond (equation 24) accompanied by formation of manganate(II), **24**.



(**17**) (**23**) (**24**)

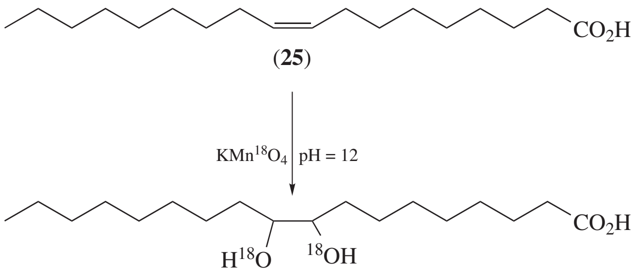
(24)

These mechanisms are supported by extensive experimental evidence in addition to the aforementioned stereochemistry. Other evidence includes the following:

Kinetic studies. The reaction rate is first order with respect to both the alkene and permanganate[51, 55–62], consistent with a bimolecular mechanism in which rate $= k[\text{alkene}][MnO_4{}^-]$.

Activation parameters. The activation parameters for the reaction of permanganate with C=C bonds are characterized by very negative entropies of activation ($\Delta S^{\mp} = -100$ to $-190\,\text{J mol}^{-1}\text{K}^{-1}$)[51, 55, 57,62–65], indicating that the transition state is highly organized compared to the ground state for these reactions. The observation (Table 1) that the activation parameters are comparable for several different kinds of compounds under a variety of conditions indicates that the mechanism for the rate-determining step is likely similar for all reactions of permanganate with compounds containing carbon–carbon double bonds. In fact, the color change that occurs when permanganate is reduced (purple → brown) has often been taken as a universal test for the presence of C=C bonds in a compound[66].

Oxygen labeling studies. When O-18 labeled permanganate is used as the oxidant, oxygen-18 is found in the product. For example, when oleic acid, **25**, was oxidized with labeled potassium permanganate (equation 25), Wiberg and Saegebarth found that the product, **26**, contained oxygen-18[69].



(**25**)

(**26**)

(25)

Analysis of the product indicated that 1.55 atoms of oxygen in **26** had come from the oxidant and 0.45 from the solvent (water). As will be discussed later, it is significant that approximately 20% of the oxygen atoms came from the solvent.

Spectroscopic detection of the intermediate[56–60,62,63,67,70–73]. Although cyclic manganate(IV) diesters have never been isolated and characterized, several authors have

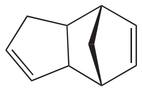
TABLE 1. Representative activation parameters for the reaction of permanganate with compounds containing carbon–carbon double bonds

C=C	Solvent	Conditions	$\Delta H^{\mp}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})	$\Delta G^{\mp}$ (kJ mol^{-1})
$CH_2{=}CH_2$[63]	Water	[a]	41	−144	84
$CH_3CH{=}CH_2$[63]	Water	[a]	45	−158	92
$CH_2{=}CHCH_2OH$[55]	Water	pH = 13	31	−100	61
$CH_2{=}CHCH_2OH$ [63]	Water	[a]	45	−158	92
$CH_2{=}CHCO_2^-$[55]	Water	pH = 13	22	−126	59
$CH_2{=}CHCN$[63]	Water	[a]	36	−128	74
$CH_3CH{=}CHCO_2H$[51]	Water	pH = 1.0	13	−150	58
$CH_3CH{=}CHCO_2^-$[55]	Water	pH = 13	20	−134	60
$CH_2{=}CHCH_2CO_2^-$[55]	Water	pH = 13	27	−117	62
$CH_2{=}CHCH_2CH_2CO_2^-$[55]	Water	pH = 13	28	−113	61
$PhCH{=}CHCO_2H$[57]	Water	1 *M* $HClO_4$	18	−126	54
$PhCH{=}CHCO_2^-$[55]	Water	pH = 13	14	−151	58
$PhCH{=}CHCO_2^-$[65]	Water	0.5 *M* NaOH	20	−121	56
$PhCH{=}CHCO_2^-$[65]	Water	pH = 11.3	19	−130	57
$PhCH{=}CHCO_2CH_3$[66]	CH_2Cl_2	Neutral	22	−164	71
$PhCH{=}CHCO_2CH_3$[66]	Acetone	Neutral	34	−139	75
$PhCH{=}CHCO_2CH_3$[66]	Toluene	Neutral	15	−185	70
$HO_2CCH{=}CBrCO_2H$[61]	Water	pH = 0.10	18	−140	60
$HO_2CCCl{=}CClCO_2H$[61]	Water	pH = 0.88	21	−134	61
$CH_2{=}CHOCH_2CH_2CH_2CH_3$[67]	THF/H_2O	0.1 *M* NaOH	18	−130	57
Dibromomaleic anhydride[61]	Water	pH = 0.10	14	−187	70
Uracil[67]	Water	pH = 6.7	22	−170	72
Thymine[67]	Water	pH = 6.7	29	−126	66
3-(3-Thienyl)-2-propanoate[68]	Water	pH = 6.83	13	−144	56
endo-Dicyclopentadiene[62]	CH_2Cl_2	neutral	16	−164	65

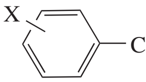
[a] The activation energies were calculated at the B3LYP/6-311++G** level[63].

reported the detection of an intermediate with an absorbance in the UV-Visible region of the electromagnetic spectrum, as documented in equations 26–28.

$$CH_3CH{=}CHCO_2H \xrightarrow[\text{pH = 7}]{KMnO_4} \text{An intermediate}^{59}\ (\lambda_{max} = 420\text{ nm}) \tag{26}$$



$$\xrightarrow[CH_2Cl_2]{QMnO_4} \text{An intermediate}^{62,\,70,\,71}\ (\lambda_{max} = 420\text{ nm}) \tag{27}$$

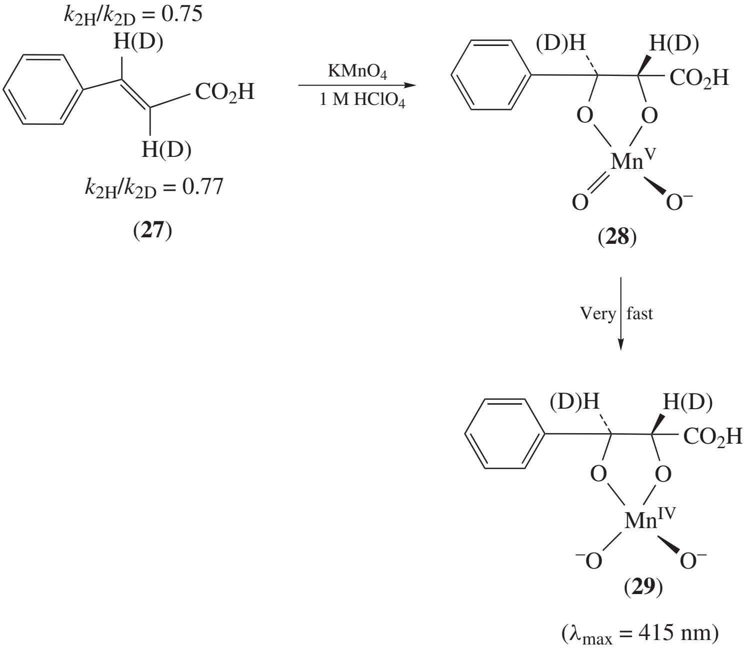


$$\text{—}CH{=}CHCO_2H \xrightarrow[\substack{\text{1 M }HClO_4\\ \text{or}\\ 50\%\ CH_3CO_2H}]{KMnO_4} \text{An intermediate}^{56,\,57} \tag{28}$$

X	λ_{max}
H	415 nm
p-CH_3	393 nm
p-Cl	405 nm
m-Cl	417 nm
p-NO_2	400 nm

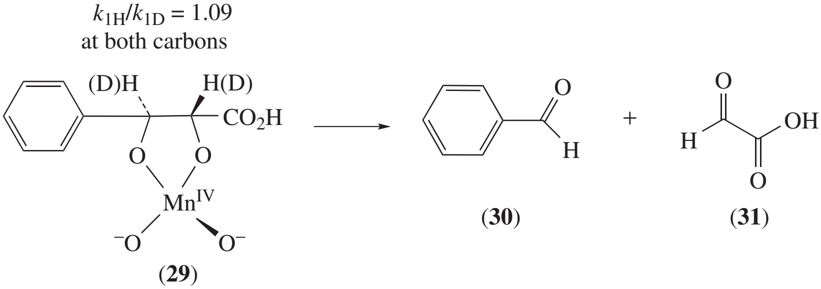
Secondary kinetic isotope effects[56,57,64,74]. It is known that deuterium substitution slightly increases the rate of a reaction in which hybridization of a carbon atom changes from sp^2 to sp^3 in the rate-limiting step. And, conversely, the rate of a reaction in which the hybridization changes from sp^3 to sp^2 in the rate-limiting step is slightly decreased[75]. When the hydrogen atoms on the double bond of cinnamic acid, **27**, were replaced by deuterium, one at a time as in equation 29, the rate of formation of the spectroscopically detected intermediate was increased for **both** substitutions ($k_{2H}/k_{2D} = 0.75$ at the α-carbon and $k_{2H}/k_{2D} = 0.77$ at the β-carbon, where k_2 is the second-order rate constant for the initial reaction between permanganate and cinnamic acid)[56,57]. This evidence is consistent with the proposed mechanism because the carbon atoms in **27** are sp^2 hybridized whereas those in the intermediates, **28** and **29**, are sp^3 hybridized.

The fact that inverse secondary isotope effects of similar size are observed at both carbon atoms indicates that the transition state is symmetrical with respect to formation of the initial intermediate—in all probability a cyclic manganate(V) diester, **28**, which is rapidly reduced to a cyclic manganate(IV) diester, **29** (the intermediate observed at $\lambda_{max} = 415$ nm), as illustrated in equation 29.



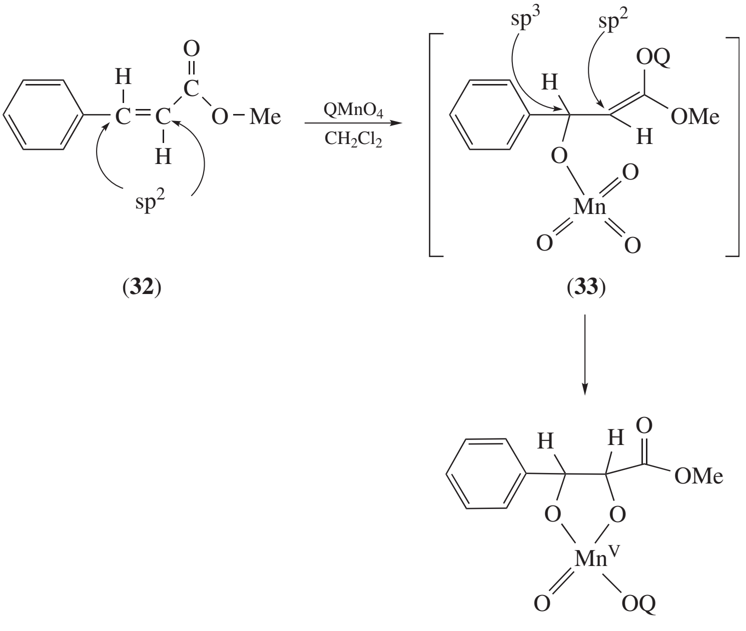
(29)

Under acidic conditions, carbon–carbon bond cleavage occurs giving benzaldehyde, **30**, and (presumably) glyoxylic acid, **31** (equation 30), in a first-order reaction, where k_1 is the rate constant for the conversion of **29** into **30** and **31**. In this process the hybridization of both carbon atoms changes from sp^3 in **29** to sp^2 in **30** and **31**. The secondary deuterium isotope effects observed ($k_{1H}/k_{1D} = 1.09$ for both the α- and β-carbons)[56,57] confirm that this or a very similar process is occurring.



(**29**) (**30**) (**31**) (30)

When the deuterium isotope effects were studied for the oxidation of methyl cinnamate, **32**, by quaternary ammonium permanganates in methylene chloride solutions, an inverse secondary isotope effect ($k_{2H}/k_{2D} = 0.94$) was observed only at the α-carbon[74]. Under these conditions the transition state for the reaction in which **32** goes to **34** is not symmetrical—the hybridization for only the α-carbon changes from sp^2 to sp^3, with the β-carbon remaining sp^2 in the transition state. This suggests that the transition state, **33**, under these conditions has enolate characteristics, as illustrated in equation 31 where Q^+ is the (p-fluorobenzyl)triethylammonium ion.



(**32**) (**33**) (**34**) (31)

The deuterium isotope effects reported for the reaction of permanganate with compounds containing C=C bonds have been summarized in Table 2.

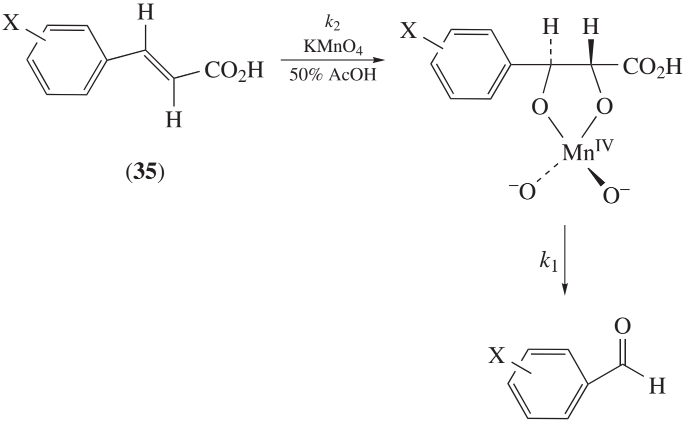
Substituent effects[57]. The first step of the reaction between permanganate ion and alkenes is relatively insensitive to the electronic effects of substituents. However, as

TABLE 2. Deuterium kinetic isotope effects

C=C	Conditions	k_{2H}/k_{2D}	k_{1H}/k_{1D}
$PhCH{=}C\mathbf{D}CO_2H$[56,57]	1 M $HClO_4$	0.77	1.09
$PhC\mathbf{D}{=}CHCO_2H$[56,57]	1 M $HClO_4$	0.75	1.09
$PhC\mathbf{D}{=}CHCO_2^-$[64]	0.5 M NaOH	0.89	
$PhCH{=}C\mathbf{D}CO_2^-$[64]	0.5 M NaOH	0.87	
$PhC\mathbf{D}{=}CHCO_2^-$[64]	pH = 11.3	0.93	
$PhCH{=}C\mathbf{D}CO_2^-$[64]	pH = 11.3	0.93	
$PhC\mathbf{D}{=}CHCO_2CH_3$[74]	CH_2Cl_2	0.91[a]	
$PhCH{=}C\mathbf{D}CO_2CH_3$[74]	CH_2Cl_2	1.0[a]	
$PhC\mathbf{D}{=}CHCO_2CH_3$[74]	CH_2Cl_2	0.94[b]	
$PhCH{=}C\mathbf{D}CO_2CH_3$[74]	CH_2Cl_2	1.0[b]	
$ArC\mathbf{D}{=}CHCO_2H$[68]	pH = 6.86	0.91[c]	

[a] The oxidant was tetrabutylammonium permanganate.
[b] The oxidant was (*p*-fluorobenzyl)triethylammonium permanganate.
[c] Ar is 2-thienyl

indicated by the data accompanying equation 32, a large effect is observed for the second (product-forming) step when substituted cinnamic acids, **35**, are oxidized in 50% acetic acid[57].



(**35**)

(32)

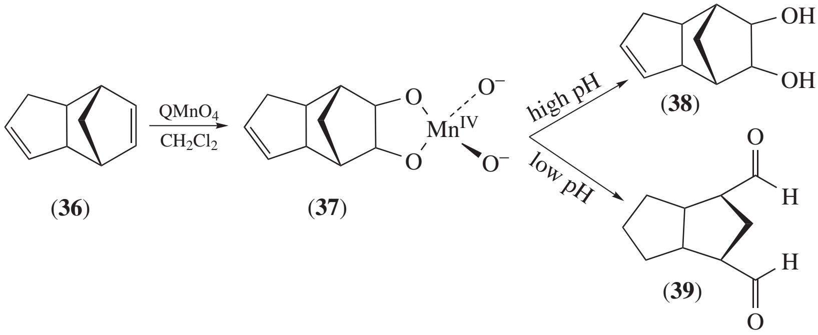
X	k_2 (l mol^{-1} s^{-1})
p-CH_3	407
H	442
p-Cl	380
m-Cl	378
p-NO_2	329

X	k_1 ($s^{-1} \times 10^3$)
p-CH_3	19.9
H	19.2
p-Cl	7.3
m-Cl	4.8
p-NO_2	2.5

The rate constants for the second step (k_1) correlate well with Hammett σ-values, giving a ρ-value of -1.1 ($r = 0.98$), whereas the Hammett plot for the first step (k_2) is slightly concave with a low slope[57].

Freeman and Kappos also found that the rate constants for the oxidation of unsaturated aliphatic carboxylates are not sensitive to the electronic impact of substituents[58]. The small changes observed were attributed primarily to steric rather than electronic effects.

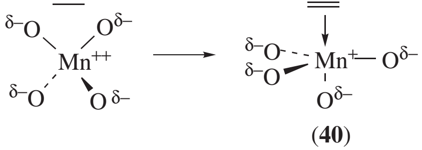
Interception of the intermediate[70,71]. Ogino and coworkers have shown that the intermediate manganate(IV) diester, **37**, formed when *endo*-dicyclopentadiene, **36**, reacts with a quaternary ammonium permanganate in dichloromethane can be intercepted by the addition of either acidic or basic aqueous solutions[70, 71]. Addition of acid to the observed intermediate results in the formation of a dialdehyde, **39**, whereas addition of base produces a diol, **38**, as illustrated in equation 33.



(33)

Some authors[68] have suggested that the intermediate detected in these reactions is nothing more than manganese dioxide. However, the interception studies reported by Ogino and coworkers[70, 71] and the isotope and substituent effects measured by Lee and Brownridge[57] provide convincing evidence that the species detected is an intermediate and not a terminal product. If it was a terminal product, such as MnO$_2$, the rate of its decay would not be subject to isotope or substituent effects and different organic products could not be obtained when it was treated with acidic or basic solutions.

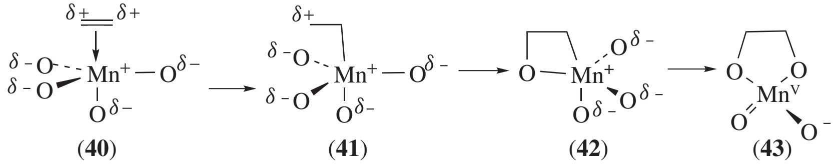
The actual way in which cyclic manganate(V) diesters form remains to be completely understood. From an electrostatic point of view, it is not likely that the initial interaction between permanganate and an alkene (which is known to be very fast) would involve an attack on the double bond by an oxygen ligand. Both the double bond and the oxygen atom are centers of electron density and would, therefore, be expected to repel rather than attract each other. Instead, it has been suggested that the initial interaction is between the double bond and the electron-deficient manganese atom to give a trigonal bipyramidal π-complex, **40**[72, 74] as in equation 34, where the sp^2 carbon atoms have been illustrated as possessing a partial positive charge because of the transfer of some electron density to the Mn atom.



(**40**)

(34)

If the manganese atom in **40** slips toward one end of the C=C bond, it would be converted from a π-complex into a σ-complex, **41**. This σ-complex could easily cyclize into **42**, a metallooxetane, which is equivalent to the product of a [2 + 2] addition between Mn=O and C=C bonds. Therefore, equation 35 is essentially an elaboration of the mechanism originally proposed by Wagner in 1895[47]. Rearrangement of **42** could result in the formation of the cyclic manganate(V) diester, **43**, originally proposed by Boeseken in 1921[48].



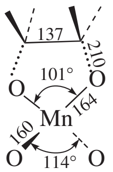
(35)

Metallocyclooxetanes, such as **42**, have been suggested as possible intermediates when alkenes are oxidized by $MnO_4{}^-$ and OsO_4[76, 77]. However, several recent theoretical calculations seem to rule out this possibility[63, 78–80].

Because it is not possible to isolate and definitively characterize the intermediates formed when permanganate reacts with alkenes, recent attention has focused on the use of theoretical methods to chart the course of the reaction. Although the initial calculations, reported by Rappe and Goddard[77], suggested that a metallocyclooxetane, such as **42**, was more stable than cyclic manganate(V) diesters, such as **43**, more recent calculations have indicated that those conclusions were incorrect. Reports of calculations from the laboratories of Houk[78], Strassner[79], Wiberg[63] and Ess[80] have all concluded that **43** is more stable than **42** by about 125 to 165 kJ mol^{-1}. Not surprisingly, calculations also indicated that the transition state leading to **43** is more favorable than the one leading to **42**.

From these calculations it appears that the difference in energies of the transition states leading to **42** and **43** can be ascribed primarily to two factors—the distortion energy expended when the transition state forms and the interaction energy required to bring the reactants together. The distortion energy involves both geometry and electronic changes as the system passes from the ground state to the transition state. The interaction energy involves unfavorable exchange-repulsions and favorable electrostatic, polarization and orbital effects[80].

Although there is not exact agreement between all of the calculations reported, the dimensions shown in **44** are typical of those calculated for the transition state for the formation of a cyclic manganate(V) diester from the reaction of permanganate with ethene[80].



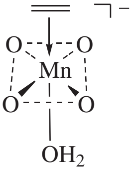
(**44**)

The distortion energy associated with geometrical changes required to transform ethene and permanganate into **44** would be less than those required to form a four-membered metallocyclooxetane, such as **42**. The distortion energy required to convert permanganate and ethene into **44** has been calculated to be 32 kJ mol^{-1} (17 kJ mol^{-1} for permanganate and 15 kJ mol^{-1} for ethene)[80]. The interaction energy for the same process was calculated to be 5 kJ mol^{-1}, giving an overall value for the activation energy of 52 kJ mol^{-1} for a gas phase reaction—an amount that is not unreasonable when compared with experimental values that have been measured for the oxidation of variously substituted ethenes by permanganate (Table 1).

Although comparable values for the distortion energies required to form metallocyclooxetanes similar to **42** have not been reported, it seems obvious that the reduced bond angles would produce greater strain and result in much higher activation energies.

It has also been demonstrated that the calculations are consistent with the secondary isotope effects previously described for this reaction[78].

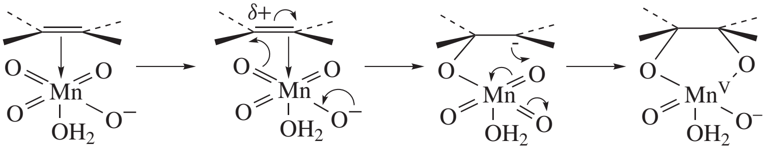
A mechanism involving formation of metallocyclooxetanes has been eliminated by theoretical studies. Despite this, ample experimental evidence exists that compounds containing metal atoms usually react with carbon–carbon double bonds by forming π-complexes[76, 81]. It has been suggested that formation of a complex between an alkene and permanganate might involve a molecule of solvent, giving an octahedral structure such as **45**[74].



(**45**)

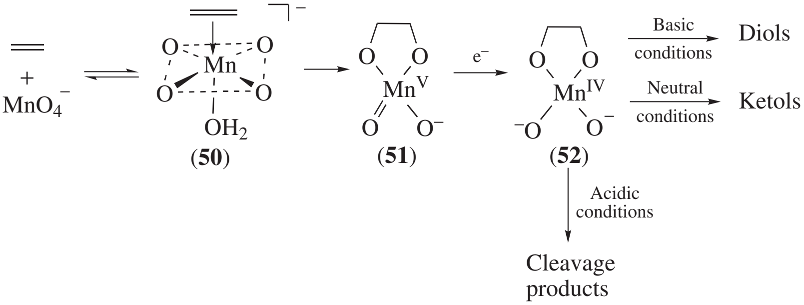
This complex, **45**, is an 18-electron organometallic system and should be somewhat stable[81]. Further, the suggestion that the coordination shell of manganese could be expanded to include a molecule of water is consistent with the oxygen-18 studies previously discussed. Wiberg and Saegebarth[69] observed that approximately 1 in 5 of the oxygen atoms present in diols prepared by the oxidation of alkenes with permanganate came from the solvent. This result seems to be in almost exact agreement with the formation of a structure similar to **45** along the reaction pathway. In addition, results of studies on the oxidation of 1,5-hexadiene by permanganate in oxygen-18 enriched water revealed that approximately one-fifth (17%) of the oxygen atoms had come from the solvent and the observed stereochemistry required that those oxygen atoms had been delivered from the coordination shell of the manganese[82].

Carbon–carbon double bonds complexed to a metal center become susceptible to nucleophilic attack, but only after the metal has slipped toward one end of the C=C bond[83]. When the manganese atom in **46** slips along the double bond, as in **47**, the most accessible nucleophile is an oxygen ligand. The next step could involve rearrangement of **47**, through **48**, into **49**, as suggested in equation 36.



(**46**) (**47**) (**48**) (**49**) (36)

In summary, a combination of experimental and theoretical evidence indicates that the reaction between alkenes and permanganate is initiated by formation of a π-complex, **50**, that rearranges to produce a manganate(V) cyclic diester, **51**, which is rapidly reduced to a manganate(IV) cyclic diester, **52**, as in equation 37. The products obtained from **52** are dependent on the reaction conditions and can be diols, ketols or C=C bond cleavage products.



(37)

The mechanism elaborated in equation 37 is consistent with all available experimental evidence including product studies, activation parameter determinations, oxygen-18 labeling experiments, and deuterium isotope effects. It is also in agreement with theoretical calculations that indicate **51** to be the first intermediate formed. Recent calculations also indicate that the cyclic manganese(IV) diester, **52**, is much more stable than the cyclic manganese(V) diester, **51**[84].

As indicated in the following sections this mechanism also accommodates the results reported for the oxidation of α,β-unsaturated esters.

E. The Oxidation of Unsaturated Esters by Quaternary Ammonium Permanganates

Although the rates of oxidation of unsaturated compounds by permanganate in aqueous solutions are not sensitive to substituent effects, the rates of the corresponding reactions in nonaqueous solvents show marked substituent effects. For example, a linear free energy analysis of rate data obtained for the oxidation of substituted methyl cinnamates by tetrabutylammonium permanganate in methylene chloride solutions at 20.0 °C indicates a Hammett ρ-value of 0.95, as illustrated in Figure 2.

As demonstrated by the data plotted in Figure 2, electron-withdrawing substituents increase the rate constants for this reaction, indicating that the transition state has greater electron density than the starting compound. This observation is consistent with the mechanism proposed in equation 38, where the transition state (**54**) for the oxidation of unsaturated esters, **53**, is assumed to have enolate characteristics.

The mechanism in equation 38 is also in agreement with the observation that an inverse secondary isotope effect is observed when the hydrogen atom in the α-position of **53** is replaced by deuterium (because the hybridization of the α-carbon atom changes from sp^2 in the starting compound to sp^3 in the transition state). However, as indicated in Table 2, replacement of the hydrogen atom in the β-position does not cause an inverse secondary isotope effect (because the β-carbon atom remains sp^2 in the transition state)[74].

Kinetic studies of the reactions of methyl cinnamates with quaternary ammonium permanganates have revealed that the rates are dependent on the identity of the quaternary ammonium ions[74]. Faster reactions are obtained when the quaternary ammonium ion is small (such as the tetrapropylammonium cation), and slower reactions are obtained with large quaternary ammonium ions (such as the tetraoctylammonium cation). If fact, as demonstrated by the data plotted in Figure 3, the magnitudes of the second-order rate constants are inversely proportional to ionic radii of the quaternary ammonium ions.

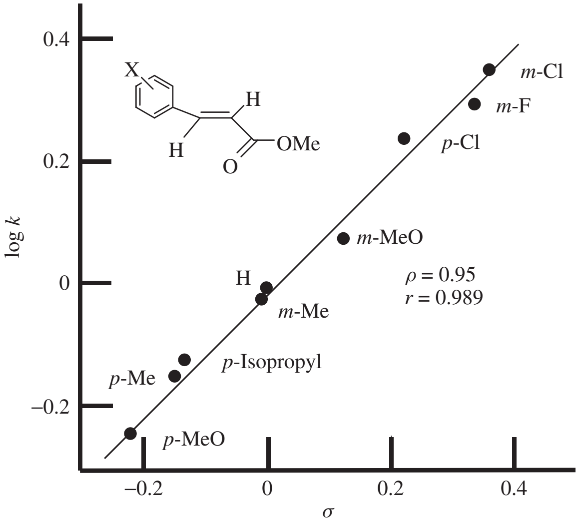
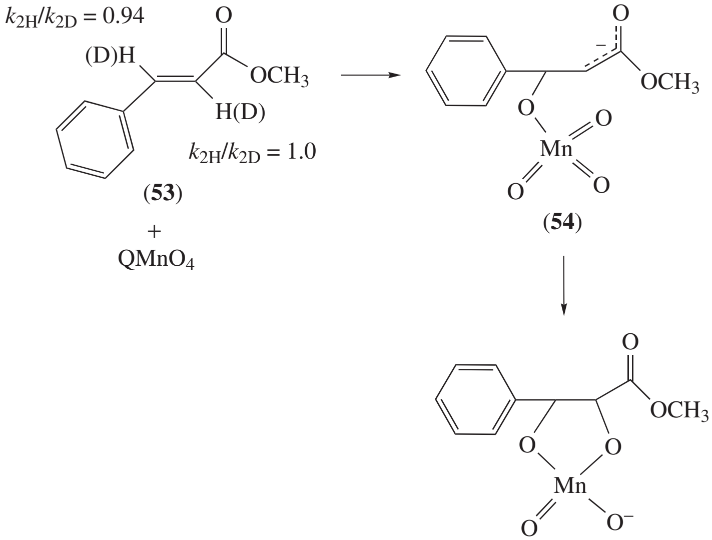


FIGURE 2. Hammett plot for the oxidation of methyl cinnamates by tetrabutylammonium permanganate in methylene chloride at 20.0 °C



(38)

The size of the quaternary ammonium ions can impact the reaction rates only if they form intimate ion pairs with permanganate and/or the transition state. If the ions were separated by solvent molecules, the size of the quaternary ammonium ions would not be expected to have any effect on the rates of reaction. The observation that the fastest rates are observed with the smallest cations suggests that the transition state benefits more from the intimacy of the ion pairs than does the starting material. This may be so because

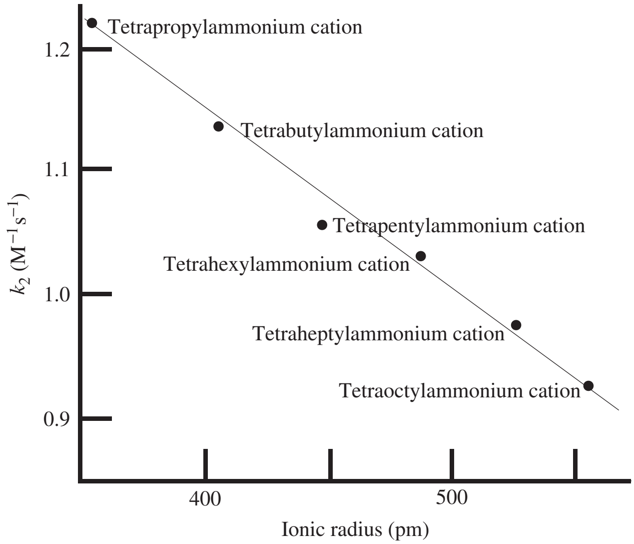


FIGURE 3. Relationship between cation size and rate constants for the oxidation of methyl cinnamate by quaternary ammonium permanganates

TABLE 3. Rate constants for the oxidation of methyl cinnamate by quaternary ammonium permanganates in methylene chloride solutions at 20.0 °C[74]

Oxidant	k_2(1 mol^{-1} s^{-1})
Tetrabutylammonium permanganate	1.15 ± 0.02
Methyltributylammonium permanganate	1.54 ± 0.02
Tetraoctylammonium permanganate	0.91 ± 0.02
Methyltrioctylammonium permanganate	1.54 ± 0.02

the negative charge on permanganate ion is dispersed over four oxygen atoms whereas the charge on the transition state, **54** in equation 38, is much more localized. A more localized negative charge in the transition state would benefit more from the formation of an intimate ion pair with the cation. This possibility is also supported by the observation that replacement of one of the longer chain alkyl groups by a methyl group results in an increase in reaction rate[74], as illustrated by the data in Table 3. Replacement of a long alkyl chain by a methyl group would facilitate the formation of an intimate ion pair, thereby giving greater stability to the transition state where the negative charge is more localized.

The size of the quaternary ammonium cation also affects the solubility of quaternary ammonium permanganates—the larger the cation, the greater the solubility, as indicated by the data plotted in Figure 4[5].

Replacement of one alkyl chain of a tetraalkyl ammonium permanganate by a methyl group allows for the formation of a closer ion pair and increases its solubility, as indicated by the data in Table 4[5].

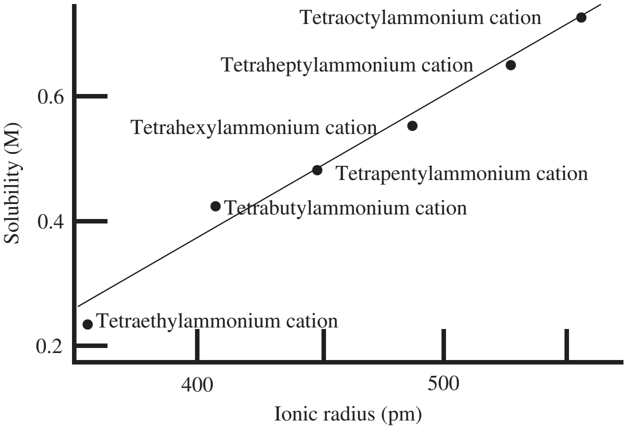


FIGURE 4. Relationship between size and the solubility of quaternary ammonium permanganates in methylene chloride

TABLE 4. Solubilities of quaternary ammonium permanganates in methylene chloride solutions at 20.0 °C[5]

Quaternary Ammonium Permanganate	Solubility (M)
Tetrabutylammonium permanganate	0.417
Methyltributylammonium permanganate	1.83
Tetraoctylammonium permanganate	0.713
Methyltrioctylammonium permanganate	1.38

The observations summarized in Figures 2–4 and Tables 3 and 4 establish that the identity of both the substituents and the quaternary ammonium cations can have an impact on the ground states and the transition states when unsaturated esters are oxidized by quaternary ammonium permanganates. Although conclusive data are not available, it is likely that similar impacts occur when other unsaturated compounds are oxidized by quaternary ammonium permanganates in nonpolar solvents.

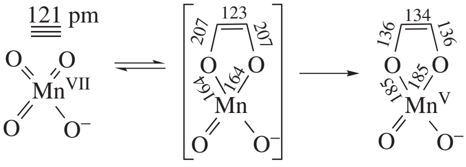
F. The Mechanism for the Oxidation of Carbon–Carbon Triple Bonds by Permanganate

Density functional theory calculations support a suggestion that the initial reaction between permanganate and carbon–carbon triple bonds is reminiscent of the corresponding reaction between alkenes and permanganate[85]. For the oxidation of acetylene, the calculated geometry for the transition state, **55**, and first intermediate, **56**, are summarized in equation 39.

As indicated from the structures in equation 39, the carbon–carbon bond length increases only slightly on going from the ground state to the transition state (from 121 pm in acetylene to 123 pm in the transition state, **55**). Also, the carbon–oxygen bonds are quite long (207 pm) in **55**, indicative of an early transition state.

TABLE 5. Activation energies for the oxidation of carbon–carbon triple bonds by permanganate

Reductant	Solvent	Conditions	$\Delta H^{\mp}$(kJ mol^{-1})	$\Delta S^{\mp}$(JK^{-1} mol^{-1})	$\Delta G^{\mp}$(kJ mol^{-1})
Sodium acetylenedicarboxylate[86]	water	pH = 3.8	25.5	−135	65.7
Propyn-3-ol[87]	water	pH = 0.98	26.4	−138	67.5
2-Butyn-1,4-diol[87]	water	ph = 0.98	22.0	−150	66.7
Propynoic acid[88]	water	pH = 3.77	25.8	−128	63.9
Phenlypropynoic acid[88]	water	pH = 3.77	30.3	−129	68.7

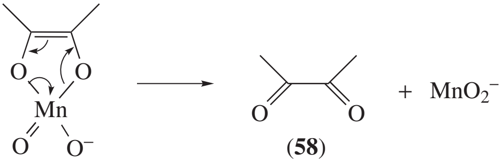


(**55**) (**56**)

(39)

The experimental observation that the entropies of activation are large and negative for the reactions between permanganate and typical compounds containing carbon–carbon triple bonds is consistent with a highly structured, cyclic transition state such as **55**. See Table 5.

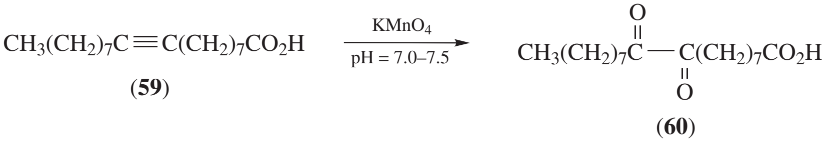
Since 134 pm is the usually observed length for carbon–carbon double bonds, it appears that the intermediate, **56**, contains a 'normal' carbon–carbon double bond. Such an unsaturated cyclic manganate(V) diester, **57**, could then undergo an internal redox reaction, as indicated in equation 40, with the formation of a vicinal diketone, **58**, and a manganese(III) species.



(**57**) (**58**)

(40)

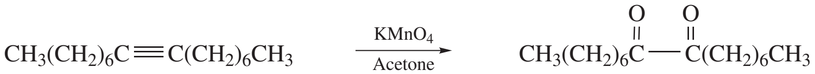
Good yields of dione are obtained in neutral aqueous solutions if the reductant contains a group that facilitates its solubility in water. For example, stearolic acid, **59**, is converted into **60** in good yields (92–96%) when treated with permanganate in a carefully buffered (pH = 7.0 to 7.5) solution[89] (equation 41). If the solutions are not buffered, cleavage products are obtained.



$$CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2H \xrightarrow[\text{pH = 7.0–7.5}]{\text{KMnO}_4} CH_3(CH_2)_7\overset{\overset{\Large O}{\|}}{C}{-}\underset{\underset{\Large O}{\|}}{C}(CH_2)_7CO_2H \qquad (41)$$

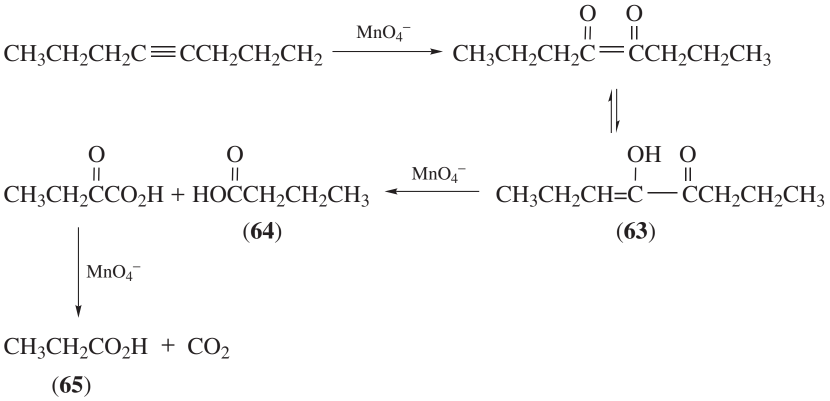
(**59**) (**60**)

Diones can also be obtained in good yields from compounds not containing polar groups (to promote water solubility) if the reactions are carried out in buffered acetone solutions[90]. For example, 8,9-hexadecanedione, **62**, is obtained in quantitative yields when 8-hexadecyne, **61**, is oxidized in an acetone solution buffered with sodium bicarbonate and magnesium sulfate (equation 42).



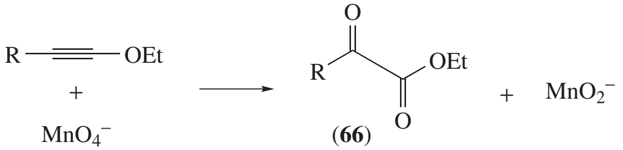
$$\underset{(\mathbf{61})}{CH_3(CH_2)_6C{\equiv}C(CH_2)_6CH_3} \xrightarrow[\text{Acetone}]{KMnO_4} \underset{(\mathbf{62})}{CH_3(CH_2)_6\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}(CH_2)_6CH_3} \qquad (42)$$

Alkynes such as 7-tetradecyne and 8-hexadecyne are also converted into the corresponding vicinal diones when oxidized by potassium permanganate in methylene chloride solutions with the aid of a phase transfer agent[91]. Under other conditions cleavage products are often obtained. For example, the reaction between potassium permanganate and 4-octyne in aqueous solutions gives butyric acid, **64**, as the primary product (73%) along with smaller amounts of propanoic acid, **65**. The latter product is the result of a reaction between the dione enol, **63**, and permanganate, as in equation 43[91]. Under certain conditions approximately equal amounts of two carboxylic acids are obtained; e.g. oxidation of 7-tetradecyne in methylene chloride by aqueous potassium permanganate with the aid of a phase transfer agent gives 78% heptanoic acid and 56% hexanoic acid[91].



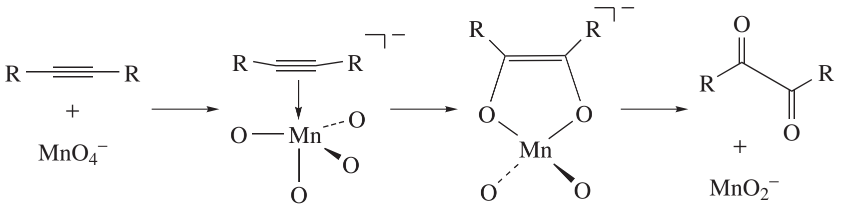
(43)

The rates at which alkynes are oxidized by permanganate are quite sensitive to the presence of substituents[92, 93]. Both carbonyl and ether groups adjacent to the triple bond accelerate the reaction. The latter observation has been exploited in the preparation of α-keto esters, **66**, as in equation 44[94].



(44)

The oxidation of alkynes by permanganate[90] requires more vigorous conditions than the corresponding oxidation of alkenes[73]. However, in numerous other studies it has been observed that nucleophiles react faster with alkynes than with the corresponding alkenes[95]. Consequently, the suggestion that the reaction between alkynes and permanganate is initiated by a nucleophilic attack (as implied by equation 39) does not seem likely. Instead, it is more reasonable to propose an initial reaction in which a manganese(VII)–alkyne complex, **67**, is formed (equation 45)[96].



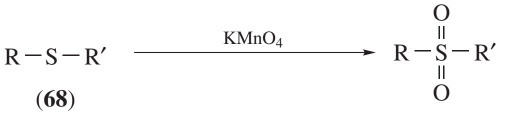
(**67**)

(45)

This mechanism is also supported by experiments using oxygen-18 tracers, which proved that the oxygen atoms in the products obtained from the oxidation of acetylenedicarboxylic acid by $KMnO_4$ come primarily from the oxidant[97].

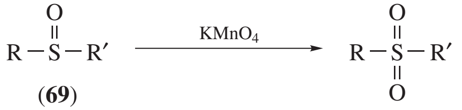
G. Mechanisms for the Oxidation of Sulfides and Sulfoxides by Permanganate

Reaction with permanganate converts sulfides (**68**) and sulfoxides (**69**) into sulfones (**70**) (equations 46 and 47)[2, 98–100]. The reactions can be carried out in acetone[101] or in methylene chloride with the aid of a phase transfer agent[102].



$$\underset{(\mathbf{68})}{R{-}S{-}R'} \xrightarrow{KMnO_4} R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}R' \qquad (46)$$

(**70**)



$$R{-}\overset{\overset{O}{\|}}{S}{-}R' \xrightarrow{KMnO_4} R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}R' \qquad (47)$$

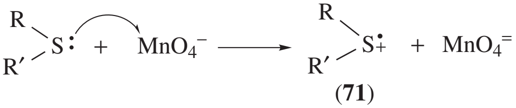
(**69**) (**70**)

The reactions in equations 46 and 47 involve only the transfer of oxygen atoms from permanganate to the reductant. Most other oxidation reactions are accompanied by extensive bond cleavages in the reductant, in addition to oxygen atom transfers. For example, as described in the preceding sections, the oxidation of arenes by permanganate involves C–H bond cleavage as well as oxygen transfer, and the oxidation of alkenes and alkynes requires the opening of π-bonds in conjunction with oxygen transfers. As a consequence, in addition to being useful synthetic procedures, the reactions of permanganate with sulfides and sulfoxides are of fundamental interest.

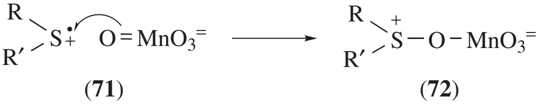
Three mechanisms have been considered for the oxidation of sulfides by permanganate:

(i) A process initiated by a single electron transfer[103, 104].
(ii) A direct, concerted oxygen atom transfer[105].
(iii) Ligand formation followed by an oxygen atom transfer[106–108].

A reaction between sulfides and permanganate, initiated by a single electron transfer, would result in the formation of a radical cation intermediate (**71**) followed by a rapid ‘oxygen rebound’ step with the formation of a manganese(V) intermediate (**72**) (equations 48 and 49).

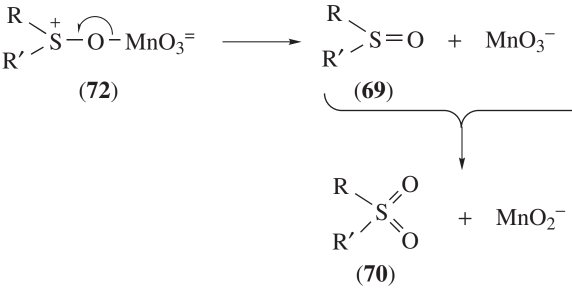


(48)



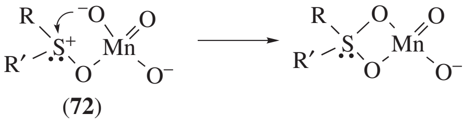
(49)

Decomposition of **72** would then give $Mn^VO_3^-$ plus a sulfoxide, which could be rapidly oxidized to the corresponding sulfone, **70**, as in equation 50.

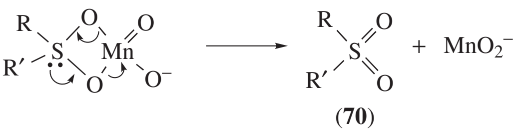


(50)

Alternatively, **72** could undergo a concerted oxidative decomposition (as in equations 51 and 52) to produce a sulfone without formation of an intermediate sulfoxide.

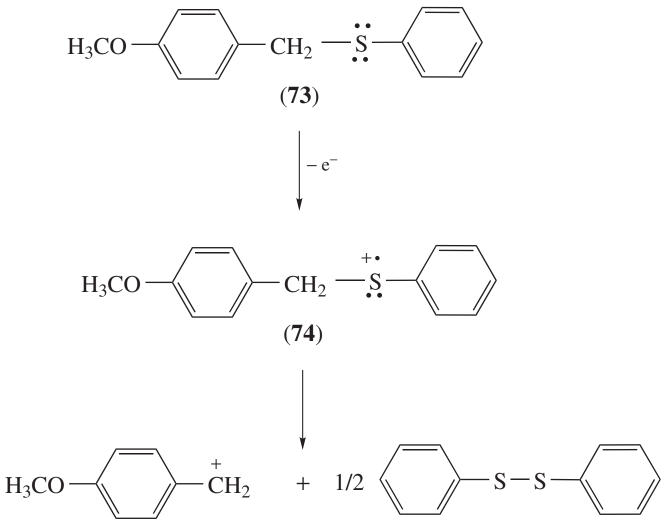


(51)



(52)

Results obtained from the oxidation of 4-methoxybenzyl phenyl sulfide, **73**, suggest, however, that the oxidation of sulfides by permanganate is not initiated by a single electron transfer. As illustrated in equation 53, a single electron transfer from **73** produces a radical cation, **74**, that readily decomposes into a benzyl carbocation, **75**, and diphenyl disulfide, **76**[109, 110].



(**73**)

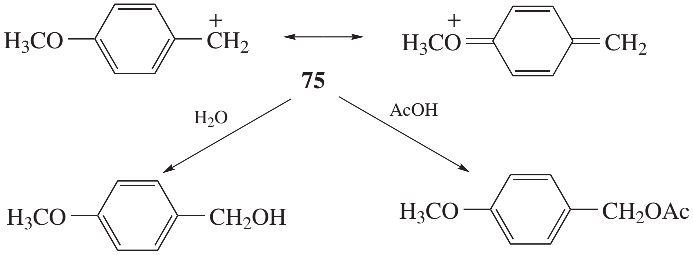
(**74**)

(**75**)

(**76**)

(53)

The 4-methoxybenzyl carbocation, **75**, which forms easily because it is stabilized by resonance, reacts with solvent to give either the corresponding alcohol, **77**, or ester, **78** (equation 54)[109].



(**77**)

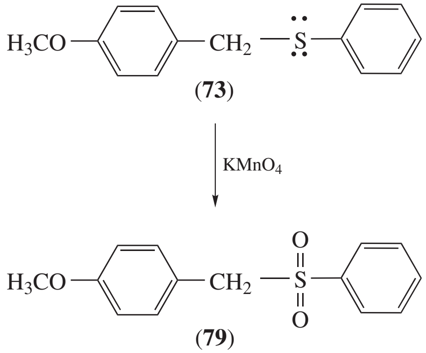
(**78**)

(54)

Because 4-methoxybenzyl phenyl sulfone, **79**, is the only product obtained when 4-methoxybenzyl phenyl sulfide, **73**, is oxidized by permanganate (equation 55), a mechanism initiated by a single electron transfer does not pertain[108].

Alternatively, a concerted mechanism (equation 56) involving nucleophilic attack concomitant with reduction of manganese(VII) to manganese(V) has been considered[105].

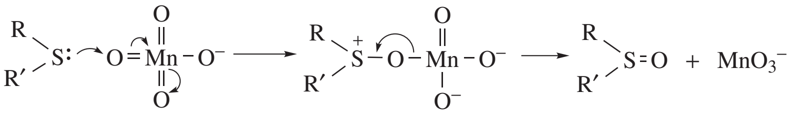
However, this mechanism requires nucleophilic attack at an electron-rich oxygen atom—a process that is unlikely. Instead, since the electron density at the manganese atom is known to be diminished[11], nucleophilic attack on the metal is more likely[106, 107]. As illustrated in equation 57, such a process could result in the formation of sulfones plus manganese(III) in a concerted or a stepwise mechanism.



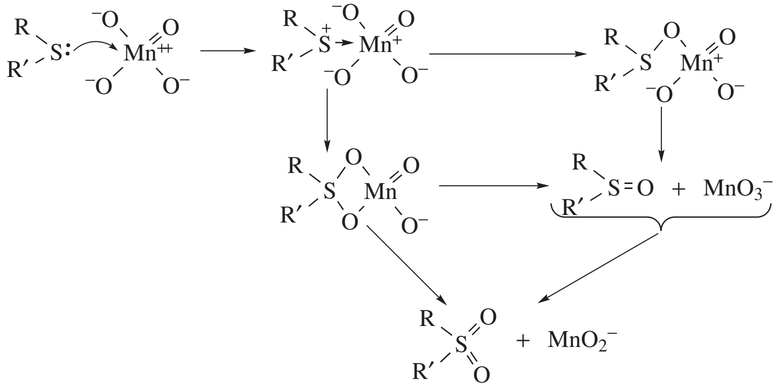
(**73**)

(**79**)

(55)

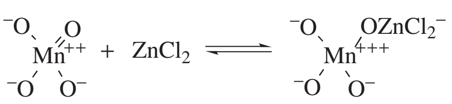


(56)



(57)

The oxidation of sulfides by permanganate is greatly accelerated by Lewis acid catalysts such as iron(III) chloride[108, 111], zinc chloride[112] and mercury(II) chloride[112]. These catalysts accelerate the reaction by combining with the oxidant (equation 58)[112].



(58)

The overall effect of combination with a Lewis acid is to decrease the electron density at the manganese atom making permanganate more susceptible to nucleophilic attack by sulfides[112]. It has also been noted that another Lewis acid, boron trifluoride, catalyzes the oxidation of alkanes by permanganate[43, 113].

The results of linear free energy relationship studies are in agreement with the mechanisms portrayed in both equations 56 and 57[105, 112]. The Hammett ρ-values, as illustrated

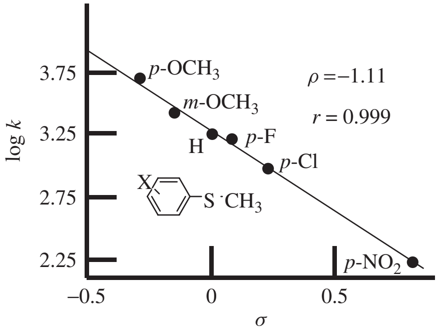
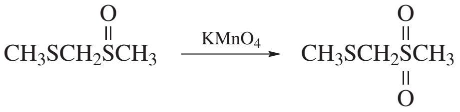


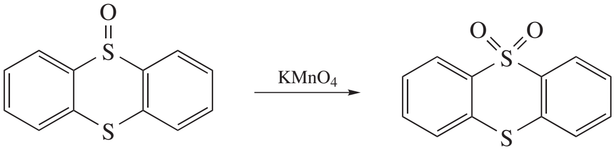
FIGURE 5. Hammett plot for the oxidation of substituted thioanisoles by permanganate in acetone solutions containing zinc chloride as a catalyst at $T = 23.0\,^{\circ}\mathrm{C}$[112]

in Figure 5, are negative—indicative of a decrease in electron density at sulfur in the transition state.

Under identical conditions the rate constant for the oxidation of thioanisole is about 16 times greater than that of the corresponding sulfoxide[112]. However, in intramolecular competitive experiments, sulfoxides are oxidized preferentially, as indicated by the reactions depicted in equations 59 and 60[114, 115].

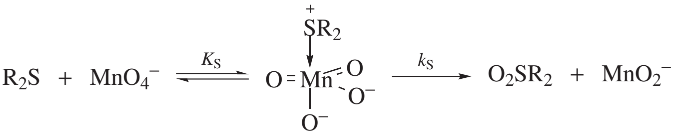


$$CH_3SCH_2\overset{\overset{O}{\|}}{S}CH_3 \xrightarrow{KMnO_4} CH_3SCH_2\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}CH_3 \qquad (59)$$

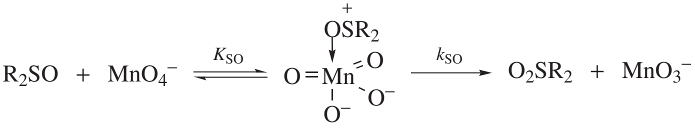


(60)

The explanation of this apparent paradox lies in the likelihood that both oxidation reactions are preceded by equilibria in which the reductants become a manganese ligand, as in equations 61 and 62.



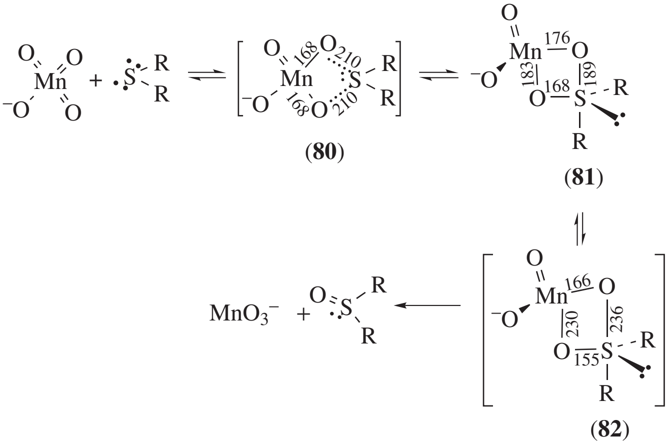
$$R_2S + MnO_4^- \overset{K_S}{\rightleftharpoons} O{=}\underset{\underset{O^-}{|}}{\overset{\overset{\overset{+}{S}R_2}{\downarrow}}{Mn}}\!\begin{smallmatrix}{=}O\\ \backslash O^-\end{smallmatrix} \xrightarrow{k_S} O_2SR_2 + MnO_2^- \qquad (61)$$



$$R_2SO + MnO_4^- \overset{K_{SO}}{\rightleftharpoons} O{=}\underset{\underset{O^-}{|}}{\overset{\overset{\overset{+}{O}SR_2}{\downarrow}}{Mn}}\!\begin{smallmatrix}{=}O\\ \backslash O^-\end{smallmatrix} \xrightarrow{k_{SO}} O_2SR_2 + MnO_3^- \qquad (62)$$

If sulfoxides are better ligands than sulfides, K_{SO} would be larger than K_S, causing the sulfoxide to be preferentially oxidized in competitive reactions, such as those depicted in equations 59 and 60. However, since k_S is apparently larger than k_{SO}, sulfides are oxidized more rapidly when sulfoxides are not present[112]. Reports that these reactions exhibit Michaelis–Menten kinetics confirms that an equilibrium precedes the oxidative step in the reaction mechanism[107, 112].

Despite the apparent internal consistency of this explanation, recent calculations[116] suggest a different mechanism in which the reaction of permanganate with dimethyl sulfide results in formation of an intermediate, **81**, wherein sulfur is bonded to manganese through two oxygen atoms giving a four-membered ring. The transition state, **80**, predicted for the formation of **81** is symmetrical, as illustrated in equation 63. The geometry around the sulfur atom in **81** is trigonal bipyramidal. One of the bonding oxygen atoms is axial with a calculated S−O bond length of 189 pm while the other is equatorial with a calculated bond length of 168 pm. In the rate-limiting step the axial S−O bond lengthens to 236 pm and the equatorial S−O bond contracts to 155 pm giving a second transition state, **82**, as the intermediate **81** is converted into products.



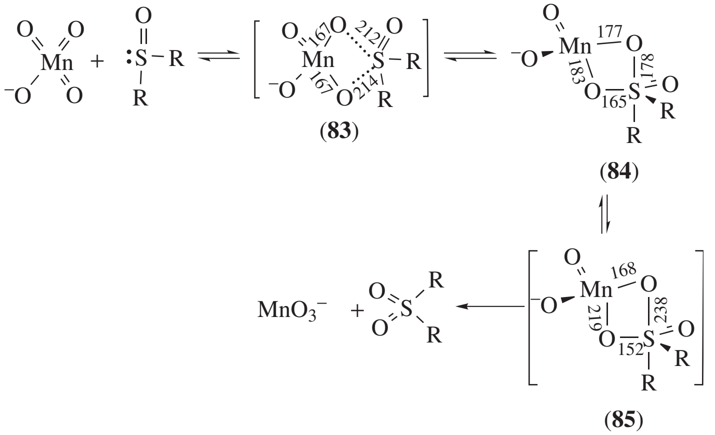
(63)

Calculations predict that a similar mechanism pertains for the oxidation of sulfoxides by permanganate, as illustrated in equation 64. The first step of the reaction has a symmetrical transition state, **83**. The geometry about the sulfur atom in the intermediate, **84**, is calculated to be trigonal bipyramidal with one of the 'R' groups and two of the oxygen atoms in the equatorial positions. The other oxygen atom and the second 'R' group are in apical positions. The transition state for the final step, **85**, is formed as the axial S−O bond stretches to 238 pm and the equatorial S−O bond contracts to 152 pm.

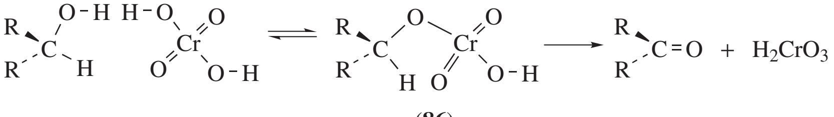
The apparent difference between the mechanisms predicted on the basis of experimental evidence and these calculations remains unresolved.

H. The Oxidation of Alcohols and Ethers by Permanganate

The mechanism for the oxidation of alcohols by some oxidants, such as chromic acid, involves formation of an intermediate chromate ester, **86** (equation 65). When this or similar mechanisms pertain, the rate at which alcohols are oxidized will exceed that of the corresponding ethers (because ethers do not form esters).


(83) (84) (85)

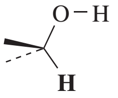
(64)

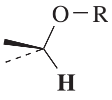

(86)

(65)

For example, Westheimer[117] found that isopropyl alcohol was oxidized by chromic acid about 1500 times faster than diisopropyl ether. On the basis of that and other evidence he concluded that chromate esters, **86**, were reactive intermediates when alcohols are oxidized by $HCrO_4^-$ or H_2CrO_4. Subsequent additional evidence—both experimental[118] and theoretical[119]—has confirmed his conclusion.

On the other hand, if the reaction is initiated by cleavage of an α-C–H bond, it is to be expected that the reaction rates for alcohols and ethers should be similar because the α-hydrogen atoms in both types of compounds are in a similar electronic environment. A comparison of the structures of alcohols, **87**, and ethers, **88**, indicates that any impact due to the oxygen atoms will be transmitted to the α-hydrogen atoms through a single carbon atom in both types of compounds.


(**87**)


(**88**)

Contrary to the results obtained for chromic acid oxidations the data in Table 6 indicate that there is not a large difference in the magnitudes of the rate constants for the oxidation of alcohols and the corresponding ethers by permanganate under neutral or acidic conditions.

Further evidence that the oxidations of alcohols[122] and ethers[123] (equations 66 and 67) likely proceed by similar mechanisms is illustrated from a comparison of the effect that substituents have on the rate constants for the oxidation of benzyl alcohol and benzyl

TABLE 6. Comparisons of rate constants for the oxidation of alcohols and ethers by permanganate

Alcohol/ether pair	Solvent	$k_2 (1\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})$
Isopropyl alcohol[120]	Aqueous, pH = 4.6	3.9×10^{-3}
Diisopropyl ether[120]	Aqueous, pH = 4.6	1.8×10^{-3}
Isopropyl alcohol[120]	$1\ M\ H_2SO_4, 0.5\ M$ NaF	13.3×10^{-3}
Diisopropyl ether[120]	$1\ M\ H_2SO_4, 0.5\ M$ NaF	9.9×10^{-3}
Benzyl alcohol[121]	Dichloromethane	6.5×10^{-3}
Benzyl methyl ether[121]	Dichloromethane	4.9×10^{-4}

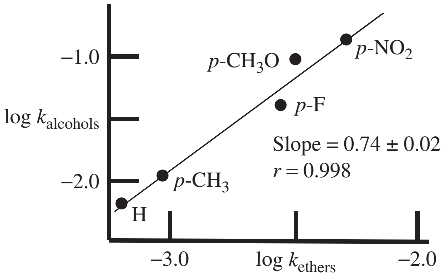
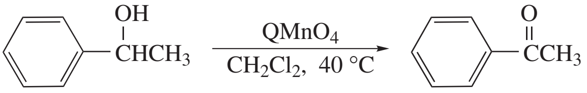
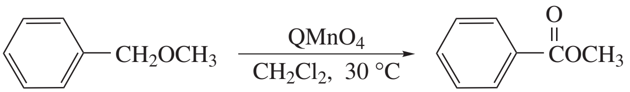


FIGURE 6. A comparison of the rate constants for the oxidation of substituted benzyl alcohols with those of the corresponding benzyl methyl ethers

methyl ether. As indicated by the data summarized in Figure 6, substituents have an almost identical impact on the relative rates of oxidation of both alcohols and ethers[121].



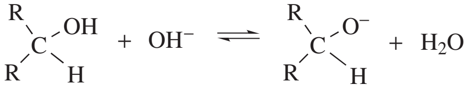
(66)



(67)

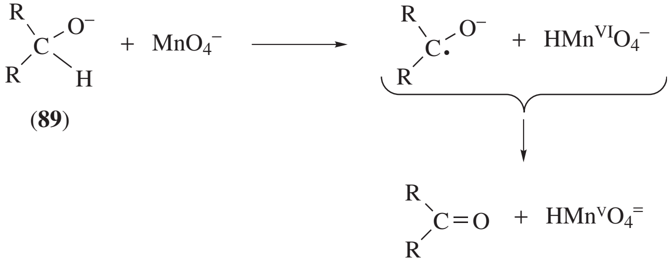
Primary kinetic isotope effects are observed for the oxidation of both alcohols[124] and ethers[125] indicating that the rate-limiting step in both reactions is cleavage of the α-C−H bonds. Other oxidants, such as ruthenium tetroxide, that readily oxidize both alcohols and ethers have also been reported to react by α-C−H bond cleavage[126]. There is, however, one major way in which the reaction of ruthenium tetroxide with alcohols differs from that of permanganate; the mechanism for ruthenium tetroxide oxidations is initiated by a hydride transfer [127], whereas oxidations of alcohols by permanganate involve the transfer of a hydrogen atom[106], i.e. a free radical process, likely reminiscent of the mechanism for the reaction of permanganate with arenes.

The rates of oxidation of alcohols by permanganate are subject to base catalysis[3, 124], suggesting that alkoxide ions (**89**) are likely intermediates, as in equations 68 and 69.



(**89**)

(68)



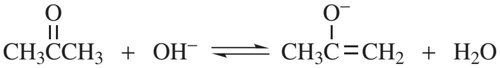
(**89**)

(69)

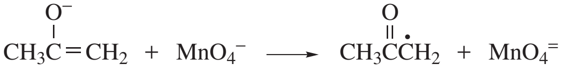
Base catalysis is observed because the oxidation of anions to radical anions is a very facile reaction[3]. Base catalysis would not be expected for the oxidation of ethers because they do not possess acidic hydrogen atoms[128].

I. The Oxidation of Ketones and Aldehydes by Permanganate

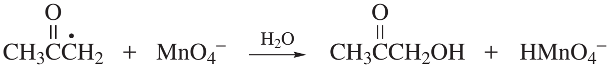
Current evidence with respect to the oxidation of aliphatic ketones and aldehydes by permanganate under basic conditions indicates that the corresponding enolate ions are the primary reductants. For example, the reaction sequence in equations 70–72 has been suggested for the oxidation of acetone in approximately 0.1 M hydroxide[129].



$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + OH^- \rightleftharpoons CH_3\overset{\overset{O^-}{|}}{C}{=}CH_2 + H_2O \qquad (70)$$



$$CH_3\overset{\overset{O^-}{|}}{C}{=}CH_2 + MnO_4^- \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\dot{C}H_2 + MnO_4^{=} \qquad (71)$$

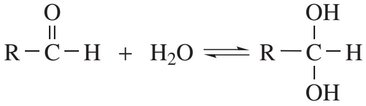


$$CH_3\overset{\overset{O}{\|}}{C}\dot{C}H_2 + MnO_4^- \xrightarrow{H_2O} CH_3\overset{\overset{O}{\|}}{C}CH_2OH + HMnO_4^- \qquad (72)$$

The mechanism for the oxidation of aldehydes (such as benzaldehyde) that cannot enolize has been subjected to greater scrutiny. Under basic conditions the rate law (equation 73) for such reactions has been found to include terms that are zero order, first order and second order in hydroxide ion concentration[130].

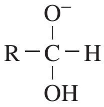
$$\text{Rate} = k_1[\text{Aldehyde}][\text{KMnO}_4] + k_2[\text{Aldehyde}][\text{KMnO}_4][\text{OH}^-] + k_3[\text{Aldehyde}][\text{KMnO}_4][\text{OH}^-]^2 \qquad (73)$$

In aqueous solutions aldehydes are known to exist in equilibrium with their corresponding hydrates, **90** (equation 74)[131]. The last two terms in the rate law (which are first order and second order in [OH$^-$], respectively) indicate the likely involvement of an anion, **91**, and a dianion, **92**, as reductants[130].



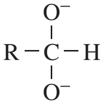
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O \rightleftharpoons R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H \qquad (74)$$

(**90**)



$$R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-H$$

(**91**)



$$R-\underset{\underset{\displaystyle O^-}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-H$$

(**92**)

Stewart and Mocek[132] have made a thorough study of this reaction using fluoral (trifluoroacetaldehyde) as a model reductant. As indicated in equation 75, fluoral is known to exist almost entirely as a hydrate in aqueous solutions. Furthermore, its first and second ionizations occur in accessible regions making it possible to study the reactions of its mono- and dianions (see Table 7).

$$2\,MnO_4^- + CF_3CH(OH)_2 + 3\,OH^- \longrightarrow 2\,MnO_4^= + CF_3CO_2^- + 3\,H_2O \qquad (75)$$

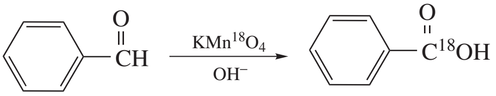
The observed primary kinetic isotope effects for the mono- and dianions indicate that C$-$H bond cleavage occurs as the reactions pass through the transition states. The entropy of activation is very unfavorable: -77 kJ mol^{-1} for oxidation of the monoanion and -130 kJ mol^{-1} when the reductant is the dianion, possibly because both the oxidant and the reductants bear negative charges. However, a low enthalpy of activation for the oxidation of the anions results in lower overall activation free energies ($\Delta G^{\mp}$) and faster reactions. This is consistent with the observation made in the previous section which indicated that alkoxide ions reacted with permanganate much faster than the corresponding neutral alcohol[3].

Oxygen-18 was found in the product, benzoic acid (**94**), when benzaldehyde (**93**) was oxidized by permanganate labeled with oxygen-18 (equation 76). Under approximately neutral conditions ($pH = 5.5$) 76% of the labeled oxygen was transferred. However, under basic conditions ($pH = 12.4$) incorporation of the labeled oxygen was reduced to 26.4%[133].

TABLE 7. Data for the oxidation of fluoral hydrate by potassium permanganate[132]

Reductant	$\Delta H^{\mp}$ (kJ mol^{-1})	$\Delta S^{\mp}$ (J K^{-1} mol^{-1})	$\Delta G^{\mp}$(kJ mol^{-1})	k_H/k_D^a
$CF_3CH(OH)_2$			large	
$CF_3CH(OH)O^-$	52	-77	75	10
$CF_3CH(O^-)_2$	28	-130	67	5

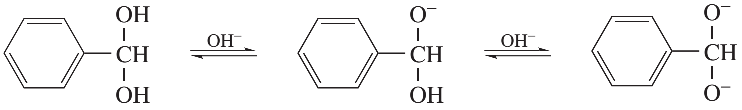
[a] Second-order rate constants for the oxidation of anions derived from $CF_3C\mathbf{H}(OH)_2$ and $CF_3C\mathbf{D}(OH)_2$.



(**93**) (**94**)

(76)

Using a combination of experimental and theoretical approaches, Wiberg and Freeman[130] have analyzed four possible mechanisms for the oxidation of benzaldehyde hydrate (**95**). They assumed that the active reductants were the corresponding anion (**96**) and dianion (**97**) formed under basic conditions (equation 77).

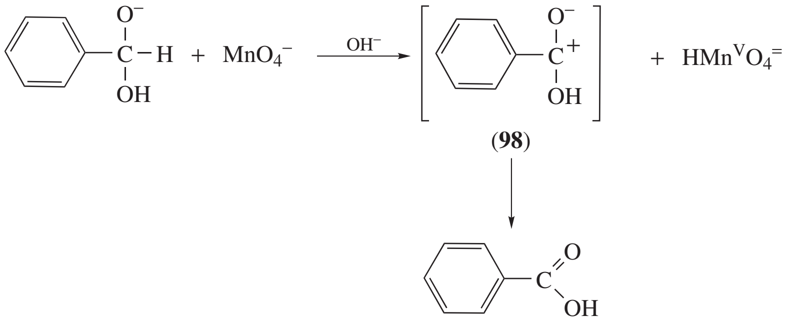


(**95**) (**96**) (**97**)

(77)

They then critically evaluated the following mechanisms.

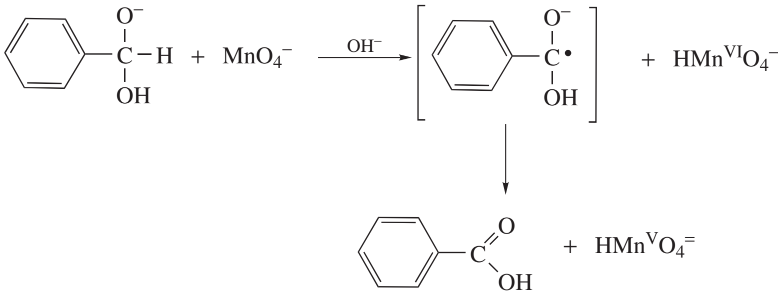
A hydride transfer mechanism (equation 78):



(**98**)

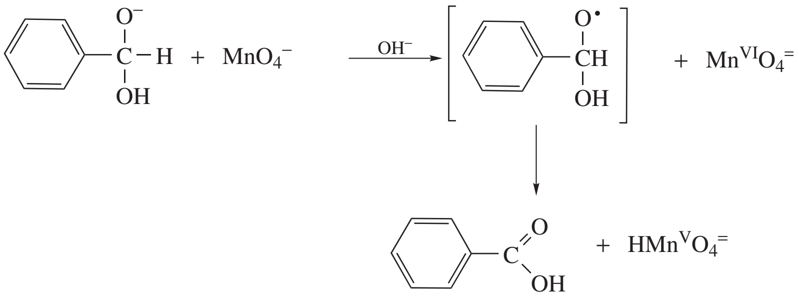
(78)

A hydrogen atom transfer mechanism (equation 79):



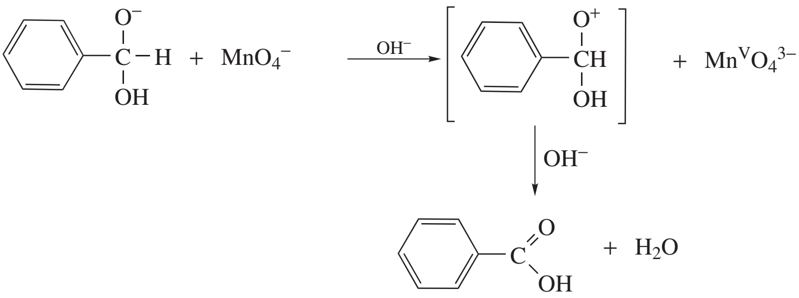
(79)

A single electron transfer mechanism (equation 80):



(80)

A double electron transfer accompanied by loss of a proton (equation 81):

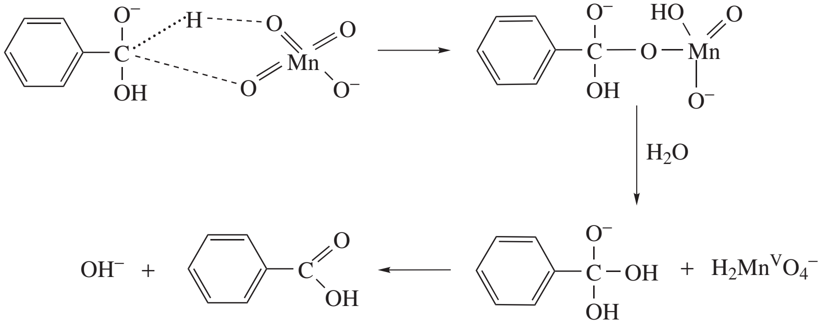


(81)

A hydride transfer mechanism (equation 78) was considered to be unlikely because the results of a linear free energy study indicate that the rate of the reaction is not sensitive to electronic effects exerted by substituents on the aromatic ring. If the first intermediate was a carbocation, such as **98**, the introduction of substituents would have caused a large change in reaction rates[134].

A mechanism in which the reaction was initiated by a single electron transfer (equation 80) was eliminated because primary kinetic isotope effects have been observed when the aldehyde hydrogen is replaced by deuterium in both fluoral[132] and benzaldehyde[133]. For similar reasons a reaction initiated by a double electron transfer (equation 81) can be eliminated unless proton transfer occurs simultaneously.

Calculations reported by Wiberg and Freeman[130] indicated that the dissociation energy for the C−H bond in benzaldehyde hydrate (**95**) is 381 kJ mol^{-1}—about the same as that of toluene. The corresponding bond dissociation energies for the anion and dianion were calculated to be much lower: 285 kJ mol^{-1} for **96** and 193 kJ mol^{-1} for **97**. Although a definitive mechanism has not emerged from these studies, the inverse relationship between bond dissociation energies and reaction rates is consistent with a mechanism initiated by homolytic C−H bond cleavage (equation 79). The incorporation of oxygen-18 in the product when benzaldehyde is oxidized by $KMn^{18}O_4$ suggests that a mechanism similar to that previously proposed for the oxidation of arenes might pertain[38, 40, 43]. In that mechanism, the transfer of a hydrogen atom to an oxygen atom of permanganate is assisted by a second oxygen atom that helps to stabilize the incipient free radical, eventually resulting in the incorporation of oxygen from the oxidant into the product, as in equation 82.



(82)

J. Heterogeneous Oxidations

Potassium permanganate is very soluble in water, making it an excellent oxidant for water-soluble reductants and for use in water-purification plants[135]. However, its lack of solubility in nonpolar solvents has decreased its value as an oxidant for organic compounds that have low solubility in water. In response to this limitation, attempts have been made to use polar organic solvents such as ethanol[136], *tert*-butyl alcohol[69] or acetone[137, 138], but with limited success. Greater use has been made of phase transfer technology where the oxidant is a quaternary ammonium or phosphonium permanganate[4].

It has also been found possible to employ permanganate salts under heterogeneous conditions in nonpolar solvents such as toluene or methylene chloride[20–27]. Hydrated sodium[139] or copper[22, 140] permanganates have been used successfully as heterogeneous oxidants in nonpolar solvents. Improved reactivity and/or selectivity can often be obtained by adsorbing potassium permanganate onto a solid support before it is used as a heterogeneous oxidant. Alumina[20, 26, 27, 141, 142], silica gel[21, 24] and molecular sieves[25] have been used as solid supports. However, the most useful solid support seems to be hydrated copper sulfate ($CuSO_4•5H_2O$)[143, 144]. Although there isn't any information in the literature that indicates why this material is such a useful solid support, it is known that the water of hydration is important—anhydrous copper sulfate is not a satisfactory solid support for permanganate oxidations[143].

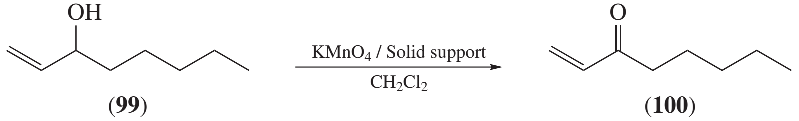
Some examples of heterogeneous oxidations using potassium permanganate adsorbed on a solid support are summarized in Table 8. An examination of these data indicates that the products obtained from a particular reductant can be modified by choice of an appropriate solid support. For example, when copper sulfate pentahydrate is used as the solid support, carbon–carbon double bonds are resistant to oxidation[22]; however, when cyclic alkenes are oxidized by permanganate using moist alumina or silica gel as solid supports, for example, the products are dialdehydes[141] and dicarboxylic acids[21], respectively.

In addition to enhancing the reactivity of permanganate, use of solid supports results in a remarkable change in selectivity. Although permanganate preferentially attacks carbon–carbon double bonds under homogeneous conditions, when mild heterogeneous conditions are used, it is possible to oxidize unsaturated alcohols to the corresponding unsaturated carbonyl compounds without disruption of the double bond. For example, as illustrated in equation 83, 1-octen-3-ol (**99**) is converted into 1-octen-3-one (**100**) in good yield[144] (equation 83).

TABLE 8. Some heterogeneous potassium permanganate oxidations

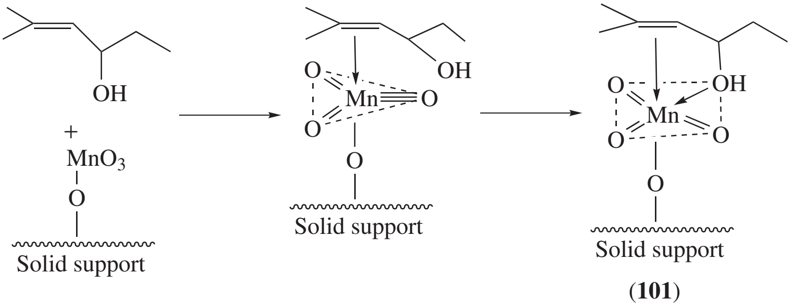
Reductant	Solid support	Product
Benzhydrol[25]	Molecular sieves	Benzophenone (100%)
Cyclododecanol[20]	Alumina	Cyclododecanone (95%)
2-Octanol[143]	Copper sulfate pentahydrate	2-Octanone (96%)
1-Octen-3-ol[144]	Bentonite	1-Octen-3-one (92%)
1-Phenyl-1-buten-3-ol[144]	Copper sulfate pentahydrate	1-Phenyl-1-buten-3-one (90%)
Cyclohexene[21]	Silica gel	Adipic acid (74%)
Cycloheptene[23]	Copper sulfate pentahydrate *tert*-Butyl alcohol	2-Hydroxycycloheptanone (59%)
1-Decene[23]	Copper sulfate pentahydrate *tert*-Butyl alcohol	Nonanoic acid (72%)
Cyclododecene[141]	Moist alumina	12-Oxododecanal (70–76%)
1-Phenylpropene[27]	Alumina	Benzaldehyde (83%)
2-Phenylpropene[27]	Alumina	Acetophenone (98%)
Ethylbenzene[26]	Alumina	Acetophenone (58%)
sec-Butylbenzene[142]	Moist alumina	2-Phenyl-2-butanol (78%)
5-Methoxyindane[142]	Copper sulfate pentahydrate	5-Methoxy-1-indanone (98%)
Diphenylethyne[145]	Silica gel[a]	Benzil (67%)
Tetrahydrofuran[145]	Silica gel[a]	Butyrolactone (52%)
Dibutyl sulfide[146]	Copper sulfate pentahydrate	Dibutyl sulfone (100%)
Butane-1-thiol[147]	Copper sulfate pentahydrate	Dibutyl disulfide (98%)
Diphenyl selenide[146]	Copper sulfate pentahydrate	Diphenyl selenone (50%)

[a] The oxidant was zinc permanganate[145].

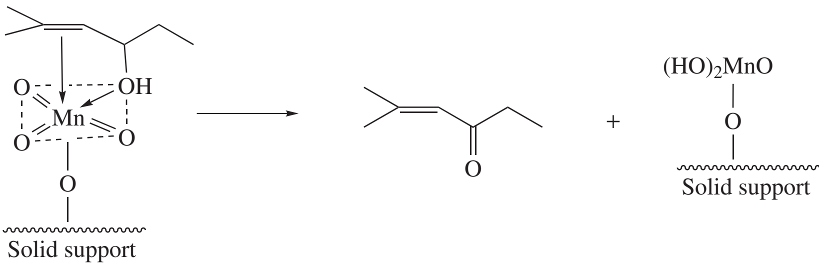


(83)

The oxidation of allylic alcohols has been explained by suggesting that manganese forms a complex with the double bond and concurrently brings the hydroxyl group into its coordination shell, as in equation 84[22]. This intermediate (**101**) then undergoes a redox decomposition giving the products indicated in equation 85. The fact that nonallylic unsaturated alcohols are resistant to oxidation under these conditions is consistent with this mechanism[22].



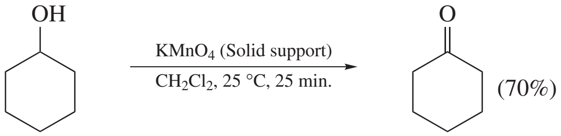
(84)



(**101**)

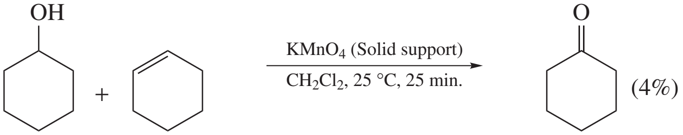
(85)

The suggestion that solid supported permanganate forms a complex with carbon–carbon double bonds is also consistent with the observation that the presence of alkenes interferes with the oxidation of alcohols. For example, as indicated in equations 86 and 87, the presence of an equimolar amount of cyclohexene, **104**, reduces the yield of cyclohexanone, **103**, obtained from the oxidation of cyclohexanol, **102**, from 70% to 4%[22].



(**102**) (**103**)

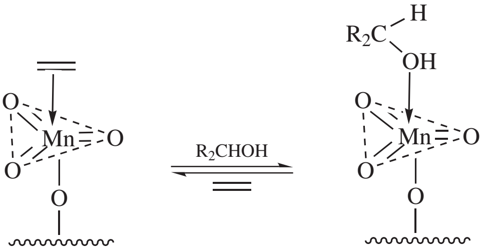
(86)



(**102**) (**104**) (**103**)

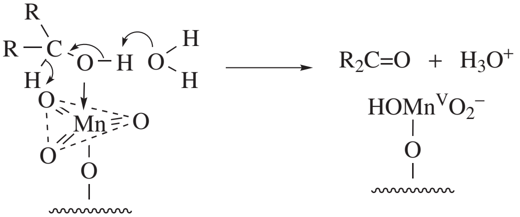
(87)

The extent of reaction therefore appears to be controlled by an equilibrium (equation 88) between complexes **105** and **106**, with **105** being unreactive. The process by which **106** is converted into products can be visualized as in equation 89.



(**105**) (**106**)

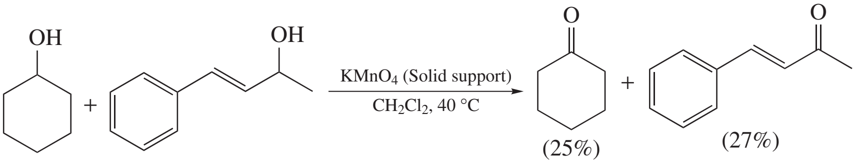
(88)



(89)

The mechanism for alcohol oxidation (equation 89) is also consistent with the observations that a primary kinetic isotope effect is observed when the rate constants for the oxidation of $PhCH_2OH$ and $PhCD_2OH$ are compared[148] and that the reaction is relatively insensitive to the electronic effect of substituents (ρ *ca* 0.3 for the oxidation of substituted benzyl alcohols)[148].

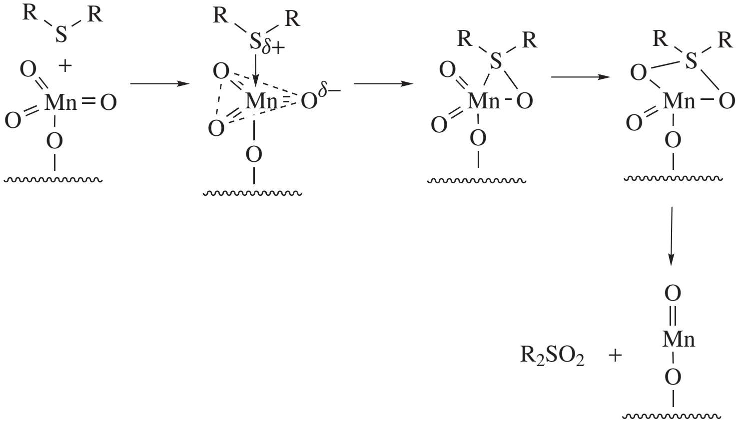
The suggestion that the oxidant forms a complex with carbon–carbon double bonds is also consistent with the observation that allylic alcohols are as readily oxidized when solid supported permanganate is treated with equimolar amounts of a saturated alcohol, **107**, and an allylic alcohol, **108**, as in equation 90[22]. This result is all the more surprising because saturated alcohols are more readily oxidized than allylic alcohols in separate, noncompetitive reactions.



(**107**) (**108**)

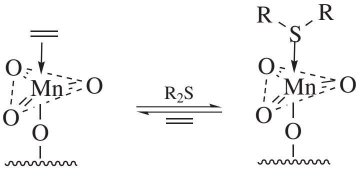
(90)

Sulfides are readily oxidized to the corresponding sulfones by permanganate adsorbed on solid supports[140, 146]. The proposed mechanism for this reaction is summarized in equation 91. Sulfoxides, which are also oxidized to sulfones under identical conditions, may be reaction intermediates; however, they are detected in only trace amounts during the oxidation of sulfides and it is not clear if they are by-products or intermediates[146].



(91)

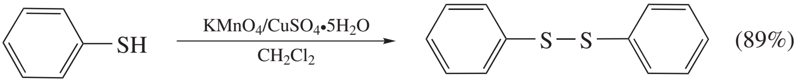
The oxidation of sulfides is also greatly inhibited when alkenes are present[146]. For example, the presence of an equimolar amount of cyclohexene reduces the yield of dibutyl sulfone from 96% to 7% when dibutyl sulfide is oxidized by permanganate adsorbed on copper sulfate pentahydrate. The inhibition is likely due to formation of an unreactive complex (**109**) that is reminiscent of the one proposed to account for the inhibition of alcohol oxidation by alkenes in equation 88. An unfavorable equilibrium between **109** and **110**, as depicted in equation 92, accounts for the observed inhibition by cyclohexene.



(**109**) (**110**)

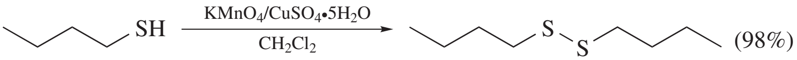
(92)

Although sulfides are oxidized by permanganate to the same products (sulfones) under both homogeneous and heterogeneous conditions, the products obtained from the oxidation of thiols are dramatically different. Under homogeneous conditions thiols are converted into sulfonic acids, while under heterogeneous conditions the products are disulfides[147]. Oxidation of both aromatic thiols (**111**) and aliphatic thiols (**113**) by permanganate adsorbed on a solid support gives the corresponding disulfides, **112** and **114** (equations 93 and 94)[147].



(**111**) (**112**)

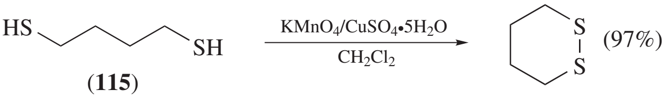
(93)



(**113**) (**114**)

(94)

The process is particularly useful for the preparation of cyclic disulfides, such as **116** from the corresponding dithiol (**115**) (equation 95)[147].



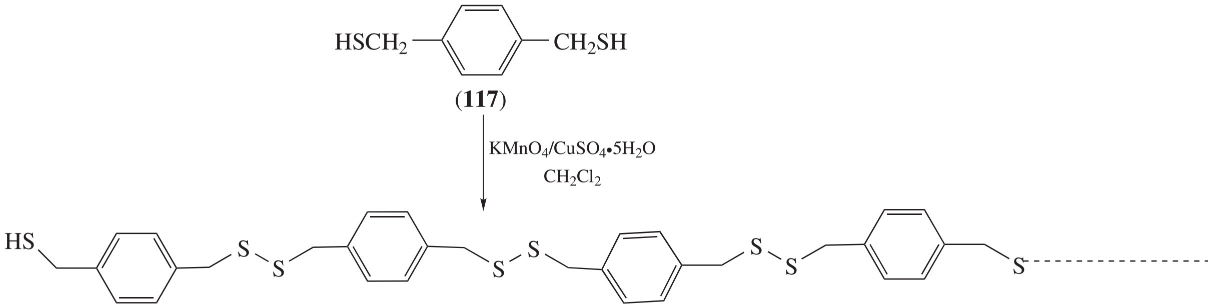
(**115**) (**116**)

(95)

The reaction of rigid dithiols such as **117**, which cannot form cyclic disulfides, results in the formation of a polymer with the proposed structure of **118**, as illustrated in equation 96[147].

The side chains of arenes are oxidized when treated with supported permanganate under heterogeneous conditions. Although the reactions are slow, good yields are usually obtained[26]. If the carbon atom attached to the aromatic ring is secondary, a ketone (**119**) is obtained (equation 97); if it is tertiary, an alcohol is formed (**120**) (equation 98).

Other examples of arene oxidations are summarized in Table 9.



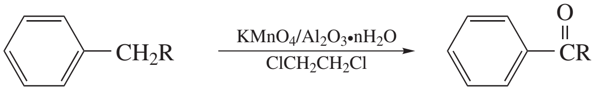
(**117**)

(**118**)

(96)

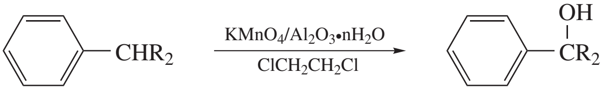
TABLE 9. Heterogeneous oxidations of arenes[26, 142]

Arene	Solid support	Product (yield)
Toluene	Moist alumina	Benzaldehyde (30%)
4-Nitrotoluene	Moist alumina	No reaction
Ethylbenzene	Copper sulfate pentahydrate	Acetophenone (95%)
Propylbenzene	Copper sulfate pentahydrate	Ethyl phenyl ketone (90%)
Butylbenzene	Copper sulfate pentahydrate	Propyl phenyl ketone (88%)
Diphenymethane	Copper sulfate pentahydrate	Benzophenone (95%)
Indane	Copper sulfate pentahydrate	1-Indanone (78%)
5-Methoxyindane	Copper sulfate pentahydrate	5-Methoxy-1-indanone (98%)
5-Nitroindane	Copper sulfate pentahydrate	No reaction
Tetralin	Copper sulfate pentahydrate	1-Tetralone (95%)
Phthalan	Copper sulfate pentahydrate	Phthalide (95%)
2,3-Dihydrobenzofuran	Copper sulfate pentahydrate	No reaction



(**119**)

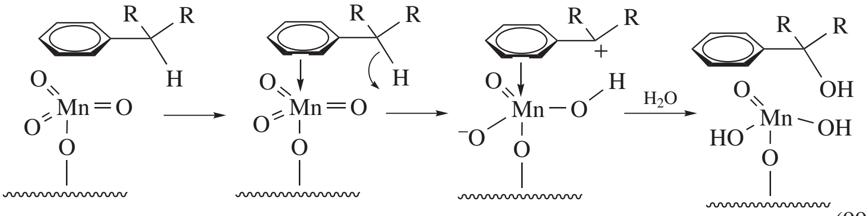
(97)



(**120**)

(98)

The data obtained for the oxidation of substituted indanes indicate that methoxy substituents on the aromatic ring activate the reaction and are *para* directing, whereas a nitro group completely deactivates the reductant[142]. On the basis of this information, it has been proposed that the reaction mechanism likely involves a hydride transfer, as outlined in equation 99[142].



(99)

The observed unreactivity of 4-nitrotoluene is also consistent with a mechanism involving hydride transfer in the rate-limiting step. A high sensitivity to electronic effects may also explain why phthalan is readily oxidized, whereas its isomer, 2,3-dihydrobenzofuran, is completely resistant to oxidation.

A good understanding of the way in which permanganate and the various solid supports interact and why different products are obtained with different supports has yet to be achieved. Two groups of researchers have found evidence that the oxidant and the solid support are not chemically bound; permanganate appears to be physisorbed[24, 149]. An IR band that is found at 900 cm^{-1} in solid $KMnO_4$ is split into two weaker bands at 910 cm^{-1} and 930 cm^{-1} when it is adsorbed onto silica gel, suggesting that two of the permanganate oxygen atoms may be interacting with the solid support[24].

Some permanganate salts can be used as heterogeneous oxidants without solid supports. For example, similar results are obtained from the use of either $KMnO_4$ with $CuSO_4{\bullet}5H_2O$ as the solid support or $Cu(MnO_4)_2{\bullet}7H_2O$ without a solid support[22, 140]. However, the cost associated with the preparation of copper permanganate has resulted in greater use being made of the solid supported system.

Solid $NaMnO_4{\bullet}H_2O$ has also been used as an efficient and selective oxidant[139]. Zinc and magnesium permanganates, on the other hand, are so reactive that they cause solvents such as tetrahydrofuran, methanol, ethanol, acetone and acetic acid to burst into flame[145]. However, when adsorbed on silica gel, zinc permanganate is a very reactive oxidant that can be used safely with methylene chloride as the solvent[145].

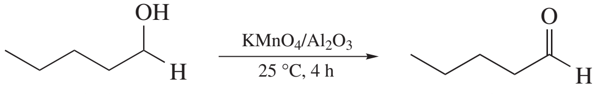
K. Solvent-free Oxidations

The use of solvent-free reactions is an emerging technology that is driven primarily by a wish to reduce costs and environmental impacts associated with chemical processes[150]. In the last decade a number of such reactions have been discovered and studied. The usefulness of permanganate in solvent-free reactions has been introduced, but as yet not extensively applied. However, the results reported to date for solvent-free permanganate oxidations have been encouraging, both for the yields obtained and the increased selectivity realized in some reactions[28].

Experimentally, potassium permanganate is first combined with a solid support similar to those used for the heterogeneous reactions described in the previous section. For example, alumina, silica gel, bentonite, manganese sulfate, manganese dioxide and copper sulfate have been used effectively as solid supports. Once the oxidant and the solid support have been thoroughly mixed, the reductant is added and the reaction is allowed to proceed as the vessel is slowly rotated to promote continuous mixing. The product is then extracted from the solid using an appropriate solvent.

Although the reactions are carried out under solvent-free conditions, it is necessary to use solvent to separate the products from the reduced oxidant and the solid support. However, the amount of solvent required for the entire process is usually much less compared to a corresponding homogeneous reaction. Furthermore, the solvent does not undergo as much degradation when used only as an extractant in the solvent-free processes.

The products obtained from the oxidation of alcohols, arenes, alkenes, ethers, sulfides, thiols and amines have been described in the literature[29, 30]. Although secondary alcohols are converted into ketones as expected, the products obtained from primary alcohols are aldehydes rather than the expected carboxylic acids[29]. As illustrated in equations 100 and 101, both aliphatic and aromatic primary alcohols (**121** and **123**) are oxidized to the corresponding aldehydes (**122** and **124**) in good yields under solvent-free conditions. Other typical reactions are summarized in Table 10.

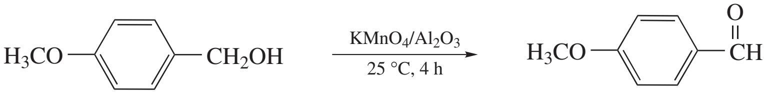


(**121**) (**122**) (100)

TABLE 10. Solvent-free oxidations

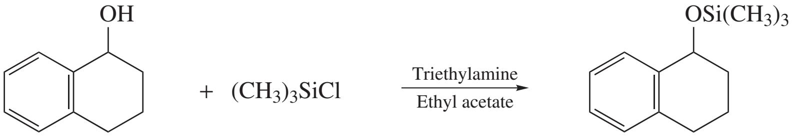
Reductant	Oxidant	Product
2-Cyclohexylethanol[29]	$KMnO_4/Al_2O_3$	2-Cyclohexylethanal (85%)
Heptanol[36]	$KMnO_4/MnO_2$	Heptanal (93%)
3-Propenol[35]	$KMnO_4/MnO_2$	Propenal (96%)
1,4-Butanediol[29]	$KMnO_4/CuSO_4{\bullet}5H_2O$[a]	γ-Butyrolactone (95%)
Tetrahydrofuran[29]	$KMnO_4/Al_2O_3/CuSO_4{\bullet}5H_2O$	γ-Butyrolactone (70%)
Dibutyl sulfide[29, 34]	$KMnO_4/CuSO_4{\bullet}5H_2O$	Dibutyl sulfone (90%)
Tetrahydrothiophene[37]	$KMnO_4/MnSO_4{\bullet}H_2O$	Sulfolane (93%)
Thiophenol[29]	$KMnO_4/CuSO_4{\bullet}5H_2O$	Diphenyl disulfide (100%)
Toluene[32]	$KMnO_4$/montmorillonite K10	Benzaldehyde (60%)
Indane[29]	$KMnO_4/CuSO_4{\bullet}5H_2O$	1-Indanone (90%)
Diphenylmethane[33]	$KMnO_4/Al_2O_3$[a]	Benzophenone (97%)
Ethylbenzene[151]	$KMnO_4$/ion exchange resin	Acetophenone (91%)
Aniline[29]	$KMnO_4/CuSO_4{\bullet}5H_2O$[a]	Azobenzene (75%)
3-Chloro-2-buten-1-ol[152]	$KMnO_4$/graphite	3-Chloro-2-butenal (92%)

[a] Microwave assisted reaction.

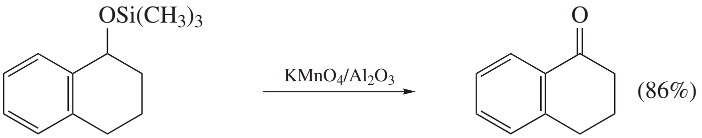


(**123**) (**124**) (101)

Solvent-free processes can also be used effectively to remove protecting groups. For example, trimethylsilyl groups, which are often used to protect alcohols as in **125**, are easily removed. As illustrated by the process summarized in equations 102 and 103, the product is a carbonyl compound[153].

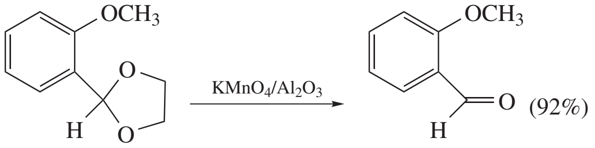


(**125**) (102)



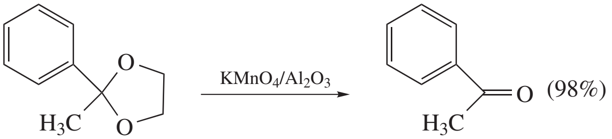
(**125**) (103)

Ethylene acetals and ketals such as **126** and **127** are protected aldehydes and ketones. As illustrated in equations 104 and 105, the protecting groups may be easily removed using permanganate under solvent-free conditions[153].



(**126**)

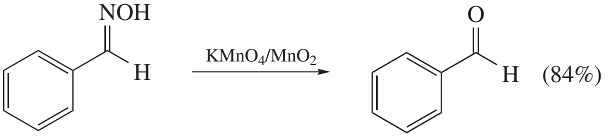
(104)



(**127**)

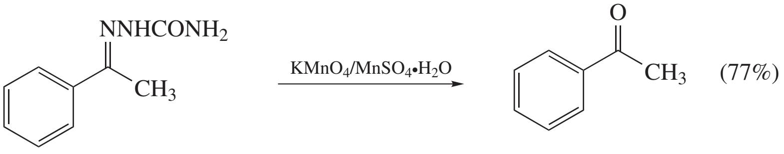
(105)

Imine derivatives of aldehydes and ketones, such as oximes (**128**) and semicarbazones (**129**), are also readily cleaved to give the parent carbonyl compounds as depicted in equations 106 and 107[154].



(**128**)

(106)



(**129**)

(107)

II. OXIDATIONS BY ACTIVE MANGANESE DIOXIDE

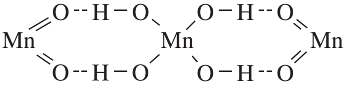
A. Preparation of Active Manganese Dioxide

Active manganese dioxide is an effective and selective oxidant. It is usually prepared by reacting manganese(II) sulfate and potassium permanganate (equation 108) or by the pyrolysis of manganese(II) carbonate or manganese(II) oxalate[6]. Variations in the procedures by which active manganese dioxide is prepared result in the formation of reagents with different selectivities[6, 155–157].

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O \rightleftharpoons 5\,MnO_2 + K_2SO_4 + 2\,H_2SO_4 \qquad (108)$$

In a typical reaction, active manganese dioxide acts as a heterogeneous oxidant in the presence of a reductant dissolved in an organic solvent. The identity of the solvent and the temperature at which the reaction is effected can have an impact on the selectivity observed[6, 155–157].

The exact structure of active manganese dioxide is difficult to define because of its amorphous nature[158]. However, on the basis of the best information available, Fatiadi[159] has proposed **130** as a likely structure for an active form of manganese(IV) oxide.



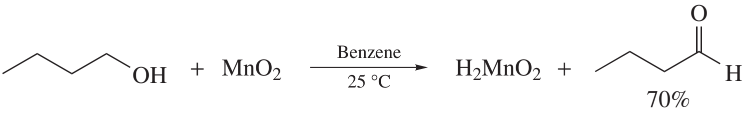
(**130**)

Extensive summaries of the transformations that can be achieved using active manganese dioxide as an oxidant have been published[6, 155, 156, 158]. While heterogeneous permanganate oxidations usually involve the transfer of one or more oxygen atoms to the reductant, active manganese dioxide most often abstracts two or more hydrogen atoms from the reductant. Oxygen transfers are less often observed when manganese dioxide is used as an oxidant.

B. Dehydrogenation Reactions

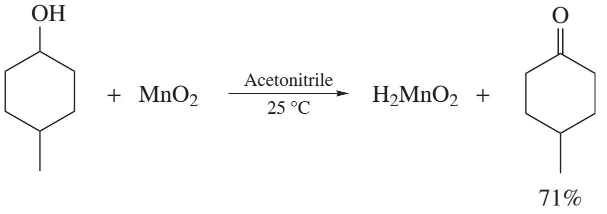
Active manganese dioxide has often been used to dehydrogenate compounds under mild, easily achievable conditions. Some typical examples of compounds that have been dehydrogenated using activated manganese dioxide are presented in equations 109–133.

Primary alcohols[160]:



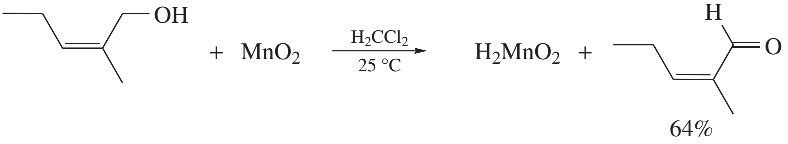
(109)

Secondary alcohols[160]:

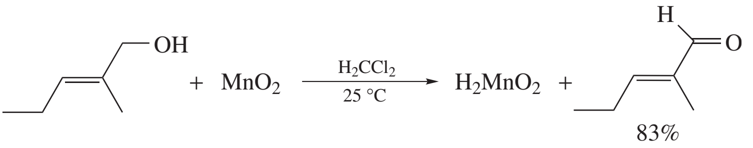


(110)

Allylic alcohols[161]:

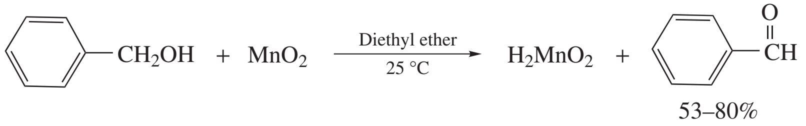


(111)

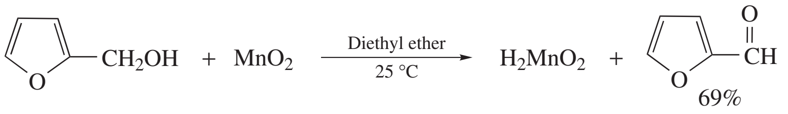


(112)

Aryl alcohols[162]:

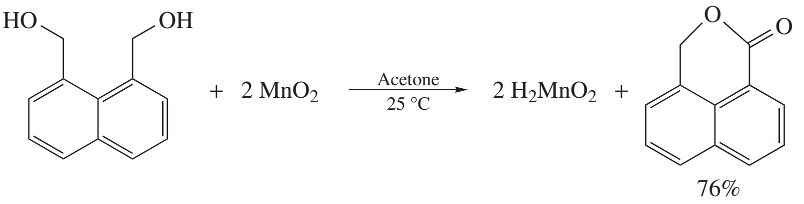


(113)

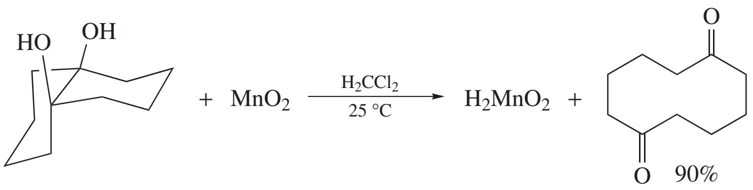


(114)

Diols[163, 164]:

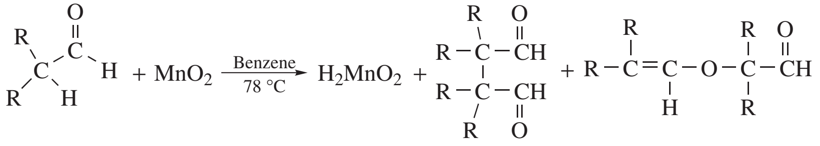


(115)

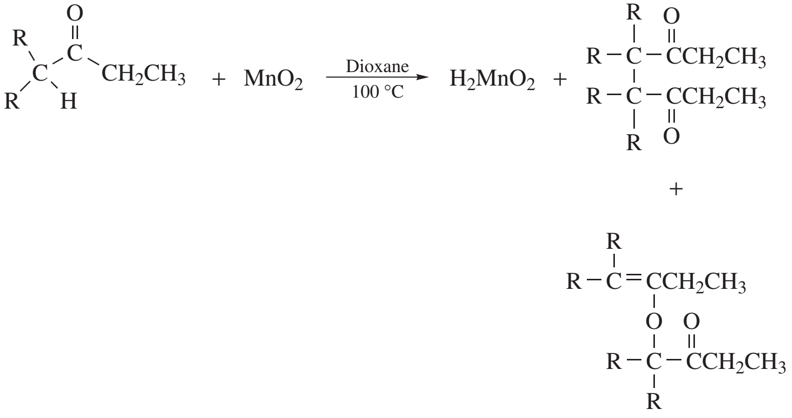


(116)

Aldehydes and ketones[155, 165]:

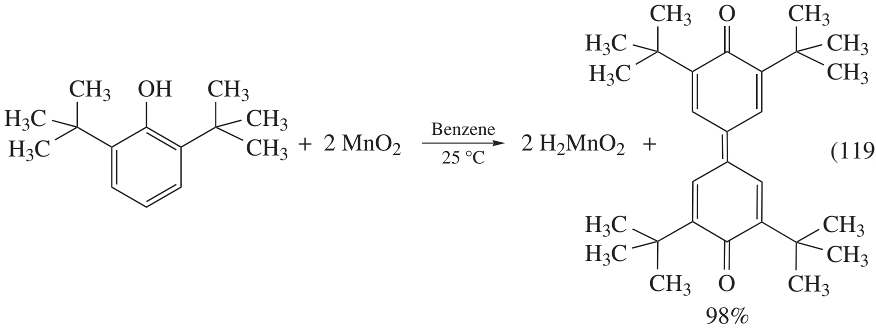


(117)



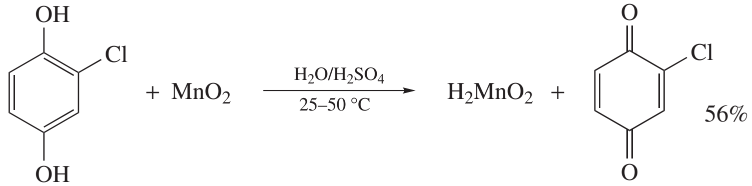
(118)

Phenols[166]:



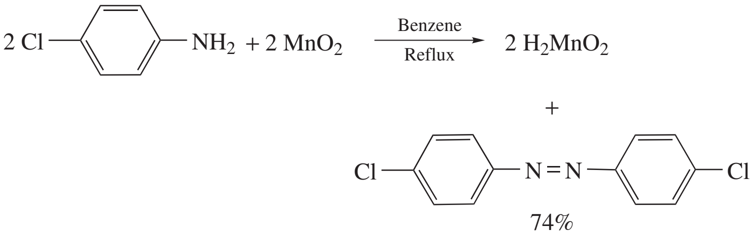
(119)

Hyrdroquinones[167]:

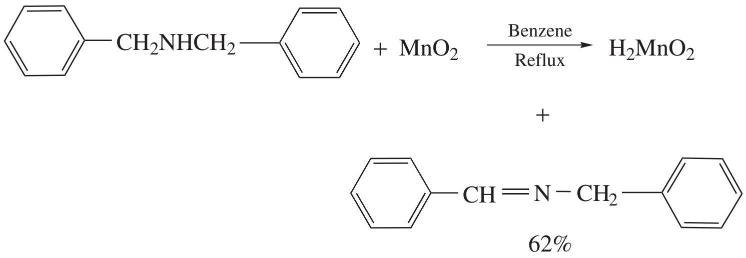


(120)

Amines[168]:

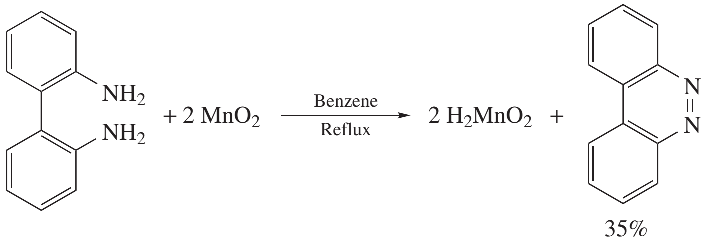


(121)

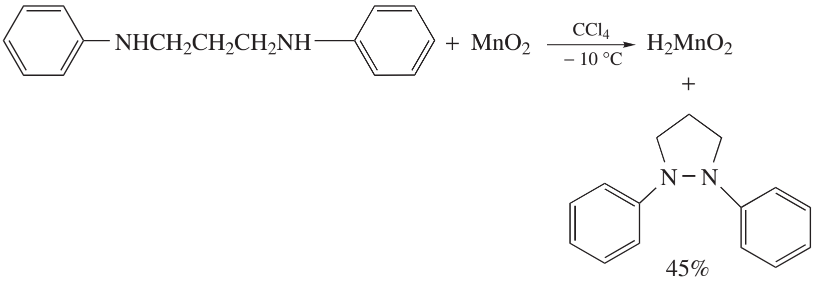


(122)

Diamines[169, 170]:

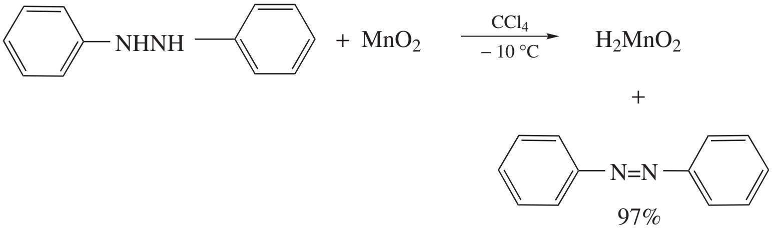


(123)

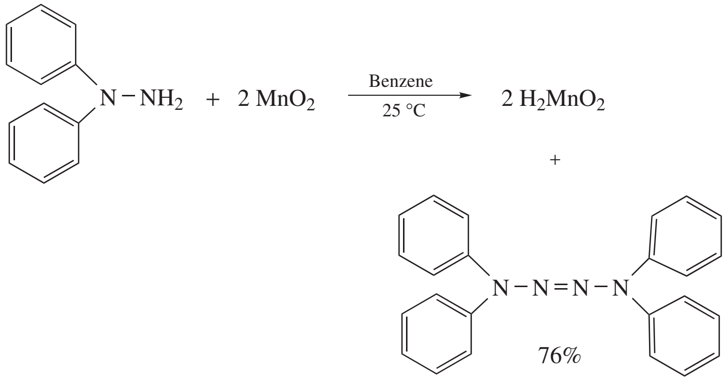


(124)

Hydrazines[168, 169]:

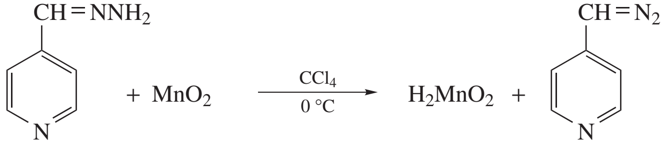


(125)

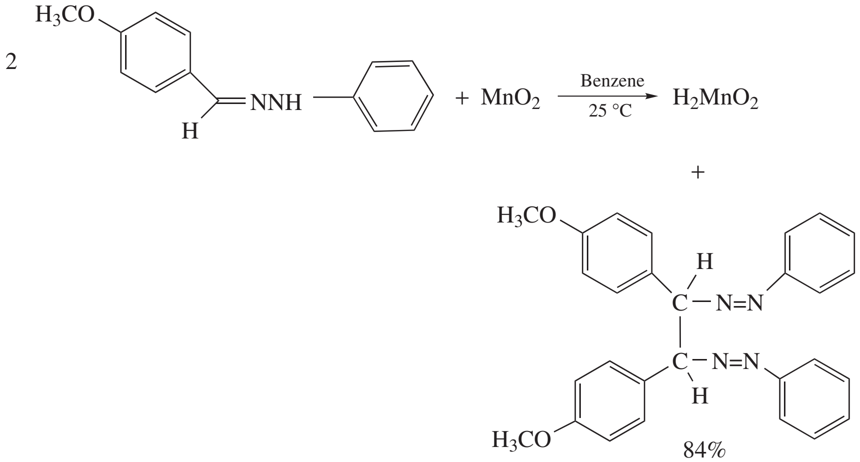


(126)

Hydrazones[171, 172]:

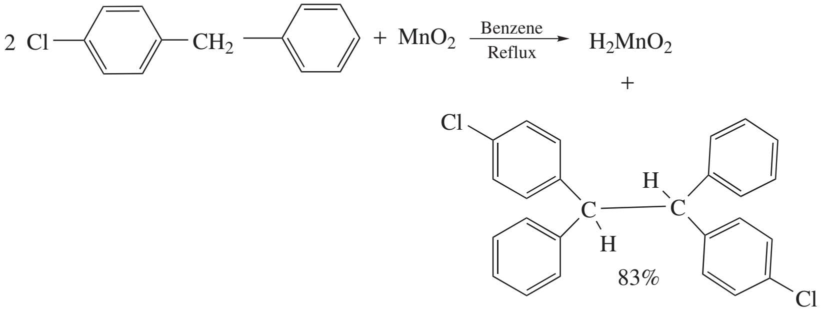


(127)

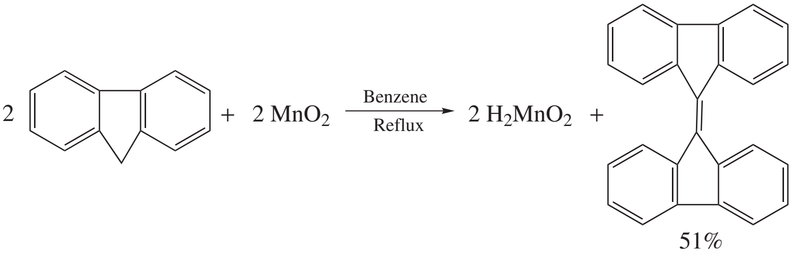


(128)

Arenes[173]:

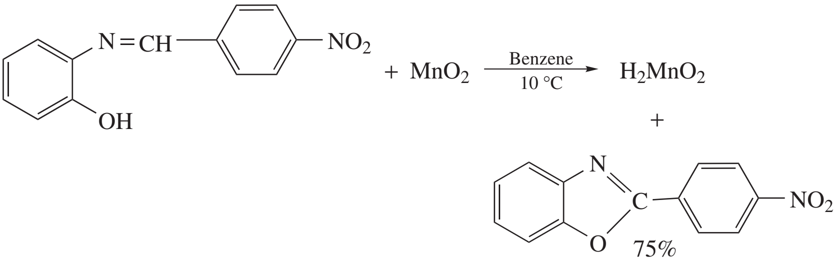


(129)

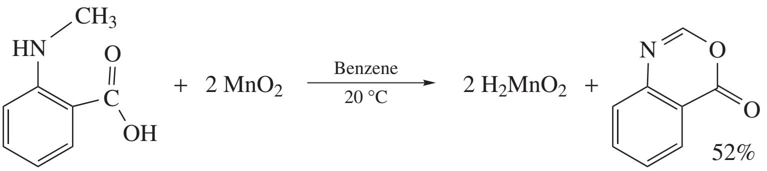


(130)

Formation of heterocycles[174, 175]:

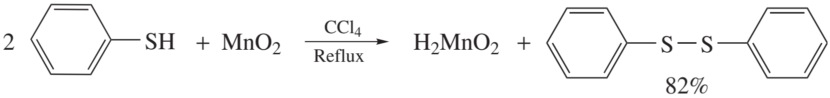


(131)



(132)

Thiols[176]:

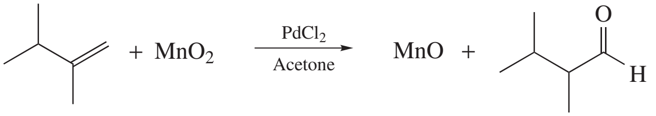


(133)

C. Oxygen Transfer Reactions

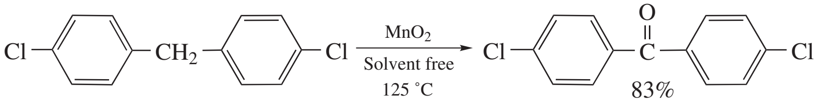
Under certain conditions, and with a limited number of reductants, manganese dioxide has also been observed to act as an oxygen transfer agent[6, 155, 156, 158, 177]. Some typical oxygen transfer reactions are summarized in equations 134–141.

Alkenes[177]:

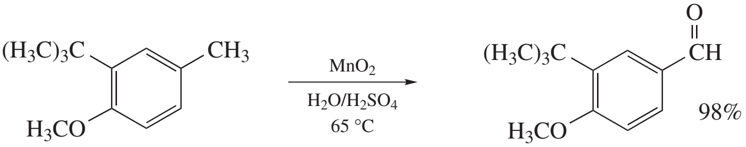


(134)

Arenes[173, 178]:

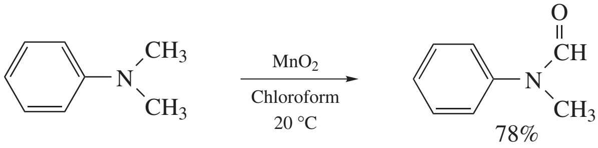


(135)

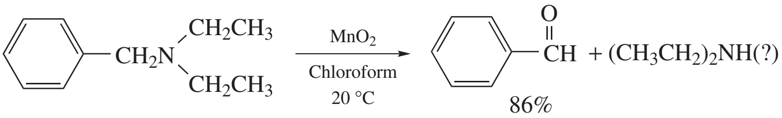


(136)

Amines[179, 180]:

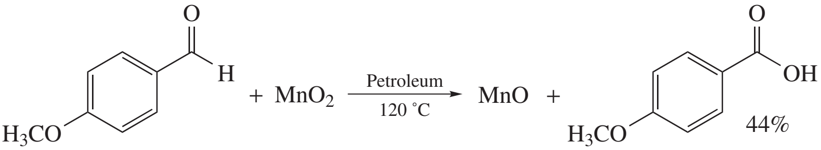


(137)



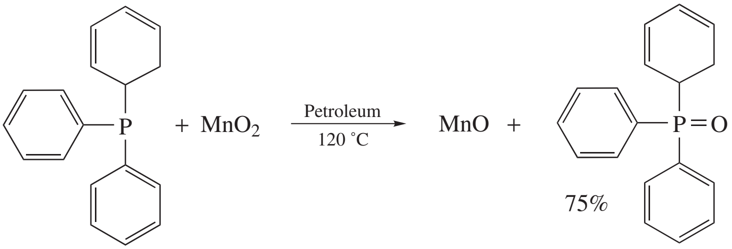
(138)

Aldehydes[181]:



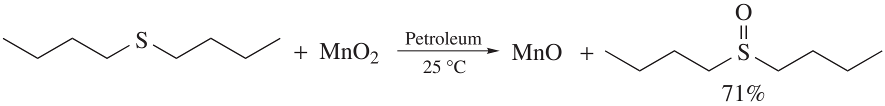
(139)

Triphenylphosphine[181]:



(140)

Sulfides[182]:



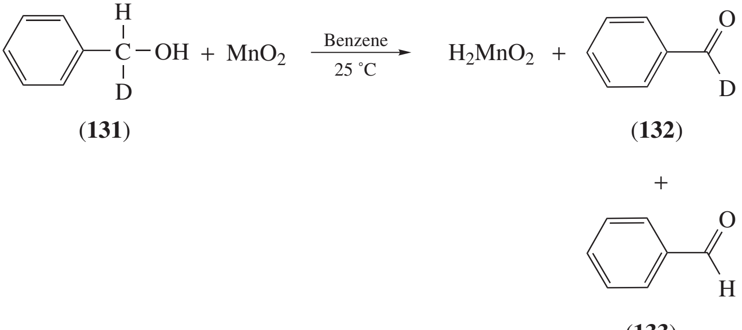
(141)

D. The Reaction Mechanism

The mechanisms of heterogeneous reactions are notoriously difficult to define. Despite this, fragmentary evidence that at least limits the mechanistic possibilities for manganese dioxide oxidations is found in the literature. The available evidence includes:

(i) The prevalence of coupling reactions (as in equations 117, 118, 119, 121, 123, 126, 128, 129, 130 and 133) is consistent with free radical mechanisms for most of the dehydrogenation reactions.

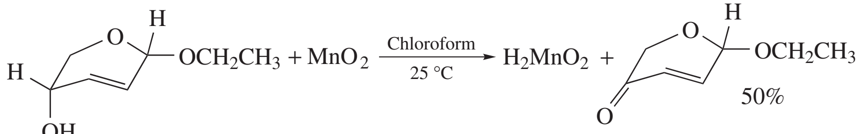
(ii) When α-deuterobenzyl alcohol (**131**) is oxidized, as in equation 142, two products are obtained with **132** in much greater amounts than **133**. From the ratio of **132** to **133**, a primary kinetic isotope effect of 14 has been calculated[183]. This is clear evidence that the rate-determining step for alcohol oxidation is cleavage of a carbon−hydrogen bond.



(**131**) (**132**) (**133**)

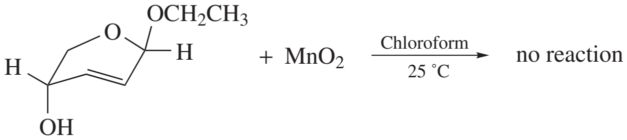
(142)

(iii) Other studies have indicated that oxidations by manganese dioxide are very sensitive to the stereochemistry of the reductants. For example, as illustrated in equations 143 and 144, compound **134** can be easily oxidized to the corresponding ketone (**135**) by manganese dioxide; but, its isomer (**136**) is completely resistant to oxidation under identical conditions[184, 185]. This, and other similar observations, suggests that in order for a reaction to occur the reductant must be adsorbed on the surface of the oxidant in a very specific way.



(**134**) (**135**)

(143)



(**136**)

(144)

From this evidence it appears as if the first step in the reaction mechanism involves adsorption of the reductant on to the oxidant followed by a rate-determining hydrogen atom transfer, producing a free radical (**137**) (equation 145). This radical could then transfer a second hydrogen atom to give a ketone (**138**), or undergo a coupling reaction to give **139** (equation 146).

$$\begin{tikzcd}
\mathrm{ArCH_2Ar} + \mathrm{Mn^{IV}O_2} \rightleftharpoons [\mathrm{Ar_2CH_2{\bullet}Mn^{IV}O_2}] \arrow[r] & \underset{(\mathbf{137})}{\mathrm{Ar_2\dot{C}H}} \arrow[d, "\mathrm{MnO_2}"] & + \ \mathrm{HMn^{III}O_2} \\
 & \underset{(\mathbf{138})}{\mathrm{Ar_2C{=}O}} &
\end{tikzcd} \qquad (145)$$

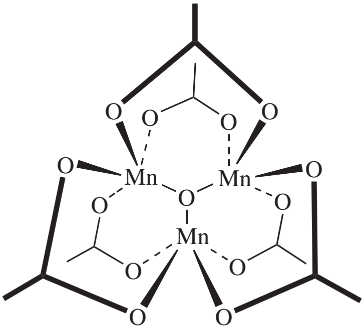
$$2\,\mathrm{Ar_2\dot{C}H} \longrightarrow \underset{(\mathbf{139})}{\mathrm{Ar_2CHCHAr_2}} \qquad (146)$$

III. OXIDATIONS BY MANGANESE(III) ACETATE

A. Preparation and Structure of Manganese(III) Acetate

Manganese(III) acetate dihydrate [$Mn(CH_3CO_2H)_3{\bullet}2H_2O$] is easily prepared by the oxidation of manganese(II) acetate tetrahydrate [$Mn(CH_3CO_2H)_2{\bullet}4H_2O$] with potassium permanganate in glacial acetic acid[6]. Anhydrous manganese(III) acetate is obtained if the preparation is carried out in glacial acetic acid containing about 7% acetic anhydride[6].

The structure of the hydrated form of manganese(III) acetate seems to be satisfactorily portrayed by its chemical formula, $Mn(CH_3CO_2H)_3{\bullet}2H_2O$. However, the structure of anhydrous manganese(III) acetate is much more complex[186]. Crystallographic studies indicate that the monomeric unit consists of three manganese atoms arranged in a planar triangular pattern around an oxygen atom, as in structure **140**. Each manganese atom is also joined to each of the other manganese atoms by double acetate bridges. Additional acetic acid molecules and acetate ions link the monomers giving a polymeric system.



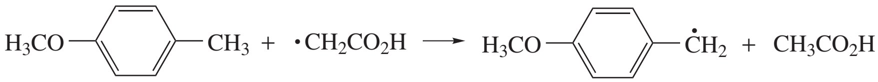
(**140**)

B. Reactions of Manganese(III) Acetate

When a solution of manganese(III) acetate is heated, carboxymethyl free radicals are formed. It isn't clear, as indicated in equation 147, if the radicals are unimolecular (**141**) or part of a more complex system (**142**). Formation of the radicals is accompanied by a reduction of manganese(III) to manganese(II).

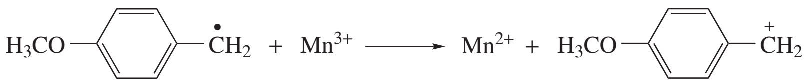
$$\mathrm{Mn(CH_3CO_2H)_2\cdot 2H_2O} \xrightarrow{\mathrm{CH_3CO_2H}} \underset{(\mathbf{141})}{\dot{\mathrm{C}}\mathrm{H_2CO_2H}} \text{ or } \underset{(\mathbf{142})}{\dot{\mathrm{C}}\mathrm{H_2CO_2HMn(CH_3CO_2H)_2}} \qquad (147)$$

It is these radicals (**141** or **142**) that oxidize the reductants. The first step usually involves hydrogen atom abstraction. For example, oxidation of *p*-methoxytoluene is initiated by abstraction of a hydrogen atom from the methyl group (equation 148). Kinetic deuterium isotope effects have demonstrated that this is the rate-limiting step[187]. Loss of an electron from **143** gives a carbocation (**144**), which then reacts with acetate to give the observed product, *p*-methoxybenzyl acetate (**145**) (equations 149 and 150).



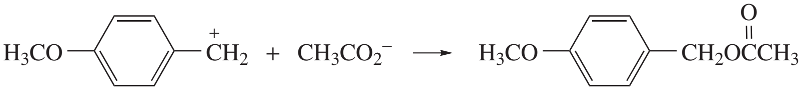
(**143**)

(148)



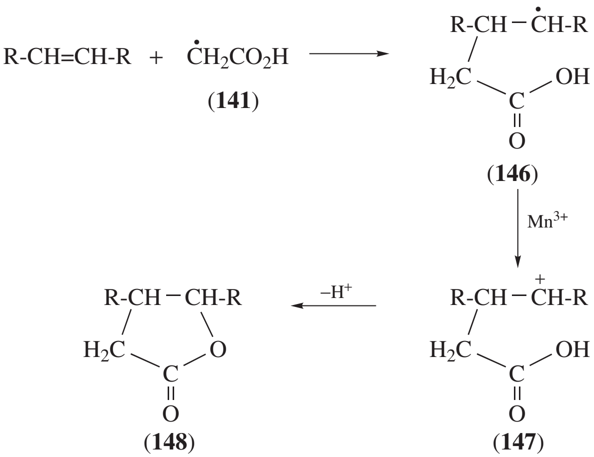
(149)

(**143**) (**144**)



(**144**) (**145**) (150)

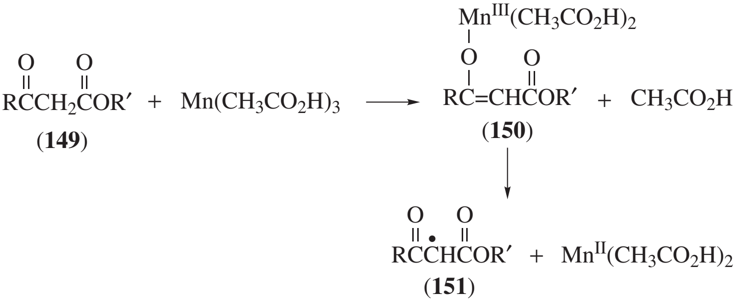
When the reductant is an alkene, the carboxymethyl free radical (**141**) attacks the double bond, forming a new radical (**146**), as in equation 151. Further oxidation produces a carbocation (**147**) that is readily converted into a lactone (**148**) with the loss of a proton[188, 189].



(**141**) (**146**) (**148**) (**147**) (151)

The use of manganese(III) acetate dihydrate as the oxidant gives the highest yields of lactones in these reactions[190]. When acetic anhydride is present in the solvent, yields are decreased, possibly because anhydrous manganese(III) acetate (**140**) is the oxidant under such conditions[190].

The reaction of manganese(III) acetate with β-ketoesters (**149**) results in the formation of metal enolates (**150**) that undergo oxidative decomposition with the formation of free radicals (**151**) and manganese(II) acetate (equation 152).

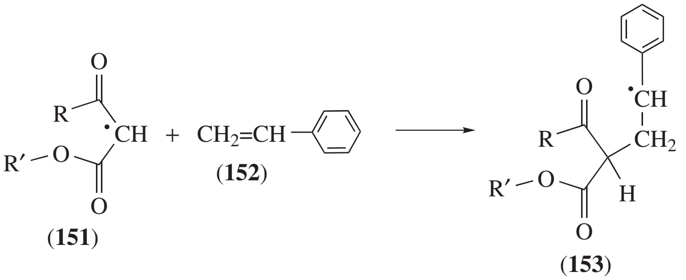


$$\underset{(\mathbf{149})}{\overset{\text{O}\quad\ \ \text{O}}{\text{R}\overset{\|}{\text{C}}\text{CH}_2\overset{\|}{\text{C}}\text{OR}'}} + \text{Mn}(\text{CH}_3\text{CO}_2\text{H})_3 \longrightarrow \underset{(\mathbf{150})}{\overset{\text{Mn}^{\text{III}}(\text{CH}_3\text{CO}_2\text{H})_2}{\text{R}\overset{|}{\underset{}{\text{C}}}(\text{O})\text{=CH}\overset{\|}{\text{C}}(\text{O})\text{OR}'}} + \text{CH}_3\text{CO}_2\text{H} \qquad (152)$$

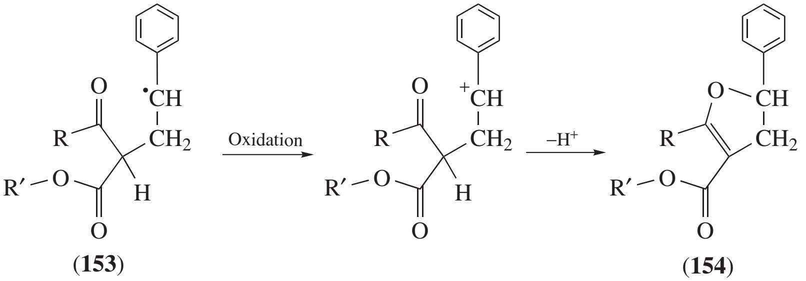
$$\downarrow$$

$$\underset{(\mathbf{151})}{\text{R}\overset{\text{O}}{\overset{\|}{\text{C}}}\dot{\text{C}}\text{H}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OR}'} + \text{Mn}^{\text{II}}(\text{CH}_3\text{CO}_2\text{H})_2$$

If an alkene such as styrene (**152**) is present, it will react with **151** to form a new radical, **153** (equation 153). Oxidation of **153**, followed by cyclization and proton loss (which may occur in one concerted process), then yields a dihydrofuran derivative, **154** (equation 154)[191].


(**151**) (**152**) (**153**)

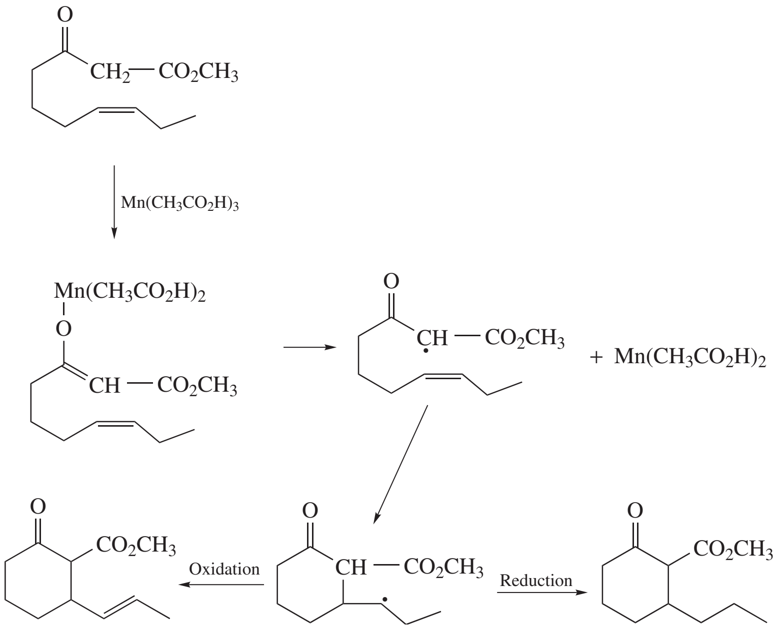
(153)



(**153**) (**154**)

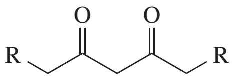
(154)

When the reductant is an unsaturated compound, a variety of intramolecular cyclizations can be realized. One example is summarized in equation 155.

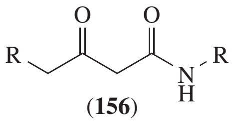


(155)

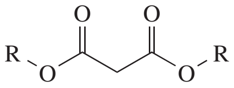
Reactions with other β-dicarbonyl compounds, such as β-diketones (**155**), β-ketoamides (**156**) and malonic esters (**157**), have permitted the synthesis of a large number of heterocyclic compounds. Other potential reductants, such as β-keto carboxylic acids (**158**), β-ketosulfoxides (**159**), β-ketosulfones (**160**) and β-nitroketones (**161**), have seen more limited use.



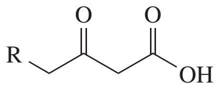
(**155**)



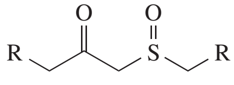
(**156**)



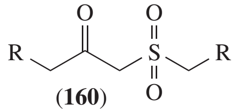
(**157**)



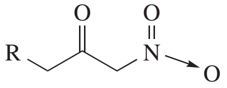
(**158**)



(**159**)



(**160**)



(**161**)

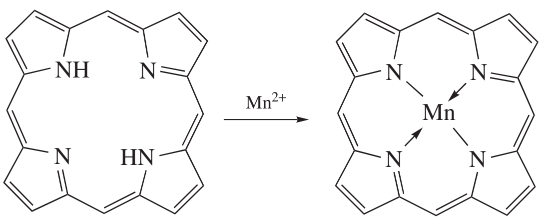
Other specific uses of manganese(III) acetate as an oxidant include the diastereoselective synthesis of substituted pyrrolidinones[192], allylic oxidations[193], aromatic coupling reactions[194, 195], the preparation of α-acetoxyenones[196] and the cyclization of unsaturated ketones[197]. Extensive compilations of products that have been prepared using manganese(III) acetate as an oxidant are available in the literature[6, 191, 196, 198, 199].

IV. OXIDATIONS BY MANGANESE PORPHYRIN AND SALEN COMPLEXES

A. Preparation and Structures of Manganese Porphyrin and Salen Complexes

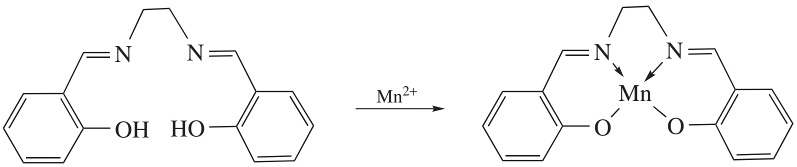
Manganese(II) porphyrin and salen complexes can be prepared by the reaction of manganese(II) acetate tetrahydrate or manganese(II) chloride tetrahydrate with porphyrin (**162**) or salen (**164**) ligands [200, 201] (equations 156 and 157). The products, manganese(II) porphyrin (**163**) or manganese(II) salen (**165**) complexes are easily oxidized to the corresponding manganese(III) complexes, **166** and **167** (equations 158 and 159).

The manganese(III) complexes are approximately flat ions with manganese having square planar geometry[200]. Reaction of **166** or **167** with an oxidant such as *m*-chloroperbenzoic acid (**168**) or iodosylbenzene (**170**) results in formation of the corresponding manganese(V) oxo complexes, **169** and **171** (equations 160 and 161).

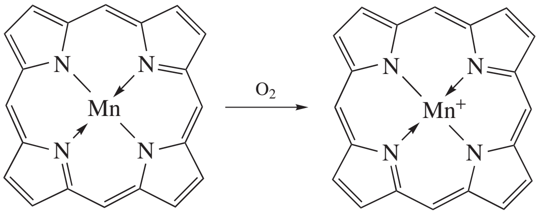


(**162**) (**163**)

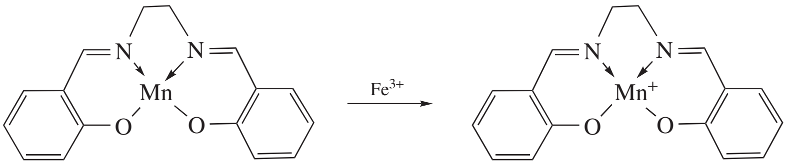
(156)



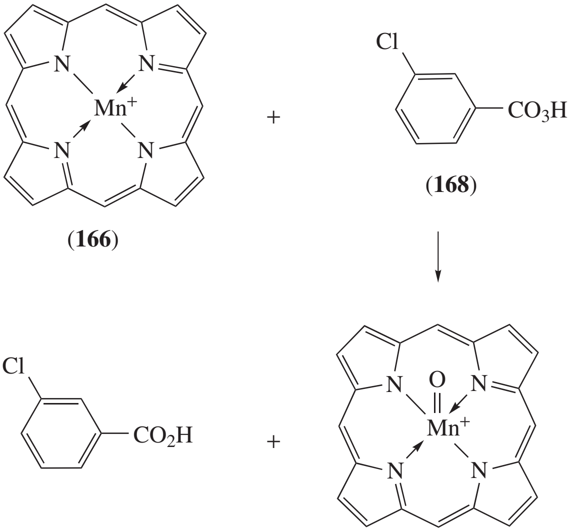
(**164**) (**165**) (157)



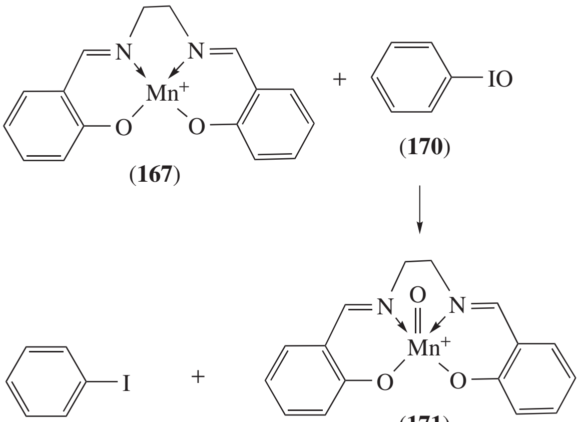
(**163**) (**166**) (158)



(**165**) (**167**) (159)



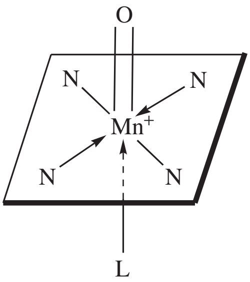
(**166**) (**168**) (**169**) (160)



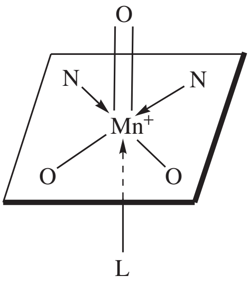
(167) (170) (171)

(161)

The oxo groups in **169** and **171** protrude out of the approximately planar complexes. If another ligand (L), such as pyridine-*N*-oxide, is present, the geometry about the manganese atom becomes octahedral with L occupying a position opposite to the oxo group, as represented by structures **172** and **173**.



(**172**)



(**173**)

B. Reactions of Manganese Porphyrin and Salen Complexes

The manganese(V) oxo complexes (**172** and **173**) can be used as stoichiometric oxidants or as catalysts in connection with terminal oxidants such as sodium hypochlorite (NaClO) or iodosylbenzene (PhIO), as illustrated in Figures 7 and 8. The literature describing the usefulness of these reactions is voluminous[200–216].

The primary importance of these oxidants is related to their use in stereoselective and enantioselective reactions[203, 209]. These selectivities have been achieved by using substituted porphyrin or salen ligands. Because the structures of the ligands can be modified by introduction of substituents in several positions, great variations in the properties of the resulting oxidants can be achieved[203, 209, 211, 212]. Structures **174** and **175** indicate the scope of substitution possibilities.

Stereoselective oxidants can be used to effect a reaction without changing the stereostructure of the reductant. For example, when the 5,5′-dinitrosalen complex (**176**) was used as a catalyst along with iodosylbenzene as the terminal oxidant, it was possible to

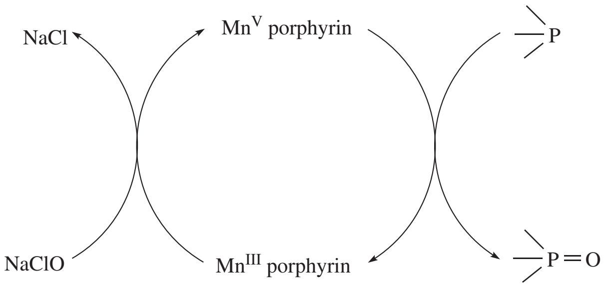


FIGURE 7. Oxidation of a phosphine using manganese(III) porphyrin as a catalyst

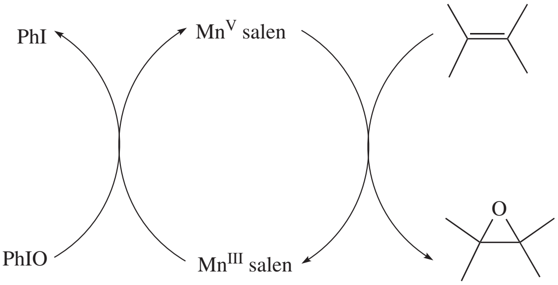
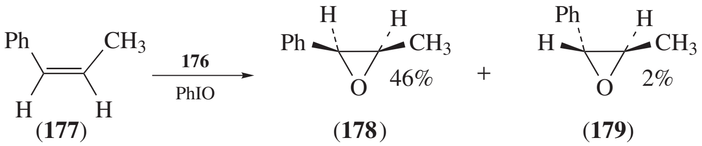


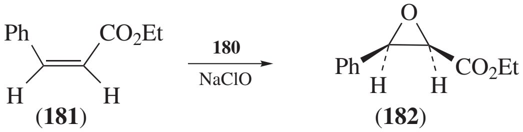
FIGURE 8. Epoxidation of an alkene using manganese(III) salen as a catalyst

convert (*Z*)-β-methylstyrene (**177**) into (*Z*)-β-methylstyrene oxide (**178**) contaminated with only a small amount of the more stable isomer, (*E*)-β-methylstyrene oxide (**179**)[200] (equation 162).

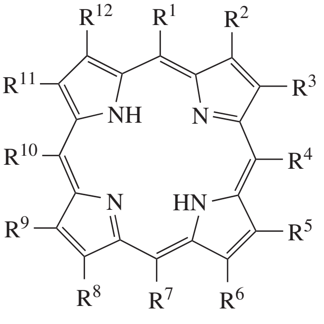
When a chiral manganese(III) catalyst is used, it is often possible to achieve an enantioselective reaction, i.e. to obtain primarily one enantiomer from a prochiral reductant[215]. For example, the oxidation of ethyl cinnamate (**181**) using **180** (commonly referred to as Jacobsen's catalyst) along with sodium hypochlorite gives the (*R*,*R*)-(+) isomer (**182**) in 95–97% enantiomer excess[202] (equation 163).



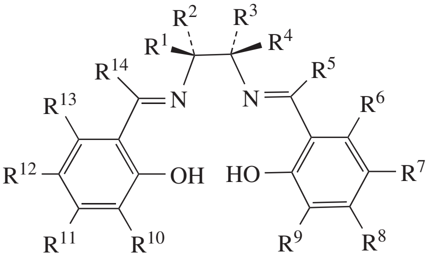
(162)



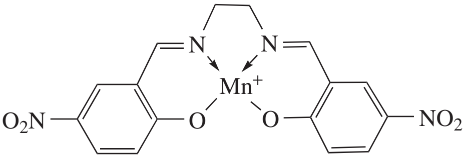
(163)



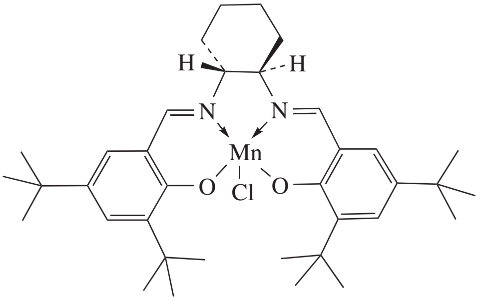
(**174**)



(**175**)



(**176**)



(**180**)

The nature of the ligand, L (see structure **173**), also has an impact on the outcome of these reactions. For example[214], best results were obtained in reaction 163 when L was 4-phenylpyridine *N*-oxide[202].

C. Reaction Mechanisms

Since the oxo group protrudes out of the equatorial plane of the porphyrin and salen complexes, **172** and **173**, it is unlikely that the approach of a reductant from the axial direction would result in a stereoselective reaction. As indicated in Figure 9, there would be no constraints on the mode of approach that would favor the formation of one stereoisomer over another.

The approach of the reductant from an equatorial direction would, however, require it to pass over space occupied by the salen ligand, as in Figure 10[216]. The possible directions of approach of the reductant could be quite limited, especially for those salens bearing appropriate substituents. Furthermore, since salen ligands are chiral, enantioselectivity

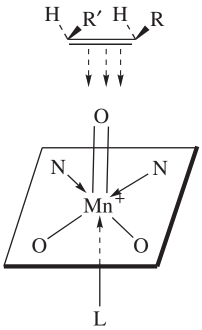


FIGURE 9. Approach of an alkene to **173** from an axial direction

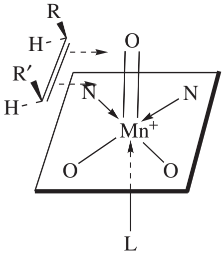
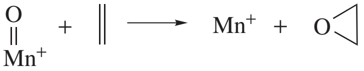


FIGURE 10. Approach of an alkene to **173** from an equatorial direction

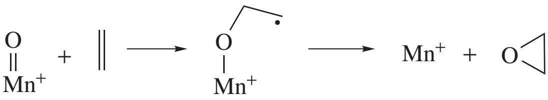
could occur. This realization has led chemists to synthesize salen ligands with an ingenious array of substituents, some of which are chiral.

Crystallographic studies have indicated that manganese(III) salen complexes are relatively flat. However, it has been suggested that the corresponding manganese(V) oxo complexes may be folded, bowl-shaped, bent or twisted[203], thereby accounting in part for the limited pathways open to approach by a reductant.

The reaction between manganese(V) oxo complexes and reductants, such as alkenes, could occur in either concerted (equation 164) or stepwise mechanisms involving the formation of intermediate free radicals (**183**), as in equation 165[203, 205].



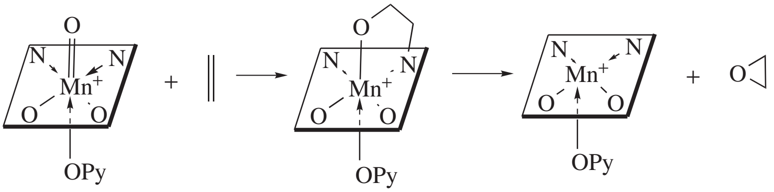
(164)



(**183**)

(165)

It is also possible that oxetane intermediates (**184**) could be involved, as indicated in equation 166[203].



(**184**)

(166)

The theoretical studies reported to date have been concerned primarily with the multiplicity of the manganese atom and the trajectory at which the reductant approaches the oxo group[205, 208].

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Organomanganese-mediated radical reactions

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I. INTRODUCTION

In comparison with organometallic nucleophiles, free radicals offer complementary functional group compatibility, so synthetic chemists have gradually developed a suite of tools based on the use of these neutral reactive intermediates[1]. An example of advantageous

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use of radical intermediates is the case of inter- and intramolecular C−C bond-forming coupling reactions; the mild conditions and neutral character often exhibited in free radical reactions could allow for the presence of diverse functionality in both precursors, including functional groups which might not survive strongly nucleophilic conditions. Unfortunately, early synthetic methods of significant scope involved hydrides of mercury and tin in reductive transformations of alkyl halides. These reagents have since fallen into disfavor due to toxicity concerns and, in the case of tin, difficulties in product purification. Numerous alternatives have been introduced to obviate these concerns[1a], and among them are reactions involving photolysis of organomanganese compounds, specifically $Mn_2(CO)_{10}$. The oxidative radical reactions of enolates in the presence of $Mn(OAc)_3$ are not included in this review; the reader may consult a number of excellent reviews on this topic[2]. Here the applications of dimanganese decacarbonyl and related organomanganese compounds in various free radical reactions will be discussed from the perspective of synthetic applications.

II. GENERATION OF RADICALS FROM ORGANIC HALIDES USING ORGANOMANGANESE REAGENTS

A. Atom Abstraction Involving Dimanganese Decacarbonyl

The thermal or photochemical homolysis of $Mn_2(CO)_{10}$ affords the metal-centered radical $^\bullet Mn(CO)_5$, which has long been known to abstract halogen atoms from alkyl halides[3–5]. Dimanganese decacabonyl[6] is a commercially available yellow solid with a molecular structure consisting of two $Mn(CO)_5$ units, each with octahedral coordination, linked by a weak manganese−manganese single bond (38 kcal mol^{-1})[7]. $Mn_2(CO)_{10}$ is UV active, with the σ to σ^* transition of the Mn−Mn bond at 324 nm (cyclohexane) associated with metal−metal bond cleavage (Scheme 1). The resulting $^\bullet Mn(CO)_5$ has been detected using EPR spectroscopy and spin-trapping techniques[8,9].

$$(CO)_5Mn\text{–}Mn(CO)_5 \xrightarrow{h\nu} 2\ (CO)_5Mn^\bullet$$

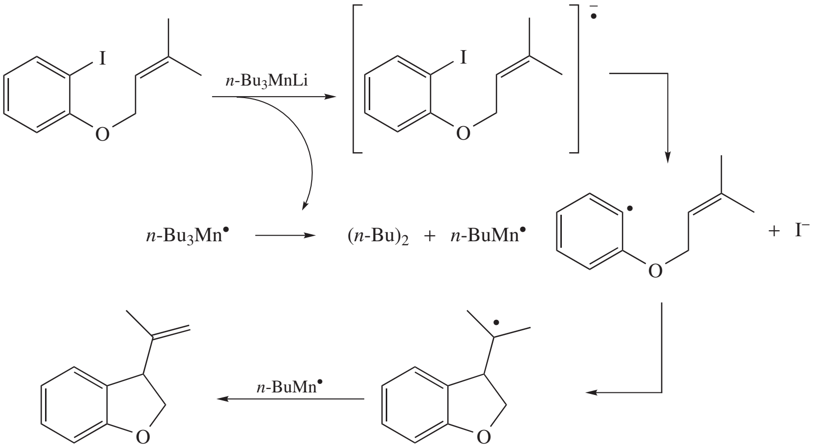
$$(CO)_5Mn^\bullet + I\text{–}R \longrightarrow (CO)_5Mn\text{–}I + {}^\bullet R$$

SCHEME 1

Halogen-atom abstraction from alkyl halides by $^\bullet Mn(CO)_5$ generates alkyl radicals along with products of the type $X{-}Mn(CO)_5$ (Scheme 1) at rates which are inversely proportional to the corresponding C−X bond strengths[10]; in this respect the halogen abstraction behavior is similar to that of $^\bullet SnR_3$. Reaction of $^\bullet Mn(CO)_5$ with 1° halides is more facile than with 2° or 3° halides, in contrast to the usual order of reactivity in the generation of alkyl radicals. Steric hindrance has been examined using phosphine ligands with varying cone angles; Brown and coworkers have shown that the rates are decreased when bulky phosphines replace carbonyl ligands at the metal center[5]. The utility of the photolysis of $Mn_2(CO)_{10}$ for Wurtz-type homo-coupling of alkyl iodides (*vide infra*) suggests that relatively high concentrations of carbon-centered radicals may be obtained under these conditions. Hydrogen atom abstractions from Si−H, S−H and P−H bonds have also been observed and exploited for subsequent radical reactions[11,12].

B. Electron Transfer Involving Trialkylmanganate Species

The organomanganese species generated upon treatment of $MnCl_2$ with three equivalents of *n*-butyllithium has been formulated as *n*-Bu_3MnLi, and a related species *n*-$Bu_3MnMgBr$ may be generated from the corresponding Grignard reagent. Such compounds can initiate radical reactions of aryl and alkyl iodides via electron transfer to the organic halide, leading to a radical anion which then releases iodide ion and an aryl or alkyl radical. After transformations of this radical, for instance by synthetically useful cyclizations, trapping by *n*-$BuMn^{\bullet}$ occurs to generate an organomanganese intermediate capable of β-H elimination as shown (Scheme 2), or in some cases reduction or further C−C bond constructions[13].



SCHEME 2

III. SYNTHETIC METHODS

A. Reduction of Alkyl Halides to Alkanes

Halogen atom abstractions are often used to initiate a variety of radical transformations; the simplest of these is reduction. Giese and Thoma reported photolytic reactions of decyl iodide in the presence of $Mn_2(CO)_{10}$ (**1**, Scheme 3), which included reductions along with a variety of other radical transformations[14]. In comparison with two other metal−metal dimers $Mn_2(CO)_{10}$ led to more efficient halogen atom abstraction from 1-iodododecane; with $Co_2(CO)_8$ there was no reaction, and with iron dimer **2** the halogen abstraction required more reactive iodides or bromides activated by neighboring functionality. Both decane and 1-decene were observed in all three cases, and the ratio decane:decene was higher using the iron dimer **2**. The product distribution was attributed to halogen atom abstraction and radical recombination to afford an alkylmetal species, which was then followed by either solvolysis of the carbon−metal bond or β-H elimination. With the use of **2**, the alkene product was suppressed in the presence of protic solvent (e.g. MeOH). The competing solvolysis and β-H elimination pathways diminish the synthetic importance of this transformation; alternative radical chain methods with stannanes or silanes as H-atom donors may be preferable.

$$C_{10}H_{21}I \xrightarrow{\text{M–M dimer, } h\nu} \text{decane} + \text{1-decene}$$

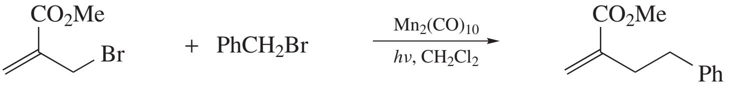
$Mn_2(CO)_{10}$ (**1**), C_6H_6	67 : 33
$Cp_2Fe_2(CO)_4$ (**2**), C_6H_6	50 : 50
$Cp_2Fe_2(CO)_4$ (**2**), MeOH	75 : 25

(**1**) (**2**)

SCHEME 3

B. Wurtz Coupling of Alkyl Halides

Halogen atom abstraction by $^{\bullet}Mn(CO)_5$ may also initiate Wurtz-type homo- and cross-coupling (equation 1), with $BrMn(CO)_5$ as the byproduct of the reaction[15]. These reactions can also be conducted with substoichiometric Mn if a biphasic medium of CH_2Cl_2 and aqueous NaOH is employed in the presence of a benzyltriethylammonium chloride as a phase transfer catalyst (equation 2), in which case $BrMn(CO)_5$ does not accumulate in the mixture[16]. When $BrMn(CO)_5$ is introduced as the starting Mn reagent, the reaction is also successful, showing that the NaOH solution converts $BrMn(CO)_5$ into $Mn_2(CO)_{10}$.



(1)

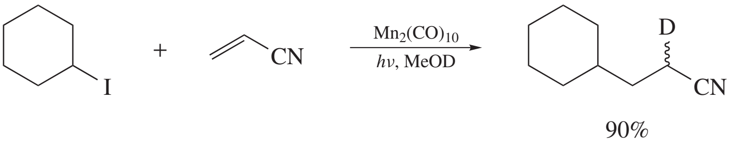
70%

$$PhCH_2Br \xrightarrow[\text{BnNEt}_3\text{Cl, NaOH/CH}_2\text{Cl}_2]{Mn_2(CO)_{10}\text{ (20 mol\%), } h\nu} PhCH_2CH_2Ph \qquad (2)$$

75%

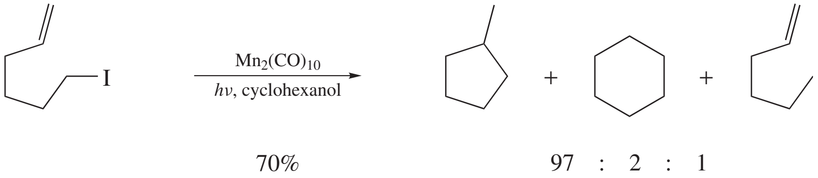
C. Radical Additions of Alkyl Halides to Alkenes

Reductive additions of alkyl halides to alkenes are among the most commonly applied radical coupling reactions, popularized with the use of mercury- and tin-mediated reagent systems (e.g. Bu_3SnH, AIBN). Early efforts by Giese and Thoma uncovered the utility of metal–metal dimers in these reductive coupling reactions, for example in the $Mn_2(CO)_{10}$-mediated addition of cyclohexyl iodide to acrylonitrile (equation 3)[14]. When this reaction was carried out in deuterated methanol, deuterium incorporation suggested solvolysis of an organomanganese intermediate generated upon trapping of the radical adduct by $^{\bullet}Mn(CO)_5$.



(3)

Both $Mn_2(CO)_{10}$ and R_3MnLi reagent systems may be used to carry out alkenyl radical cyclizations. A prototypical 5-hexenyl cyclization (equation 4) results in a ratio of 5-*exo* and 6-*endo* cyclizations consistent with other radical cyclizations[14]. A representative Ueno–Stork haloacetal cyclization[17] also proceeded as expected, affording a mixture of diastereomeric 5-*exo* cyclization products (equation 5)[14].



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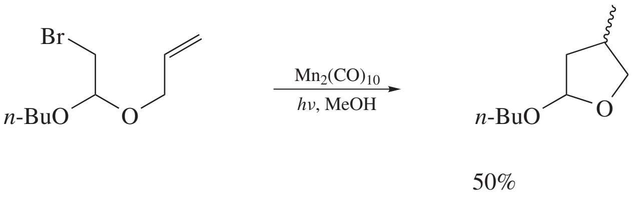
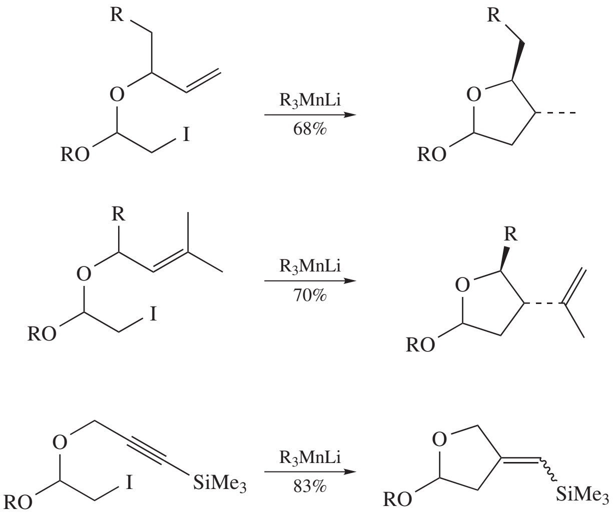


(5)

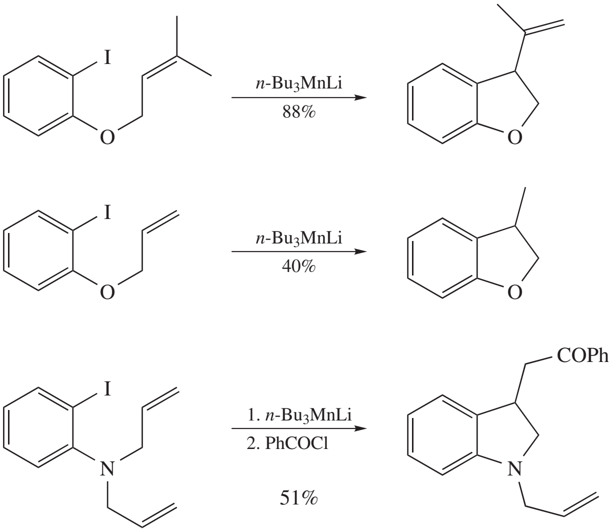
Similar Ueno–Stork reactions have been achieved with electron transfer initiation by R_3MnLi, using either alkene or alkyne as the radical acceptor moiety (Scheme 4)[18]. Reductive cyclizations are observed when the cyclized radical is primary or vinylic, whereas secondary or tertiary alkyl radicals undergo an elimination to regenerate the alkene functionality after cyclization. Excellent diastereoselectivity is delivered from a stereogenic center at the allylic position of the acceptor, consistent with other haloacetal cyclizations[19]. A related reagent system involving *in situ* generation of active Mn(0) as a reductant has also been successful in initiation of Ueno–Stork cyclizations[20].

An advantage of the electron transfer initiation with R_3MnLi is its applicability to generating aryl radicals. Thus, various alkenyl 2-iodoaryl ethers, as well as the corresponding amines, have been cyclized using the R_3MnLi initiation (Scheme 5). Non-reductive cyclization products, presumably arising via β-H elimination after Mn trapping of the cyclized radical, are formed in excellent yield. As noted above, this β-H elimination is apparently suppressed when the cyclized radical is primary, and reductive cyclization is observed. The intermediacy of radicals was supported by the diastereomer ratio, which matched that obtained in other radical cyclizations, and by ring opening of cyclopropanes attributed to the presence of a cyclopropyl carbinyl radical. Cyclized organomanganese intermediates may be intercepted by other electrophiles including allyl bromide and acyl halides, as exemplified by PhCOCl (Scheme 5).



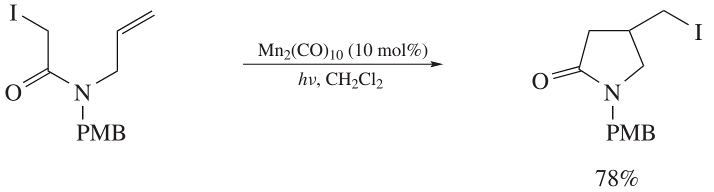
R = *n*-Bu

SCHEME 4



SCHEME 5

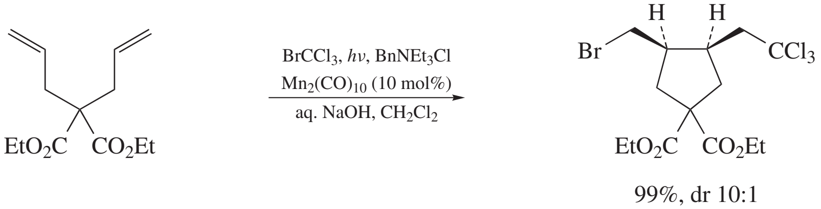
The photolysis of $Mn_2(CO)_{10}$ is also suitable for initiating atom transfer cyclizations of electrophilic radicals; such a process is observed upon reaction of an *N*-allyliodoacetamide (equation 6)[21]. Stoichiometric amounts of $Mn_2(CO)_{10}$ offered no yield improvements in this reaction.



(6)

D. Tandem Radical Addition/Cyclization Reactions of Dienes

Tandem addition and cyclization reactions of $BrCCl_3$ with unactivated 1,6-dienes (Kharasch reactions) occur with initiation via photolysis of $Mn_2(CO)_{10}$; here also the biphasic media of CH_2Cl_2 and aq. NaOH may be employed with a phase transfer catalyst to reduce the loading of $Mn_2(CO)_{10}$ to substoichiometric levels[16, 22]. For example, diethyl 2,2-diallylmalonate affords a quantitative yield and excellent diastereocontrol (*cis*/*trans* = 10:1) in construction of a cyclopentane bearing four substituents (equation 7). Such Kharasch reactions end with atom transfer to afford alkyl bromide functionality; the secondary alkyl bromide which forms upon Kharasch addition of $BrCCl_3$ to diethyl allylmalonate offers an electrophilic partner for subsequent carbanion cyclization. Thus under the basic conditions of the biphasic media, the malonate functionality underwent 3-*exo-tet* cyclization (equation 8), providing a key intermediate for synthesis of coronamic acid[16].



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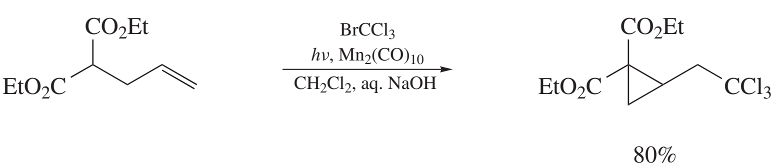
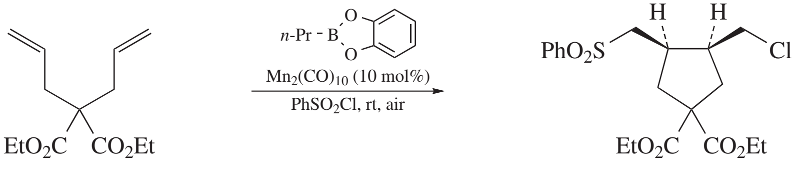


(8)

As an alternative to the Kharasch reaction, tandem addition and cyclization of 1,6-heptadienes may also be accomplished with $PhSO_2Cl$ under the Mn-mediated photolysis conditions[16]. The reaction also occurs using a non-photolytic initiation system of 0.3 equiv of *B*-propyl-catecholborane in the presence of 0.1 equivalents of $Mn_2(CO)_{10}$ (equation 9)[23].



(9)

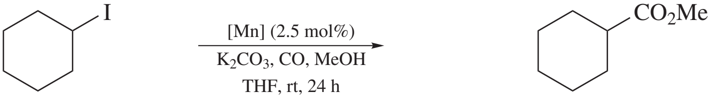
69% yield, dr 5.7:1

E. Radical Carbonylations

Dimanganese decacarbonyl was found to promote carbonylation of alkyl iodides to afford methyl esters under basic conditions during photolysis or electrochemical reduction; good yields were obtained from secondary alkyl iodides (equation 10)[24]. In further discussion of the mechanism of this transformation, Watanabe and coworkers proposed that pentacarbonylmanganate anion was the catalytically active species, and this was supported by the finding that $NaMn(CO)_5$ was more efficient than $Mn_2(CO)_{10}$ in catalyzing the reaction in the absence of photolysis or electrochemical reduction (equation 11).

$$\text{R–I} \xrightarrow[\text{K}_2\text{CO}_3\text{, CO, MeOH, Et}_4\text{NOTos} \atop \text{THF, rt, 24 h}]{\text{e}^-\text{, Mn}_2(\text{CO})_{10}\ (10\ \text{mol\%})} \text{R–CO}_2\text{Me} \qquad (10)$$

R = cyclohexyl: 60%
R = 2-octyl: 76%
R = *n*-hexyl: 20%

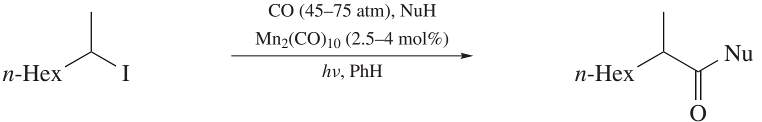


(11)

[Mn] = $Mn_2(CO)_{10}$: 22%

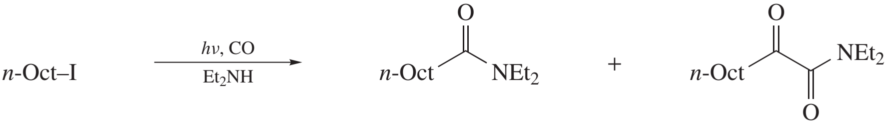
[Mn] = $NaMn(CO)_5$: 84%

In a study of atom transfer carbonylation of alkyl iodides, Ryu and coworkers discovered that such reactions are more facile in the presence of $Pd(PPh_3)_4$ or $Mn_2(CO)_{10}$[25]. This process involves trapping a primary or secondary radical with carbon monoxide to afford an acyl radical; halogen atom abstraction or radical recombination with a metal-centered radical then provides acylating agent which may be trapped by an alcohol or amine, providing access to esters or amides (equation 12). Primary alkyl iodides, which normally are sluggish in such reactions, become suitable substrates with these metal additives, which suppress destructive side reactions of the alkyl iodides by accelerating the desired carbonylation. In the amide synthesis, bis-carbonylation occurs with $Pd(PPh_3)_4$, but is not observed with $Mn_2(CO)_{10}$ (equation 13).



(12)

NuH = *n*-BuOH: 91%
NuH = Et_2NH: 86%

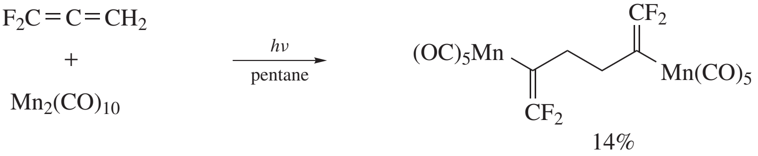


with $Pd(PPh_3)_4$:	29%	52%
with $Mn_2(CO)_{10}$:	91%	0%

(13)

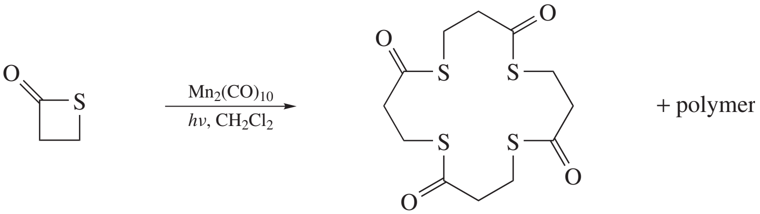
F. Dimerizations and Polymerizations

The radical initiating behavior of $Mn_2(CO)_{10}$ may be exploited for alkene dimerization[3, 11] and polymerization reactions[26–28], including less conventional types of dimers, telomers and polymers. An interesting dimerization reaction of 1,1-difluoroallene with $Mn_2(CO)_{10}$ affords C−C bond construction leading to a bimetallic complex in which two Mn atoms are bridged by four carbons (equation 14)[29]. The lithium trialkylmanganate species also are known to initiate polymerization[30].



(14)

Photolysis of *β*-propiothiolactone in the presence of $Mn_2(CO)_{10}$ or $Re_2(CO)_9(NCMe)$ leads to a macrocyclic tetramer polythioester in about 20% yield (equation 15); hexameric and higher polymeric macrocyclic polythioesters were also obtained[31]. This transformation may involve radical substitution at the sulfur atom.



(15)

G. Intermolecular Radical Addition to Chiral *N*-Acylhydrazones

1. Design of chiral N-acylhydrazones

Simple imines exhibit modest reactivity of the C=N bond toward nucleophilic radicals, and therefore have been of limited utility in intermolecular radical additions. Bertrand and coworkers found that α-iminoesters, bearing an electron-withdrawing substituent adjacent to the C=N bond, were more effective[32]. Oxime ethers are active radical acceptors, and have been exploited extensively, mainly through the longstanding efforts of Naito and coworkers[33]. Hydrazones offer enhanced reactivity similar to oxime ethers, but offer some extra advantages: The additional valence of nitrogen presents more options for design of conformational constraints. And from a practical standpoint, the E/Z mixtures frequently observed with oxime ethers are not an issue with aldehyde hydrazones, which generally adopt C=N E-geometry. Although chiral *N,N*-dialkylhydrazones are prominent in asymmetric α-alkylation of carbonyl compounds[34], and have also been applied to addition of organometallic reagents to C=N bonds[35–37], there was a need for a new type of chiral hydrazone specifically designed for use in free radical addition reactions.

We introduced chiral *N*-acylhydrazones in 2000 to meet this need, with a design built upon Lewis acid activation[38] and restriction of rotamer populations[39]. Hydrazone **A** (Figure 1) constrains the C−N bond within a ring and includes a carbonyl group for two-point binding of a Lewis acid in a rigid chelate structure (**B**). The Lewis acid would also increase reactivity toward nucleophilic alkyl radicals by lowering the LUMO energy of the C=N bond, ensuring that the chelated structure would react preferentially. Finally, there is a notable potential for reductive cleavage of N−N bonds[40], whereby an *N*-linked auxiliary could be released for reuse after stereoisomer purification.

2. Preparation of chiral N-acylhydrazones

To exploit the design described above, oxazolidinones **3a**–**3e**[41, 42] (Scheme 6) were chosen to provide the ring-templated stereocontrol element and the carbonyl for Lewis acid chelation. Electrophilic amination provided the *N*-aminooxazolidinones (e.g. **4a**–**4e**), and condensation with aldehydes and ketones in turn afforded chiral *N*-acylhydrazones, e.g. **5**–**16**. The preferred reaction conditions for the *N*-amination involve deprotonation of the oxazolidinones with NaH or KH and introduction of an NH_2^+ equivalent. Several such reagents have been used with success, including *O*-(*p*-nitrobenzoyl)hydroxylamine ($NbzONH_2$)[43], *O*-(diphenylphosphinyl)hydroxylamine ($Ph_2P(=O)ONH_2$) or NH_2Cl[44].

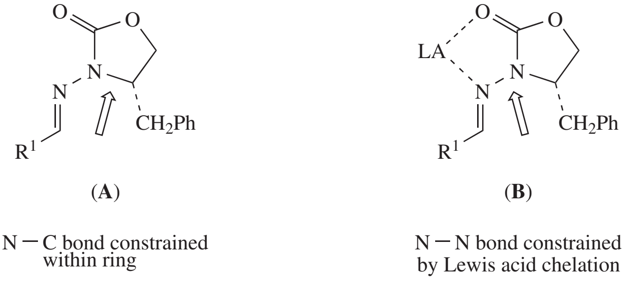
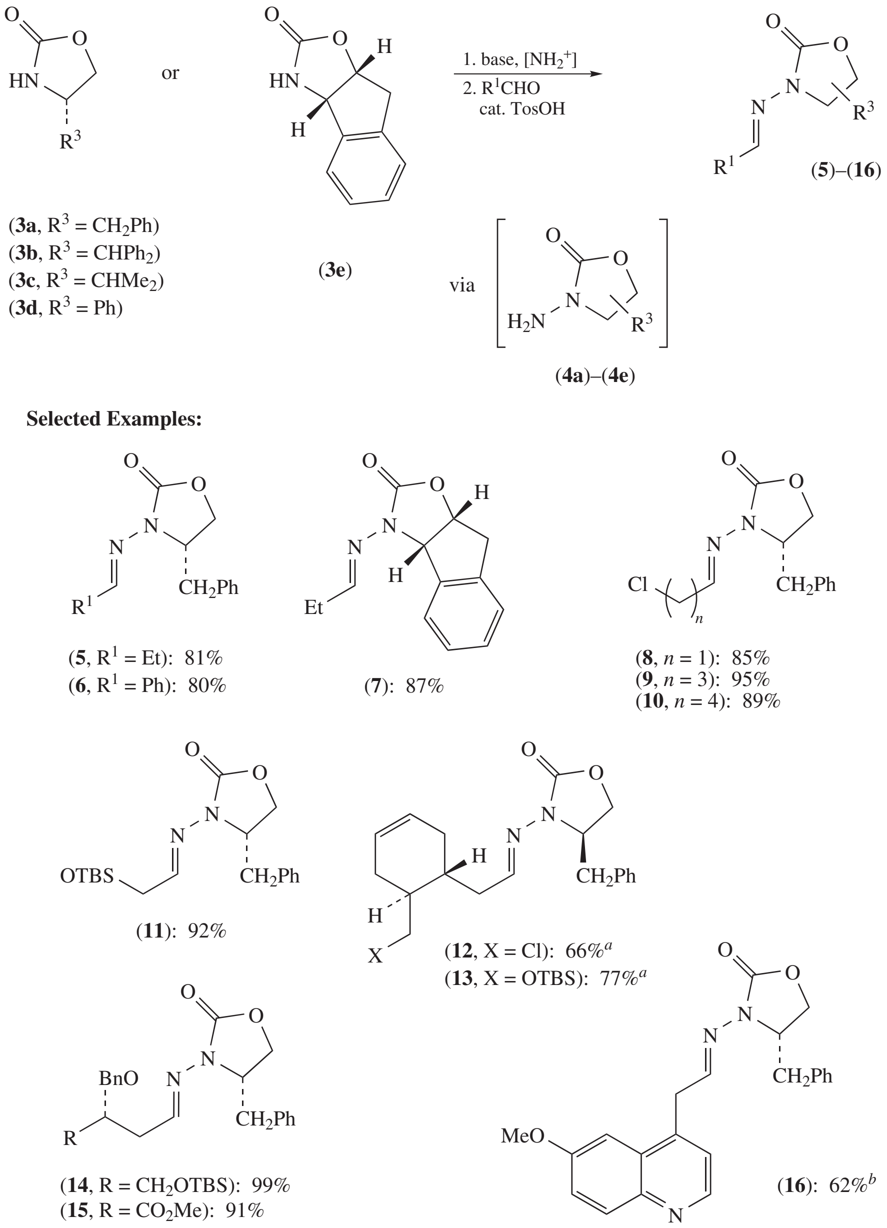


FIGURE 1. A hypothetical *N*-linked auxiliary approach for stereocontrolled addition to C=N bonds, based on chelation inducing a rigid, electron-deficient imino acceptor (LA = Lewis acid)



[a] Yield for two steps including reduction of R^1CN to R^1CHO.

[b] Yield from 6-methoxy-4-methylquinoline via ArCH=CHNMe$_2$.

SCHEME 6

Condensation with aldehydes proceeds reliably, with or without isolation of the intermediate *N*-aminooxazolidinones **4**, to afford a wide range of chiral hydrazones in good overall yields (Scheme 6). The sequence has been conducted successfully on multigram scale: Benzaldehyde hydrazone **6**, obtained in 80% yield on mmol scale (253 mg) by chromatographic purification, was obtained on larger scale in 74% yield (9.4 g) from **3a** with purification by recrystallization. The material may be stored and exchanged to other hydrazones as desired by equilibrating with excess of the carbonyl compound of choice[43].

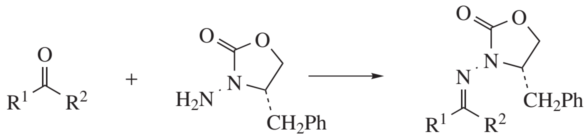
Chiral *N*-acylhydrazone derivatives have also been prepared from condensations of various ketones (**17** and **18**, R^1 = alkyl, R^2 = Et, Ph) with *N*-aminooxazolidinone **4a** (Table 1)[45,46]. Unlike the aldehyde examples, mixtures of *E*/*Z* isomers were usually obtained, although the more highly branched ketone *N*-acylhydrazones **22** and **26** were formed as single isomers. These amination and condensation procedures have been extended to prepare a variety of similar chiral *N*-acylhydrazones for different purposes[47].

3. $Mn_2(CO)_{10}$ in radical additions to C=N

After proof-of-concept was established for stereoselectivity in radical additions to chiral *N*-acylhydrazones, with radicals generated under tin hydride-mediated conditions[48], broader scope was sought. In particular, primary alkyl iodides were ineffective under the tin-mediated conditions, so various other methods for radical initiation were evaluated. This led to the discovery that $Mn_2(CO)_{10}$ is in fact well-suited to this purpose; it requires no sensitizer (λ_{max} 340 nm, $\sigma_{Mn-Mn} \rightarrow \sigma^*_{Mn-Mn}$) for homolytic metal–metal bond cleavage, and had already been known to be effective in generation of primary alkyl radicals.

Indeed, initial experiments with $Mn_2(CO)_{10}$ were very promising: Ethyl iodide addition to the propionaldehyde *N*-acylhydrazone (Table 2, entry 1) in the presence of $Mn_2(CO)_{10}$ under photolysis conditions (300 nm, Rayonet) using $InCl_3$ as a Lewis acid furnished the ethyl adduct in 85% yield[49].

TABLE 1. Preparation of ketone hydrazones



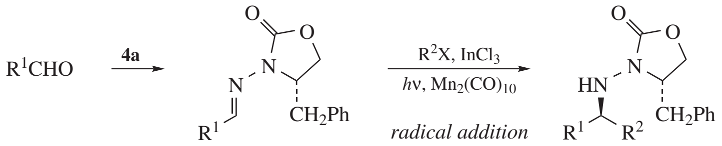
(**17**, R^1 = alkyl, R^2 = Et)
(**18**, R^1 = alkyl, R^2 = Ph)

(**4a**)

(**19**)–(**27**)

Entry	R^1	R^2	Hydrazone (yield)	*E*/*Z* Ratio
1	*i*-Pr	Et	**19** (84%)	77:23
2	*c*-C_5H_9	Et	**20** (49%)	79:21
3	*c*-C_6H_{11}	Et	**21** (64%)	85:15
4	*t*-Bu	Et	**22** (67%)	>98:<2
5	*i*-Pr	Ph	**23** (55%)	19:81
6	*c*-C_5H_9	Ph	**24** (59%)	26:74
7	*c*-C_6H_{11}	Ph	**25** (55%)	13:87
8	*t*-Bu	Ph	**26** (73%)	<2:>98
9	Me	CO_2Me	**27** (75%)	92:8

TABLE 2. Initial scope studies of Mn-mediated radical addition to chiral *N*-acylhydrazones[a]



Entry	Aldehyde (or acetal)	Hydrazone[a]	Halide R^2X	Yield, config[b]	*dr*[e]
1	CH_3CH_2CHO	81%	CH_3CH_2I	85%	-
2			CH_3I	48%[c,d], S	95:5
3			$CH_3CH_2CH_2I$	66%, R	94:6
4			$CH_3(CH_2)_2CH_2I$	78%, R	95:5
5			$CH_3(CH_2)_3CH_2I$	79%, R	96:4
6			*i*-BuI	54%[c], R	95:5
7			*i*-PrI	75%, R	95:5
8			$ClCH_2I$	63%, R	93:7
9			$Cl(CH_2)_3I$	52%, R	96:4
10			$Cl(CH_2)_4I$	55%, R	96:4
11			Cl_2CHBr	38%[c,d], R	98:2
12	CH_3CHO	66%	CH_3CH_2I	66%, R	95:5
13	$CH_3(CH_2)_2CHO$	87%		63%, S	95:5
14	$CH_3(CH_2)_3CHO$	89%		72%, S	97:3
15	$CH_3(CH_2)_4CHO$	88%		77%, S	97:3
16	*i*-BuCHO	85%		65%, S	95:5
17	$ClCH_2CH(OMe)_2$	85%		57%, S	93:7
18	$Cl(CH_2)_3CHO$	95%		60%, S	93:7
19	$Cl(CH_2)_4CHO$	89%		62%, S	97:3
20	$Cl_2CHCH(OEt)_2$	54%		34%[c], S	89:11

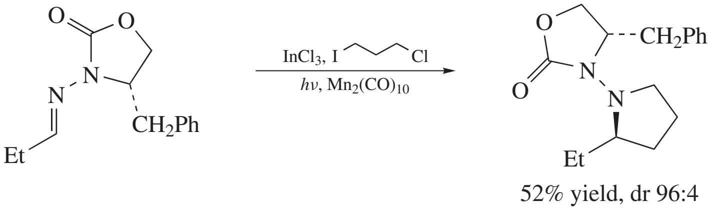
[a] Reaction conditions: (1) Aldehyde or acetal (5–10 equiv), **4a**, TosOH, CH_2Cl_2, rt. (2) Hydrazone in deoxygenated CH_2Cl_2 (0.1 M), $InCl_3$ (2.2 equiv), $Mn_2(CO)_{10}$ (1–2 equiv), R^2X (10 equiv), *hν* (300 nm, pyrex), 1–2 d, *ca* 35°C. [b] Isolated yield. [c] Isolated yield, diastereomer mixture. [d] 20 equiv of R^2X was used. [e] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was used in removal of Mn byproducts. [f] Ratios determined by HPLC (Chiralcel OD, *i*-PrOH/hexane) or by integration of ^1H NMR spectra.

A variety of primary and secondary halides, including methyl iodide and difunctional halides, led to good yields of radical adducts with excellent stereocontrol (Table 2, entries 1–11). Exceptions are benzyl, *tert*-butyl and 2-chloroethyl additions (not shown); these presumably are ineffective due to Wurtz-type homocoupling, steric hindrance to atom abstraction and radical fragmentation, respectively. The scope of hydrazones was examined by carrying out additions of ethyl iodide to a variety of hydrazones (entries 12–20); all occurred in synthetically useful yields and reliably high diastereomer ratios, with some adducts bearing additional functionality for further elaboration. It should be emphasized that these adducts are epimeric to the first set of examples (i.e. entries 2–6 and 8–11) with respect to the new stereogenic center; N−N bond cleavage of complementary members of these two sets of adducts would afford enantiomeric chiral amines. This allows for flexibility in synthetic design as a result of simply changing the roles of the aldehyde and iodide precursors.

With respect to mechanism, control experiments revealed a requirement for both irradiation and $Mn_2(CO)_{10}$[49,50]. Other mechanistic roles for $InCl_3$ were considered, but it appears to function only as a Lewis acid activator of the radical acceptor; without $InCl_3$, the reaction proceeded, but slowly (21% yield after 2 d). In CH_2Cl_2, solubility was a problem with most Lewis acids, but $InCl_3$ promoted the reaction despite inhomogeneity, and therefore is a Lewis acid of choice for these reactions. Potential intermediate (alkyl)$Mn(CO)_5$ compounds were synthesized independently, but attempted use of these for alkyl addition to *N*-acylhydrazones under various reaction conditions gave only traces of the alkyl adduct[50]. Thus a carbometallation mechanism for the addition reactions is inconsistent with observed results.

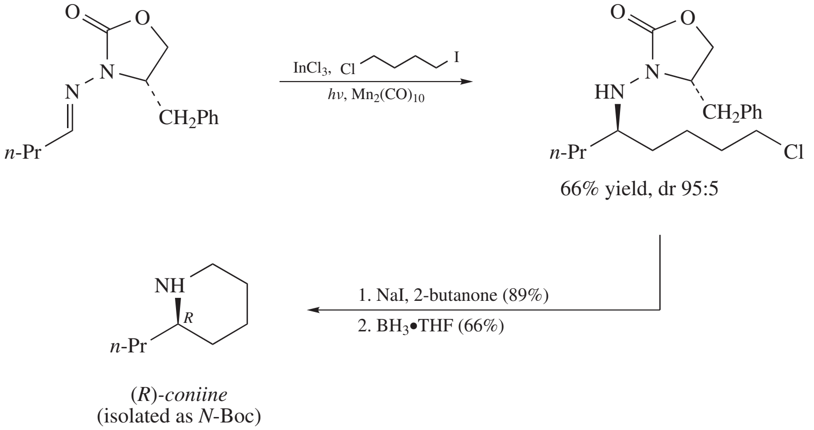
4. Hybrid radical–ionic annulation

Interestingly, the 3-chloro-1-iodopropane addition in Table 2 (entry 9) led exclusively to a pyrrolidine (equation 16); none of the acyclic adduct was found[49, 50]. Presumably radical addition was followed by *in situ* S_N2−type cyclization. The same cyclization (giving the epimeric pyrrolidine) occurs upon ethyl addition to the 3-chlorobutyraldehyde hydrazone. These reactions are hybrid radical–ionic annulations of the C=N bond, a class of radical–polar crossover reactions[51] with potential utility in alkaloid synthesis.



(16)

The piperidine alkaloid coniine[52] (Scheme 7) offers a simple test case. Starting with the chiral *N*-acylhydrazone derived from butyraldehyde, Mn-mediated addition of 4-chloroiodobutane afforded the acyclic adduct in 66% yield with a diastereomer ratio of 95:5[49, 50]. Cyclization occurred upon exposure to Finkelstein conditions, and reductive removal of the auxiliary afforded coniine in 34% overall yield for 4 steps. This reaction sequence

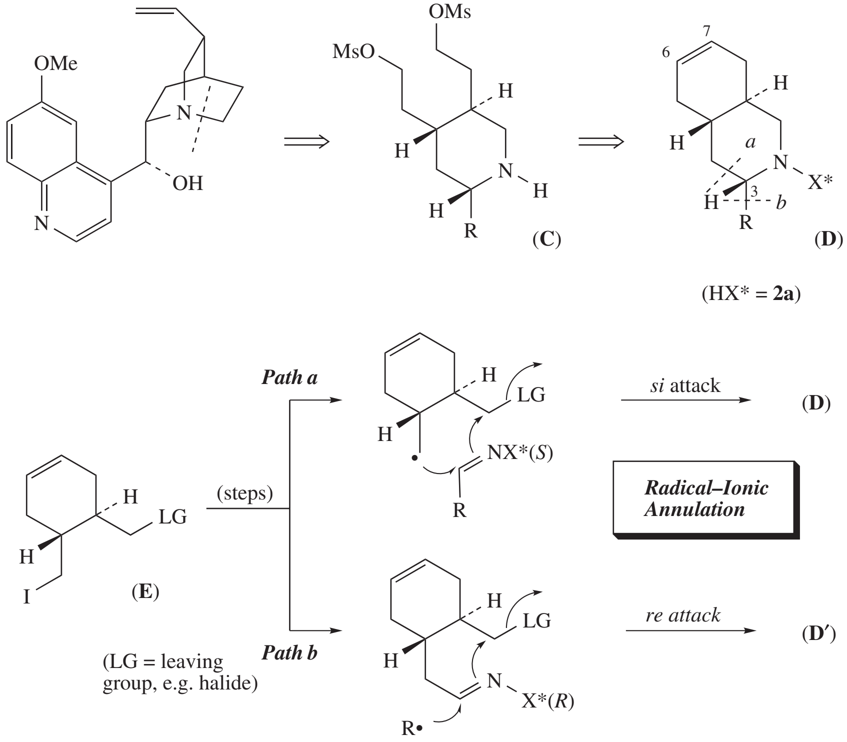


SCHEME 7

compares quite favorably to carbanion-based syntheses via the same retrosynthetic disconnection, where additional steps are needed to protect the electrophilic functionality prior to cyclization[52b,f]. Thus, for multifunctional precursors there is potential for improved efficiency and complementary functional group compatibility via radical addition strategies.

5. Applications in synthesis of complex targets

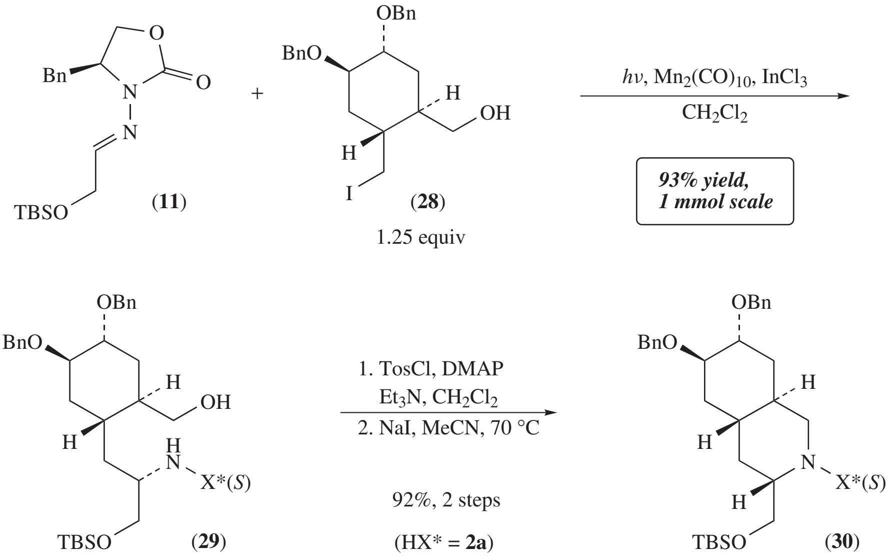
a. Quinine. The antimalarial alkaloid quinine has a colorful history of inspiring synthetic efforts[53]. Our approach to quinine focuses on strategic application of our Mn-mediated hybrid radical–ionic annulation[54]. Initial retrosynthetic analysis followed the disconnection employed in the Stork synthesis[55], wherein the azabicyclo[2.2.2]octane ring system would be constructed by cyclization of a piperidine of the functionalization pattern denoted in structure **C** (Scheme 8). This in turn would be derived from oxidative cleavage of the $\Delta_{6,7}$ bond of an azadecalin of type **D**. From this point, the flexibility of the Mn-mediated coupling enabled two alternative pathways for the radical–ionic annulation to forge the piperidine ring (i.e. bonds **a** and **b**). Here the iodide and hydrazone functionality of the two components could be interchanged such that either component could serve as radical precursor or acceptor (paths **a** and **b**). These stereoconvergent paths lead to adducts **D** and **D**′ which are identical except for the configuration in the removable chiral auxiliary.



SCHEME 8

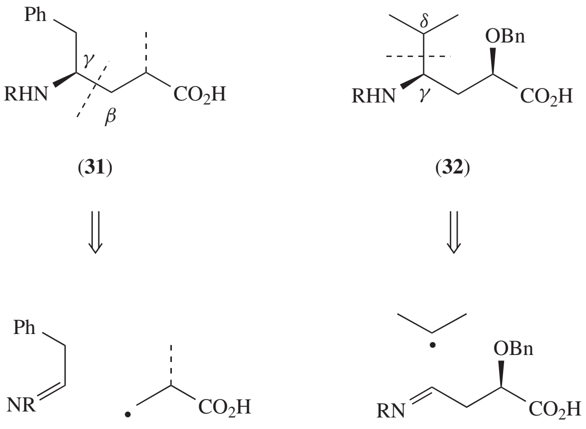
Further strategic impact of the radical–ionic annulation arises by its suggestion of a C2-symmetric progenitor for cyclohexene component **E**, facilitating an efficient access to **E** from simple materials.

In attempts to apply Mn-mediated radical–ionic annulation to this strategy, the alkene in precursors of type **E** appeared to interfere with the radical coupling[54]. As the strategy called for $\Delta_{6,7}$ cleavage by ozonolysis or the like, it was decided to partially oxidize the alkene at an earlier stage, while preserving the C2-symmetric aspects of the strategy. Thus the alkene was oxidized to a *trans*-1,2-diol, then processed on to iodide **28** (Scheme 9). In the key radical addition step, stoichiometry was a concern. In most intermolecular radical additions to imino compounds, large excesses (10–20 equivalents or more) of radical precursors are required. Clearly this would be a prohibitive stoichiometric requirement for an iodide such as **28**, prepared through several synthetic steps. To our great delight, the Mn-mediated coupling of **28** with only 1.25 equivalents **11** proceeded in 93% yield in 1 mmol scale, giving **29** as a single diastereomer. Although completion of the hybrid radical–ionic annulation *in situ* during the Mn-mediated coupling has not yet been achieved, a stepwise process provided decahydroisoquinoline **30** in a quite satisfactory overall yield (85% for 3 steps). The low stoichiometric requirement in the coupling of the multifunctional alkyl group of **28** to an imino compound is quite attractive and should enable broader applications of this Mn-mediated coupling process in complex target synthesis.



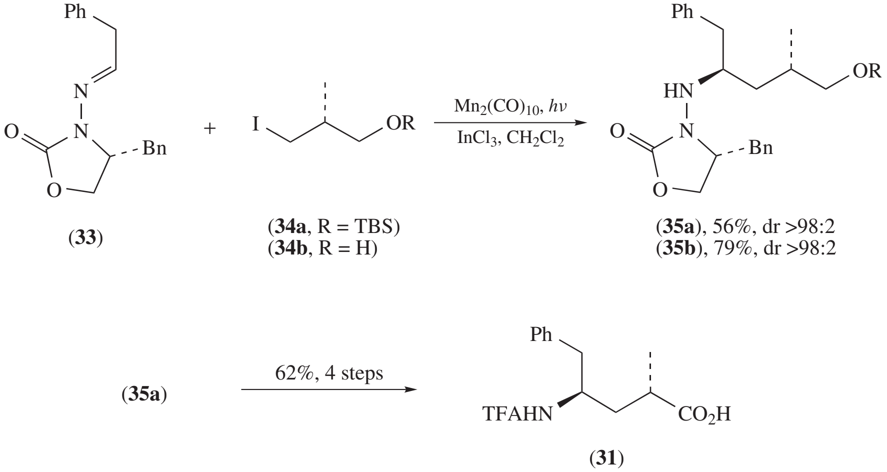
SCHEME 9

b. γ-Amino acids. As homologs of the more common α- and β-amino acids, γ-amino acids have attracted attention as building blocks for bioorganic and medicinal chemistry[56–59]. The Mn-mediated coupling of alkyl iodides and chiral *N*-acylhydrazones has led to syntheses of γ-amino acids **31** and **32** (Scheme 10)[60], as well as a series of analogous γ-hydrazino esters[61]. The C–C bond disconnections shown would require additional oxygen functionality in either the iodide or hydrazone components, and this would challenge the synthetic versatility of the Mn-mediated coupling reactions.



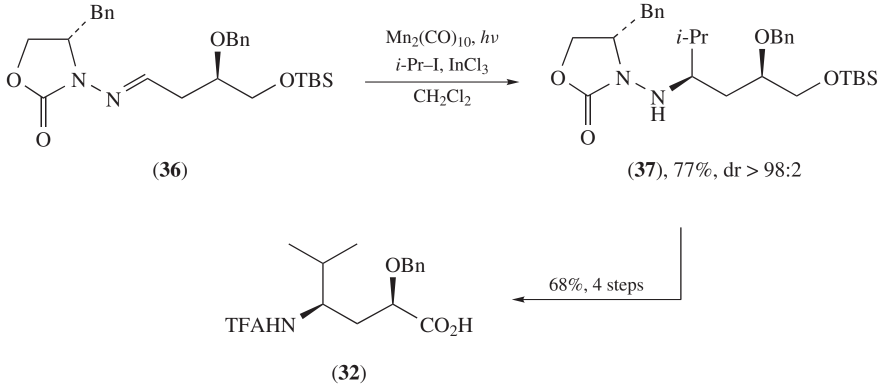
SCHEME 10

For the γ-amino acid **31**, phenylacetaldehyde N-acylhydrazone **33** was employed as the radical acceptor (Scheme 11). Mn-mediated addition of difunctional iodide **34a** (5 equivalents) proceeded in 56% yield, affording **35a** as a single diastereomer[60]. Adduct **35a** was transformed, through a simple 4-step sequence entailing N−N bond cleavage and oxidation, to γ-amino acid **31**. Recently we have found that iodide **34b** bearing an unprotected hydroxyl group couples with hydrazone **33** in 79% yield, using 3.5 equivalents of the iodide. In comparison with other types of stereocontrolled additions to imino compounds, e.g. diorganozinc reagents used in 3- to 5-fold excess with only one of the groups transferred, the stoichiometry is quite attractive. This, together with the functional group compatibility, suggests potential for expanding the applications of radical addition chemistry to more complex and precious precursors.



SCHEME 11

The synthesis of α-alkoxy-γ-amino acid **32** (Scheme 12) must address the potential complication of β-elimination of the benzyloxy group from an imino compound such as **36**. Using Mn-mediated photolysis conditions, isopropyl iodide coupled with the hydrazone, with no evidence of β-elimination, furnishing **37** as a single diastereomer in 77% yield. After N−N bond cleavage and oxidation, carboxylic acid **32** was obtained in good overall yield[60]. This sequence emphasizes the non-basic character of C−C bond constructions using Mn-mediated coupling of alkyl iodides and *N*-acylhydrazones.

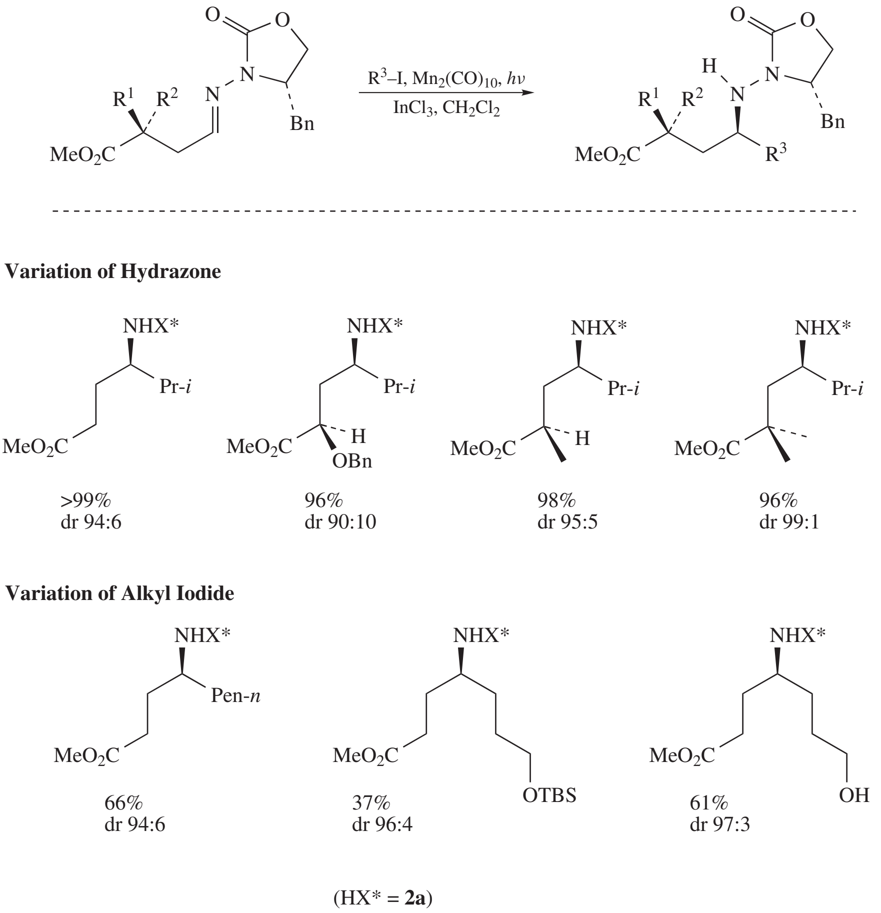


SCHEME 12

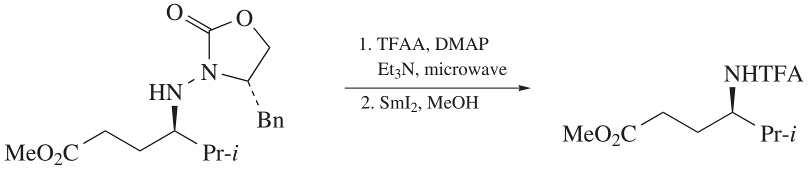
Efforts to develop a γ-amino acid synthesis in which the oxidation state need not be adjusted after coupling led to the hypothesis that γ-hydrazonoesters may be competent radical acceptors[61]. The Mn-mediated radical addition conditions had already exhibited excellent chemoselectivity, but an important question came to light: Would the chelation of In(III) implied by the stereocontrol model be disrupted by the presence of an additional Lewis basic ester function in the hydrazone?

Prototypical radical additions were examined under Mn-mediated photolysis conditions with $InCl_3$ as the Lewis acid, coupling isopropyl iodide with a variety of γ-hydrazonoesters (Scheme 13) bearing varied substitution at the position α to the ester. The α-methyl, α,α-dimethyl and α-benzyloxy substituents appeared to have little effect on reaction efficiency and selectivity, as all provided the isopropyl adducts with consistently high diastereoselectivities and excellent yields (91–98%). Surprisingly, the selectivity was only slightly diminished in the absence of $InCl_3$; the yield in the absence of Lewis acid activation was modest but synthetically useful. The $InCl_3$ coordinates to the imino nitrogen and the oxazolidinone carbonyl, without significant interference by the ester function, as judged by ^1H NMR and ^{13}C NMR spectra obtained in the presence and absence of $InCl_3$.

A range of iodides was also examined in reactions with and without $InCl_3$. With primary iodides, the desired adducts were obtained in moderate yields (37–66%, Scheme 13) and excellent diastereoselectivities. Silyl ether and alcohol functionality were accommodated. Trifluoroacetylation of **38** under microwave irradiation[62] in the presence of Et_3N and DMAP, followed by exposure to SmI_2, smoothly furnished known γ-aminoester **39** (equation 17). Proof of absolute configuration was obtained by enolate allylation of **39** to afford a known derivative whose specific optical rotation matched the published data[63].



SCHEME 13

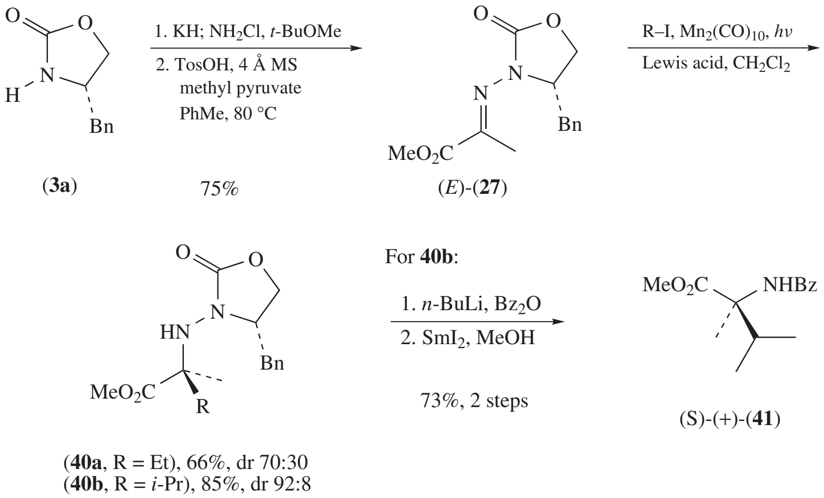


(**38**) (**39**) (17)

c. α,α-Disubstituted α-amino acids. Despite the aforementioned developments with aldimine-type acceptors, there are few examples of the corresponding radical additions to ketimine acceptors[64]. This strategy may provide a diverse range of *tert*-alkyl amines not conveniently prepared by nucleophilic substitution. Using the Mn-mediated coupling methodology, the radical addition approach was expanded to afford α,α-disubstituted α-amino acids[46].

In contrast to aldimines, which generally are obtained with *E* geometry, a key issue in additions to ketimine derivatives is ensuring the reaction takes place exclusively through one *E*/*Z* geometry. Ketones generally afford mixtures of *E*- and *Z*-hydrazones. The efforts began with identifying a ketone hydrazone which would be well-behaved with respect to *E*/*Z* isomerism. Amination of the potassium salt of commercially available (*S*)-4-benzyl-2-oxazolidinone (**3a**, Scheme 14) and condensation with methyl pyruvate furnished hydrazone **27** (*E*/*Z* 92:8). Fortunately, the minor (*Z*)-isomer could be separated by flash chromatography, and (*E*)-**27** was obtained in 75% yield.

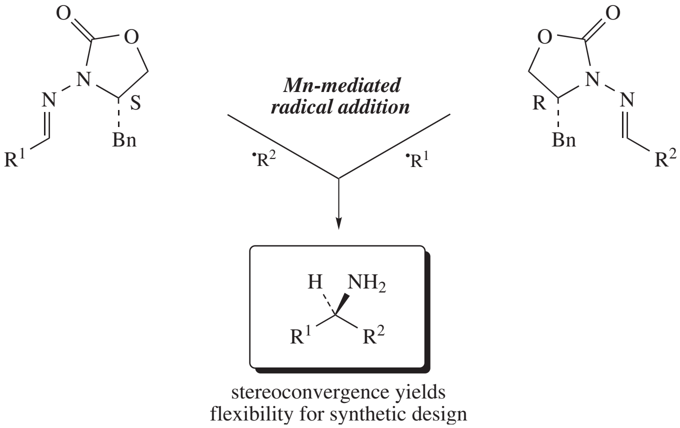
Addition of ethyl iodide to (*E*)-**27** using the Mn-mediated photolysis conditions (Scheme 14) gave 66% yield of the ethyl adduct **40a**, with a modest diastereomer ratio of 70:30, while the corresponding isopropyl addition was very effective (85% yield of **40b**, dr 92:8). Variation of the stoichiometry indicated that amounts less than 2 equivalents of Lewis acid proportionally lowered the diastereoselectivity. This suggested that, in contrast to γ-hydrazonoesters, the α-hydrazonoester may involve the ester function in Lewis acid coordination along with the *N*-acylhydrazone. Cleavage of the N−N bond was achieved upon sequential treatment of isopropyl adduct **40b** with *n*-butyllithium, benzoic anhydride and SmI_2/MeOH (Scheme 14). This sequence afforded known benzamide (*S*)-(+)-**41**[65] in good yield, confirming the assigned configuration.



SCHEME 14

6. Flexibility for synthetic design

Because of the broad functional group compatibility in these Mn-mediated radical additions, they offer an inherently flexible carbon−carbon bond construction approach to synthesis of a range of multifunctional chiral amine targets. The tolerance for functionality in both the radical precursor and hydrazone acceptor allows for potentially feasible retrosynthetic disconnections of a chiral amine at any of the C−C bonds to the stereogenic center. For a secondary amine, epimeric configurations can be selected by either (A) employing the enantiomeric auxiliary, or (B) interchanging the roles of R^1 and R^2 in the alkyl halide and aldehyde precursors[66]. Combining these two tactics, two alternative routes to the target become stereoconvergent (Scheme 15), and the optimal roles of R^1 and R^2 with respect to yield and selectivity can be chosen. Such strategic flexibility contributes to the synthetic potential of these radical addition reactions.



SCHEME 15

IV. CONCLUDING REMARKS

Radical reactions are advantageous in many respects, particularly in the fact that their functional group compatibility complements that of anionic reaction conditions. While initial studies of applications in cyclizations and small molecule coupling reactions resulted in a rather unfortunate focus on mercury and tin reagent systems, many alternatives are now available. In this context, some of the organomanganese-mediated reactions described in this review have reached a sufficiently broad scope and reliability that they may be called upon in synthetic design. Numerous fruitful applications are already envisioned, and yet further inspiration for this review derives from anticipating the unexpected innovations in organomanganese chemistry that may be on the horizon.

V. ACKNOWLEDGMENT

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Energetics of organomanganese compounds

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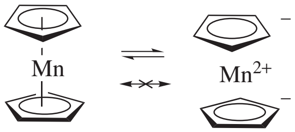
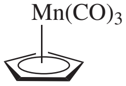
I. INTRODUCTION

Almost 30 years ago, the thermochemistry of organometallic species was reviewed by Pilcher and Skinner in an earlier volume of the Patai/Rappoport series[1]. The periodic table was traversed and the following organomanganese species were cited: the homoleptic carbonyl $Mn_2(CO)_{10}$, the cyclopentadienyl derivatives manganocene and cymantrene, Cp_2Mn (**1**) and $CpMn(CO)_3$ (**2**), and the pentacarbonyl derivatives $RMn(CO)_5$, R = Me, Cl and Br. The Mn^{III} acetylacetonate species $Mn(acac)_3$ was also discussed, even though this species lacks any Mn−C bond: presumably the dual presence of Mn and C sufficed although manganese carbonates, oxalates, formates and acetates were ignored as were their measured enthalpies of formation[2]. The current chapter updates this earlier thermochemical review by inclusion of many other species.



(**1**)



(**2**)

However, stylistically and scientifically, this chapter does not parallel the aforementioned chapter[2] nor those thermochemical reviews we have written for other metal-containing species where more abundant thermochemical information was available[3]. Rather, we will discuss bond energies and indirect existential evidence and reaction-derived results from a wide variety of techniques. Notably scarce in both the current and earlier review is combustion calorimetry with oxygen. Among the reasons for this absence is the perceived lack of accuracy of this technique for organomanganese species. Manganese forms a variety of oxides and oxyhydroxides, many of which have known enthalpies of formation and interconversion[4−6] despite their diverse stoichiometry. However, proper compositional and thermochemical analysis, and then correction for this, is no doubt much more difficult than correcting for the products resulting from the combustion of nonmetallic organic compounds, the so-called 'Washburn correction'[7] that is now a major part of 'classic' calorimetry. Another reason for the comparative absence of oxygen combustion calorimetry is that many of the species of interest have not been isolated but are reagents and/or products of solely gas-phase reactions.

II. BINARY MANGANESE−CARBON CONTAINING SPECIES

The simplest species nominally with manganese−carbon bonds are manganese carbides, Mn_xC_y with stoichiometries that lack the small integer ratios of $x{:}y$ normally associated with binary compounds. The energetics of MnC, either as a crystalline solid[8,9] or as a gaseous diatomic molecule or its ions[10−14], have been studied only by theoreticians to date. Electron affinities, ionization energies and dissociation energies were among the properties computed. The diatomic structure is simply described as $\cdot\dot{:}\mathrm{Mn}{\equiv}\mathrm{C}{:}$, as befits its $^4\Sigma^-$ ground state with its three unpaired electrons. (MnC^+ and MnC^- are both calculated to have $^3\Sigma^-$ ground states with two unpaired electrons apiece.)

Although they are solids, the main group metal carbides such as Mg_2C_3, Al_4C_3 and CaC_2 have simple compositional descriptions. From both their reaction chemistry and crystal structure, these species are easily recognized as completely metallated, hydrogen-free organometallic derivatives of allene/propyne, methane and acetylene, respectively. In contrast, the manganese carbides with x or $y > 1$ seem to defy such characterization.

TABLE 1. Enthalpies of formation, ΔH_f (solid), for Mn_xC_y species ($kJ\,mol^{-1}$)

Mn_xC_y	ΔH_f	Temperature (K)	Reference
Mn_3C	5	298	2
	-54 ± 9		20
	-45 ± 2	*ca* 1100	21
Mn_5C_2	-70 ± 4		22
	-62 ± 11		23
	-83 ± 3	*ca* 1100	21
Mn_7C_3	-91 ± 13		23
	-120 ± 4	*ca* 1100	21
$Mn_{23}C_6$	-246 ± 29		24
	-353 ± 8	*ca* 1100	21

The only experimental thermochemically relevant quantities we know of for MnC_2 are (a) the gas-phase electron affinity, *ca* 205 $kJ\,mol^{-1}$, and (b) that there are two distinct low-lying excited states, both *ca* 100 $kJ\,mol^{-1}$ higher in energy than the ground state[15]. The authors conclude that their measurements on Mn and the other 3d transition metals support the bonding as $Mn^{2+}C_2{}^{2-}$ in analogy to Mn^{2+} O^{2-} and in accord with the long-known similarity of corresponding C_2- and O-containing metal derivatives[16], i.e. acetylide (ethynediide) and oxide ($C_2{}^{2-}$ and O^{2-}).

Gaseous MnC_3 and $MnC_3{}^-$ are also known[17] where they are interrelated by an electron affinity of *ca* 187 $kJ\,mol^{-1}$ for the former. Interestingly, $MnC_4{}^-$ and $MnC_6{}^-$ [18] have both been observed but not $MnC_8{}^-$, where the latter is the formal analog of $MnO_4{}^-$ which, as its potassium salt, is undoubtedly the best known species containing manganese. (Neutral MnC_8, unlike MnO_4, has been reported in the solid phase, however[19], but the C_8/O_2 analogy seems to hold only in terms of stoichiometry, not structure.)

The solid state enthalpies of formation that are available for Mn_xC_y species appear in Table 1. Zaitsev and coworkers deduce[21] that the enthalpy of formation for $Mn_{23}C_6$ decreases only slightly (*ca* 3 $kJ\,mol^{-1}$) when recalculated from 1100 K to 298 K and conclude that their results are more accurate than those from Reference 24 due to uncertainty in the combustion products. At the standard temperature of 298 K, the enthalpy per atom is most generally nearly 10 $kJ\,mol^{-1}$, while at the higher temperature, the enthalpy per atom is *ca* 12 $kJ\,mol^{-1}$.

How do we understand the enthalpies of formation (reported at $T = 1100$ K) for the superficially simpler, Mn_3C and its derivatives wherein the manganese atoms may be, in total or in non-stoichiometric part, replaced by iron, cf. $Mn_{3-x}Fe_xC$[21]? A governing principle for the understanding of these species and related transition metal carbides is the average number of valence electrons[25].

III. HOMOLEPTIC MANGANESE CARBONYL COMPOUNDS AND RELATED SPECIES

A. Dimanganese Decacarbonyl, $Mn_2(CO)_{10}$

The sole isolable homoleptic manganese carbonyl compound is the Mn−Mn σ-bonded species, $Mn_2(CO)_{10}$. Oxygen bomb calorimetry[26] with H_2O_2 and HNO_3 as oxidants results in a solid phase enthalpy of formation of -1677 $kJ\,mol^{-1}$. A calorimetric study of the iodination reaction[27, 28] to form MnI_2 resulted in the nearly identical enthalpy of formation of -1675 ± 8 $kJ\,mol^{-1}$. From vacuum sublimation[28] and the solid phase formation enthalpy, the enthalpy of formation of the gaseous species is deduced to be $-1585 \pm 5\,\mathrm{kJ\,mol^{-1}}$. A more recent investigation[29] used electron impact mass spectrometry. From the appearance potentials for diverse fragment cations, the rather disparate value of $-1510\,\mathrm{kJ\,mol^{-1}}$ was found for the gas phase quantity. As acknowledged for related experiments of mononuclear carbonyl cations, $\mathrm{Mn(CO)}_n{}^+$, there are nonzero energies of activation for metal−CO bond cleavage. These activation energy barriers affect the value of the measured bond energies and derived enthalpies of formation. As such, special care must be taken in their analysis. We prefer the most recent and more direct calorimetric measurement for the enthalpy of formation of gas-phase $\mathrm{Mn_2(CO)_{10}}$.

B. Heteronuclear and Polynuclear Carbonyls

The heteronuclear carbonyl species $\mathrm{MnCo(CO)_9}$ (i.e. the Mn−Co σ-bonded $\mathrm{Mn(CO)_5Co(CO)_4}$) undergoes the disproportionation reaction[30] shown in equation 1. The reaction is almost thermally and entropically neutral, with $\Delta H_\mathrm{r} = 1.3 \pm 0.3\,\mathrm{kJ\,mol^{-1}}$ and $T\Delta S_\mathrm{r} = 2.9 \pm 3.3\ \ \mathrm{J\,mol\,K^{-1}}$. From iodination and sublimation calorimetric measurements[31], it was deduced that $\mathrm{MnCo(CO)_9}$ and $\mathrm{MnRe(CO)_{10}}$ (i.e. $\mathrm{Mn(CO)_5}$ $\mathrm{Re(CO)_5}$) have solid phase enthalpies of formation of -1450 ± 36 and $-1630 \pm 24\,\mathrm{kJ\,mol^{-1}}$, respectively, with corresponding gas phase values of -1388 ± 42 and $-1544 \pm 28\,\mathrm{kJ\,mol^{-1}}$.

$$\mathrm{Mn_2(CO)_{10} + Co_2(CO)_8} \rightleftharpoons \mathrm{2MnCo(CO)_9} \tag{1}$$

Thermochemical data are sparse for species that have fewer CO molecules than the most stable, conventional species. The $\mathrm{Mn_2(CO)_9}$−CO bond energy has been found to be *ca* $160\,\mathrm{kJ\,mol^{-1}}$[32] from which an enthalpy of formation of $-1345\,\mathrm{kJ\,mol^{-1}}$ may be deduced for $\mathrm{Mn_2(CO)_9}$ given the above recommended value for $\mathrm{Mn_2(CO)_{10}}$.

While the corresponding $\mathrm{MnRe(CO)_9}$−CO bond energy has not been measured, it has been shown[33] that the bond energy is smaller for the Mn−CO than for the Re−CO dissociation process, at least in the radical cation[33] and excited state[34, 35] of the mixed carbonyl.

The binuclear carbonyl reaction 2 has an equilibrium constant of 2.13 at 190 °C with an enthalpy and entropy of the reaction of $34.4\,\mathrm{kJ\,mol^{-1}}$ and $80.3\,\mathrm{J\,(K{\bullet}mol)^{-1}}$, respectively[36].

$$\mathrm{Mn_2(CO)_{10} + Re_2(CO))_{10}} \rightleftharpoons \mathrm{2MnRe(CO)_{10}} \tag{2}$$

The trinuclear Mn and Re carbonyls interconvert as shown in equation 3[37].

$$\begin{aligned} &\mathrm{(CO)_5Re(\mu\text{-}H)Mn(CO)_4Mn(CO)_5 + HRe(CO)_5} \rightleftharpoons \\ &\qquad\qquad \mathrm{(CO)_5Re(\mu\text{-}H)Mn(CO)_4Re(CO)_5 + HMn(CO)_5} \end{aligned} \tag{3}$$

An equilibrium constant of 1.00 ± 0.05 was determined. No data are to be found for the individual enthalpy or entropy terms—from the above binuclear example where both quantities are significantly nonzero, we hesitate to assume both are close to 0.0 for this trinuclear case. No data are available involving the valence isoelectronic homonuclear $\mathrm{HMn_3(CO)_{14}}$—its intermediacy has been invoked but seemingly without any thermochemical consequences discussed[38].

C. Sequential CO Bond Energies, $Mn_2(CO)_n{}^+{-}CO$

Sequential $Mn_2(CO)_n{}^+{-}CO$ bond energies have been determined[39] for $n = 0$ through 9. These values ($kJ\,mol^{-1}$) are clearly not monotonic: $n = 9$, 67 ± 5; $n = 8$, 67 ± 5, $n = 7$, 67 ± 5; $n = 6$, 67 ± 5; $n = 5$, 67 ± 5; $n = 4$, 200 ± 5; $n = 3$, 131 ± 5; $n = 2$, 183 ± 5; $n = 1$, 111 ± 5; $n = 0$, 111 ± 5. The energetics for the direct process shown in equation 4 have also been studied[40] for $n = 6$, 5 and 4 and found to be 270, 357 and 405 $kJ\,mol^{-1}$, respectively.

$$Mn_2(CO)_{10} \longrightarrow Mn_2(CO)_n{}^+ + (10 - n)CO + e^- \tag{4}$$

Related processes as shown in equation 5 for a variety of Mn:CO stoichiometries have also been measured[41] but only a common upper bound for all of these processes of *ca* 180 $kJ\,mol^{-1}$ was reported.

$$Mn_2(CO)_x{}^+ \longrightarrow Mn_2(CO)_y{}^+ + (x - y)CO \tag{5}$$

D. Mononuclear Manganese Carbonyls

The simplest (at least to study) mononuclear manganese carbonyl is $Mn(CO)_5$, formed by homolytic Mn−Mn bond cleavage of $Mn_2(CO)_{10}$. The various Mn−Mn bond homolysis enthalpies are $172 \pm 40\,kJ\,mol^{-1}$ from gas-phase ion measurements[42], $158 \pm 17\,kJ\,mol^{-1}$ and free energy of $117 \pm 17\,kJ\,mol^{-1}$ from a solution-phase electrochemical study[43], and $155 \pm 21\,kJ\,mol^{-1}$ from photoacoustic calorimetry[44]. From these, a consensus value of $165 \pm 20\,kJ\,mol^{-1}$ is derived. This is somewhat in accord with the value[45] of $142 \pm 54\,kJ\,mol^{-1}$ suggested some thirty years earlier from a combination of various estimates and thermochemical and spectroscopic values. Combining the consensus enthalpy with the value for the gaseous enthalpy of formation of $Mn_2(CO)_{10}$, we derive a value of $-875 \pm 20\,kJ\,mol^{-1}$ for the enthalpy of formation of $Mn(CO)_5$.

E. Sequential CO Bond Energies, $Mn(CO)_n{}^+{-}CO$ and $Mn(CO)_n{}^-{-}CO$

Gas-phase guided ion mass spectrometry experiments, far more sophisticated and reliable than direct electron impact often used above, result in the following $Mn(CO)_n{}^+{-}CO$ bond energies for the dissociation of the mononuclear cations[46] ($kJ\,mol^{-1}$): $n = 5$, 139 ± 21; $n = 4$, 67 ± 13; $n = 3$, 84 ± 13; $n = 2$, 130 ± 26; $n = 1$, <105 and $n = 0$, >19. Like the isoelectronic $Cr(CO)_6$, $Mn(CO)_6{}^+$ has no unpaired electrons while ground state Mn^+ has 6 unpaired electrons. The decarbonylation of the hexacarbonyl cation (the sole carbonyl ion here obeying the '18 electron rule') is thus a spin-modulated bumpy, barrier-laden path since many of the decarbonylation reactions are spin forbidden. Presumably this 'bumpiness' also affects the decarbonylation enthalpies of the above multiply carbonylated dimanganese cations.

Bond energies for $Mn(CO)_n{-}CO$ are[47]: $n = 4$, $193 \pm 9\,kJ\,mol^{-1}$; $n = 3$, $179 \pm 14\,kJ\,mol^{-1}$; $n = 2$, $114 \pm 8\,kJ\,mol^{-1}$. In the absence of barriers or other complications, summing the decarbonylation enthalpies of $Mn(CO)_5{}^-$ and $Mn(CO)_4{}^-$ should equal the one-step double decarbonylation enthalpy $Mn(CO)_5{}^-{-}2CO$ as found by direct reaction. Likewise, summing the decarbonylation enthalpies of $Mn(CO)_4{}^-$ and $Mn(CO)_3{}^-$ should equal that of the direct reaction of $Mn(CO)_4{}^-$ to form $Mn(CO)_2{}^-$. This was found[47] to be the case within $10\,kJ\,mol^{-1}$. There being no data connecting any of these species with $Mn(CO)^-$ and then Mn^-, however, deprives us of connecting the energetics of $Mn(CO)_5{}^-$ with that of Mn^-, for which the enthalpy is obtainable from the enthalpy of formation of atomic Mn and its electron affinity. This is not surprising, however, because Mn itself (unlike the vast majority of elements, as atoms) does not bind an electron to form a bound anion[48].

The energetics of these ions relate to neutral mononuclear carbonyls. For example, the electron affinity[49] of $Mn(CO)_5$ is 2.4 ± 0.3 eV ($232 \pm 29\,kJ\,mol^{-1}$), and the ionization potential of $Mn(CO)_5$ was suggested[50] as 7.7 eV ($743\,kJ\,mol^{-1}$), thereby interrelating the enthalpies of formation of $Mn(CO)_5$ and its anion and cation. $NaMn(CO)_5$ has been studied as solid and as a solution phase solvent and contact ion pair[50]. Should not its enthalpies of formation and complexation be available and compared with other alkali metal salts? A comparatively simple synthesis of crystalline $Mn(CO)_6{}^+\ BF_4{}^-$ has been reported[51]. Conventional reaction calorimetry, e.g. by reaction with Br_2 or I_2, to form the manganous halide, is thus not unreasonable to ask for both of these salts.

F. Species with Excess CO

We briefly mention $Mn(CO)_6$ and $Mn_2(CO)_{11}$, species that have nominally more carbonyls than the most stable carbonyl:Mn ratio of 5:1 as found in the sole isolable homoleptic manganese carbonyl, $Mn_2(CO)_{10}$. The simplest description of the latter species is $[Mn(CO)_5]_2CO$. To the best of our knowledge, the energetics of neither is known. Nonetheless, they are plausible intermediates in the solution-phase carbonyl transfer reaction[52] between (duly labeled) $Mn(CO)_5{}^-$ and $Mn(CO)_6{}^+$, a reaction that ultimately yields as the decarbonylated product, the normal, classical neutral homoleptic manganese carbonyl $Mn_2(CO)_{10}$ [53]. $Mn_2(CO)_{11}$ and its decarbonylation is discussed along with other $Mn(CO)_5$ derivatives.

G. Manganese Oxocarbon Salts

Manganese squarate containing Mn^{2+} and the oxocarbon anion $(C_4O_4)^{2-}$ is known as the thermally labile anhydrous salt[54], the hydrate[55], and some related hydrated species with the coordinating ligands 1,10-phenanthroline and 1,2-bis(4-pyridyl)ethane[56, 57].There are related salts with the oxoanion croconate, $(C_5O_5)^{2-}$, the hydrated complexes without[58] and with the above nitrogenous ligands[59, 60]. A hydrated ligated complex with $x = 6$, a manganese rhodizonate, has also been synthesized[61] and a complex of Mn^{2+} with the tetraanion $C_6O_6{}^{4-}$ has been observed[62]. No comparison is yet available with the isomeric neutral mononuclear carbonyls, i.e. other species with the same MnC_nO_n formula. Indeed, the decomposition products where $n = 4$ are seemingly too ill-defined to be calorimetrically useful[54]. Reaction calorimetry (acidification) may be efficacious except that squaric acid stands alone among the carbon/oxygen containing products with a measured enthalpy of formation. Although no evidence for manganese oxocarbon π interactions have seemingly been suggested, we note π–π interanion interactions in ammonium[63] and potassium[64] squarate and π–π cation/anion interactions in cobalticenium and chromocenium hydrogen squarate[65]. Such stabilization mechanisms may confound simple interpretation of any derived enthalpy of formation of these manganese oxocarbon salts.

IV. HOMOLEPTIC MANGANESE CYANIDE COMPLEXES AND RELATED SPECIES

CN can be bonded to a metal atom with either C or N, cyano or isocyano, just like alkyl cyanides and isocyanides. In principle, the CN group can also be η^2-bonded (i.e. π-bonded) to a single metal atom as well as bridged between two metal atoms, e.g. M–CN–M.

A. Polycyanomanganates

The enthalpy of formation of aqueous $[Mn^{II}(CN)_6]^{4-}$ is 556 kJ mol^{-1}[2]. $[Mn^{III}(CN)_6]^{3-}$ is known[66] to readily form $[Mn^{IV}(CN)_6]^{2-}$ in a disproportionation reaction on acidification in aqueous medium and this latter ion slowly decomposes to form Mn^{2+} (aq) and cyanogen, C_2N_2. From the known Gibbs free energies of these products[2] we thus determine a lower bound of 670 kJ mol^{-1} for the Gibbs free energy of $[Mn(CN)_6]^{3-}$. A lower bound to the enthalpy of formation of aqueous $[Mn(CN)_6]^{3-}$ may be offered as 502 kJ mol^{-1} if we assume the same difference between the enthalpy and Gibbs free energy[67] for $[Mn(CN)_6]^{3-}$ for $[Fe(CN)_6]^{3-}$, namely 168 kJ mol^{-1} [2]. $[Mn^{I}(CN)_6]^{5-}$ has also been observed[68]. It would be of interest to compare the energetics of these four $Mn(CN)_6$ ions, although the high degree of solvation necessarily complicates any analysis. As also found[69] for solid potassium salts, the volumes of the −3, −4 and −5 $Mn(CN)_6$ ions are not monotonic with charge (123, 144 and 122 cc mol^{-1}, respectively). As noted by the original authors, the size is dependent on whether the 18 electron rule is obeyed or not, and the length of the Mn−C bond is not simply dependent on oxidation state. Finally, while manganese (II) cyanide is actually[70] a salt of Mn^{2+} and $[Mn^{IV}(CN)_4]^{2-}$, what might have been manganese (III) cyanide is likewise[71] a salt of $[Mn^{II}]^{2+}$ and $[Mn^{IV}(CN)_6]^{2-}$ (quite inexplicably with 0.57 waters of hydration). The thermochemistry of 'Prussian blue' species like the latter has been discussed[72]. Many questions remain, for example, why isn't manganese(II) cyanide a 2:1 salt of Mn^{2+} with $[Mn^{II}(CN)_6]^{4-}$; after all, MCN (M = K, Rb) and Mn^{2+} in aqueous solution react[73] to form crystallographically characterizable $M_2MnMn(CN)_6$ with two distinct types of manganese.

In the above species, the manganese is found in oxidation states +1 through +4. What about Mn^0 cyanide complexes? A mixed valence Mn^0/Mn^I complex $K_{11}Mn(CN)_{12}\cdot 2\,NH_3$ has been isolated[74] from the reduction of $[Mn^{III}(CN)_6]^{3-}$ salts by potassium in liquid ammonia and characterized as a mixture of $[Mn^{I}(CN)_6]^{5-}$ and $Mn^0(CN)_6{}^{6-}$ salts. We do not know of any homoleptic manganese cyano complex in which the Mn has a formal negative oxidation state; the mixed cyano nitroso anions, $Mn(NO)(CO)_3CN^-$ and $Mn(NO)_3CN^-$ are well-characterized[75].

We do not know of any Mn^V homoleptic cyanide complex, i.e. $[Mn(CN)_6]^-$. Presumably, Mn(V) is too strongly oxidizing—we recall the instability of Mn^{IV} relative to Mn^{II} as found in $[Mn(CN)_6]^{2-}$. However, the Mn^V nitridocyanide ion $[MnN(CN)_5]^{2-}$ has been isolated[76] as a labile salt which readily decomposes on recrystallization to form the 5-coordinated $[Mn^VN(CN)_4]^-$ by loss of CN^-. A fortiori, we do not know of any Mn^{VI} and Mn^{VII} cyanide complex to accompany the well known oxyanions of Mn in these oxidation states, manganate and permanganate ion.

B. Cationic Manganese Cyanides

Cationic manganese cyano complexes also exist. For example, Mn^{II} complexed with one or two pyridines undergoes collision induced dissociation[77] to form $[Mn(CN)]^+$ either as free cation or complexed with one remaining pyridine. The structure of this cation is unknown. Neutral MnCN has been shown by quantum chemical calculations[78] to be nearly isoenergetic to the isomeric MnNC. This last finding is not surprising. CN^- can be regarded as essentially a spherical ion[79] and the ion pair can be viewed as Mn^+ CN^-.

C. N-Substituted Derivatives

By N-substituted derivatives are meant manganese isonitrile complexes for which both homoleptic and heteroleptic derivatives are well-studied. An electrochemical study[80] interrelates the singly and doubly positively charged $Mn(CO)_{6-n}(CNPh)_n$ ions for $n = 2$

(both *cis* and *trans* isomers), 3 (both *fac* and *mer* isomers), 4 (only *cis*), 5 and 6. The electrochemical processes interconverting the corresponding +1 and +2 ions are quasi-reversible, indicating considerable stability of these species. Each substitution of CO by isocyanobenzene decreases the redox potential $E^0_{1/2}$ by a nearly constant 0.30 V (*ca* 29 kJ mol^{-1}). Quasi-reversible redox reactions for $n = 5$ and 6 to the +3 species is also observed. Similar behavior over a more narrow range of *n* had been observed[81, 82] for the related methyl isocyanide species, $Mn(CO)_{6-n}(CNMe)_n$+1 and +2 ions. The solution-phase Gibbs energy changes may thus be derived using the Nernst equation.

V. PENTACARBONYLMANGANESE DERIVATIVES

Through a combined calorimetric study involving enthalpies of sublimation, decomposition, bromination and iodination, as well as some plausible assumptions, the enthalpies of formation for a variety of $RMn(CO)_5$ species were deduced[83]. It was noted that the R−$Mn(CO)_5$ bond energies generally correspond to those of R−H and R−CH_3, although those for R = CF_3 and $COCH_3$ are 'slightly higher than expected from direct comparison with *D*(R−H)'. References 84 and 85 provide data for additional R groups. In summary, the difference between the enthalpies of formation of $RMn(CO)_5$ and RCH_3, and between $RMn(CO)_5$ and RH, should be rather constant. All of the values as originally determined are given in Table 2. Also included are the values for R = $Mn(CO)_5$, Br, I and H. The assumption for a nearly constant difference is realized for R = H and the various hydrocarbyl groups; perhaps not surprisingly, the same difference is not found for R = $Mn(CO)_5$, Br and I although these groups exhibit a constant difference among themselves.

TABLE 2. Enthalpies of formation, ΔH_f, for $RMn(CO)_5$ species (kJ mol^{-1})

R =	ΔH_f(s)	ΔH_f(g)	Reference	ΔH_f(RCH_3, g)	Difference (g)[a]
$Mn(CO)_5$	−1675 ± 8	−1585 ± 5	83	−753	−832
Br	−964 ± 4	−876 ± 5	83	−35	−841
I	−911 ± 5	−834 ± 5	83	14	−844
H	−778 ± 10	−740 ± 10	83	−74	−666
CH_3	−813 ± 4	−753 ± 4	83	−84	−669
$CH_2CH{=}CH_2$	−727 ± 20	−679 ± 25	85	0	−679
C_6H_5	−675 ± 5	−590 ± 7	83	51	−641
$CH_2C_6H_5$	−726 ± 8	−642 ± 8	83	30	−672
CF_3	−1464 ± 4	−1386 ± 4	83	−745	−641
$COCH_3$	−977 ± 7	−897 ± 10	83	−217	−680
$COCF_3$	−1587 ± 5	−1508 ± 8	83	−832[b]	−681
COC_6H_5	−848 ± 5	−725 ± 6	83	−87	−638
$CO(AlBr_3)CH_3$	−1621[c]		84		

[a] The difference between ΔH_f(g) and ΔH_f(RCH_3, g).

[b] The enthalpy of formation of 1,1,1-trifluoroacetone is unavailable from the experimental literature. The number that appears here is a consensus value of the nearly identical results found (a) by equating the enthalpy of formation difference between acetylacetone and its 1,1,1-trifluoro-derivative, namely −610 kJ mol^{-1}, with that of acetone and trifluoroacetone, and (b) quantum chemical calculations at the G3(MP2)B3 level[86].

[c] From summing the enthalpies of formation of the $COCH_3$ species[83] (−977 kJ mol^{-1}) and $AlBr_3$ (−524 kJ mol^{-1}) and the calorimetrically measured[84] reaction enthalpy (−120 kJ mol^{-1}). The enthalpy of solution of $AlBr_3$ is but a few kJ mol^{-1} (in toluene, deduced from the data in Reference 2) and it was assumed that the enthalpies of solution of $CH_3COMn(CO)_5$ and its $AlBr_3$ complex are not that different[84].

There are some other studies that give relevant thermochemical data. For reaction 6 in supercritical CO_2 solution, with and without cobalt carbonyl catalysis under 34 atm pressure of H_2 at 165 °C, values of 35 ± 1 kJ mol^{-1} and 31 ± 3 J mol^{-1}K^{-1} for the reaction enthalpy and entropy were directly determined[30].

$$\tfrac{1}{2}\,Mn_2(CO)_{10} + \tfrac{1}{2}\,H_2 \longrightarrow HMn(CO)_5 \tag{6}$$

From the data in Table 2, an enthalpy of reaction for equation 6 of about 105–119 kJ mol^{-1} is obtained, the exact value depending on the phase assumed relevant for the comparison.

There is also solution-phase confirmation of some of the above values. The enthalpy of solution-phase carbonylation of $CH_3Mn(CO)_5$ to give $CH_3COMn(CO)_5$ has been determined by evaluation of the equilibrium reaction at 30 °C in diethoxydiethyl ether[87] (-52.9 ± 0.4 kJ mol^{-1}) and by direct high pressure calorimetry[84] (-56.1 ± 4.2 kJ mol^{-1}). Using the consensus value of -54.5 ± 5.8 kJ mol^{-1}, the archival enthalpy of formation of CO, -110.5 kJ mol^{-1}, and neglecting all solvation enthalpies, results in a predicted enthalpy of formation difference between methyl and acetylmanganese pentacarbonyl of -165 kJ mol^{-1}. From Table 2, the difference is -164 ± 8 kJ mol^{-1} for the condensed phase species and -144 ± 11 kJ mol^{-1} for the gases.

Earlier in this chapter we briefly mentioned $Mn_2(CO)_{11}$ with the suggested structure $(Mn(CO)_5)_2CO$. How thermodynamically stable is this carbonyl compared to its decarbonylation products, $Mn_2(CO)_{10}$ and CO, as shown in equation 7? To determine this, let us estimate the enthalpy of formation of $(Mn(CO)_5)_2CO$ by assuming thermoneutrality for reaction 8.

$$(Mn(CO)_5)_2CO \longrightarrow (Mn(CO)_5)_2 + CO \tag{7}$$

$$2CH_3COMn(CO)_5 \longrightarrow (Mn(CO)_5)_2CO + CH_3COCH_3 \tag{8}$$

The derived enthalpy of formation value is -1577 kJ mol^{-1}. The decomposition reaction 7 is thus expected to be -119 kJ mol^{-1} exothermic. In that the decomposition reaction involves an increase in gaseous product molecules, the fragments have a significantly higher entropy as well. Although the reaction is thermodynamically favorable, the rate of decomposition might be slow enough to isolate $(Mn(CO)_5)_2CO$.

The lability and reactivity of most members of the homologous series of C_1–C_{18} *n*-alkyl and alkanoylmanganese pentacarbonyls have been studied[88]. Except for ethyl-, *n*-propyl- and *n*-butylmanganese pentacarbonyls, the alkyl derivatives are relatively stable to air and heat for a short time. The rate of alkyl group migration, the presumed rate-determining step in reaction 9, increases for $n = 1$ to $n = 3$, rapidly decreases for $n = 4$–7 and then levels off or decreases slowly for the higher homologs. Thermal decarbonylation (equation 10), for which the rate-limiting step is loss of a terminal carbonyl group, shows a similar reactivity for the lower series members: the rate increases for $n = 1$–3 and then rapidly decreases throughout the remainder of the series. The authors argue that increasing electron donation from the lengthening of the alkyl group initially dominates and then steric interaction dominates thereafter for both reactions. A DFT study[89] of the structures and reaction pathways of reaction 9 asserted that the simplifying kinetic assumptions in the experimental study were not justified. However, even when the observed rate constant expression is not simplified, a combination of electronic and steric effects still explains the experimental rate differences according to the later authors. Of particular interest to organic chemists is the conclusion that of the three possible acyl intermediates formed by the migration of a methyl group to a carbonyl, only the η^2-acyl ligand and the agostically-stabilized structure are found by calculation of the potential energy surface; the traditional

η^1-acyl ligand is not found[90].

$$\text{RMn(CO)}_5 + \text{Ph}_3\text{P} \longrightarrow \textit{cis}\text{-RCOMn(CO)}_4\text{PPh}_3 \tag{9}$$

$$\text{RCOMn(CO)}_5 \longrightarrow \text{RMn(CO)}_5 + \text{CO} \tag{10}$$

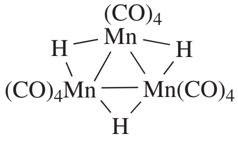
VI. TETRACARBONYLMANGANESE DERIVATIVES

The $Mn(CO)_4$ group is a 15-electron species; this means it is missing 3 electrons from the idealized 18 and so is coordinatively unsaturated. Accordingly, $Mn(CO)_4$ is found bonded to other atoms or groups of atoms in a variety of structural environments.

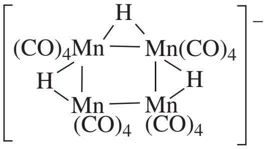
Earlier presented was the $BrMn(CO)_4{-}CO$ bond energy for both the cation and anion species, 67 ± 13 and $193 \pm 9\,\text{kJ mol}^{-1}$[46,47]. The $BrMn(CO)_4{-}CO$ bond energy is $184\,\text{kJ mol}^{-1}$[32]. Equating this with the decarbonylation reaction enthalpy of $BrMn(CO)_5$ in equation 11, one may derive the enthalpy of formation of $BrMn(CO)_4$ as $-702\,\text{kJ mol}^{-1}$.

$$\text{BrMn(CO)}_5 \longrightarrow \text{BrMn(CO)}_4 + \text{CO} \tag{11}$$

The simplest manganese tetracarbonyl is the hydride, $HMn(CO)_4$, which is found in its most stable form as a trimer[91,92] (**3**) like the isoelectronic iron compound, $Fe_3(CO)_{12}$. Laser desorption studies show[93] the presence of higher oligomers as their corresponding deprotonated anions $[H_{n-1}(Mn(CO)_4)_n]^-$ (**4**, $4 \le n \le 9$, $n = 4$ shown). These species are isolobally analogous to cycloalkane carbanions. The values of the proton affinities of these cycloalkyl carbanions do not change[94] monotonically with n; a comparison with these manganese carbonyl anions is thus welcomed.



(**3**)



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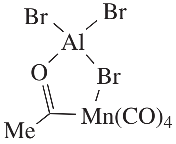
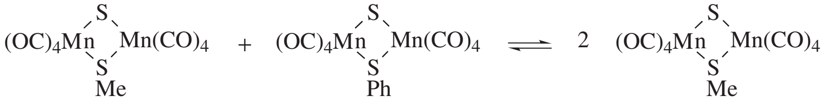


(**5**)

The enthalpies of reaction interrelating the cyclic (bromine bridged) $CH_3CO(AlBr_3)Mn(CO)_4$ (**5**), and the pentacarbonyls $CH_3CO(AlBr_3)Mn(CO)_5$ and $CH_3COMn(CO)_5$ have been measured[84]. Accompanying the enthalpy of formation data for η^1-allylmanganese pentacarbonyl found in Table 2 is the enthalpy of formation of related η^3-allyl manganese tetracarbonyl of $-650 \pm 12\,\text{kJ mol}^{-1}$ for the solid and $-570 \pm 15\,\text{kJ mol}^{-1}$ for the gaseous-phase species[85].



(12)

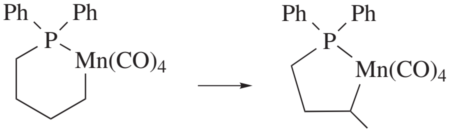
Thiolato derivatives, $RSMn(CO)_4$ are dimeric (with two bridging SR groups) for which the enthalpies of formation of the methyl and ethyl derivatives have been determined by reaction calorimetry[95] as -1521 ± 30 and $-1555 \pm 30\,\text{kJ mol}^{-1}$ for the solids with R = Me and Et respectively, and $-1407\,\text{kJ mol}^{-1}$ for the gaseous R = Me species.

The light-induced equilibration shown in equation 12[96] readily proceeds, while the non-manganese phosphine-catalyzed reaction shown in equation 13 proceeds slowly[97]. In both cases the equilibrium constant appears close to unity and hence the Gibbs energy is close to 0 kJ mol^{-1}.

$$\mathrm{MeSSMe + PhSSPh \rightleftharpoons 2MeSSPh} \qquad (13)$$

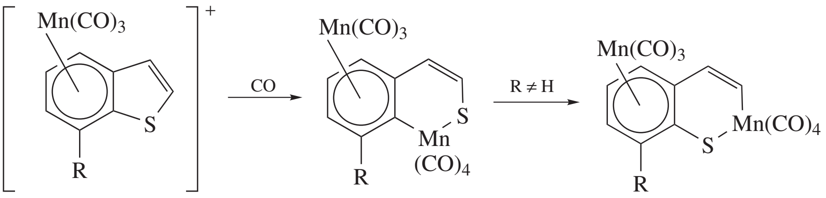
Another type of manganese tetracarbonyl derivative are the anionic $[\mathrm{Mn(CO)_4X_2}]^-$ species for X = Cl, Br, I and CN. In all cases[98], the *cis* isomer is observed and not the *trans*: it is plausible that the *cis* isomer is more stable. For a different set of X_2 derivatives, namely 1,2-disubstituted ethylenes, the *cis* isomer is more stable than the *trans* isomer for X = Cl and Br[99, 100], they are of nearly identical stability for X = I, and for X = CN [101]. The *trans* isomer is generally the more stable for most other X such as most organic groups.

1,1-Diphenyl-2,2,2,2-tetracarbonyl derivatives of 1(λ^4)-phospha-2(λ^6)-manganacycloalkanes thermally rearrange[102] to the corresponding 3-methyl-1-phospha-2-manganacyclopentane (equation 14). This violates what is expected from their carbocyclic counterparts, cyclohexane and methylcyclopentane, where the 6-membered ring species is more stable. However, the two different ring-sized species with sulfur, thiacyclohexane and 2-methylthiacyclopentane, have the same enthalpy of formation to within 1 kJ mol^{-1}. Alternatively, consider the equilibrium in equation 15 involving an acyclic manganese phosphine hydride and a 1-phospha-2-manganacycloalkane, or more precisely, the 1,1-diphenyl-2,2,2,2-tetracarbonylcycloalkanol derivative. As discussed[103], for $n = 2$, both the aldehyde and the cycloalkanol are observed species. For $n = 2$ with a benzo group replacing the dimethylene chain, the latter cyclic species is the sole form observed. When nitrogen replaces phosphorus, the cyclic 1-aza-2-manganacycloalkane derivative is also the preferred form. For $n = 0$ the chemistry is somewhat more complicated with a higher concentration of the acyclic species[104]. We note that cyclopentanol is more stable than pentanal, but cyclopropanol is unequivocally less stable should we assume that cyclopropane and cyclopropanol have the same strain energy.



(14)

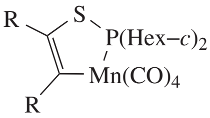
$$\mathrm{(OC)_4Mn(H)PPh_2(CH_2)_nCHO \rightleftharpoons cyclo\text{-}Mn(CO)_4PPh_2(CH_2)_nCHOH} \qquad (15)$$



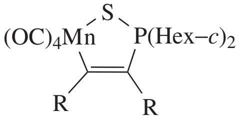
(16)

Reduction of 7-substituted η^6-benzothiopheneMn(CO)$_3^+$ derivatives in the presence of CO results in the corresponding η^6-complex of 1(λ^6)-mangana-2-thianaphthalene-1,1,1,1-tetracarbonyl. This last species then rearranges to the 2(λ^6)-mangana-1-thia isomer (equation 16)[105]. No such rearrangement is seen in the absence of a 7-substituent. It would appear that the instability of the 1-Mn-2-S-species is due to *peri*-type repulsion between the 7-substituent and the CO groups on the Mn, analogous to destabilization of 1,8-disubstituted naphthalenes.

Finally, we note the synthesis of 1,2,3- and 1,2,5-thia(λ^4)phospha(λ^6)mangole and 1,2,3-thia(λ^4)phospha(λ^6)mangepin tetracarbonyl derivatives (6–8)[106]. Two thermochemical questions immediately arise: do any of these species enjoy any homoaromatic stabilization and what is the relative stability of the two isomeric mangoles.

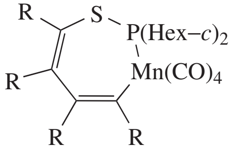


(**6**)



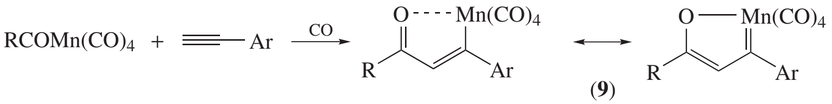
R = COOMe

(**7**)



(**8**)

There are also $Mn(CO)_4$ containing species in which Mn is part of a stabilized ring, namely derivatives of 1,2-(λ^6)manganoxole-1,1,1,1-tetracarbonyl (**9**). By crystallographic structural determination, reaction chemistry[107] and NMR spectroscopy[108], it was suggested that these species should be related to the aromatic furan. These species were readily formed[109] by reaction of phenylacetylenes with acyl$Mn(CO)_4$ (in transient equilibrium with the isolable, more stable, alkyl$Mn(CO)_5$ derivatives) accompanied by the loss of CO (equation 17): the corresponding reaction of olefins to form the saturated metallocycle requires much higher pressure condition. This suggests enhanced stability of the unsaturated ring system. While thermochemical documentation of enhanced resonance structure-derived stability is absent, it is also absent for many other more conventional aromatic species, and certainly most other species that are considered metalloaromatic[110].



(**9**) (17)

VII. MANGANOCENE (BISCYCLOPENTADIENYL MANGANESE) AND DERIVATIVES

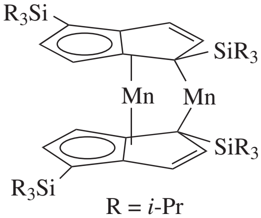
A. Manganocene and Substituted Derivatives

Ferrocene, or biscyclopentadienyl iron, is probably the best known organometallic species, or at least the best known species involving transition metals. The corresponding manganese compound, with one less proton and one less electron than iron, is known as manganocene or biscyclopentadienyl manganese. Comparisons between these compounds are not so simple because ferrocene is a covalent, totally spin-paired, species that may be formally described as a sandwich compound with ionic Fe^{2+} and cyclopentadienide ions, Cp^-, bonded in a η^5- or pentacoordinated manner. Manganocene may likewise be understood as being composed of Mn^{2+} and Cp^-. However, in that Mn^{2+} is a high spin cation (with 5 unpaired electrons) it disallows a simple, spin-allowed combination with the Cp^- aromatic anion to form a covalent species Cp_2Mn that is isoelectronically and isostructurally analogous to ionized ferrocene with one unpaired electron, i.e. ferricenium ion. In the solid state, it has long been known that solid manganocene is not a simple sandwich compound[111]. So, before discussing the energetics of manganocene as defined by its enthalpy of formation, we need to know about its spin state and thereby its description as a molecular entity as opposed to a salt or ion triplet. In other words, we now consider the equilibrium in equation 18. From temperature-dependent NMR spectroscopy[112], the following thermodynamic values favoring the high spin species were found: $\Delta H^0 = 21 \pm 5\,\text{kJ mol}^{-1}$ and $\Delta S^0 = 100 \pm 20\ \text{J mol}^{-1}\text{K}^{-1}$. These values result in manganocene being a slowly exchanging mixture of these two spin states in solution. Substituent effects on the equilibrium have been of interest. While there are no thermochemical data for metallocenes with more 'extreme' organic substituents such as amino, methoxy and carbethoxy, a good generalization for manganese is that alkyl substituents, acting as electron-donating groups, stabilize low spin species while silyl substituents, as electron-withdrawing groups, favor high spin species[112, 113]. Nonetheless, bis(1,2,4-tri-*t*-butylcyclopentadienyl)manganese prefers the high spin species as well and this was ascribed to repulsion between the rings[113] resulting in lengthened bonds between the rings and the central metal atom. We note that 1,2,4-tri-*t*-butylbenzene is destabilized by *ca* 80 kJ mol^{-1} relative its to its 1,3,5-isomer[114, 115] suggesting intra-ring effects may also be operative.

$$^{2}\text{Cp}_2\text{Mn} \rightleftharpoons {}^{6}\text{Cp}_2\text{Mn} \tag{18}$$

The recommended[83] enthalpies of formation of solid and gaseous manganocene are 201.0 ± 2.8 and $276.7 \pm 3.3\,\text{kJ mol}^{-1}$; the recommended sublimation enthalpy is $75.7 \pm 1.7\,\text{kJ mol}^{-1}$. This last value is very much the same to within a 'few' kJ mol^{-1} to those recommended for other biscyclopentadienyl metal derivatives, most notably of Fe, Co and Ni. This is fortuitous, because manganocene is polymeric in the solid with CpMn units bridged by η^2:η^3-cyclopentadienyl groups[116]. Ion energetics studies either accept these values within some small variation[117] or rederive the gas phase value, e.g. $275 \pm 29\,\text{kJ mol}^{-1}$ [29] in good agreement. Unlike the case of ferrocene and bisbenzenechromium, there are seemingly no substituted derivatives for which there are enthalpy of formation values.

We noted above that manganocene is not simply describable as the bis-η^5-cyclopentadienyl derivative of Mn$^{\text{II}}$. Crystallographic and magnetic investigations show[118] that pentalene, as its 1,4-bis(triisopropylsilyl)derivative, does form a bis-η^5-cyclopentadienyl sandwich with manganese$^{\text{II}}$ accompanied by bis η^1- bonding (i.e. simple σ-bonded) of its second ring to a second Mn$^{\text{II}}$ (**10**). The two manganese centers respectively have 0 and 6 unpaired electrons (with a very low lying excited state that has 0 and 4 unpaired electrons) and so this species is more reminiscent of a mixed valence complex of Mn$^{\text{I}}$ and Mn$^{\text{III}}$.



R = *i*-Pr

(**10**)

B. Manganocene Ions

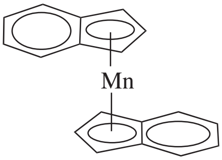
Manganocene has one less electron than ferrocene. Although ferrocene is well known to readily oxidize to the stable cation ferrocinium ion, there is no evidence for a stable

Cp_2Mn^- ion, corresponding to reduced manganocene[119]. Following from the finding that decamethylmanganocene is a ground state doublet with a low spin configuration, its low spin anion $[Cp^*{}_2Mn]^-$ has been isolated as the THF solvated sodium salt, that on heating forms the unsolvated compound[120]. Not surprisingly, this species is a strong reducing agent and reverts to decamethylmanganocene on reaction with both protic acids and alkyl halides rather than form any Mn(I) or Mn−R containing species. Salts of Cp_3Mn^- and its ring methylated derivatives have been structurally characterized[121]. This suggests measurements of gas-phase anion affinities of manganocene should be made.

The adiabatic ionization energy of manganocene is suggested[117] to be 6.12 ± 0.07 eV, resulting in an enthalpy of formation of Cp_2Mn^+ of 890 ± 7 kJ mol^{-1}. The recommended enthalpy of formation of $CpMn^+$ is 935 ± 16 kJ mol^{-1} [117]. The $CpMn^+$−Cp and Cp−Mn^+ bond energies are nearly the same, 331 ± 16 and 326 ± 14 kJ mol^{-1}.

C. Related Ring Systems

The metallocene species with indenyl ion, $(Ind)_2Mn$ (**11**), was recently isolated[122] as the di-THF solvate wherein one ring apiece exhibited η^1- and η^3-coordination. Both 1,3- and 2-substitution on the 5-membered ring resulted in the corresponding classical (η^5-) ‘manganocene’ sandwich structure while 4,7-substitution on the 6-membered ring resulted in an octamer with both η^1- and η^5-bonding. In no case described was there bonding of manganese with the 6-membered ring. In all cases studied, the high spin species was observed. Differences between these indenylmanganese compounds and manganocene cannot be ascribed to degrees of covalency of the C−Mn bonds in that the gas acidities of indene[123, 124] and cyclopentadiene[125, 126] are nearly identical.



(**11**)

D. Heteroanalogs

The complexation of Mn^+ with the 6π aromatic heterocycles pyrrole and furan has been studied. Pyrrole participates with an arene–Mn^+ binding energy of 180 kJ mol^{-1} for the 1:1 complex with much weaker binding for the 2:1 complex[127]. There was no binding observable for furan under these authors’ gas-phase reaction conditions[128]. Related complexes[129] of the dimeric cation, Mn^{2+}, with up to five pyrrole and furan ligands have been observed. Much as pyrrole binds Mn^+ more strongly than does furan, pyrrole binds $Mn_2{}^+$ more strongly than does furan. It was also suggested that the dimeric cation maintains its identity in the complex, rather than a reverse sandwich arrangement such as $(\eta^5\text{-Pyrrole})_2Mn(\mu\text{-pyrrole})Mn(\eta^5\text{-Pyrrole})_2$. This seems surprising given Mn^+ is bound more strongly to pyrrole than to Mn, i.e. the structure is not $[(\eta^5\text{-pyrrole})_2MnMn(\eta^5\text{-pyrrole})_3]^+$.

VIII. CYCLOPENTADIENYLMANGANESE TRICARBONYL (CYMANTRENE) AND RELATED SPECIES

A. The Parent Species and Ring-Cyano Analogs

Like manganocene, cyclopentadienylmanganese tricarbonyl, η^5-CpMn(CO)$_3$, is important enough to have its trivial name, cymantrene, enter the standard chemical vocabulary. The recommended solid and gas phase enthalpies of formation determined by classical calorimetry are -528.1 ± 6.8 and $-475.7 \pm 7.5\,\mathrm{kJ\,mol^{-1}}$, respectively[83]. Ion studies have suggested other values for the gas phase value, $-377 \pm 29\,\mathrm{kJ\,mol^{-1}}$ [29] and $-424 \pm 17\,\mathrm{kJ\,mol^{-1}}$ [117]. The discrepancy between the latter ion study and the calorimetric measurement is partially remediated by considering the enthalpy of sublimation that interrelates the solid and gaseous species. A recent study[130] reports a value of $76.0 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$, compared to the earlier value[83] of $52.4 \pm 3.1\,\mathrm{kJ\,mol^{-1}}$. Using the new value for the sublimation enthalpy with the solid-phase calorimetric enthalpy of formation results in a gas-phase enthalpy of formation of $-452.1 \pm 7.4\,\mathrm{kJ\,mol^{-1}}$, nearly overlapping one of the ion study values[117]. We will use this value of $-452\,\mathrm{kJ\,mol^{-1}}$ in our subsequent analysis.

Cyanocyclopentadienide complexes show the manganese to be either η^5-bonded to the five ring carbons or nitrogen-bonded as the ketenimine >C=C=N−Mn. Only the former are of the class of compounds to be explicitly discussed here, but the distinction is important to make. With but one cyano group, the η^5-complex with Mn(CO)$_3$ is formed, as is found also for the 1,2-dicyano species[131]. There are no data for the 1,3-dicyanocyclopentadienide species. For the isomeric 1,2,3- and 1,2,4-tricyano species, only polymeric complexes bonded through nitrogen are found[132]. The reduction of π electron density in the ring by the cyano substituents would be expected to destabilize sandwich compound formation. We also note that polymer formation for the dicyano species would be inhibited by steric repulsion and dimerization would require bent, and hence destabilized, cyano groups. (We are reminded of the analysis of the formation of halogen-bridged dimers and cyano-bridged oligomers of organo-Pd(II) and Au(III) species in which there are bent cyano groups bridging the metals[133].) In contrast, pentacyanopentadienide only forms polymeric complexes[132].

Isocyanocyclopentadienide forms[134] an air-stable but light and heat labile η^5-complex with Mn(CO)$_3{}^+$. The ligand, isocyanocyclopentadienide, is presumably less stable than cyanocyclopentadienide by analogy to other isocyano compounds[135], and isocyanomethanide is less stable than cyanomethanide ion by *ca* $107 \pm 15\,\mathrm{kJ\,mol^{-1}}$ [136]. However, no isomerization of isocyanocyclopentadienideMn(CO)$_3{}^+$ has been described.

Finally, η^6-phenylazideMn(CO)$_3{}^+$ thermally converts to the ring contracted η^5-cyanocyclopentadienylMn(CO)$_3$ [137] wherein N$_2$ and H$^+$ are lost. This reflects the relative stability of benzene and cyclopentadienyl derivatives of manganese. No azepine complex is formed corresponding to thermal ring expansion reactions[138] of uncomplexed phenylazide accompanying N$_2$ loss.

B. Anions of Cyclopentadienylmanganese Tricarbonyl Formed by Electron Addition

The gas-phase electron affinity of methylcyclopentadienylmanganese tricarbonyl has been experimentally determined[139] to be $48 \pm 9\,\mathrm{kJ\,mol^{-1}}$. No corresponding bound state for the anion of the unsubstituted species has been observed[140] as opposed to a resonance, i.e. long-lived low lying but still unbound state. In solution, the unsubstituted and methylated anions are presumably formed on electrochemical reduction[141] en route to diverse dimerized (both C−C and Mn−Mn) products as well as Mn(CO)$_5{}^-$.

Methylcyclopentadienylmanganese tricarbonyl may be reduced[142] to the presumed η^3-dianion by the novel two-electron reductant K^-. On reaction with more than 2 equivalents of the strong acid CF_3SO_3H, only the monoanion was found as a product. This shows the extremely high acidity of η^3-methylcyclopent-1-en-3-ylMn$(CO)_3$, the putative diprotonated species, even though one might have thought it would have stabilized by agostic interactions much like the isomeric cyclohex-1-en-3-ylMn$(CO)_3$ [143]. The monoanion containing a η^4-methylcyclopentadiene ring is readily displaced by naphthalene, suggesting this arene is more stabilizing than the alicyclic diene despite some loss of aromaticity on complexation.

C. Cyclopentadienylmanganese Dicarbonyl Species

Gas-phase ion studies[144] give values of -137 ± 17 and $-92 \pm 18\,\mathrm{kJ\,mol^{-1}}$ for the enthalpies of formation of $CpMn(CO)_2CS$ and $CpMn(CO)_2CSe$, respectively. The very large difference between these values and the all-oxygen species reflects the difference between the enthalpies of formation of CO, and of CS and CSe. The CO displacement reactions 19 are exothermic by 99 ± 8 and $145 \pm 8\,\mathrm{kJ\,mol^{-1}}$ for X = S and Se, respectively.

$$CpMn(CO)_3 + CX \longrightarrow CpMn(CO)_2CX + CO \qquad (19)$$

One carbon monoxide molecule may be photochemically cleaved from cyclopentadienylmanganesetricarbonyl to form the corresponding dicarbonyl species. By use of photoacoustic calorimetry[145] the Mn−CO bond energy was determined to be $249\,\mathrm{kJ\,mol^{-1}}$. If we accept the value of $-452\,\mathrm{kJ\,mol^{-1}}$ suggested for the enthalpy of formation of $CpMn(CO)_3$ and the archival enthalpy of formation of CO of $110\,\mathrm{kJ\,mol^{-1}}$, the enthalpy of formation for neutral $CpMn(CO)_2$ is $-93\,\mathrm{kJ\,mol^{-1}}$. The related[146] MnCO bond enthalpy in $CpMn(CO)_2{}^-$ is $200\,\mathrm{kJ\,mol^{-1}}$. Subsequent loss of CO from the so-formed monocarbonyl anion, $CpMn(CO)^-$, to form $CpMn^-$ costs but $120\,\mathrm{kJ\,mol^{-1}}$.

Appearance potential data are available for $CpMn(CX)^+$ and $CpMn(CO)CX^+$ (X = O [117, 147], S[144] and Se[144]) as well as for $CpMn(CO)_2(CX)^+$ ions (see Table 3). However, data are lacking to derive the enthalpies of formation of the vast majority of the corresponding neutral species.

$CpMn(CO)_2$ forms complexes with diverse ligands. The lower bounds for its binding energy[148] to the following hydrocarbons are: CH_4, 39 ± 1; C_2H_6, 36 ± 2, c-C_5H_{10}, 24 ± 2, 34 ± 3, n-C_7H_{16}, $36 \pm 2\,\mathrm{kJ\,mol^{-1}}$. It also forms bonds with alkyl chlorides and bromides[149]. With CH_2Cl_2 and n-BuCl the bond energies are 69 and $79\,\mathrm{kJ\,mol^{-1}}$, while with CH_2Br_2, n-BuBr and n-PenBr the bond energies are 84, 88 and $88\,\mathrm{kJ\,mol^{-1}}$.

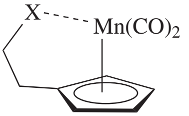
The bond energy between $CpMn(CO)_2$ and tetrahydrofuran is *ca* $100\,\mathrm{kJ\,mol^{-1}}$ [149, 150]. The binding energies of furan and 2,3-dihydrofuran, both in their η^2-coordination modes,

TABLE 3. Enthalpies of formation, ΔH_f, for $CpMn(CO)_nCX^+$ ($\mathrm{kJ\,mol^{-1}}$)

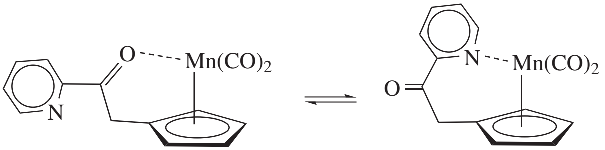
ΔH_f		X	
n	O	S	Se
0	938 ± 15	1012 ± 17	1045 ± 18
1	719 ± 15	827 ± 17	861 ± 18
2	546 ± 15	597 ± 17	642 ± 18
3	325 ± 15		

to $CpMn(CO)_2$ have been shown[151] to be *ca* 46 and 88 kJ mol^{-1}, respectively. This difference of 42 kJ mol^{-1} for the unsaturated heterocycles reflects the aromaticity of furan, as also shown by the 42 kJ mol^{-1} difference in hydrogenation enthalpies between these two heterocycles[152]. It was assumed that the furan binds via C_2 and C_3. As calculational theory was also employed[151], and a thermochemical comparison of 2,3 and 2,5-dihydrofuran was reported[153], we wonder now about the binding energy of 2,5-dihydrofuran with $CpMn(CO)_2$. The ligand is assumed to be η^2-bonded and involve C_3 and C_4. $CpMn(CO)_2$(2,3-dihydrofuran) exists as two isomers, the η^1-O- and the η^2-olefinic bonded species. The latter is formed irreversibly from the former[154]. This is not surprising since we would expect the oxygen in 2,3-dihydrofuran to have diminished, and the C=C bond to have enhanced, donor properties because of the vinyl ether conjugation.

The intramolecularly halogen bonded species $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2X]Mn(CO)_2$ (**12**, X = Br, I) are stable to Mn−X cleavage up to *ca* −20 °[155]. 2-Pyridinyl-2-oxoethylcyclopentadienylmanganese dicarbonyl, $[2\text{-}C_5H_4NCOCH_2C_5H_4]Mn(CO)_2$, exists as two equilibrating isomers[156]; the metal is attached to the acyl oxygen in one isomer and to the pyridine nitrogen in the other (equation 20). The latter is more stable. These authors also prepared isomers of the related thioamide, $[NH_2C(S)CH(2\text{-}Py)CH_2C_5H_4]Mn(CO)_2$, and showed that the stability order for bonding decreases in the order S> pyridyl N > amide N ∼ 0.

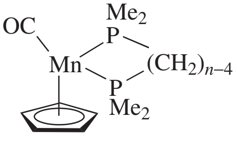


(**12**) X = Br, I

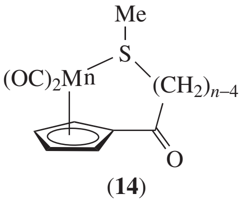


(20)

By photoacoustic calorimetry, the ring strain in $CpMn(CO)(PMe_2(CH_2)_{n-4}PMe_2)$ (**13**) has been determined[157] as a function of the size of the n-membered ring, where the n-membered ring includes one carbon atom of the cyclopentadienyl. For $n = 4$, the strain energy is *ca* 49 ± 13 kJ mol^{-1}, while for $n = 5$ and 6 no strain was found. Likewise, the strain energy in cyclo-$[MeS(CH_2)_{n-4}COC_5H_4]Mn(CO)_2$ (**14**) was shown[158] to be negligible for $n = 5$ and 6. The latter study also showed that the strain energy is essentially the same for $n = 5$ and 6 in $[MeOOC(CH_2)_{n-4}C_5H_4]Mn(CO)_2$ (**15**). From these findings we conclude that both 5- and 6-membered rings containing manganese are generally unstrained.



(**13**)



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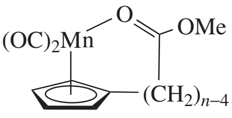
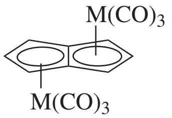


(**15**)

D. Benzo and Other Fused Analogs: Indenyl, Fluorenyl and Pentalene Derivatives

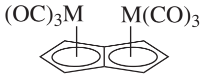
As shown by mass spectrometry[159], benzoannelation results in successively weakened bond strengths in the $Mn(CO)_3$ complexes of cyclopentadienyl, indenyl and fluorenyl. This makes sense in terms of the decreased charge and less 6π character of the 5-membered ring because of greater delocalization through this series. We note the successful synthesis[160] of η^1-9-fluorenylMn$(CO)_5$ and its subsequent thermolysis to form the η^5-fluorenylMn$(CO)_3$, 9,9′-bifluorenyl and $Mn_2(CO)_{10}$. In that the enthalpy of formation of $Mn_2(CO)_{10}$ (see Section II) and of the C−C bonded ‘dimer’[161] are both available, we welcome a calorimetric measurement of this process that would help interweave the thermochemistry of manganese pentacarbonyl and tricarbonyl derivatives.

Pentalene forms[162] a bis manganesetricarbonyl derivative in which the two metals and appended ligands are on opposite sides of the hydrocarbon (**16a**). It may be thought that this is to allow the two metals to avoid each other for steric reasons. This is too simplistic a picture because with the isoelectronic, but larger, rhenium tricarbonyls both *syn* and *anti* isomers are known (**16a**, **16b**, M = Re). Also, the two manganese atoms are favorably interacting as shown by the facile and reversible electrochemical formation of the mono and dianion of this pentalene bismanganese complex. In η^5-cyclopenta[*c*]thienyl (2-thiapentalene) $Mn(CO)_3{}^+$ derivatives[163], it is the carbocyclic ring to which the metal prefers to coordinate.



M = Mn, Re

(**16a**)



(**16b**)

E. Fulvene Derivatives

By use of literature measurements of the gas phase acidity[164] and electron affinity[139] of methylcyclopentadienylMn$(CO)_3$, a H−$[CH_2C_5H_4Mn(CO)_3]^-$ bond energy of 210 ± 77 kJ mol^{-1} was derived[139, 165]. $[CH_2C_5H_4Mn(CO)_3]^-$ is a fulvene derivative. While the uncertainty in the latter measurement is high, it was nonetheless deduced that the anion is considerably stabilized relative to benzyl anion. Benzyl cation is also stabilized. While the cationic counterpart of the aforementioned fulvene derivative. i.e. $[CH_2C_5H_4Mn(CO)_3]^+$, remains unknown, 6, 6-disubstituted species[166] have been shown to be stabilized (and $pK_R{}^+$ values measured) as befits a η^5:η^1-18 valence electron complex description[166].

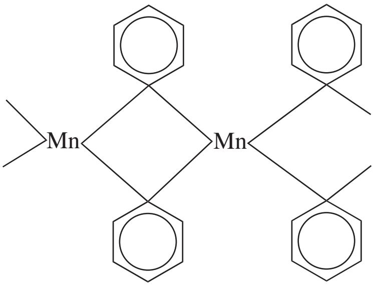
No data are available to compare the fulvene–Mn bond energy of this analogous pair of anion and cation, or of any substituted derivatives, and the large error bar inherent in the former quantity discourages our making estimates. What about neutral fulvene complexes? No data are available here either. η^5-CyclohexadienylMn$(CO)_3$ readily reacts with 6,6-dimethylfulvene under UV irradiation[167] to form isopropylcyclopentadienylMn$(CO)_3$ by hydrogen atom and ligand transfer. That benzene is more aromatic than fulvene and cyclopentadienyl is a better ligand than cyclohexadienyl provide a thermodynamic driving force for this photochemical reaction. Whether any neutral $CH_2C_5H_4Mn(CO)_3$ radical, or, more properly, its dimethyl derivative, is formed is moot. Gas-phase bracketing and solution-phase electrochemical experiments on $[CH_2C_5H_4Mn(CO)_3]^-$ and/or $[CPh_2C_5H_4Mn(CO)_3]^+$ are welcomed as probes of these fulvene complexes in their −1, 0 and +1 charge states. Diverse fulvenes photochemically react[168] with CpMn$(CO)_3$ and Cp*Mn$(CO)_3$ to displace one and/or two CO groups. It was shown that the endocyclic fulvene double bonds preferably reacted. This may be understood in terms of decreased steric hindrance of these ring double bonds. 6-(Dimethylamino)fulvene[169] reacts with $[HMn(CO)_4]_3$ to form η^5-(dimethylaminomethyl)cyclopentadienyl$Mn(CO)_3$ by a formal simple addition reaction and subsequent decarbonylation; the aromatization of the cyclopentadienyl ring provides a strong driving force.

IX. ARYL AND ARENE DERIVATIVES

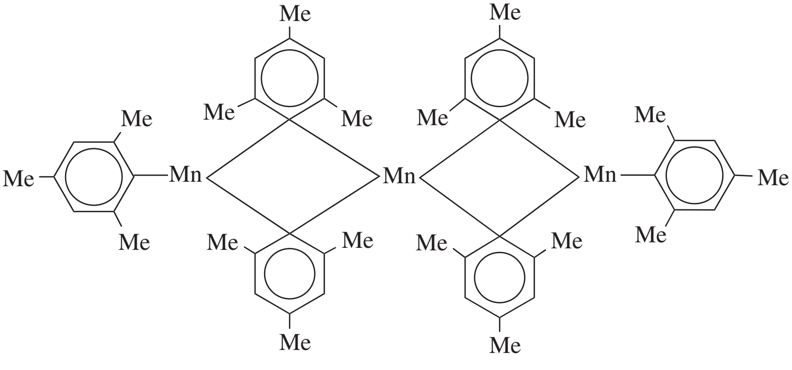
By an aryl derivative, we mean a substituted benzene, naphthalene, or any of a plethora of benzenoid species containing a σ Mn−C bond (i.e. η^1-coordination) while an arene derivative means a multiply coordinated π complex of benzene, naphthalene, or any of a plethora of benzenoid species. A wide variety of hapticities is found. Some of the species discussed in this section employ both modes of bonding; sometimes, it is not clear from the literature which mode is meant. Arene manganese derivatives also include $Mn(CO)_3{}^+$ containing species.

A. Phenyl and Substituted Phenyl Species

As elsewhere mentioned in this chapter, the enthalpy of formation of the σ-bonded $PhMn(CO)_5$ had been determined as -675 ± 5 and $-590 \pm 7\,\mathrm{kJ\,mol^{-1}}$ for the solid and gas phase species, respectively[83]. There are no enthalpy of formation values for the



(**17**)



(**18**)

formally simple diphenyl manganese species, Ph_2Mn, save the conclusion that it must be greater than *ca* 100 kJ mol^{-1} because, in THF, it reacts[170] with elemental hydrogen to form benzene and elemental manganese. As shown crystallographically[171], diphenylmanganese is an infinite doubly carbon bridged polymer $[Mn(\mu\text{-}Ph)_2]_\infty$ (**17**) while the more hindered dimesitylmanganese is trimeric[172]. It was shown that this latter species[171] is not a 6-membered ring with three metal atoms alternating with three bridging mesityl rings but rather is the 'acyclic', $MesMn(\mu\text{-}Mes)_2Mn(\mu\text{-}Mes)_2MnMes$ (**18**). Dimesitylmanganese•THF is a dimer, bridged by the *ipso*-carbons of the benzene ring[171]. The still more hindered bis(2,4,6-tri-*t*-butylphenyl)manganese[173] and bis(2,6-dimesitylphenyl)manganese[174] are monomeric. There are no equilibrium constant data for any aggregation reactions or for solvation of these diarylmanganese compounds, unlike those for the related aryl copper species[175].

It has been determined crystallographically[176] that the $Li(THF)_4{}^+$ salt of $[Mn(Mes)_3]^-$ is monomeric while the corresponding salt of $[MnPh_3]^-$ is a phenyl bridged dimer much as hexaphenylethane is not $Ph_3C{-}CPh_3$ but rather a phenyl bridged dimer[177]. Another steric aspect is that with diethyl ether as the ligand for lithium, the nominal Li^+ $MnPh_3{}^-$ salt is better described as $[Li(Et_2O)_2{}^+]_2$ $[Ph_2Mn(\mu\text{-}Ph)_2MnPh_2]^{2-}$. The Mn in $[MnMes_3]^-$ has a spin of 5/2 as it does in 'free' Mn^{2+}; the spin in the dimer is significantly less than twice 5/2 owing to significant antiferromagnetic spin coupling, if not Mn−Mn bond formation. The anion $[MnPh_4]^{2-}$ has been isolated as its $Li(tmeda)^{2+}$ salt[178]; we know of no attempt at synthesizing $[MnMes_4]^{2-}$ salts. We also know of no study of the equilibrium between monomeric and dimeric $[MnPh_3]^-$ and/or with $[MnPh_4]^{2-}$.

B. Naphthyl and Other Derivatives

Naphthalene can be manganated in the presence of Na(tmp) (sodium tetramethylpiperidide) and tmeda to form a complexed 2-naphthylmanganese derivative[179]. The preference for β-manganation is clear in that 1- and 2-methoxynaphthalene form the corresponding 2- and 3-manganese substituted product where the methoxy group is complexed with the *ipso* sodium and the adjacent ring carbon is η^1-bound to Mn. While varying metallation sites for both the Mn and Na are plausible, their energy difference remains unknown from experiment. However, high level quantum-chemical calculations show 2-naphthyl sodium, i.e. with no manganese or ligands, to be less stable than its 1-isomer by *ca* 4 kJ mol^{-1} [180]. No such theoretical studies have been reported on the isomeric naphthylmanganese species.

The synthesis of *m*- and *p*-$C_6H_4(Mn(CO)_5)_2$, *m*- and *p*-$C_6H_4(COMn(CO)_5)_2$ and diverse other polymetallated benzenes was reported[181]. No evidence was shown for any *o*-isomer. We welcome information as to the relative thermodynamic stability of the various sets of isomers noting thermochemical calorimetry data for other sets of disubstituted benzenes that are either strained[182, 183] or carry two electron-withdrawing substituents [184].

C. Homoleptic Manganese Arene Species

$Mn(C_6H_6)^+$, as the ion−molecule complex of manganese and benzene, has been found to have a 0 K bond dissociation energy[185] of 133 ± 9 kJ mol^{-1}; the related $(MnC_6H_6)^+{-}C_6H_6$ bond energy has the significantly greater bond energy, 203 ± 18 kJ mol^{-1}. The 0 K binding energies of $Mn(C_6H_6)^+$ and $Mn(C_6H_6)_2{}^+$ were also derived[186] to be between 170 and 202 kJ mol^{-1}.

A vast variety of hydrocarbons react with $MnCl^+{\cdot}H_2O$ by displacement of the water molecule[187]. Among these are benzene and coronene. If we casually equate the hydration energy[188] of $MnCl^+$ to that of general 3d transition metal cations such as Mn^+ itself, *ca* 120 kJ mol^{-1}, we thus derive a complexation energy of this quantity as a lower bound for that of $MnCl^+$ with these hydrocarbons. We would think that collision assisted dissociation measurements could be used on these $MnCl^+$ with both water and the above arenes and so provide another measurement for the arene–Mn^+ binding energy.

Gas-phase $C_6H_6Mn^+$ and O_2 exclusively react[189] to form a $C_6H_6O_2Mn^+$ ion of unknown structure in a reaction with Gibbs energy of $-41\,kJ\,mol^{-1}$. Benzene reacts[190] with atomic Mn in the presence of the oxidizing agent I_2 to form $Mn(C_6H_6)_2{}^+$, which was isolated as a salt. No reaction is observed in the absence of the iodine, suggesting the instability of neutral $Mn(C_6H_6)_2$.

In a study[191] of the reaction chemistry of Mn^+ with monohalobenzenes, the following was found: F, no reaction; Cl, no reaction; Br, abstraction to form $MnBr^+$; and I, reaction to form an ion with the stoichiometry $C_6H_5MnI^+$ which was suggested to be the ion–molecule cluster $Mn^{+\bullet}$ C_6H_5I and not the ionized, but otherwise classical, organometallic C_6H_5MnI.

Coronene is known[192] to form 1:1 and 2:1 complexes with Mn^+ with individual ligand–metal binding energies greater than *ca* $150\,kJ\,mol^{-1}$.

Both endohedral and exohedral isomers of $C_{60}-Mn^+$ have been observed[193], the former quite naturally requiring higher energy Mn^+ as a reagent to enter the cage. There is no evidence as to which is the more stable isomer—the endohedral isomer has a higher activation energy for demetallation because this would require at least temporary opening of the cage.

The neutral endohedral manganese-fullerene $C_{84}Mn_2$ has also been observed[194]. Related to the endohedral complexes of Mn and the fullerenes are the intercalation (lamellar) complexes of Mn and graphite. Such species have been prepared[195] and, from the crystallographically determined 'thickness of the filled sheets', it was suggested that the Mn/graphite interaction was scarcely stronger than that expected from van der Waals interactions. The energies of such metal–graphite interactions are known to be small, e.g. for LiC_6 and LiC_{12}, the enthalpies of formation are -13.9 ± 1.2 and $-24.8 \pm 1.0\,kJ\,mol^{-1}$, respectively[196]. However, these enthalpies of formation are defined relative to graphite and elemental metal, respectively, and so both their interplanar (*ca* $6.1\,kJ\,mol^{-1}$ per C[197]) and intermetallic (sublimation, atomization) binding energies must be overcome to form these species and hence the net bond energies are, in fact, quite substantial[198]. Assume a zero enthalpy of formation, i.e. no net binding energy, for MnC_8, the most manganese-rich of these manganese–graphite compounds described in Reference 195. To form MnC_8 costs $330\,kJ\,mol^{-1}$, and so the sheet-metal, the graphite–manganese interaction binding energy is at least $165\,kJ\,mol^{-1}$.

D. Ambiguous Bonding: σ and/or π Bonding

Gas-phase MnO^+ reacts with benzene to form $C_6H_4Mn^+$ (and H_2O). From this, the binding energy of C_6H_4 to Mn^+ was determined to be bounded by 155 and $280\,kJ\,mol^{-1}$ where it was assumed that this ligand was *o*-benzyne[199]. It remains unproven if the ligand is not (*Z*)-3-hexen-1,5-diyne or even fulvenylidene, both ligands having the possibility of alternate hapticity other than two that would naturally be assumed for *o*-benzyne, the former in a η^6- and the latter in a η^1-and/or η^5-coordination mode.

There are two modes of η^1-bonding of an aryl group to manganese in the monomeric amido complex $Ar'MnN(H)Ar^{\#}$ wherein $Ar' = C_6H_3\text{-}2,6\text{-}[C_6H_3\text{-}2,6\text{-}(Pr\text{-}i)_2]_2$, $Ar^{\#} = C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2$ to use the terminology of the original authors[200]. The same structure is found for the corresponding Fe and Co, the latter at 'high temperatures'. At low temperatures ($<240\,K$), the Co species forms the related η^6-$Ar^{\#}$ species. We wonder if replacement of the H on nitrogen by some alkyl group would not decrease the $C-Mn-N$ angle and so encourage this latter means of coordination. In turn, this would provide information as to the energetics of arene–Mn interactions.

E. Species with More Metals Than Rings

In the above discussions there were always at least as many cyclopentadienyl or benzene rings as manganese atoms in any complex presented. There is no reason why this need be the case. A reverse sandwich bonding mode, i.e. an Mn$-\eta^6$-Mn, has been found[201] in the toluene complex (η^6:η^6-PhMe)[MnAr]$_2$ where the aryl group that is σ-bonded (η^1-) to the Mn is the hindered *m*-terphenyl, 2,6-(C_6H_2-2,4,6-Pr-*i*)$_3$)$_2$-3,5-*i*-Pr-C_6H-.

Both thiophene and selenophene form complexes[202] wherein a Mn(CO)$_5$ group is σ-bonded to the ring (η^1- with the 2-carbon) and Cr(CO)$_3$ is likewise η^5-bonded to the ring. These species have been shown to be thermodynamically and kinetically unstable with respect to their isomers wherein the Cr(CO)$_5$ is η^1-bonded and the Mn(CO)$_3$ is η^5-bonded. It was shown that the isomerization most likely proceeds through a dimeric intermediate rather than a unimolecular *ipso*-Mn/Cr carbonyl bridged intermediate. We know of no analogous study involving a benzenoid analog although both phenylMn(CO)$_5$ and η^6-benzeneCr(CO)$_3$ are well-known compounds. Likewise, while we know of no phenyl dimanganese complex, i.e. $[C_6H_5(\eta^1\text{-Mn(CO)}_5)(\eta^6\text{-Mn(CO)}_3)]^+$ involving both η^1- and η^6-bonded manganese, the former as the pentacarbonyl and the latter as the tricarbonyl, we see no reason to deny its plausibility.

Finally, for the reaction of transition metal clusters with benzene[203] it was shown that $(C_6H_5-M_a)^-$ dominates the anions while $(C_6H_6-M_b)^+$ dominates the cations, where *a* and *b* are the varying number of metals in the anionic and cationic complexes. In principle, the energetics of the following processes (equations 21–24), in one or both directions, can be quantitated for a variety of stoichiometries, i.e. different values of *a* and *b*.

$$(C_6H_5-M_a)^- \longrightarrow C_6H_5-M_a + e^-\text{, the electron affinity of } C_6H_5-M_a \quad (21)$$

$$(C_6H_5-M_a)^- + H^+ \longrightarrow C_6H_5-M_a\text{, the gas phase acidity of } C_6H_5-M_a \quad (22)$$

$$(C_6H_5-M_b)^+ + e^- \longrightarrow C_6H_5-M_b\text{, the ionization energy of } C_6H_5-M_b \quad (23)$$

$$(C_6H_5-M_b)^+ \longrightarrow C_6H_5-M_b + H^+\text{, the proton affinity of } C_6H_5-M_b \quad (24)$$

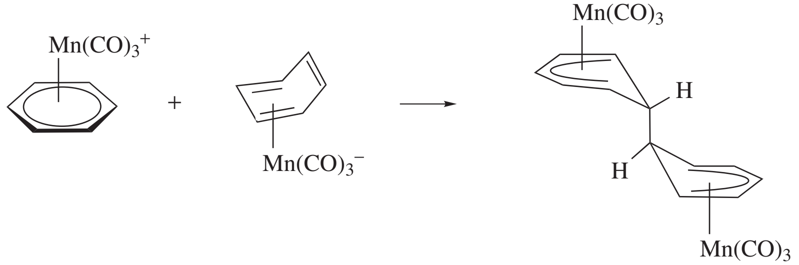
Letting $a = b$ allows for a closed thermochemical cycle to be generated and the binding energies of phenyl and benzene to cationic, neutral and anionic clusters of Mn determined. By analogy to the energetics of hydrocarbon ions and radicals[204], comparison with the values for the above quantities in C_6H_5-Mn(CO)$_5$ and C_6H_6-Mn, monometallic analogs to the above cluster species, would be most intriguing.

X. ARENE MANGANESE TRICARBONYL COMPLEXES AND RELATED SPECIES

These species have been actively studied and this section provides but a brief analysis for the understanding of their energetics. There are various hapticities and charges for these complexes, most often consistently determined by adherence to the 18-electron rule.

A. Benzene Derivatives

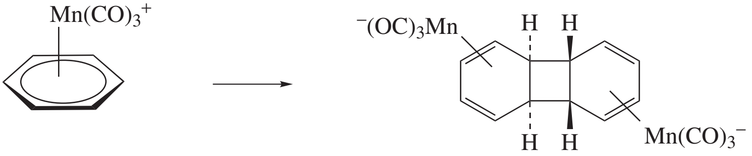
The reaction of η^6-C_6H_6Mn(CO)$_3{}^+$ with η^4-C_6H_6Mn(CO)$_3{}^-$ results[205] in the dimeric [η^5-C_6H_6Mn(CO)$_3$]$_2$ with a C$-$C bond between the two 6-membered rings (equation 25). From solution studies of isotopically labeled species, the authors suggest that reaction 26 is more favorable than reaction 25. In fact, the authors found no evidence by either IR or EPR spectroscopy of equilibration of the dimer with the monomer C_6H_6Mn(CO)$_3$.



(25)

$$\eta^6\text{-}C_6H_6Mn(CO)_3{}^+ + \eta^4\text{-}C_6H_6Mn(CO)_3{}^- \longrightarrow \eta^6\text{-}C_6H_6Mn(CO)_3{}^- + \eta^4\text{-}C_6H_6Mn(CO)_3{}^+ \qquad (26)$$

Whatever is the hapticity of the neutral monomeric species, earlier studies[206] showed that η^6-$C_6H_6Mn(CO)_3{}^+$ can be reduced to the cyclobutane-containing (1*a*,4*a*,5*a*,8*a*-tetrahydrobiphenylene) dimer of η^4-$C_6H_6Mn(CO)_3{}^-$ (equation 27). Such loss of aromaticity of benzene and destabilization of neutral $C_6H_6Mn(CO)_3$ is profound. Charge transfer studies of both $C_6H_6Mn(CO)_3{}^+$ and $C_6H_6Mn(CO)_3{}^-$ with a well-defined set of added neutrals could establish the degree of destabilization of neutral $C_6H_6Mn(CO)_3$. For example, still unknown is the binding energy of neutral $C_6H_6Mn(CO)_3$ relative to $C_6H_6Mn(CO)_2$ and CO.



(27)

The $Mn(CO)_3{}^+$ complex of [10]paracyclophane was reported[207] to have a decreased ring current, and presumably decreased aromaticity, relative to the parent hydrocarbon. The same trend was found for the isoelectronic neutral $Cr(CO)_3$ complex. No corresponding $Mn(CO)_3{}^+$ complex has seemingly been reported for any of the smaller, and more strained[208], [*n*]paracyclophanes nor for any of the two ring [*m.n*]paracyclophanes. For the latter, one might anticipate the additional formation of bis($Mn(CO)_3{}^+$) complexes as well as mixed metal $Mn(CO)_3{}^+$/$Cr(CO)_3$ complexes, although only the latter are found for the 'acyclic', singly bridged diphenylmethane[209]. Comparison with paracyclophane$Cr(CO)_3$ complexes is welcomed; no [*n*] and but few [*m.n*]$Cr(CO)_3$ (and fewer still bis$Cr(CO)_3$) complexes of the diverse paracyclophanes have been synthesized[210]. Likewise, the study of the synthesis and aromaticity of the $Mn(CO)_3{}^+$ complexes of small and strained [*n*] and [*m.n*]metacyclophanes is a worthy goal, paralleling the recent report of the $Cr(CO)_3$ complexes of [5] and [6]metacyclophane[211].

SmI_2 reacts[212] with (η^6-PhCl)$Mn(CO)_3{}^+$ to produce both PhCl and (η^5-C_6H_6Cl)$Mn(CO)_3$. By contrast, dechlorination is observed with the isoelectronic (η^6-PhCl)$Cr(CO)_3$ because of significant stabilization of the metallated phenyl radical in the latter case. Studies with the complexes of other halobenzenes is of interest—for example, there is structural[213], but not yet thermochemical, documentation that there is significant I•••CO interaction in η^5-$C_5H_4IMn(CO)_3$. All four monohalocyclopentadienyl$Mn(CO)_3$ species have been synthesized[214]. We await the requisite physical chemical measurements.

η^5-CyanocyclohexadienylMn(CO)$_3$ derivatives[215], including the cyano derivatives of p-xylene, mesitylene and hexamethylbenzene, can be synthesized by reacting the arene•Mn(CO)$_3{}^+$ complex with CN$^-$ to form the corresponding η^5-cyanocyclohexadienyl Mn(CO)$_3$. In turn, these cyanocyclohexadienyl complexes can be oxidatively rearomatized to form the cyanobenzene complexes by p-benzoquinone, iodine or Fe$^{\text{III}}$. Alternatively, heating the cyanocyclohexadienyl species results in CO elimination to form the rearomatized arene•Mn(CO)$_2$CN. These data suggest that cyanobenzene complexes Mn(CO)$_3{}^+$ more poorly than does C$_6$H$_6$, a not surprising result as it is assumed that the aromatic ring donates electron density to the cationic metal. Other reaction chemistry shows that the CN group in the cyclohexadienyl complex energetically prefers to be on a carbon bearing a methyl group. This tendency of the cyano group to be on the more substituted carbon is in contradistinction to the endothermicity of reaction 28 in the all-hydrocarbon (non-organometallic) case.

$$\mathrm{Me_2CHCN + Me_3CH \longrightarrow Me_2CH_2 + Me_3CCN} \tag{28}$$

This tendency for CN to be attached to an aliphatic carbon without a methyl group is apparently countervened by the considerable weakening of the π-donating ability of η^5-cyclohexadienyl rings by cyano substituents, as mentioned earlier for cyclopentadienyl rings substituted by cyano groups.

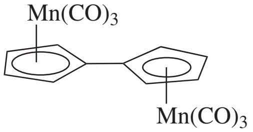
Benzene and its substituted derivatives may also bind by other than η^6-coordination modes. Toluene binds[216] to CpMn(CO)$_2$ in an η^2-mode with a bonding energy of 59 ± 3 kJ mol^{-1}. Relative rates for the dissociation of CpMn(CO)$_2$ArH, where ArH is a substituted benzene, have been investigated[217] and shown to depend on both electronic and steric factors, e.g. both mesitylene and trifluoromethylbenzene bind more weakly than benzene, while toluene and the isomeric xylenes bind more strongly. Another, here multimetallated mode, was found[218] in (OC)$_5$Re-μ-(η^1:η^5-C$_6$H$_6$)Mn(CO)$_3$. Both coordination modes were documented crystallographically but thermochemical information remains absent. Perhaps the former species is a σ or η^1-aryl manganese species, albeit with a sterically hindered phenyl group, that needs solvation so that two of them will share a common toluene molecule between them. Perhaps the latter species is a η^5-cyclohexadienylMn(CO)$_3$ derivative where the saturated carbon is substituted by a singly bonded Re(CO)$_5$ group. Other η^5-cyclohexadienylMn(CO)$_3$ derivatives are long known from the early synthetic and structural chemistry of metal arene π complexes (e.g., see References 219 and 220). A more recent example of a η^5-cyclohexadienylMn(CO)$_3$ derivative is the C−C bonded dimer of C$_6$H$_7$Mn(CO)$_3$ itself[25]. It is then surprising that the studies of the corresponding bis-manganese compound (OC)$_5$Mn-μ-(η^1:η^5-C$_6$H$_6$)Mn(CO)$_3$ and the posssilibility of scrambling of both Mn and CO remains unreported, especially since the isomeric fulvene (a CpMn(CO)$_3$ derivative with a CH$_2$Mn(CO)$_5$ substituent) has long been known[221]. We additionally wonder about the relative stability of these isomers in that fulvene is well known to be much less stable than benzene.

7-Substituted benzothiophenes form η^6-complexes with Mn(CO)$_3{}^+$ in which it is the benzene ring that is bonded to the metal. What does that tell us about the relative binding of Mn(CO)$_3{}^+$ to benzene and thiophene? 2-(2-Arylvinyl)thiophenes preferably bind Mn(CO)$_3{}^+$ on the thiophene ring rather than the benzene as shown by reactions[222] of these heterocycles (Ar = p-XC$_6$H$_4$, X = MeO, Me, H, Br, NO$_2$) with NpHMn(CO)$_3{}^+$. The reverse ring selectivity was shown for the Ar = p-dimethylaminophenyl case.

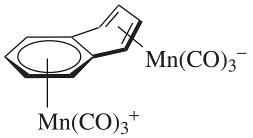
B. Naphthalene Derivatives

NaphthaleneMn(CO)$_3{}^+$ has been shown to readily transfer Mn(CO)$_3{}^+$ to diverse benzene derivatives and also to 1-methylnaphthalene, 2-naphthol and acenaphthene[223]. Other transfer reactions were also observed. It would appear that the relative binding strengths in these $Mn(CO)_3{}^+$ complexes reflect the relative donating abilities and ionization potentials of the parent arene.

A long-known derivative of cyclopentadienylmanganese tricarbonyl is bicymantryl[224], also known as fulvalene bis(manganese tricarbonyl) (**19**). Isomeric to this species is the highly labile, and destabilized, *syn*-naphthalene (η^4-,η^6-) bismanganese tricarbonyl (**20**)[225] which is both zwitterionic and nonplanar. We wonder about the relative stabilities of these two species, in light of the destabilizing structural features for the latter and the relative stabilities of naphthalene and fulvalene, the parent hydrocarbons of these manganese complexes. (For a review of the energetics of distorted aromatic species, see Reference 208.) One more isomer, *anti*-azulene (η^5, η^5-) bis(manganese tricarbonyl) (**21**), which is likewise nonplanar[226], is nonetheless stable until it melts at 153 °C[227]. Azulene itself is intermediate in stability between the aforementioned parent hydrocarbons. The isomer cyclobutacyclooctatetraene is much less stable[228] than azulene, but no quantitative comparison is available with the above fulvalene. While its η^4-$Fe(CO)_3$ complex appears to be quite stable[229], its $Mn(CO)_3{}^+$ complex remains unstudied, precluding any comparisons. The $Mn(CO)_3$ containing complex of cyclobutacyclooctatetraene, isoelectronic to the iron complex, is also unknown. The remaining isomer, bicyclo[7.1.0]decapentaene, is experimentally unknown as are any derivatives thereof.



(**19**)



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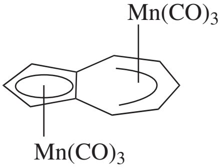


(**21**)

C. Three-Ring Species: Anthracene, Phenanthrene and Biphenylene Derivatives

Anthracene forms[230] a stable anionic η^4-$Mn(CO)_3$ complex wherein carbons 1–4 of the aromatic are bound to the metal. This species was formed by the stepwise reactions shown in equation 29. This shows that anthracene binds $Mn(CO)_3{}^-$ better than benzene, presumably because less aromaticity is lost upon complexation and loss of planarity. Additionally, anthracene also has a lower ionization potential and higher electron affinity than benzene. This suggests that a plausible species is the manganese anthracene complex, $C_{14}H_{10}Mn$, analogous to the corresponding compound of Mg and the heavier alkaline earth metals[231, 232] in which the metal is bonded to the aromatic at its 9,10-positions: the electron-donating ability of these metals, as defined by gaseous ionization potentials, is $Mg \sim Mn > Ca > Sr > Ba$[233].

$$\begin{aligned}[\eta^6\text{-}C_6H_6Mn(CO)_3]^+ + C_{14}H_{10}{}^- &\longrightarrow [\eta^4\text{-}C_6H_6MnCO)_3]^- + C_{14}H_{10}\\ &\longrightarrow [\eta^4\text{-}C_{14}H_{10}Mn(CO)_3]^- + C_6H_6 \qquad (29)\end{aligned}$$

Phenanthrene$Mn(CO)_3{}^+$ (it is the A ring that is bonded to the metal) transmetallates benzene and diverse benzene derivatives[223]. Yields, generally high, were given for a variety of reactions. However, no equilibrium constants connecting different benzene derivatives, or for intra-phenanthrene isomerization, have been measured.

The aromaticity/antiaromaticity of biphenylene has been a source of considerable contention. After all, biphenylene is an isolable, thermally stable hydrocarbon unlike the related cyclobutadiene[234] and benzocyclobutadiene[235] with fewer benzene rings. Nonetheless, the bonds between the two benzene rings appear quite labile. Activated (on one side) by $Mn(CO)_3{}^+$, one such bond is readily cleaved[236] by an organoplatinum species to form the 9-platinafluorene derivative. Additionally, this biphenylene$Mn(CO)_3{}^+$ complex is readily, but reversibly, reduced[237] to form a pair of C−C bonded dimers. As shown crystallographically, per biphenylene 'monomer', one benzene ring has been sacrificed to form a neutral cyclohexadienyl$Mn(CO)_3$ moiety and the remaining bridgehead carbon of one 'monomer' is bonded to its counterpart on the other 'monomer'. Again as documented crystallographically, these dimers are easily thermally rearranged to form new dimers that may be described as indenyl$Mn(CO)_3$ derivatives wherein ring annulation results in a benzopentalene ligand that is simultaneously hydrogenated, dimerized and the benzene ring dearomatized. A useful thermochemical comparison of $Mn(CO)_3{}^+$ binding energies would be between biphenylene and biphenyl (the formal cleavage product by H_2) where we note that the latter hydrocarbon is more stable than the former by some $220\,kJ\,mol^{-1}$. We are hesitant to discuss in the current context the stability of uncomplexed biphenylene and benzopentalene because both of these hydrocarbons are too distorted in the complexes of interest. Additionally, benzopentalene remains unisolated and any thermochemical data for it needs to be estimated.

D. Benzene vs. Cyclopentadienyl Bonding to $Mn(CO)_3{}^+$

Let us now contrast bonding with benzene and cyclopentadienyl rings. The first illustration is a comparison of the deprotonation reactions of the η^6-$Mn(CO)_3{}^+$ cations of toluene, ethylbenzene and isopropylbenzene[238] with those of indane and trisindane[239]. The three alkylbenzenes produce the parent, and the exocyclically methylated, η^5-methylenecyclohexadienyl$Mn(CO)_3$ complexes respectively, all simply formed by deprotonation of the benzylic hydrogen of the alkylbenzenes. By contrast, indane and trisindane demonstrate metal migration and ring dehydrogenation to form the parent and biscyclopentane annelated η^5-indenyl$Mn(CO)_3$ complexes. This study invites the question of whether the complex of *n*-propylbenzene would result in the corresponding complex of the η-deprotonated anion and/or that of allylbenzene formed by dehydrogenation as well as deprotonation. The formal deprotonation reaction of indane to give indenide is endothermic by *ca* $1585 \pm 10\,kJ\,mol^{-1}$, making use of the archival enthalpies of formation of indane, indene and the gas-phase acidity of indene[123, 124]. The sequential deprotonation[124, 125] and dehydrogenation of *n*-propylbenzene, approximated by those of the isomeric isopropylbenzene, is endothermic by very much the same value, $1580 \pm 15\,kJ\,mol^{-1}$. We thus conclude that the migration of the $Mn(CO)_3$ group reflects the greater strength of its bonding as a η^5-ligand to cyclopentadienyl compared to benzyl rather than the greater ease of formation of the 'cyclopentadienyl' over that of the 'benzylic' ion.

Deprotonation of benzene bound η^6-$Mn(CO)_3{}^+$ complexes of fluorene and of 4*H*-cyclopenta[*def*]phenanthrene result[240] in neutral complexes wherein the $Mn(CO)_3$ now is η^5-bonded to the final central cyclopentadienide ring.

The mixed cyclopentadienyl/biphenyl manganese complex Cp(PhPh)Mn has been synthesized in high yield[241] from manganocene and biphenylide ion and found to be a useful reagent. Given the aromaticity of cyclopentadienide ion and the loss of aromaticity upon the formation of biphenylide, we are not surprised at the facility of reaction 30.

$$Cp_2Mn + Ph_2{}^{-\cdot} \longrightarrow CpMn(PhPh) + Cp^- \tag{30}$$

Variously substituted benzenemanganese dicarbonyl cyanides, η^6-$ArHMn(CO)_2CN$, have been made[242] by the sequential reactions of the arene with $BrMn(CO)_5$ and $AlCl_3$, and then with KCN. We wonder about using any ionic cyclopentadienide, $(Cp'')^-$, as the nucleophile in the second step—would this produce η^6-ArHMn$(CO)_2(\eta^1$-Cp$'')$? Alternatively writing it as η^1-Cp$''{}'$Mn$(CO)_2(\eta^6$-ArH) invites the question of whether this would equilibrate with, or spontaneously rearrange to, η^5-Cp$''{}'$Mn$(CO)_2(\eta^2$-ArH) or with any other intermediate hapticity species.

The archetypal fullerene, C_{60}, reacts[243] with the Na and pnp (Ph_3PNPPh_3) salts of $Mn(CO)_5{}^-$ to form a η^2-derivative of $[C_{60}Mn(CO)_4]^-$ wherein the Mn is attached at a six-ring/six-ring junction. The same product is produced by the reaction of $Mn_2(CO)_{10}$ and NaC_{60}. No evidence for loss of CO is found except in mass spectrometry, where the fragment ions $C_{60}Mn(CO)_x{}^-$ ($x = 1, 2, 3$) accompany the parent $x = 4$ ion. No $Mn(CO)_3$ derivative analogous to cyclopentadienyl$Mn(CO)_3$ has been observed.

XI. MANGANESE [*n*]-ANNULENE DERIVATIVES

The [5]- and [6]-annulene derivatives, cyclopentadienyl and benzene and benzene-related species, have already been considered in this chapter. Here we discuss annulenes with other values of n in the cyclo-$(CH)_n$ ligands and their substituted derivatives.

A. Cyclopropenyl, $n = 3$

2,3-Diphenylcycloprop-2-ene-1-carbonyl chloride reacts with $Mn(CO)_5{}^-$ to form the acylmanganese pentacarbonyl[244]. On standing, this species readily decomposes to form 1,2,4,5-tetraphenylbenzene (a rearranged dimer of the cyclopropenyl radical), CO and $Mn_2(CO)_{10}$. It is tempting to invoke the formation of an aromatic product as the thermodynamic driving force. However, the related decomposition reaction of $CH_3COMn(CO)_5$ to form C_2H_6 (dimerized methyl) is highly exothermic (by nearly $400\,kJ\,mol^{-1}$) but does not readily proceed. No evidence is offered for either a η^1- or η^3-cyclopropenylmanganese intermediate.

B. Cyclobutadienes, $n = 4$

From the vantage point of enthalpy of formation, cyclobutadiene is slightly more stable than two acetylene molecules, 428 ± 16 [234] vs $456 \pm 1\,kJ\,mol^{-1}$. Nonetheless, in that acetylenes are much more common than cyclobutadienes, we note with some surprise the facile reaction[245] of 2-butyne with $Mn(CO)_5F{\bullet}BF_3$ to form the ionic cyclobutadiene derivative $Me_4C_4Mn(CO)_4{}^+\ BF_4{}^-$, presumably via isomerization of the bis alkyne complex (both of which have been isolated for the related Re species)[246]. It is likewise noteworthy that diphenylacetylene reacts (thermally, but not photochemically)[247] with $Mn(CO)_4NO$ to form $Ph_4C_4Mn(CO)_2NO$, albeit in low yield. This last species, without the phenyl substituents, is isoelectronic to cyclobutadienedicarbonylnitrosyl iron cation. The ease of attack by nucleophiles on iron carbonyl cation is bounded[248] by those of the likewise cationic cycloheptatriene$Mn(CO)_3{}^+$ and cyclobutadiene$Mn(CO)_3{}^+$ (respectively more and less reactive) documenting a lack of correlation of the aromaticity of the π system when appended to a metal and when as free ligand. (For discussions of the thermochemistry and aromaticity/antiaromaticity of cycloheptatriene and cyclobutadiene, see References 249 and 234, respectively.)

C. Cycloheptatrienyl (Tropyl), $n = 7$

While η^1-cycloheptatrienylcarbonyl manganese pentacarbonyl is quite stable[250] under ambient conditions, heat or UV irradiation decomposes it to bis(cycloheptatrienyl) and

$Mn_2(CO)_{10}$. η^1-Cycloheptatrienyl manganese pentacarbonyl can also be sequentially photochemically decomposed[251] to the η^3-tetracarbonyl, η^5-tricarbonyl and η^7-dicarbonyl. An equilibration study under high CO pressure of these diverse species is desirable. Study of the isomeric benzyl series shows that the η^1-species, $PhCH_2Mn(CO)_5$, may be thermally decomposed[252] to form 2.3.4.5.6-η^5-[(1-methylene)cyclohexadienyl]$Mn(CO)_3$ as identified by NMR and chemical reactions; relatedly p-$C_6H_4(CH_2Mn(CO)_5)_2$ can be thermolyzed[252] to form p-xylylene. A study on the related m-species is welcomed: after all, the two starting organometallics should have nearly the same enthalpies of formation while m-xylylene has a much higher enthalpy of formation than that of its p-isomer (m-, $340 \pm 13\,\mathrm{kJ\,mol^{-1}}$ [253]; p-, $210\,\mathrm{kJ\,mol^{-1}}$ [254]).

The sequential decarbonylation energies for the benzyl manganese carbonyl cations, $C_6H_5CH_2Mn(CO)_n{}^+$, are $n = 5$, 42; 4, 88; 3, 50; 2, 105; 1, $126\,\mathrm{kJ\,mol^{-1}}$ [42]. From the earlier enunciated enthalpy of formation of benzylmanganese pentacarbonyl and the archival value for CO, in principle we may deduce the enthalpy of formation of all of the above cations. We may thus derive the C−Mn bond energy in the $n = 0$ species, $C_6H_5CH_2Mn^+$, and compare it with that of CH_3Mn^+. We are hesitant to do so. Not only is there uncertainty about the hapticity of the benzyl group as COs are stripped off, but also there is the possibility of rearrangement to the isomeric cycloheptatrienyl complexes. For the $n = 5$ ion, there is less concern because less excitation energy was imparted to the species in its formation. These authors say that $C_6H_5CHMn(CO)_5{}^+$ has a lower hydride affinity than $CH_2Mn(CO)_5{}^+$ by at least $105\,\mathrm{kJ\,mol^{-1}}$. For comparison, we may ask about the hydride affinities of other phenylated cations. For example, consider $C_6H_5CHOH^+$ and CH_2OH^+. This is simply expressed as the enthalpy of the reaction involving protonated aldehydes and alcohols (equation 31) (using proton affinities and neutral enthalpies of formation from References 255 and 2, respectively). The phenylated species has a hydride affinity *ca* $150\,\mathrm{kJ\,mol^{-1}}$ smaller than its unsubstituted counterpart.

$$C_6H_5CHOH^+ + CH_3OH \longrightarrow C_6H_5CH_2OH + CH_2OH^+ \qquad (31)$$

The monocationic mixed ring (η^7-tropylium)(η^5-cyclopentadienyl) manganese sandwich species has been prepared and shown to reversibly interconvert[256] with the neutral (η^6-cycloheptatriene)(η^5-cyclopentadienyl)manganese. This quantitates the H^- donating abilities as $LiAlH_4$ > (η^6-cycloheptatriene)(η^5-cyclopentadienyl)manganese > triphenylmethane. Given the seeming affinity of cyclopentadienyl for manganese as shown by the richness of products from its tricarbonyl, it is not surprising that the isomeric (η^7-cycloheptatrienyl)(η^4-cyclopentadiene)manganese is not the neutral species.

Another example of the preference of manganese for cyclopentadienyl over tropyl is found in the structure of dimeric azulenemanganese tricarbonyl[257]. Crystallographic studies showed this species to have two $Mn(CO)_3$ groups, individually η^5-bonded to the respective 5-membered rings of the two azulenes, and the two azulenes bonded to each other via their 4-carbons of the 7-membered rings. As explained in the original paper, plausibly for steric reasons, the metal fragments are 'attached to the "outer" surface of the 5-membered rings.' It was noted that this species with its two saturated >CH− carbons exists as the racemate, rather than the *meso* diastereomer, in contradistinction to the isolobally related dimeric bis $Mo(CO)_3CH_3$ complex. No explanation was offered for this stereochemical surprise other than the ease of crystal formation. Unanswered, and indeed unasked, was why the two azulenes were bonded through their respective 4-carbons as opposed to both 6- or even one apiece. We do not know the relative stability of the monocyclic 1,2-divinyl and 1-(1,3-butadienyl)cyclopentadienyl species (the underlying conjugated framework for these isomeric options), or, for that matter, the simpler related substituted benzenes.

A manganese tricarbonyl complex of sesquifulvalene was characterized[258]. It has Mn bonded to the cyclopentadienide, not the tropylium ion: no isomerization between these two forms has been observed.

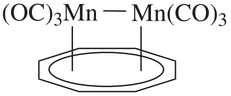
Tropone reacts with $MnCl_2$ to form a simple Mn(II)−O bonded complex[259, 260]. This complex is not surprising given the polarity of the C−O bond in tropone. By contrast, tropone reacts with $Mn_2(CO)_{10}$ to form the crystallographically characterized 1-*syn*-(1',2'-dihydro-2'-oxo-1'-oxaazulen-3'-yl)cyclopentadienyl$Mn(CO)_3$[261,262]. Thermochemical data are absent for this species—what is the driving force for the Mn^0-catalyzed near-dimerization of tropone? The synthesis of 2-oxo-1-oxaazulenes (cyclohepta[*b*]furan-2-one) have been described[263, 264]. The enthalpy of formation of tropone is known, from which discussions of the degree of its aromaticity follow[249], and we recognize that structurally 2-oxo-1-oxaazulene is to azulene as coumarin is to naphthalene, a −C(O)−O− group in the former species replaces a −CH=CH− in the latter. The enthalpy of formation of the last three species is known (of coumarin recently reinvestigated[265]); we welcome a calorimetric study of 2-oxo-1-oxaazulene.

Derivatives of 1,2,3,4,5-η^5-6-oxocycloheptadienyl $Mn(CO)_3{}^+$ have been synthesized[266], and suggestively formed by thermal rearrangement of a comparatively substituted, and also isolable 6-vinyl-η^5-2-pyranyl derivative[267]. We recognize the ligand as C-protonated tropone and so inquire about its rearrangement to the hydroxytropylium (O-protonated tropone) isomer and deprotonation to the tropone complex itself. After all, tropone is 'only' a relatively strong base[255].

D. Cyclooctatetraene, *n* = 8

As befits the four double bonds of cyclooctatetraene, numerous coordination modes have been studied. These include the η^2-mode as in dicarbonyl-1,2-η^2-cyclooctatetraene-η^5-cyclopentadienylmanganese[268], η^4- as in the $Mn(CO)_3{}^-$ complex of the parent hydrocarbon[269], and η^6- as in the cyclooctatetraene cyclopentadienyl mixed sandwich[270]. There are no thermochemical data interrelating these species.

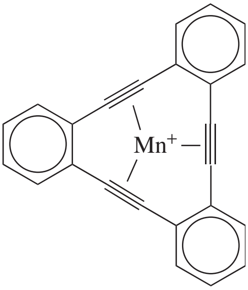
Early in the study of organomanganese compounds[271] it was shown that acetylene reacts with $Mn_2(CO)_{10}$ to form a hydropentalene–$Mn(CO)_3$ complex, while cyclooctatetraene (nominally acetylene tetramer) forms the trihydropentalene–$Mn(CO)_3$ complex. Both of these complexes are cyclopentadienyl $Mn(CO)_3$ derivatives, as opposed to those of cyclooctatetraene. Cyclooctatetraene reacts[169, 272] with the trimeric $[HMn(CO)_4]_3$ to yield η^5-1,4-cyclooctadien-5-yl$Mn(CO)_3$ and cyclooctatetraene (η^4-1,2,3,4:η^4-5,6,7,8)bis($Mn(CO)_3$) (**22**) with an additional Mn−Mn bond. Relatedly, a mixture of 1,3,5- and 1,3,6-cyclooctatriene results[169] in the former product as well as the η^6-complex of the latter olefin. There is related novelty in the energetics of the corresponding all-hydrocarbon species, pentalene[273, 274] and cyclooctatetraene[275] and their hydrogenated counterparts. In addition[276], cyclooctatetraenyl anion (more correctly described as the CH_2 deprotonated 1,3,5,6-cyclooctatetraene) may be exothermically isomerized in the gas phase to the above hydropentalene anion.



(**22**)

E. Higher Annulenes

Few complexation studies of any manganese species with any higher annulene have been reported. $\eta^{3:2}$-Cyclonona-2,6-dien-1-yl (tetrahydro-[9]-annulenyl) $Mn(CO)_3$ derivatives were readily formed[277] by [5+4] cycloaddition reactions of suitably substituted pentadienyl $Mn(CO)_3$ and butadiene derivatives. We know of no dehydrogenation study to form the corresponding totally unsaturated [9]-annulenyl derivatives: we would think that loss of one more H_2 molecule to form the indenyl compound is more probable because of enhanced aromaticity and decreased strain. A benzo derivative of a multiply unsaturated [12] annulene (alternatively called tribenzocyclyne and tribenzocyclotriyne) (**23**) has been shown to bind Mn^+ in the gas phase by at least 150 kJ (mol-ligand)$^{-1}$ in both a 1:1 and 2:1 complex[278]. For the doubly bridged *anti*-dimethyldihydropyrene, a surrogate [14]-annulene, fused with cyclopentadienide, $Mn(CO)_3$ has been shown to preferably bond to the 5-membered ring with both isomers (the nearest CH_3 *syn* and *anti* to the Mn fragment) found[279] in a competitive synthesis. The ratio of these two isomers is 1:2.5, but it is not obvious if this reflects a plausible thermodynamic 2.3 kJ mol^{-1} difference in stability as defined by enthalpy as opposed to the Gibbs free energy. Tetraaza[14]annulene, or more properly the dianion of a dibenzo derivative, forms a stable complex with Mn^{III} [280]. However, it is its four nitrogens that are engaged in the bonding and so further comparison with [14]annulene itself is as educational as that of $Mn(py)_n{}^{2+}$ compared with phenylmanganese derivatives.



(**23**)

XII. ORGANOMANGANESE SPECIES WITH ONE OR TWO LIGATING CARBONS

In this section we consider those species in which at least one of the groups attached to the manganese have one or two carbons. We will, however, disregard in this section cases where the ligands are CO or CN^- as these are discussed elsewhere in this chapter. We defer to elsewhere in this chapter fluorinated species such as CF_3 containing compounds.

A. Cations, Neutrals and Mn^+

There are no direct measurements of the enthalpy of formation of Me_2Mn. This quantity is greater than *ca* − 140 kJ mol^{-1} as may be derived from the observation[170] that dimethylmanganese dissolved in THF reacts with elemental hydrogen to form methane and elemental manganese, the latter in presumably some amorphous and somewhat destabilized form[281].

Much of the remaining discussion in this section refers to gas phase species, or at least isolated species as found in cryogenic matrices. It has been found that $MnCH_2$ is readily formed along with $MnCH_2N_2$ by the matrix reaction of atomic Mn with diazomethane [282]. Accepting the value of 269 kJ mol^{-1} for the enthalpy of formation of diazomethane[283], the archival value of 281 kJ mol^{-1} for atomic Mn, the definitional 0.0 value for N_2, and making no temperature corrections to these enthalpies, results in an upper bound of 550 kJ mol^{-1} for the enthalpy of formation of $MnCH_2$, a value undoubtedly too high because we have neglected the manganese–carbon bond energy. The accompanying spectroscopic analysis suggests the $Mn{=}CH_2$ structure for the primary product. A $Mn(CH_2N_2)$ complex was likewise observed[282]. UV irradiation converts this species into its $HMnCH{\bullet}N_2$ isomer; visible light with $\lambda \geq 410$ nm reverses that isomerization process. Gas-phase ion-guided mass spectrometry ion–molecule experiments of Mn^+ with diverse hydrocarbons[284] give a $Mn^+{-}CH_2$ bond energy in CH_2Mn^+ of 295 ± 13 kJ mol^{-1}.

Related ion–molecule experiments[284, 285] give a $Mn^+{-}CH_3$ bond energy of 215 ± 19 kJ mol^{-1} in CH_3Mn^+ and, for $Mn{-}CH_3$ in CH_3Mn, between 38 and 125 kJ mol^{-1}, where it was suggested that the higher numerical value is more plausible. From this value (which is actually a lower bound) of -145 kJ mol^{-1} for the enthalpy of formation of dimethylmanganese, we obtain a bond energy of no more than 359 kJ mol^{-1} for the $Mn{-}CH_3$ as found in $(CH_3)_2Mn$. The great disparity between the methyl–metal bond in monomethyl manganese neutral and cation, and between neutral mono and dimethylmanganese, and monomethyl manganese neutral and cation is precedented by the corresponding organomagnesium and organozinc species[286]: in all three cases the atomic metal has an S (^1S or ^6S) ground state and spherical symmetry, and must expend promotion energy to form the carbon–metal bond.

The methyl transfer reaction between Mn^+ and CH_3F is thus significantly endothermic and so this reaction[287] does not yield CH_3Mn^+; the cluster ions $Mn^+ (CH_3F)_n$ are found instead. The sequential $n = 1$ and $n = 2$ binding Gibbs free energies are more negative than the essentially identical -35 ± 2 and -37 ± 2 kJ mol^{-1}, respectively. The relative weakness of the Mn–C bond in $Mn^+{-}CH_3$ compared to the stronger C–C bonds in alkanes and alkenes is consistent with the finding[288] that it is excited state, not ground state Mn^+, that reacts with propane and propene to form CH_3Mn^+ in 38% and 23% yields, respectively, in a spark plasma.

Indirect spectroscopic evidence (stretching frequency-bond strength correlations) suggests[289] that the $CH_3{-}Mn$ bond in $CH_3Mn(CO)_5$ is some 67 kJ mol^{-1} weaker than in *cis*-$CH_3Mn(CO)_4N_2$.

Long-lived solution-phase $Mn^{2+}{-}CH_3$ species of significant, but undetermined, Mn–C bond strength have been suggested[290] to explain product yields (increased ethane, decreased methane) in the metal-assisted decomposition of di-*t*-butyl peroxide.

Two photochemically interconverting $MnCH_4$ complexes have been observed[282] from the reaction of the $MnCH_2N_2$ species with adventitiously formed H_2; the two assigned structures are $Mn{\bullet}CH_4$ and CH_3MnH. Mn^+, like main group metal and lanthanide cations, but unlike most other monoatomic transition metal cations, does not react with CH_4[291]. Ion–molecule reaction studies suggest[292] an upper bound of 71 ± 21 kJ mol^{-1} for the binding energy of Mn^+ and CH_4 (and likewise C_3H_8 and n-C_4H_{10}). Electronically excited Mn^+ reacts[293] with CH_4 to result in ground state Mn^+; the intermediacy of CH_4Mn^+ in this quenching reaction was invoked.

There are no experimental measurements for any thermochemically relevant quantity for MnC_2H, MnC_2H_2 or MnC_2H_3, or any of their ions. Mn^{2+}, as the microporous formate salt, binds acetylene[294] with a binding energy of *ca* 43 kJ ‘per unit pore’ but there is no evidence for a specific π complex: indeed, the suggested stabilizing interaction is between the negative carboxylate oxygens and the protic acetylenic hydrogens. $MnC_2H_4{}^+$, as the ion–molecule complex of manganese and ethene, has been found to have a bond dissociation energy[295] of 91 ± 12 kJ mol^{-1}; the related $(MnC_2H_4)^+-C_2H_4$ bond energy has the essentially indistinguishable bond energy of 92 ± 12 kJ mol^{-1}. In solution, it is found[296] that $Mn(C_2H_4)(CO)_5{}^+$ is less bound than the corresponding rhenium species as in reaction 32, where the countercation is pnp$^+$ $[(Ph_3PNPPh_3)^+]$ and the counteranion is $BF_4{}^-$.

$$Mn(C_2H_4)(CO)_5{}^+ + Re(CO)_5{}^- \longrightarrow Mn(CO)_5{}^- + Re(C_2H_4)(CO)_5{}^+ \qquad (32)$$

There are likewise no thermochemical data for neutral MnC_2H_4, nor for the neutral or cationic MnC_2H_5 or MnC_2H_6 species in the gas phase: neutral gaseous Mn does not react with ethylene, or for that matter with propene (or propane or cyclopropane), 1-butene (or any of its olefinic isomers), or with 1,3-butadiene nor butane[297]. There is an anion formally containing manganese and ethylene, and indeed synthesized from this latter hydrocarbon, but this ion with the formula $[Mn(py)(C_4H_8)_2]^-$ has been crystallographically shown[298] to be a [4.4]spiromanganolane $Mn[(CH_2)_4]_2$ derivative and so may be identified as a cyclic counterpart of a tetraalkylmanganate(III).

Mn^+ and C_2H_6 complex with a binding energy of no less than 46 kJ mol^{-1}; Mn^+ and C_3H_8 likewise form an ion–molecule complex with a binding energy of no less than 54 kJ mol^{-1} [299]. A stronger lower bound of 95 kJ mol^{-1} for the Mn^+ bond to propane, and also *n*- and isobutane and neopentane, may be presented from the observations that (a) these latter hydrocarbons displace Cl to form such a complex[300] and (b) the difference between the appearance potentials[301] of Mn^+ and $MnCl^+$ as formed from the fragmentation of $MnCl_2$ is 95 ± 10 kJ mol^{-1}, a difference that may be equated with the bond energy in $MnCl^+$.

All the above reactions involve single manganese atoms associated with some collection of carbons. Looking at the reverse stoichiometry, gas-phase manganese-rich carbide cations readily react[302] with hydrogen to form $Mn_nCH_2{}^+$ and $Mn_nCH_3{}^+$. The latter three-hydrogen species have been suggested to have a methyl group with a $Mn-CH_3$ bond energy of 117 ± 9 kJ mol^{-1}.

B. Oxygen-containing Species: Manganese and Carbon Oxides

Laser ablated MnO reacts[303] with CH_4 to form the weakly bound complex $CH_4{\bullet}MnO$. Ultraviolet irradiation irreversibly produces CH_3MnOH, shown to be the more stable isomer by quantum chemical calculations[303]. The corresponding cation has been formed by gas phase reaction of $Mn_2{}^+$ and CH_3OH from which a $CH_3-(MnOH)^+$ bond energy of *ca* 200 kJ mol^{-1} has been suggested[292]. MnO^+ reacts with CH_4 only by H atom abstraction[304], while with C_2H_6, Mn^+ (and mechanistically presumed C_2H_4 and H_2O) are formed. With C_3H_8, $C_2H_4{\bullet}MnOH^+$ is formed presaging alkene complex formation from the higher alkanes.

Matrix isolated MnO_2 reacts with acetylene[305] and ethylene[306] to form their respective η^2-complexes. We are surprised that these reactions do not form η^2-OCH=CHO and η^2-OCH_2CH_2O species, i.e. a manganese ethenediolate and ethanediolate, although the formation of a Mn(H)C=C=O derivative upon irradiation is suggestive of the intermediacy and rearrangement of the former. (The reaction of uncomplexed acetylene and O_2 to form uncomplexed glyoxal is exothermic by *ca* 440 kJ mol^{-1}.) $Mn_2O_2{}^+$ reacts[307] with acetylene and ethylene in the gas phase to form mostly $Mn_2{}^+$ and Mn_2O^+: no organic or organometallic products were characterized.

In principle, manganese may bind with CO_2 at carbon, as well as at the oxygen, or at both sites. In the matrix, laser ablated atomic Mn reacts with CO_2 to form OMnCO and its corresponding anion[308]. New IR absorption bands from the chemisorption of $Mn_2(CO)_{10}$ on the surface of MgO have been interpreted[309] as arising from an ion pair of $CO_2{}^-$ and

Mg^+. Had the chemisorption been on MnO, would a $CO_2{}^-{-}Mn^+$ ion pair be formed? Mn^+ forms[310] a cluster ion with CO_2 with an associated Gibbs energy more negative than $24 \pm 2\,kJ\,mol^{-1}$. $CpMn(CO)_2CO_2$ has been prepared photochemically[311] with the oxygen η^1-mode of coordination, while the valence isoelectronic rhenium species binds with the combined carbon + oxygen η^2-mode. In any case, the well-studied[312] manganese oxalate should not be confused with the unknown $Mn(CO_2)_2$. There is a study of the relative gas-phase Mn^+ (MeNCO) binding free energy compared to some other bases[313]. No evidence was given as to which ligand atoms of the NCO backbone were involved in this complexation; this species is 'isoelectronic' to CO_2. A related study[314] showed sequential binding gas-phase Gibbs free energies of CS_2 to Mn^+ more negative than 27 ± 2 and $43 \pm 2\,kJ\,mol^{-1}$.

C. Anions, as Found in Free Species, Solutions and Salts

Using pulse radiolysis, the equilibrium constant for the aqueous reaction 33 with M = Mn (nta = nitrilotriacetate) was found[315] to be 8.3×10^{-4}, compared to values of 4.3×10^{-4} and 1.4×10^{-8} for Fe and Co, respectively. These correspond to Gibbs energies of reaction of 33, 19 and $45\,kJ\,mol^{-1}$, respectively, for M = Mn, Fe and Co.

$$[(nta)(H_2O)MMe]^- \longrightarrow [(nta)(H_2O)M]^- + CH_3\bullet \qquad (33)$$

A series of homoleptic polymethylmanganate dianions[316], $[Li(tmeda)_2]^+$ salts of $[MnMe_4]^{2-}$, $[MnMe_5]^{2-}$ and $[MnMe_6]^{2-}$, contain Mn(II), Mn(III) and Mn(IV), respectively. Except for their colors (pale orange, deep red and yellow-orange), these species seem to be quite normal in that their crystal structures show tetrahedral, trigonal bipyramidal and octahedral anions following simple structural predictions from their coordination numbers of 4, 5 and 6. We would think that calorimetric measurements of enthalpies of reaction, say of iodination to form manganous and methyl iodides, and ethane, could be used to derive enthalpies of formation. Likewise, this would tell us about the various Mn−Me bond energies, and particularly $[MnMe_{n-1}]^{2-}{-}Me$ ($n = 4$, 5 and 6) to compare with the above $[(nta)(H_2O)Mn]^-{-}Me$ value. Lacking this information, we merely note for now that the solution-phase conproportionation reaction 34 proceeds cleanly as written, as might be expected from a simple redox reaction that is slow because methyl ligand transfer must accompany electron transfer.

$$[Mn^{II}Me_4]^{2-} + [Mn^{IV}Me_6]^{2-} \longrightarrow 2[Mn^{III}Me_5]^{2-} \qquad (34)$$

$[MnOMe_3]^{2-}$ salts have also been characterized[317] both in solution and as crystals. There are few Mn^{III} species with which comparison can be made. It is not obvious how to compare this oxo organometallic with $Mn(acac)_3$ or any other manganese compound. The formal reaction 35, where solvent and lattice effects should largely cancel (although admittedly these ions are tetrahedral, tetrahedral and square planar, respectively), might be useful in that regard.

$$[MnO_4]^{2-} + 3[MnMe_4]^{2-} \longrightarrow 4[MnOMe_3]^{2-} \qquad (35)$$

$[MnEt_4]^{2-}$ is known[316] as are a variety of other tetraalkylmanganate dianions; these $[MnR_4]^{2-}$ also include R = n-Bu, t-Bu and t-$BuCH_2CH_2$. It is not surprising that $[Mn(Bu\text{-}t)_4]^{2-}$ salts could not be isolated as there is ethylene available to form the more stable neohexyl manganate from the strong base-assisted decomposition of the ethyl ether solvent. Most assuredly, the dealkylation reaction of ethyl ether by t-butyl lithium is exothermic as is the addition of ethylene to any t-butyl derivative to form a derivative of neohexane.

Gas phase $Mn(CO)_3{}^-$ does not react with methane[318]. It reacts with ethane to form $C_2H_4Mn(CO)_3{}^-$ and hydrogen. Assuming no entropy change as two gas-phase species form two gas-phase species, the ethylene–$Mn(CO)_3{}^-$ binding energy must exceed the ethylene–H_2 binding energy in ethane. This latter quantity may be recognized as the difference between the enthalpy of formation of ethane and ethylene or 136 kJ mol^{-1}.

$Mn(CO)_n{}^-$ complexes ($n = 3$ and 4) with a single acetylene or ethylene ligand are formed [319] by reaction of $Mn(CO)_n{}^-$ with the corresponding hydrocarbon; with acetylene the decarbonylated product $C_2H_2Mn(CO)_{n-1}{}^-$ is also observed. This suggests that the binding energy of acetylene with manganese carbonyls is larger than that of Mn with CO, or at least with the 'last' CO. We note that $(C_2H_2)_2MnCO^-$ and $Mn(C_2H_2)_3{}^-$ were observed while no corresponding complexes with more than one ethylene ligand were found. Steric hindrance was suggested by the original authors. Given the small size of ethylene—not that much larger than acetylene—this seems unlikely to us. The structures of these ions are not known—while the original authors suggested a η^2-complex, there is also the possibility of a vinylidene isomer associated with isomerism of the acetylene while we know of no ethylidene manganese complex.

D. Other Methylmanganese Species

An estimate for the enthalpy of formation of gaseous CH_3MnCl, an archetypical organomanganese halide, begins with the observation [320] that the hydride affinity of $MnCl^+$ is 994 ± 6 kJ mol^{-1}. From the measured gas-phase enthalpies of formation[301] of gaseous $MnCl_2$ (-262 kJ mol^{-1}), appearance potential[301] of $MnCl^+$ (820 kJ mol^{-1}) and enthalpy of formation[2] of Cl^- (-233 kJ mol^{-1}), the enthalpy of formation of $MnCl^+$ is derived as 849 kJ mol^{-1}. Combined with the enthalpy of formation of H^- (139 kJ mol^{-1} [2]), the enthalpy of formation of HMnCl is -6 kJ mol^{-1}. If we now make the assumption that reaction 36 is thermoneutral (both the Mn–H and Mn–Me bonds involve neutral dicoordinated metal), then we deduce the enthalpy of formation of monomeric, unsolvated gas-phase methylmanganese chloride to be -19 kJ mol^{-1}.

$$MeMn(CO)_5 + HMnCl \longrightarrow HMn(CO)_5 + MeMnCl \tag{36}$$

It is not obvious with what we can compare this value: we find the enthalpy of decomposition to methyl chloride and solid, elemental manganese is exothermic by *ca* 60 kJ mol^{-1} and lack all solvation enthalpy data with which to estimate the enthalpy of its formation in solution, and a fortiori that of any of the organomanganese halides that appear in other chapters in this volume.

XIII. MANGANESE–ALKENE AND ALKYNE INTERACTIONS

A. Alkenes

As mentioned earlier in the discussion of the binding of ethene[295] to Mn^+, the binding energies of the first and second neutrals were nearly the same, namely 91 ± 12 kJ mol^{-1}. How does this compare to dienes? Conjugated 1,3-butadiene has a binding energy of 120 ± 6 kJ mol^{-1} while the nonconjugated 1,4-cyclohexadiene has a binding energy of 151 ± 21 kJ mol^{-1} [321]. For this study, the former complexed species was produced by reaction 37 and the latter by reaction 38.

$$Mn^+ + CH_3CH{=}CHCH_2Cl \longrightarrow Mn(C_4H_6)^+ + HCl \tag{37}$$

$$Mn(C_4H_6)^+ + C_2H_2 \longrightarrow Mn(C_6H_8)^+ \tag{38}$$

The so-formed cyclohexadiene Mn ion complex readily decomposes to benzene, H_2 and uncomplexed Mn^+. As is reflected by the aromaticity of benzene and the antiaromaticity of cyclobutadiene, the butadiene complex seemingly does not dehydrogenate to form cyclobutadiene. On the other hand, the $MnCl^+$ ion–olefin molecule complexes formed[320] from the reaction of $MnCl^+ \cdot H_2O$ with 1,3- and 1,4-cyclohexadiene seem stable to decomposition or dehydrogenation to form benzene or its complex.

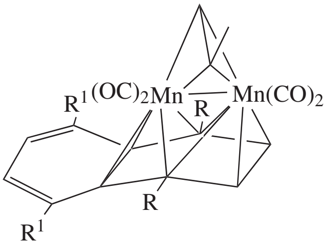
n-Propyl chloride reacts[313] with Mn^+ to form an ion with the formula $MnC_3H_6^+$. This requires the propene–Mn^+ bond energy to be greater than the propene–HCl bond energy of *ca* 60 kJ mol^{-1}. It is natural to assume that it is a propene–Mn^+ complex because of other metal cation induced dehydrochlorinations.

However, it was found that $Mn(CO)_3^-$ reacts with propane to form $C_3H_6Mn(CO)_3^-$ [318]. Based on the relative reactivity with other alkanes (e.g. the inertness of neopentane) and application of the 18 electron rule, it was suggested that this complex is the η^3-$C_3H_5Mn(CO)_3H$ anion. As such, we wonder if the aforementioned $MnC_3H_6^+$ ion is likewise a complexed allylmanganese hydride.

By solution calorimetry[322] the binding energy of $MnCl_2$ with formamide has been shown to be greater than that with acrylamide despite the possibility of C=C/Mn^{2+} stabilizing interactions for the latter. There is seemingly no bonding enhancement due to the dipolar resonance structure, $^+CH_2{-}CH{=}C(O^-){-}NH_2$, in acrylamide. Then again, recent studies have suggested the absence of enhanced conjugation-derived resonance in acrylic acid[323] and acrylonitrile[324], even to the extent of butadiene, and so why we may ask, should any be expected for acrylamide?

B. Alkynes

2-Butyne photochemically reacts[325] with bicymantryl, 1,1'-bis[cyclopentadienyl ($Mn(CO)_3$)], by a carbonyl displacement reaction. No cycloaddition to the 'fulvalene' backbone was observed. The $Mn_2(CO)_5$ complex from an isomerically related 1,4-dimethylnaphthalene ligand forms a pentacarbonyl(μ-$\eta^{4:6}$-1,4-dimethylnaphthalene)dimanganese–(Mn–Mn) complex, and this reacts[326] with 2-butyne to form (μ-$\eta^{2:2}$-2-butyne)(μ-1,2,3,4-η:1,4,4*a*,8*a*-η-1,4-dimethylnaphthalene)dimanganese tetracarbonyl (**24a**) in which the metals are bridged by the 2-butyne and the two Mn atoms are complexed by only one ring of the hydrocarbon. The latter species isomerizes to (μ-$\eta^{2:2}$-2-butyne) (μ-4*a*,5,8,8*a*-η:5,6,7,8-η-1,4-dimethylnaphthalene)dimanganese tetracarbonyl (**24b**). That ring methylation results in destabilization suggests that steric effects from the methyl groups are more important than any enhanced σ donation ability from the ring.



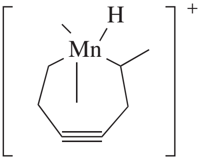
(**24**) (**a**) R = Me, R^1 = H

(**b**) R = H, R^1 = Me

$CpMn(CO)_2THF$ reacts[327, 328] with phenylacetylene to form the corresponding η^2-complex, $CpMn(CO)_2$ (PhC≡CH), which in turn rearranges to form the vinylidene complex $CpMn(CO)_2C{=}CHPh$. Although no experimental measurements exist as to the enthalpy of rearrangement of this or other alkyne manganese complexes[329], for the corresponding unsubstituted species containing the archetypal acetylene itself, the difference has been shown to be *ca* 40 kJ mol^{-1} from calculational theory[330].

The reaction chemistry of 4-octyne with Mn^+ results in a rich collection of organomanganese products[331]. Among them is the cation from 5-hydrido-4,5-dimethyl-5-manganacycloheptyne (**25**) for which the strain energy was deduced to be less than 63 kJ mol^{-1}. The strain energy of the parent hydrocarbon cycloheptyne or any other all-hydrocarbon derivative remains unavailable from the experimental literature. High level quantum chemical calculations suggest a value of 106 kJ mol^{-1} [332] for cycloheptyne itself. Unlike cycloheptyne, the cationic center of the manganacycloheptyne can coordinate with the 'distant' acetylene as well.

The bond between $CpMn(CO)_2$ and *cis*-cyclooctene is 12 ± 4 kJ mol^{-1} weaker than between Mn and Bu_2S[333].



(**25**)

The $CpMn(CO)_2$ complex of cyclooctyne has been shown to rearrange[334] to the complex of 1,2-cyclooctadiene. The energetics of this process are unknown: however, the enthalpy of formation of cyclooctyne, derived from the enthalpy of hydrogenation, has been calculated to be 33 kJ mol^{-1} higher than that of 1,2-cyclooctadiene[332]. Nothing is known about complexes with other cycloalkynes and whether they also rearrange.

A 1:2 complex of Mn^{-2} and 1,5-cyclooctadiene has been synthesized and crystallographically characterized[241]. This species is a 17-electron complex. As such, we wonder what is its α-C−H bond strength to form the 18-electron η^2-cyclooctene-(1,2,3-η^3-cyclooctenyl)manganese. Relatedly, what is its Mn−H bond strength to form its 18-electron hydrido complex, $(cod)_2MnH$. Accordingly, we ask about its disproportionation to form the latter two complexes.

XIV. ACIDITY, BASICITY AND OTHER HYDROGEN TRANSFER REACTIONS

The recommended proton affinity and gas phase basicity[255] of $HMn(CO)_5$ are 835.5 and 803.0 kJ mol^{-1} respectively, values reduced to 765.4 and 735.4 kJ mol^{-1} for $CH_3Mn(CO)_5$. As methylation almost invariably increases the basicity of a given compound, we conclude that it is the H of the former species that is the basic site, a finding corroborated by its reaction with both Brønsted[335] and Lewis acids[336] alike. The gas phase acidity[337] of $HMn(CO)_5$ is 1391 ± 17 kJ mol^{-1}, among the strongest neutral gas phase acids. In acetonitrile solution[338], $HMn(CO)_5$ is a relatively weak acid with a pK_a of 15.1, somewhere near the protonated aromatic pyridine and the protonated secondary amine, morpholine. This is consistent with the earlier finding of a pK_a of 7.1 of $HMn(CO)_5$ in water[339]. The difference between gas- and solution phase results is due to the poor solvation of $Mn(CO)_5^-$ [340].

The comparison between $HMn(CO)_5$ and $CH_3Mn(CO)_5$ shows that metal carbonyl derivatives with M−H bonds not only can donate H^+, they can also donate H^-. That is, isomeric to metal carbon carbonyl hydrides are metal formyl derivatives for which the energetics of the formal reaction 39 may be determined.

$$\mathrm{M{-}CHO} \longrightarrow \mathrm{(M{-}CO)^+ + H^-} \tag{39}$$

This has been done through a study[341] of reaction 40 where M_a and M_b are suitably coordinated metals.

$$\mathrm{M_a{-}H^+ + M_b{-}CO^+ \longrightarrow M_a{}^{2+} + M_b{-}CHO} \tag{40}$$

These include *trans*-$Ph_3PMn(CO)_4{-}CHO$ for which the solution-phase Gibbs energy for hydride donation is 210 kJ mol^{-1}. There are no data for this quantity for either $Mn(CO)_5{-}CHO$ or $Mn(CO)_4{-}CHO$. The latter is isomeric to $HMn(CO)_5$. Indeed, the former species remains unknown, unlike the analogous acetyl derivative. This is reminiscent of the instability of formyl halides compared to their acetyl counterparts.

XV. FLUORINATED MANGANESE SPECIES

A. Aliphatic Examples

Ion molecule chemistry continues to provide bond enthalpies for some formally simple species. As one successively fluorinates the methyl group in $CH_3{-}Mn(CO)_5$, the C−Mn bond dissociation enthalpy varies thus[342]: 192 ± 11, 139 ± 11, 144 ± 11 and 182 ± 11 kJ mol^{-1}. From calculational theoretical results[343] it has been suggested that the intermediate values for $CH_2FMn(CO)_5$ and $CHF_2Mn(CO)_5$ are too low. We concur—we do not understand why the $CH_2F{-}Mn$ and $CHF_2{-}Mn$ bonds would be particularly weaker than both $CH_3{-}Mn$ and $CF_3{-}Mn$.

Earlier in this chapter we discussed the $Mn^+{-}CH_2$ complex. The Mn−C bond strength in the corresponding carbonylated derivative, $(Mn(CO)_5CH_2)^+$ has been measured[344] as well as those in the fluorinated species $(Mn(CO)_5CHF)^+$ and $(Mn(CO)_5CF_2)^+$ and found to be 289 ± 33, 318 ± 38 and 331 ± 13 kJ mol^{-1}, respectively. An earlier study gave the value of 322 ± 21 kJ mol^{-1} for the $(Mn(CO)_5{-}CH_2)^+$ bond energy[345]. To the best of our knowledge, there are no measurements of the gas phase acidity of $CH_3Mn(CO)_5$, nor of its mono and difluoro derivatives. Such gas-phase acidity studies would allow the determination of the $(Mn(CO)_5{-}CH_2)^-$ bond energy and that of its mono and difluoro derivatives. Photodetachment studies of these anions would provide information about the energetics of the corresponding neutral $(Mn(CO)_5{-}CH_2)$ and fluorinated species.

It has been reported that gas phase $Mn(CO)_3{}^-$ reacts[346] with 1,2-di- (both *Z* and *E*), tri- and tetrafluoroethylenes to form anionic complexes of MnF_2 with acetylene and its mono and difluorinated derivatives, respectively (equation 41).

$$\mathrm{Mn(CO)_3{}^- + CXF{=}CYF \longrightarrow [XC{\equiv}CY{\bullet}MnF_2]^- + 3CO} \tag{41}$$

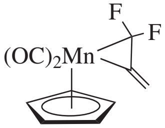
The related reaction with C_2F_6 also forms $MnF_2{}^-$ bonded to C_2F_2 (and presumably $COF_2 + 2CO$). $Mn(CO)_4{}^-$ reacts with C_2F_4 to form both $Mn(C_2F_4)(CO)_3{}^-$ and $Mn(C_2F_4)(CO)_4{}^-$ while $Mn(CO)_5{}^-$ does not react with C_2F_4 at all. No study has been made of reactions with mono or difluoroacetylene—both of these species are highly unstable and highly reactive. Perhaps these acetylene complexes are those of vinylidene instead. The enthalpy of formation[347] and electron affinity[348] of MnF_2(g) have both been measured. Dissociative electron attachment[349] by mono, di and trifluoroethylenes result in the vinylidene anions $[XYCC]^-$; indeed $[CHFC]^-$ is formed from 1,2- but not

1,1-difluoroethylene with nearly zero energy electrons[350]. The enthalpy of formation of C_2H_2 is well known from experiment, while calculational theory gives conflicting values for mono and difluoroacetylene[351–353] and the corresponding vinylidene isomers[353]. The electron affinities of the three acetylenes are negative, while the vinylidenes all bind electrons with measured values[354, 355].

Gas phase $Mn(CO)_3^-$ and $Mn(CO)_4^-$ react[356] with acetylene to form $C_2H_2Mn(CO)_2^-$ and both $C_2H_2Mn(CO)_3^-$ and $C_2H_2Mn(CO)_4^-$, respectively. The related reactions with ethylene form $C_2H_4Mn(CO)_3^-$ and $C_2H_4Mn(CO)_4^-$, respectively.

Cyclopentadienyl$Mn(CO)_3$ and perfluoro-2-butyne react[357] to form the $CpMn(CO)_2$ alkyne complex. Relatedly, the more labile $CpMn(CO)_2$THF complex photochemically reacts[358] with 2-butyne. We know of no exchange reaction reported to compare their relative Mn−alkyne bond energies. Nonetheless, the above relative ease of syntheses is suggestive that the fluorinated species is more tightly bound.

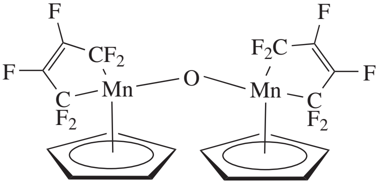
$CpMn(CO)_2$THF reacts[359] with allene and its 1,1-difluoro and tetrafluoro derivatives to form the corresponding $CpMn(CO)_2$ complex. It is the CH_2C of the difluoroallene that forms the complex or nominal manganacyclopropane resulting in an exocyclic CF_2 group (**26**). This parallels the relative stability of the two *gem*-difluoromethylenecyclopropanes[360] as shown by thermal equilibration, but runs counter[361] to the relative stability of their counterparts, the acyclic 1,1- and 3,3-difluoropropenes.



(**26**)

1,1-Difluoroallene has been shown[362] to react with $HMn(CO)_5$ to form the η^1-1,1-difluoroprop-1-en-2-yl, 3,3-difluoroprop-1-en-2-yl and 1,1-difluoroallyl (1,1-difluoroprop-2-en-1-yl) $Mn(CO)_5$ complexes in roughly 8:24:1 ratio. No η^1-3,3-difluoroallyl (3,3-difluoroprop-2-en-1-yl) $Mn(CO)_5$ or η^3-(1,1-difluoroallyl) $Mn(CO)_4$ complex was observed. It is not obvious how much relative stability of the diverse organometallics determines the product yield. On the other hand, in the much faster reaction of tetrafluoroallene, the corresponding reaction produces 1,2,3,3-tetrafluoropropen-2-yl$Mn(CO)_5$ which may be thermally rearranged, albeit slowly, to the (*Z*)-1,3,3,3-tetrafluoropropen-2-yl isomer where again no allyl product was observed.

Conjugated polyenes can bind to form either π or σ complexes. An example of this dichotomy is found[363] with hexafluorobutadiene (isomeric to the above perfluoro-2-butyne) and cyclopentadienyl$Mn(CO)_3$ from which both the half sandwich η^5-$CpMn(CO)(\eta^4$-$C_4F_6)$ and the 1,4-CF_2−CF=CF−CF_2−containing μ-oxo-bis[(cyclopentadienyl)(η^1, η^1-1,1,2,3,4,4-hexafluorobut-2-ene-1,4-diyl)manganese(IV)] (**27**) may be synthesized.



(**27**)

B. Aromatic and Related Examples

On the interface of aliphatic and aromatic examples are thiopheniumMn$(CO)_3$ species wherein the S-substituted thiophene (thiophenium) ring is significantly non-planar and the sulfur significantly pyramidalized. No significant structural differences were seen for S-phenylated[364] and 2,3,4,5-tetrakis trifluoromethylated and S-pentafluorophenylated[365] thiophene rings. These species have been described as zwitterions containing sulfonium ions, and so may be understood as containing dieneMn$(CO)_3$ anions. They are also valence isoelectronic to substituted cyclopentadienylMn$(CO)_3$ species, although we are leary of comparing the unstable thiophenium and stable cyclopentadienide ions.

Pentafluorophenyl[366] is a normal substituent for $Mn(CO)_5$ with respect to the carbonyl stretching force constants and thus the understanding of inductive and mesomeric effects. 'A fair straight line relationship exists'[367] between ^{19}F chemical shifts and substituent electronegativities—the manganese-containing group $Mn(CO)_5$ shows no anomalies.

Diverse pentafluorophenyl containing compounds were shown[368] to react with $MnO_2{}^-$ and $MnO_3{}^-$ by either electron transfer or F^- displacement. The final products of the latter set of reactions are presumably of the general type $ZC_6F_4MnO_2$ and $ZC_6F_4MnO_3$; cf. the S_NAr reaction 42.

$$C_6F_5Z + MnO_x^- \longrightarrow ZC_6F_4MnO_x + F^-(x = 2, 3) \qquad (42)$$

However, it is not obvious whether these contain C−Mn bonds and so are analogous to iodoxy- and nitrobenzene ($x = 2$), and perchlorylbenzene and tosylate ion ($x = 3$). Species of the type $RRe(CO)_3$ containing the valence isoelectronic Re are well-established and quantum chemical calculations[369] suggest the C−Mn bonded permanganyl derivative, $C_6F_5MnO_3$, is 'a promising target for future synthesis'. The enthalpy of formation of C_6F_6 is well-established as is that of F^-. Mn−O bond energies and electron affinities have been measured[370] for both gaseous $MnO_2{}^-$ and $MnO_3{}^-$, from which the enthalpies of formation of these anions may be derived. Accordingly, upper bounds for the enthalpies of formation of $C_6F_5MnO_2$ and $C_6F_5MnO_3$ may thus be deduced as well. The data[370] allow us to determine the enthalpies of formation for MnO_2 and MnO_3, that of C_6F_5 has been found from the chemistry of some other pentafluorophenyl derivatives[371] and so $C_6F_5{-}MnO_2$ and $C_6F_5{-}MnO_3$ bond energies may be determined and compared with some species with unequivocal C−Mn bonds. However, this analysis is thwarted because the electron affinities of MnO_2 and MnO_3 as reported in References 368 and 370 differ by at least $100\,\mathrm{kJ\,mol^{-1}}$ and no reconciliation is apparent: we note a plethora of geometries and spin state possibilities for MnO_2, MnO_3 and their ions, and it is not obvious to what species the measurements from Reference 368 correspond.

The square-planar $[(C_6F_5)_4Mn^{III}]^-$ ion has been observed as a solid salt[372]. No corresponding $[(C_6F_5)_4Mn^{II}]^{2-}$ is known. This is surprising since the Mn^{III} species was formed from the corresponding Grignard reagent and $MnBr_2$. By contrast, $[(C_6H_5)_4Mn^{II}]^{2-}$ with a distorted tetrahedral geometry is known, but not $(C_6H_5)_4Mn^-$, formed by analogous reaction[178] involving organolithiums. It is not surprising that C_6H_5 preferably stabilizes Mn^{II} and the more electronegative C_6F_5 likewise stabilizes Mn^{III}: quantitation via electrochemical redox measurements is yet unreported.

Elsewhere in this chapter we described the interaction of Mn^+ with benzene. The gas phase reaction[373] of Mn^+ with C_6F_6 is dominated (90:10) by formation of the related $C_6F_6{\cdot}Mn^+$ complex versus that of formation of MnF^+. We know of no corresponding reaction with partially fluorinated benzenes.

Hexafluorobenzene reacts[374] with $Mn(CO)_5{}^-$ salts to form pentafluorophenylMn$(CO)_5$. By contrast, the corresponding reaction[375] with the valence isoelectronic pentafluorohalobenzenes (Cl, Br, I) yield aroyltetracarbonylhalometallates, *cis*-$[C_6F_5COMn(CO)_4X]^-$

salts via S_N2 reactions on the heavier halogens. This reflects the difficulty of nucleophilic displacement on fluorine[376].

The η^6-cyclooctatetraene complexes C_8X_8MnCp with $X = H$ and F have been prepared and contrasted[377]. The hydrocarbon species is much more labile (both to heating and the presence of air) than the fluorinated species. The cyclooctatetraene–Mn bonds are 0.1 Å longer for the fluorinated species and the colors of the two species are very different, yellow and red-brown respectively. Although both species were synthesized using displacement reactions of the cyclooctatetraene with $CpMn(CO)_3$, disappointingly no studies were reported attempting displacement of one cyclooctatetraene by the other to determine their relative thermodynamic stability. Nonetheless, the above relative kinetic stabilities is suggestive of the perfluorinated species being the more tightly bound.

There is also the perfluorinated η^1-derivative, $C_8F_7Mn(CO)_5$, for which the dynamics of its interconversion with its valence isomers has been studied[378] as has that of its precursor perfluorocyclooctatetraene[379], C_8F_8. There are no data for the corresponding C_8H_7 containing organomanganese or one with a partially fluorinated ring. We also do not know of any organomanganese species with multiple C_8F_7 groups.

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The chemistry of organomanganese ate complexes

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I. INTRODUCTION

Ate complexes of transition metals have been an interesting class of compounds in coordination chemistry and organic synthesis. After two decades since organomanganese(II) compounds, PhMnI and Ph_2Mn, were first reported in 1937[1], Nast and Griesshammer prepared the first organomanganate by simply mixing $Mn(SCN)_2$ and alkali metal acetylides (equation 1) and discussed the chemical, electronic and magnetic properties[2]. Subsequently, preparations of Me_3MnLi and Ar_3MnLi from MnI_2 and organolithium reagents were reported[3]. In these reports, elemental and electromagnetic analyses were the only methods for characterizing the manganates, and no information about the precise structure and the reactivity toward organic compounds was disclosed. Thereafter, organomanganates had been ignored for more than one decade. In the 1970s, organomanganates started to attract significant attention of both organometallic chemists and synthetic organic chemists. Now organomanganates, as well as other organomanganese compounds[4–6], represent structurally intriguing entities and useful reagents in organic synthesis.

$$4\ \mathrm{R{-}C{\equiv}C{-}M} + \mathrm{Mn(SCN)_2} \xrightarrow[\substack{\text{(R = H, Me, Ph;}\\ \text{M = Na, K)}}]{} \left(\mathrm{R{-}C{\equiv}C}\right)_4\mathrm{MnM_2} + 2\ \mathrm{MSCN} \qquad (1)$$

This chapter comprises two main sections. The first section describes the organometallic chemistry of organomanganates. The second section details the application of organomanganates to organic synthesis.

II. ORGANOMETALLIC CHEMISTRY OF ORGANOMANGANATES

A. σ-Bonded Organomanganates

Following the research around 1960[2, 3], several reports about the synthesis and characterization of manganates appeared from 1975 to 1977 ($Li_2[Mn(o,o'\text{-lithiophenyl ether})_2]\bullet 6thf$ and $Li[Mn(o,o'\text{-lithiophenyl ether})_2]\bullet 2thf$[7], $Li_2[Mn(CH_2N(CH_2)_5)_2]\bullet 2dioxane$[8], $LiMn(mesityl)_3\bullet dioxane\bullet thf$)[9]. However, no X-ray data were available. Only elemental analysis or magnetic moment measurement was performed to elucidate the structures. Wilkinson and coworkers reported their extensive and careful investigation on dilithium tetraalkylmanganates as well as dialkylmanganese[10]. They obtained the structure of dineopentylmanganese and bis(trimethylsilylmethyl)manganese by X-ray crystallographic analysis. However, it seems that they failed to present the exact structure of the manganate species. Instead, they evidenced the synthesis of $Li_2[MnR_4]$ (R = Me or CH_2SiMe_3) by very careful elemental analysis, IR and magnetic moment measurement. For instance, the magnetic moment of crystalline $Li_2[MnR_4]\bullet 2TMEDA$ was $5.5\,\mu_B$, which suggests essentially high-spin Mn(II).

In the 1980s, Eaborn and coworkers succeeded in obtaining the first X-ray crystallographic analysis, albeit with significant disorder, of anionic manganate $[Li(thf)_4]$-$[\{(Me_3Si)_3C\}_3Mn_3Cl_4(thf)]$ (Figure 1) upon treatment of $MnCl_2$ with $(Me_3Si)_3CLi$ in THF[11a,b]. They observed the interaction between the manganese atoms, which is indicated by the mean magnetic moment of $3.8\,\mu_B$. The value is similar to that in $MnMes_2$ ($3.65\,\mu_B$) but considerably lower than the spin-only values, $5.8–5.95\,\mu_B$, found for $MnCl_4^-$. Later, they also synthesized a similar manganate $[Li(thf)_3][\{C(SiMe_3)_2SiMe_2CH_2CH_2SiMe_2C(SiMe_3)_2\}MnCl]$[12].

Power and coworkers reported the first X-ray structural characterizations of compounds of type $LiMnR_3$[13]. $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$ and $[\{Li(thf)_4\}]_2[Mn_2Ph_6]$ crystallized as a centrosymmetric dimer (Figures 2a and 2b). The structure of the former may be described as a

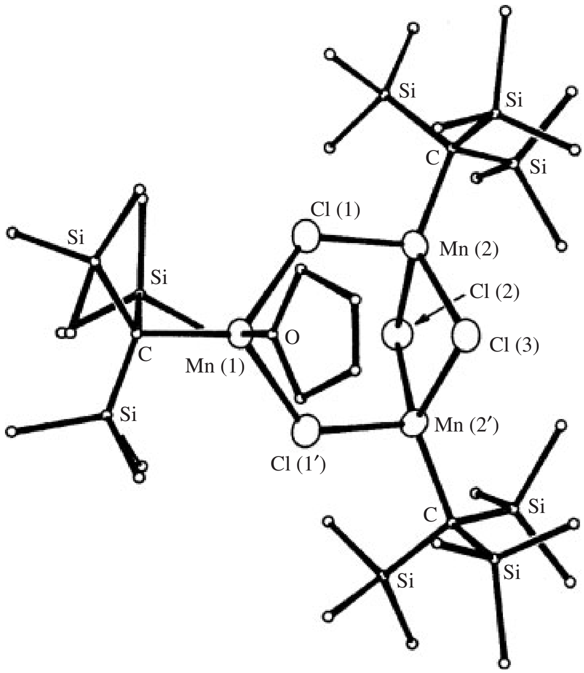
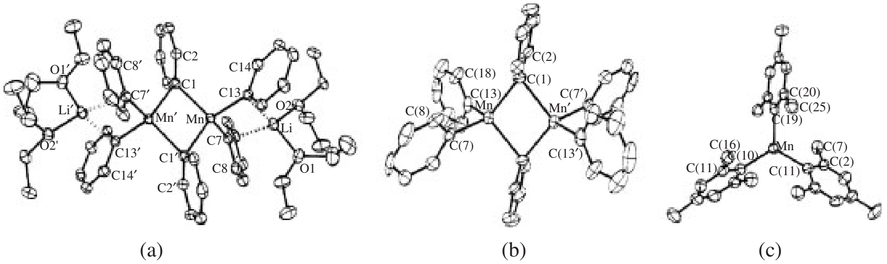


FIGURE 1. The structure of the anion $[\{(Me_3Si)_3C\}_3Mn_3Cl_4(thf)]^-$. Reproduced by permission of The Royal Society of Chemistry from Reference 11a



(a) (b) (c)

FIGURE 2. The structures of (a) $[\{Li(Et_2O)_2\}_2Mn_2Ph_6]$, (b) $[Mn_2Ph_6]^{2-}$ of $[\{Li(thf)_4\}]_2[Mn_2Ph_6]$ and (c) $[MnMes_3]^-$ of $[Li(thf)_4][MnMes_3]$. Reprinted with permission from Reference 13. Copyright 1988 American Chemical Society

linear Li-Mn−Mn−Li array. Each metal is located at the centers of four edge-sharing distorted tetrahedra. Both manganese atoms are surrounded by four bridging phenyl groups, and the lithiums bear two phenyls and two ethers. In the latter complex, strongly coordinating THF isolates $\{Li(thf)_4\}^+$, leaving the free dimeric $[Mn_2Ph_6]^{2-}$. The bulkier mesityl group makes the corresponding manganate monomeric, $[Li(thf)_4][MnMes_3]$ (Figure 2c).

Around the same time, Morris and Girolami started to report their elegant serial work on manganates. Alkylation of $MnCl_2$ with 4 equivalents of MeLi in ether in

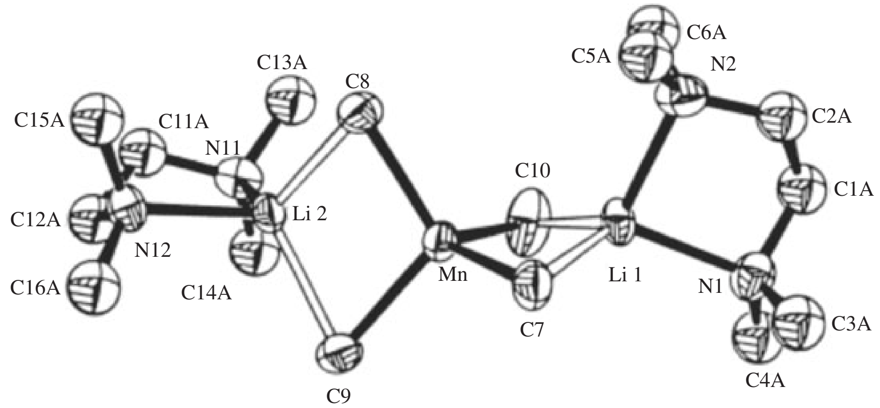


FIGURE 3. The structure of $[Li(tmeda)]_2[MnMe_4]$[14]. Reprinted with permission from Reference 14. Copyright 1988 American Chemical Society

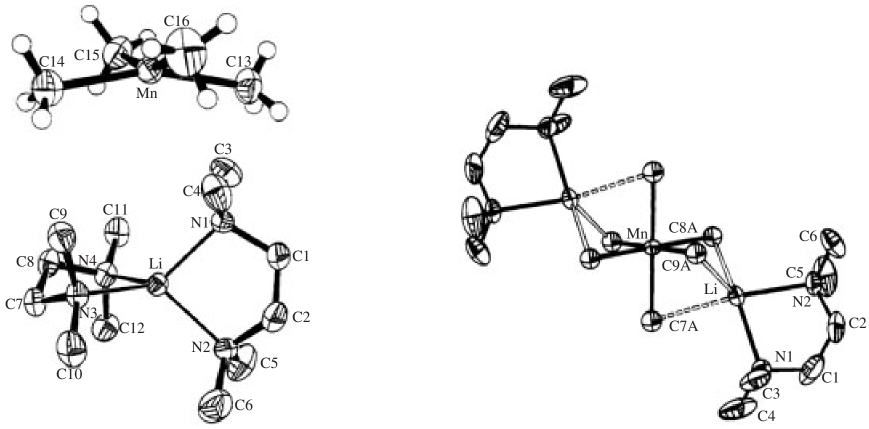
the presence of TMEDA gave pale-colored $[Li(tmeda)]_2[MnMe_4]$[14, 15] (Figure 3). The 13-electron manganate is stable at room temperature and has nearly ideal tetrahedral symmetry. $[Li(tmeda)]_2[MnEt_4]$ was prepared in a similar fashion. Treatment of $MnCl_2$ with 4 equiv of t-BuLi in ether led to the formation of $[Li(tmeda)]_2[Mn(CH_2CH_2Bu\text{-}t)_4]$ via an ethylene-forming side reaction with diethyl ether. Notably, the tetraethyl- and tetrakis(3,3-dimethylbutyl)manganates are the first structurally characterized alkyl transition metal complexes that contain β-hydrogen atoms.

Stereochemistry and spin state in four-coordinate transition metal complexes including manganese have attracted significant interest. Very recently, a DFT computational study for tetramethylmanganate was presented[16].

High valent organomanganese complexes are rare. Morris and Girolami succeeded in preparing trivalent pentamethylmanganate $[Li(tmeda)]_2[MnMe_5]$ and tetravalent $[Li(tmeda)]_2[MnMe_6]$[14, 17]. The reaction of $Mn(acac)_3$ with excess MeLi afforded a red solution of $[Li(tmeda)]_2[MnMe_5]$. The trivalent manganate was EPR-silent and exhibited a solution magnetic moment of $4.9\,\mu_B$, which is consistent with the presence of four unpaired electrons. Single crystals of $[Li(tmeda)_2][MnMe_4]$, which would be formed via decomposition of $[Li(tmeda)]_2[MnMe_5]$, were grown from toluene at $-20\,^\circ C$ (Figure 4a). The structure analysis shows that the crystals are composed of charge-separated $[Li(tmeda)_2]^+$ and $[MnMe_4]^-$ ions and that $[MnMe_4]^-$ unit exhibits a slight tetrahedral distortion from a square plane, which is an exceedingly rare structure for manganese(III) complexes. Tetravalent $[Li(tmeda)]_2[MnMe_6]$ was prepared from $MnMe_4(PMe_3)_2$, MeLi and TMEDA as an orange solution. Single crystals of $[Li(tmeda)]_2[MnMe_6]$ were grown from ether at $-20\,^\circ C$ (Figure 4b). The hexamethyl complex takes an octahedral geometry for the d^3 Mn with the lithium atoms capping the opposite faces.

Morris and Girolami also reported the synthesis and characterization of the first alkyl oxomanganese $[MnOMe_3]^{2-}$[18]. Treatment of $Mn(acac)_3$ with 5 equivalents of MeLi in diethyl ether followed by an addition of TMEDA gave the rare trivalent organomanganese.

Recently, Forniés and coworkers synthesized the first structurally characterized homoleptic trivalent arylmanganates[19]. Arylation of $MnBr_2$ with C_6F_5MgBr in THF



(a) (b)

FIGURE 4. The structures of (a) [Li(tmeda)$_2$] and [Mn^{III}Me$_4$]. Reprinted with permission from Reference 17. Copyright 1991 American Chemical Society and (b) [Li(tmeda)]$_2$[Mn^{IV}Me$_6$]. Reprinted with permission from Reference 17. Copyright 1991, American Chemical Society

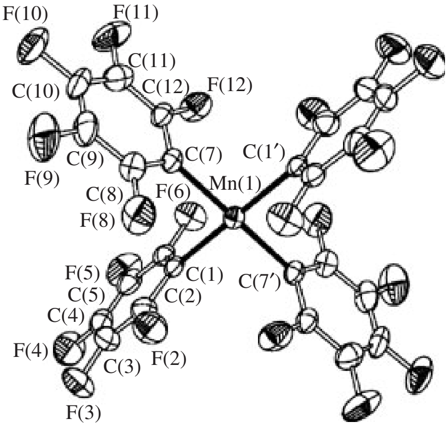


FIGURE 5. The structure of one of the two crystallographically independent [Mn(C$_6$F$_5$)$_4$]$^-$ in [Mg(thf)$_6$][Mn(C$_6$F$_5$)$_4$]$_2$. Reprinted with permission from Reference 19. Copyright 2005 American Chemical Society

proceeded with oxidation of the manganese to afford [Mg(thf)$_6$][Mn(C$_6$F$_5$)$_4$]$_2$ (Figure 5). The crystal structure contains [Mn(C$_6$F$_5$)$_4$]$^-$ with approximate square-planar geometry around the manganese.

During their research on bis(pentadienyl)metal, Ernst and coworkers obtained K[Mn{3-Me-1,5-(Me$_3$Si)$_2$C$_5$H$_4$}$_3$][20] (Figure 6). An X-ray diffraction study revealed that the Mn

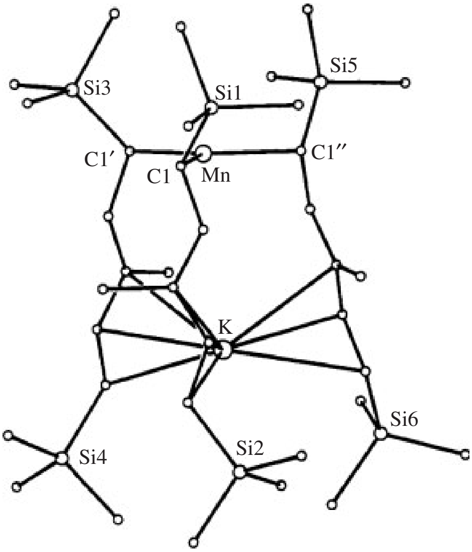
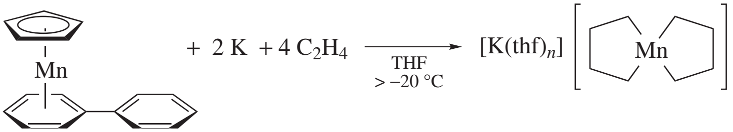


FIGURE 6. The structure of K[Mn{3-Me-1,5-$(Me_3Si)_2C_5H_4$}$_3$]. Reprinted with permission from Reference 20. Copyright 1992 American Chemical Society

center experiences trigonal planar coordination with the three η^1-bound dienyl anions, while potassium cation is coordinated in η^3 modes.

Addition of organolithium or organomagnesium to manganese salts is not the only way to synthesize organomanganates. The reaction of CpMn(biphenyl) with potassium in the presence of ethylene in THF proceeded to yield manganaspirononane $[K(thf)_n][(C_4H_8)_2Mn]$ (equation 2)[21a,b]. The crystal structure of a similar potassium manganate is shown in Figure 7.



(2)

Gambarotta and coworkers synthesized an interesting zerovalent manganate complex (Figure 8) by treatment of an *N*,*N*,*N*-pincer complex with trimethylsilylmethyllithium (equation 3)[22]. The complex displays a magnetic moment consistent with the presence of three unpaired electrons on a tetracoordinated high-spin d^7 zerovalent manganese. The complex has a distorted square-planar geometry. The Mn atom is coplanar with the three nitrogen atoms and has the alkyl group considerably deviating from planarity.

Organomanganates with a salen ligand were prepared from a manganese(salen) dimer complex (equation 4)[23]. The reaction of the dimer with mesityllithium in DME provided a red solution, from which crystals were grown upon addition of ether. The structure shown in Figure 9 reveals that the Mn(salen) unit has an umbrella conformation with the dihedral angles between the O−Mn−N planes being 69°. The distance of Mn from the N_2O_2 plane is remarkably longer than those in other trivalent [RM^{III}(salen)] derivatives.

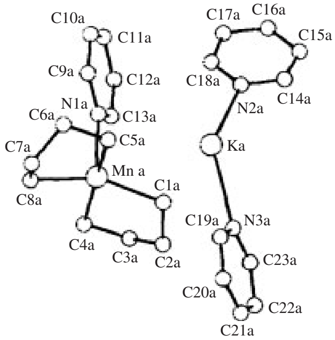


FIGURE 7. The structure of one of the two crystallographically independent [K(pyridine)$_2$]-[(pyridine)Mn(C$_4$H$_8$)$_2$]. Reproduced by permission of Wiley-VCH from Reference 21a

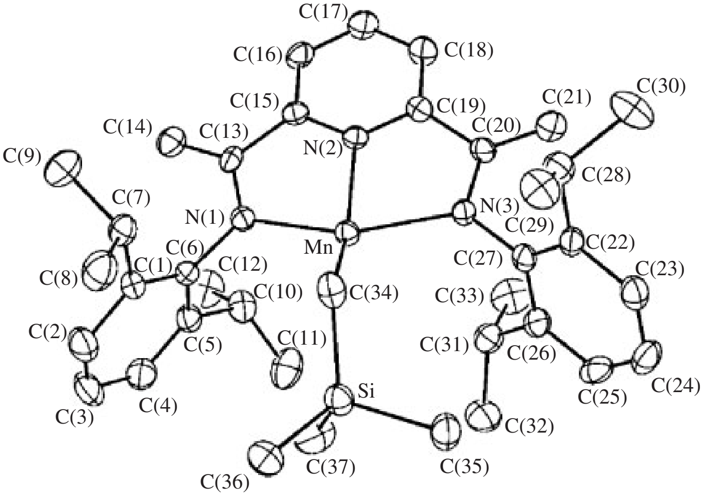
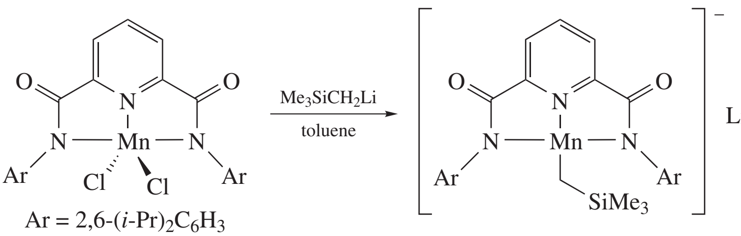
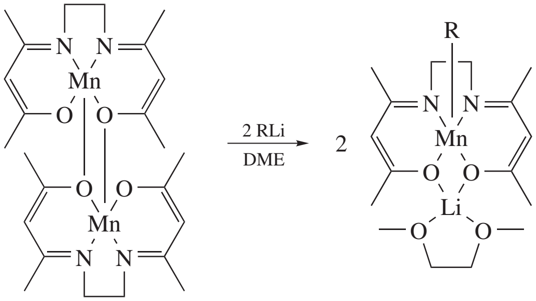


FIGURE 8. The structure of zerovalent manganate in equation 3. Reprinted with permission from Reference 22. Copyright 2002 American Chemical Society



(3)

Ar = 2,6-(i-Pr)$_2$C$_6$H$_3$



(4)

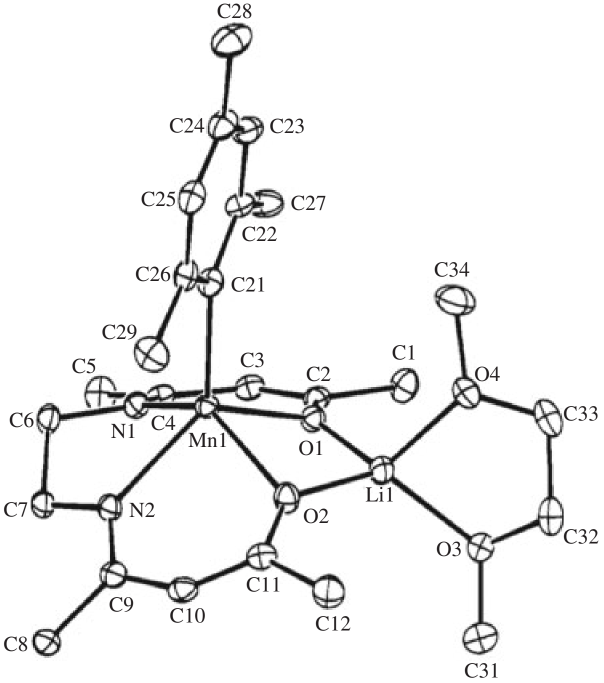


FIGURE 9. The structure of mesitylmanganate in equation 4 (R = mesityl). Reprinted with permission from Reference 23. Copyright 1995 American Chemical Society

B. Organomanganates Bearing π Ligands

Although organomanganates bearing C−Mn σ-bonds are popular, those bearing π ligands such as Cp^- are less common.

Jonas pioneered the synthesis of π-bonded manganates[21]. Except for $Na[Mn(CO)_5]$ and $Na_3[Mn(CO)_4]$, $[Li(dme)]_2[Mn(cod)_2]$ is the first homoleptic manganate with manganese in a negative oxidation state (Figure 10). The manganate is prepared from Cp_2Mn, lithium naphthalenide and 1,5-cyclooctadiene in DME (equation 5). The reductive formation of manganates is also applicable to the synthesis of $[K(thf)_n][CpMn(biphenyl)]$ and

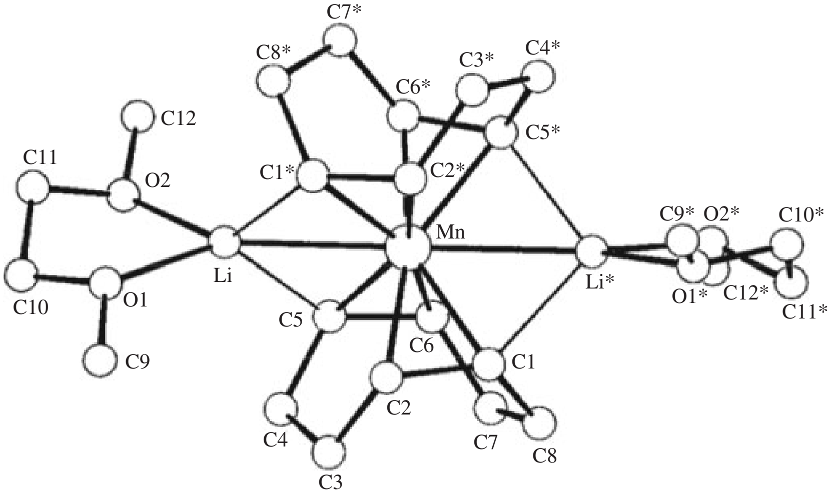
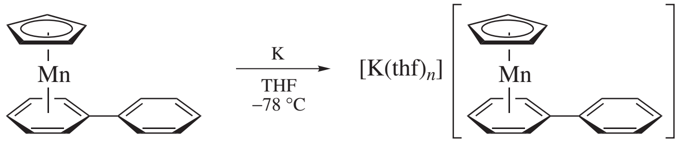


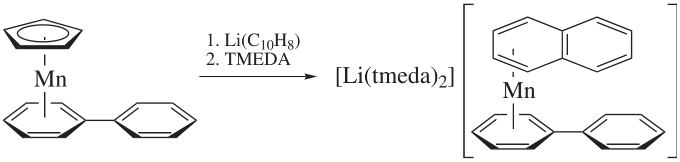
FIGURE 10. The structure of $[Li(dme)]_2[Mn(cod)_2]$. Reprinted from Reference 21b. Copyright 1992, with permission from Elsevier

$[Li(tmeda)_2][Mn(biphenyl)(naphthalene)]$ (equations 6 and 7).

$$Cp_2Mn + Li(C_{10}H_8) + COD \xrightarrow[DME]{} [Li(dme)]_2[Mn(cod)_2] \tag{5}$$



(6)



(7)

Wright and coworkers reported in 2001 the first complex containing $[Cp_3Mn]^-$ anion by the reaction of manganocene with CpK or Cp_2Mg in THF[24]. $[(\eta^2\text{-}Cp)_3MnK\bullet 1.5thf]$ consists of the manganate anions associated via Mn-(μ-Cp)-K interactions into cyclic $[(\eta^2\text{-}Cp)_3MnK]$ units, which build into a honeycomb sheet structure (Figure 11). Interestingly, the Mn centers are clearly coordinated by three η^2-Cp ligands. The $[(\eta^2\text{-}Cp)_3Mn]$ anion is the first transition metal triscyclopentadienide anion. Around the same time, the cesium analogues, $[Cs(18\text{-}crown\text{-}6)_2][(\eta^2\text{-}Cp)_3Mn]$ and $Cs[(\eta^2\text{-}Cp)_3Mn]$, were shown to have similar η^2-Cp coordination[25]. It is noteworthy that the latter cesium salt is a rare example of a racemic interpenetrating network that crystallizes in the orthorhombic space group *Pbca*.

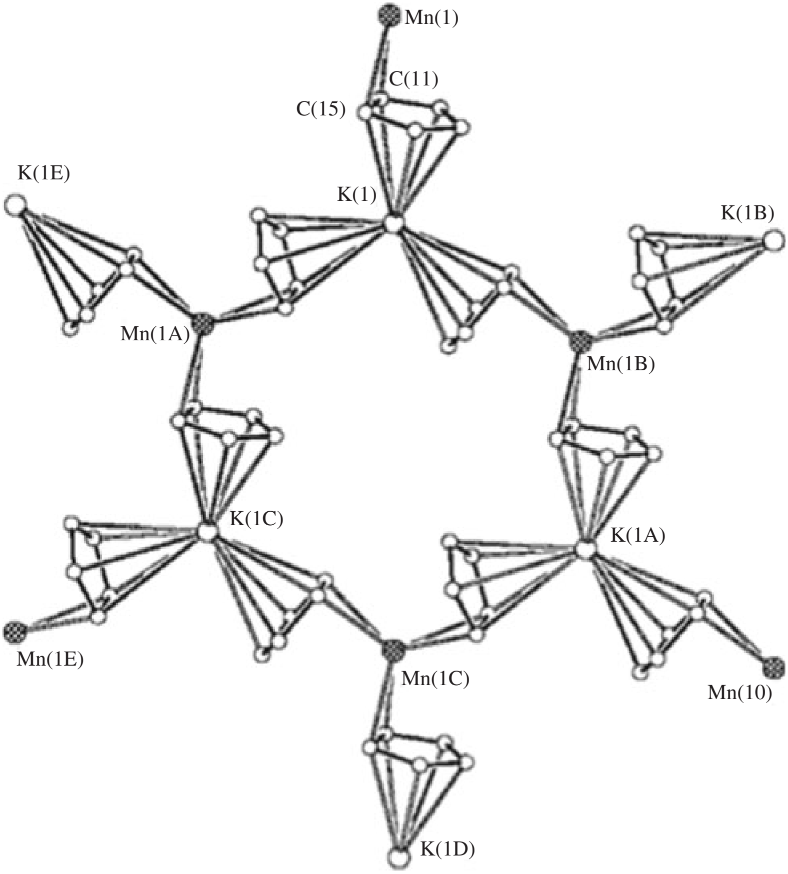


FIGURE 11. The sheet structure of [(η^2-Cp)$_3$MnK•1.5thf]. Reproduced by permission of The Royal Society of Chemistry from Reference 24

Layfield and Humphrey reported the synthesis, structure and magnetic properties of [Li(thf)$_4$][Mn{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}{η^1-(Me$_3$Si)$_2$C$_3$H$_3$}$_2$] (Figure 12), which is the first structurally authenticated allyl complex of manganese(II)[26]. The observation of both η^3- and η^1-allyl coordination to a Mn^{II} center is unprecedented for an ionic metal(allyl) complex. They also performed DFT calculations on manganates [Mn{η^x-(C$_3$H$_3$R$_2$)$_3$}]$^-$ ($R = H$, SiMe$_3$; $x = 1$ or 3) to develop an understanding of allylmanganates[27].

C. Additional Interesting Organomanganates

Treatment of (MeC$_5$H$_4$)Mn(CO)$_3$ or {(Me$_3$Si)$_2$CH}$_2$Mn with an anionic gallium heterocyclic complex afforded the corresponding manganate bearing a Ga−Mn bond[28] (Scheme 1). The former reacted with extrusion of one carbon monoxide to yield dimer

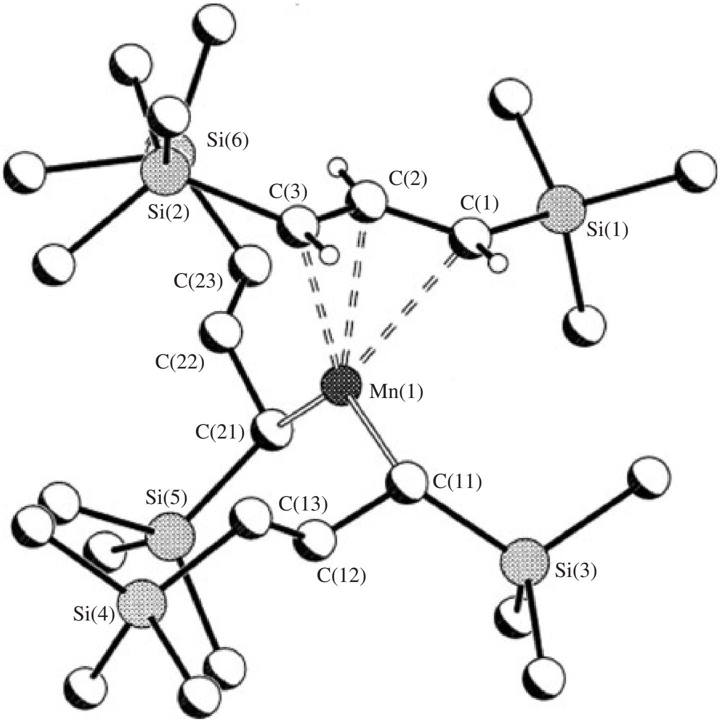
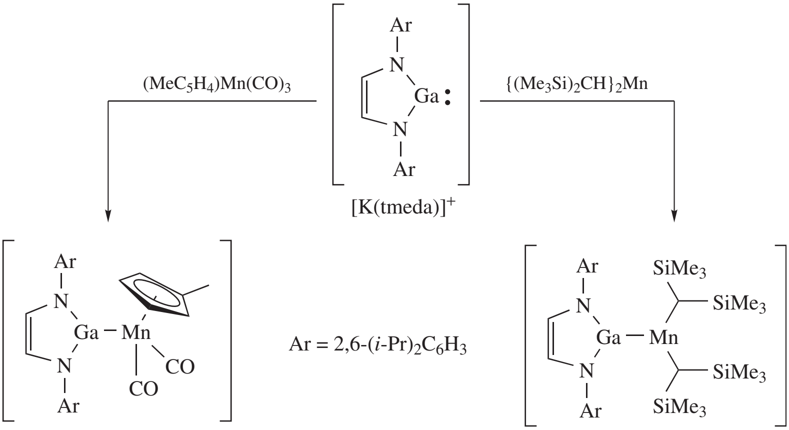


FIGURE 12. The structure of $[\mathrm{Mn}\{\eta^3\text{-}(\mathrm{Me_3Si})_2\mathrm{C_3H_3}\}\{\eta^1\text{-}(\mathrm{Me_3Si})_2\mathrm{C_3H_3}\}_2]^-$. Reproduced by permission of Wiley-VCH from Reference 26



SCHEME 1

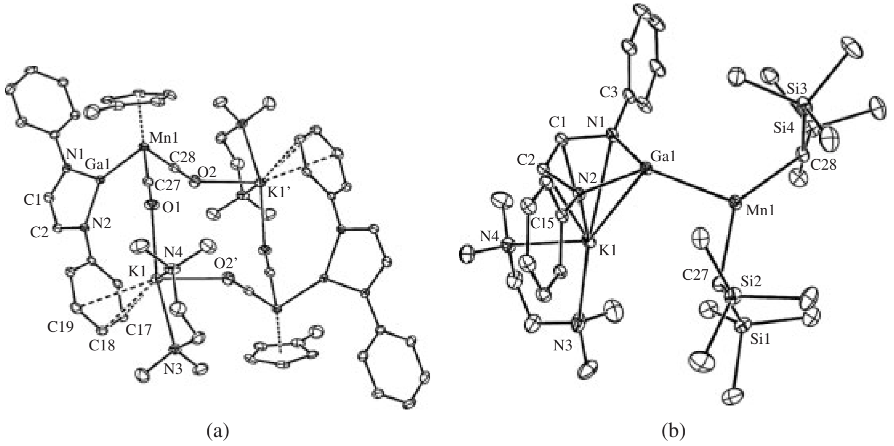


FIGURE 13. The structures of (a) dimer of **1** and (b) **2**. Reproduced by permission of The Royal Society of Chemistry from Reference 28

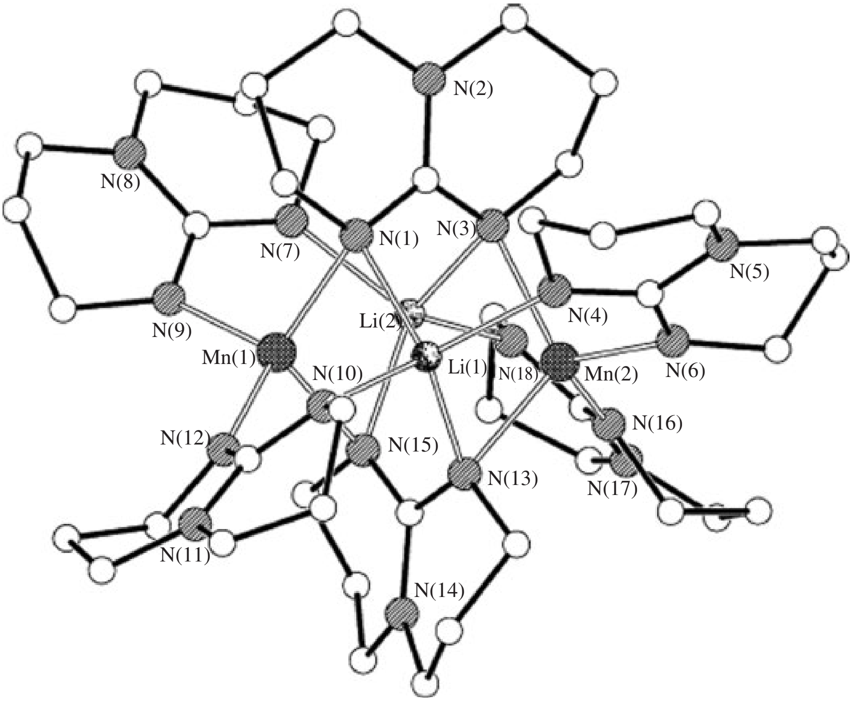


FIGURE 14. The structure of $[LiMn(hpp)_3]_2$. Reproduced by permission of the Royal Society of Chemistry from Reference 29

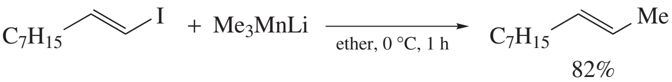
of **1** through bridging potassium cations (Figure 13a), while the latter was converted to monomeric anionic complex **2** (Figure 13b).

The nucleophilic substitution reaction of Cp_2Mn with excess Li(hpp) (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2,a]pyrimidine) afforded unusual manganate cage $[LiMn(hpp)_3]_2$[29] (Figure 14).

III. REACTIONS OF ORGANOMANGANATES IN ORGANIC SYNTHESIS

A. General Introduction of Organomanganate Reagents in Organic Synthesis

Although the importance of organocuprates is self-evident, the use of organomanganates in organic synthesis has been much less explored. Corey and Posner reported in 1970 that manganates behave as cuprates in the reactions of organic halides[30] (equation 8). Lithium trimethylmanganate and tributylmanganate react with organic halides to afford the corresponding cross-coupling products.



(8)

Following the pioneering work by Corey and Posner, Normant and Cahiez extensively investigated the preparation of triorganomanganates and their reactions, especially with carbonyl compounds[4]. The most convenient way to prepare manganates for organic synthesis is transmetalation between manganese(II) halides and organolithium or organomagnesium in ether or THF (equations 9 and 10). According to a molar ratio of manganese halide and organometallic reagent, tri- or tetraorganomanganate is formed. One can prepare a wide range of organomanganates such as alkyl-, aryl-, alkenyl-, alkynyl-, allyl- and benzylmanganates. Lithium trialkylmanganates are the most stable organomanganese compounds, more than the corresponding monoalkylmanganese halide and dialkylmanganese. For instance, while dibutylmanganese and butylmanganese chloride are unstable above −30 °C and 25 °C in ether, respectively, lithium tributylmanganate is stable above 35 °C and thus easy to use.

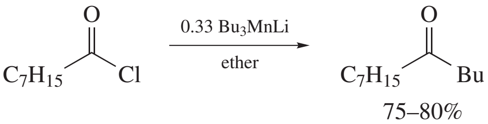
$$\begin{array}{l} 3\,RM + MnX_2 \longrightarrow R_3MnM\ (+\ 2\,LiX \text{ or } 2\,MgXX^1) \\ (M = Li,\ MgX^1) \end{array} \qquad (9)$$

$$\begin{array}{l} 4\,RM + MnX_2 \longrightarrow R_4MnM_2\ (+\ 2\,LiX \text{ or } 2\,MgXX^1) \\ (M = Li,\ MgX^1) \end{array} \qquad (10)$$

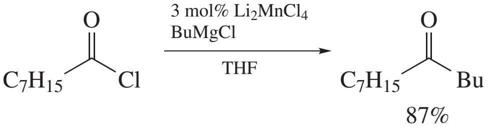
B. Nucleophilic Addition to Carbonyl Compounds and Related Reactions

Organomanganates are reactive enough to undergo nucleophilic attack to aldehydes and ketones. Such reactions are useless when simple organomanganates such as Bu_3MnLi are employed. However, when manganese-mediated reactions provide highly functionalized organomanganese species *in situ*, the reactions of aldehydes and ketones are useful as further C−C bond forming events (see Sections III.D and III.E).

Historically, Cahiez, Normant and coworkers started to develop organomanganates as reagents for nucleophilic attack in organic synthesis. The reactions of saturated carboxylic acid chlorides with monoalkylmanganese iodides provide the corresponding ketones[31]. Thus, similar reactions proceed with 0.33 equivalents of lithium trialkylmanganates[32] (equation 11). Tetraorganomanganates are supposed to be the key intermediate in manganese-catalyzed reactions of acyl chlorides with Grignard reagents[33] (equation 12). Carboxylic anhydrides react with manganates with slightly lower efficiency[34].

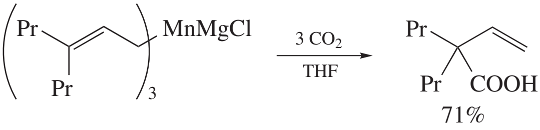


(11)

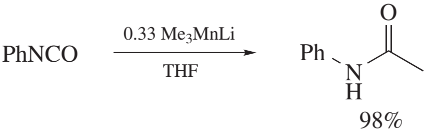


(12)

Triorganomanganates also react smoothly with 3 equivalents of carbon dioxide to yield the corresponding carboxylic acid[35] (Table 1). The scope of triorganomanganates is wide, and no overreactions that produce ketones take place, which is in sharp contrast to carboxylation of organolithium and organomagnesium reagents. The reactions of tri(1-alkenyl)manganates proceed with retention of configuration. Allylic manganates react with carbon dioxide exclusively at the more substituted carbon (equation 13). Manganates react with sulfur dioxide and phenyl isocyanate in a similar fashion (equation 14).



(13)



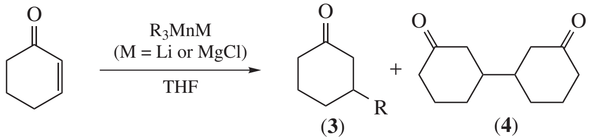
(14)

TABLE 1. Reactions of triorganomanganates with carbon dioxide

$$\underset{(M = Li\ or\ MgCl)}{0.33\ R_3MnM + CO_2} \xrightarrow[\text{THF, 20 °C}]{} RCOOH$$

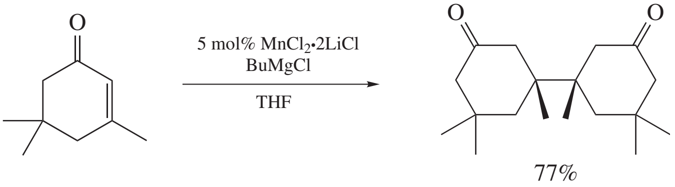
Manganate	Yield (%)
$(C_7H_{15})_3MnLi$	83
$(C_7H_{15})_3MnMgCl$	72
s-Bu_3MnLi	77
(t-amyl)$_3$MnMgCl	50
Ph_3MnLi	89
$(Me_2C{=}CH)_3MnLi$	96
$[(Z)\text{-}BuCH{=}CH]_3MnLi$	80
$(BuC{\equiv}C)_3MnLi$	83

TABLE 2. Reactions of triorganomanganates with cyclohexenone



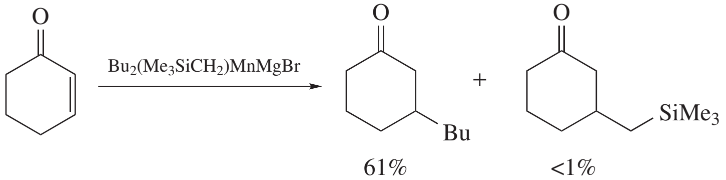
Manganate	Yield of **3** (%)	Yield of **4** (%)
$Me_3MnMgCl$	42	21
$Bu_3MnMgCl$	20	74
Bu_3MnLi	18	74
$(i\text{-}Pr)_3MnMgCl$	13	74
$Ph_3MnMgCl$	45	16

Organomanganates participate in 1,4-addition to a variety of α,β-unsaturated carbonyl compounds without forming 1,2-adducts. In the 1,4-addition reactions of cyclohexenone derivatives[36], reductive dimerization at the β-positions always competes, and the yields of the 1,4-adducts are low to modest[37] (Table 2). The addition of $BF_3 \bullet Et_2O$ can suppress the reductive dimerization albeit with still modest yields of 1,4-adducts[38]. Clean reductive dimerization takes place upon treatment of cyclohexenone with butylmagnesium chloride in the presence of $MnCl_2 \bullet 2LiCl$ catalyst (equation 15).



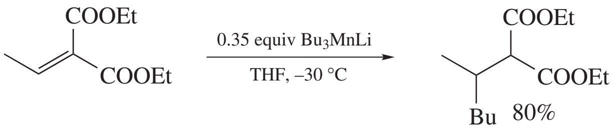
(15)

The reactions of cyclohexenone with unsymmetrical triorganomanganates ($R^1_2R^2MnMgX$) were examined to probe the reactivity order of organic groups on manganese[39] (equation 16). The order was approximately allyl > Bu > Ph > Me, Me_3SiCH_2, HexC≡C. Thus, the least reactive three groups can serve as nontransferable dummy ligands.

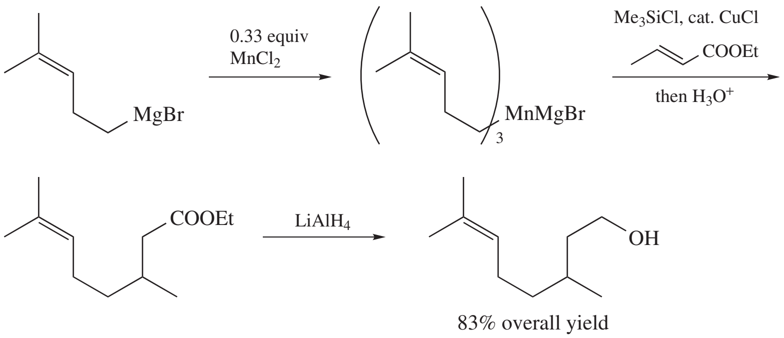


(16)

Highly reactive ethylidene- and isopropylidenemalonates undergo 1,4-addition of organomanganates without reductive dimerization at the β position[40] (equation 17). The reaction of the less reactive ethyl crotonate with trialkylmanganate requires both the presence of copper-catalyst and Lewis acid, as demonstrated in the short synthesis of citronellol[41] (Scheme 2).

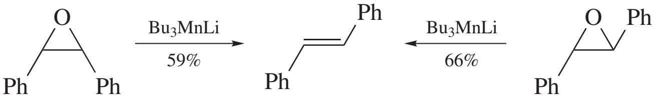


(17)



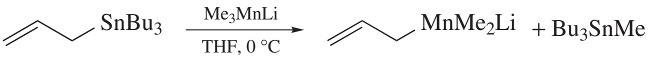
SCHEME 2

Different from organocuprates, lithium tributylmanganate does not participate in ring-opening of epoxides but in deoxygenative olefination of stilbene oxide[36] (equation 18). Unfortunately, the deoxygenation is not stereospecific: both *cis*- and *trans*-stilbene oxides are reduced to *trans*-stilbene selectively.



(18)

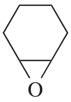
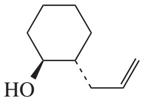
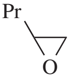
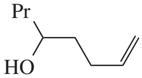
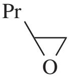
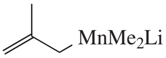
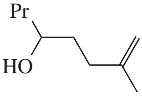
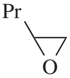
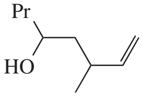
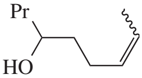
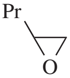
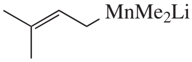
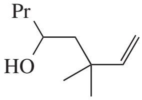
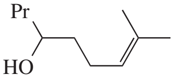
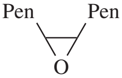
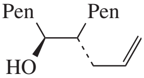
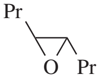
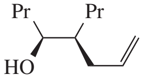
In contrast, allylic manganates, which are prepared from lithium trimethylmanganate and allylic tributyltin (equation 19), effect allylation of epoxides without conceivable methyl transfer[42] (Table 3). In the formation of allylic manganates, the counter metal cation of the trimethylmanganate plays a critical role, i.e. $Me_3MnMgBr$ does not undergo transmetalation. The allylic manganates attack the less hindered carbon of monosubstituted epoxide (entries 2–5). Crotyl- and prenylmanganates react preferentially at the more substituted carbon although the selectivities are inferior to those obtained with the corresponding cuprates (entries 4 and 5). It is worth noting that the ring-opening proceeds stereospecifically (entries 6 and 7).



(19)

Combined with $BF_3{\bullet}OEt_2$, magnesium triorganomanganates are useful for converting acetals to the corresponding alkylated ethers at low temperatures[43] (Table 4). The reaction is so powerful that dibutyl ketone dimethyl acetal was transformed to *tert*-alkyl ether in excellent yield (entry 5). This result implies that the corresponding oxonium cation intermediate may be involved in the reaction. However, interestingly, cyclopropanecarboxaldehyde dimethyl acetal is alkylated smoothly without cationic rearrangement

TABLE 3. Reactions of lithium allyldimethylmanganates with epoxides

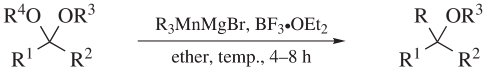
Entry	Substrate	Manganate	Product	Yield (%)
1				80
2				81
3				75
4				54
				18
5				52
				13
6				65
7				61

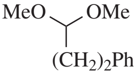
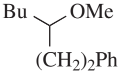
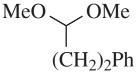
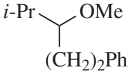
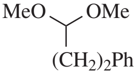
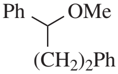
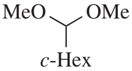
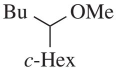
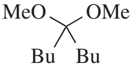
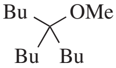
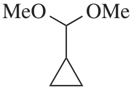
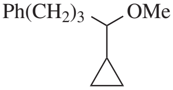
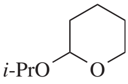
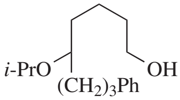
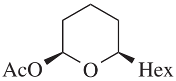
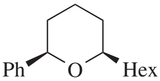
(entry 6). The exact mechanism of the reactions is not clear. The THP ether of isopropyl alcohol undergoes selective ring-opening alkylation without conceivable substitution of the isopropoxy group (entry 7). Lactol acetate also reacts under the manganate–BF_3 system (entry 8).

C. Cross-coupling Reactions of Organic Halides with Organomanganates

Organomanganates were first used in organic synthesis by Corey and Posner for the cross-coupling reactions of organic halides with lithium trimethylmanganate and tributylmanganate[30] (equation 8). While the methylation of aryl or alkenyl halides

TABLE 4. Alkylation of acetals with manganate–BF_3 combination

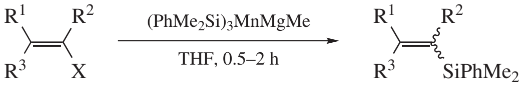


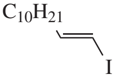
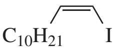
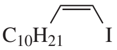
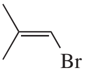
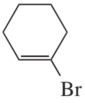
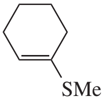
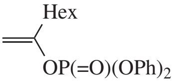
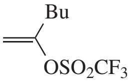
Entry	Acetal	Manganate	Temp (°C)	Product	Yield (%)
1		$Bu_3MnMgBr$	−78		94
2		$(i\text{-Pr})_3MnMgBr$	−78		94
3		$Ph_3MnMgBr$	−78		71
4		$Bu_3MnMgBr$	−50		81
5		$Bu_3MnMgBr$	−78		96
6		$[Ph(CH_2)_3]_3MnMgBr$	−50		99
7		$[Ph(CH_2)_3]_3MnMgBr$	−50		59
8		$Ph_3MnMgBr$	−20		86

proceeds smoothly, the butylation suffers from a side reaction, replacement of halides with hydrogen, because of the occurrence of β-hydride elimination from butylmanganese species. Kauffmann and coworkers reported that manganates are comparable or inferior to the corresponding iron or cobalt ate complexes in reactivity[44]. Thus, cross-coupling reactions with stoichiometric manganates are rather useless.

Cahiez and coworkers reported manganese-catalyzed organolithium-mediated reductive dimerization of iodoalkenes to dienes[45]. In this report, they suggested that the catalytic cycle involves lithium manganates, which is also the case for manganese-catalyzed cross-coupling reactions[46].

TABLE 5. Synthesis of 1-alkenylsilanes by cross-coupling silylation with silylmanganate

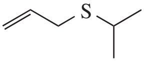
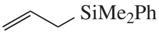
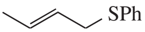
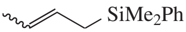
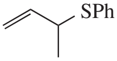
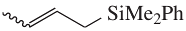
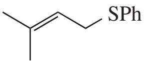
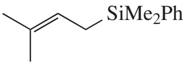
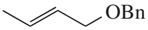
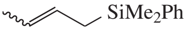


Entry	Substrate	Temp (°C)	Yield (%)	*E/Z*
1		0	72	100/0
2		0	73	20/80
3		−95	40 (70% conv.)	0/100
4		0	70	—
5		0	93	—
6		0	75	—
7		25	74	—
8		0	99	—

Silylmanganates $(R_3Si)_3MnMgMe$, prepared from MeMgI, R_3SiLi and Li_2MnCl_4, react with 1-alkenyl halides, sulfides, phosphate and triflate to give the corresponding 1-alkenylsilanes in good yields[47, 48] (Table 5). Unfortunately, the reactions of alkenyl halides are not stereospecific at 0 °C, and the reactions at temperature as low as −95 °C proceed with stereospecificity, yet with lower efficiency (entries 1–3). It is noteworthy that the amount of Li_2MnCl_4 could be reduced to a catalytic amount. Allylic sulfides and ethers couple with the silylmanganate to yield the corresponding allylic silanes with high regioselectivity (Table 6).

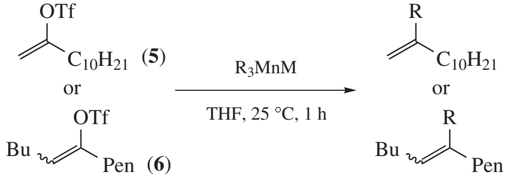
Not only silylmanganates but also other triorganomanganates react with 1-alkenyl triflates[49] (Table 7). Similar transformations can be performed with phenyl, allyl and benzyl Grignard reagents under manganese catalysis (equation 20). The corresponding

TABLE 6. Synthesis of 2-alkenylsilanes by cross-coupling silylation with silylmanganate[a]

Entry	Substrate	Product	Yield (%)
1			91
2			75
3			88
4			89
5			65

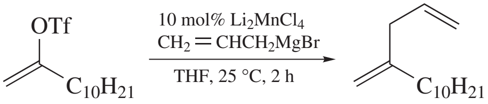
[a] Performed at 0 °C for 30 min.

TABLE 7. Cross-coupling reactions of 1-alkenyl triflates with manganates

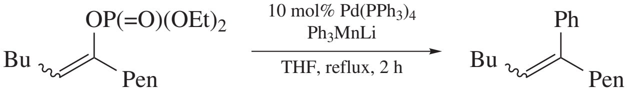


Entry	Substrate	Manganate	Yield (%)
1	**5**	Me_3MnLi	86
2	**5**	Bu_3MnLi	93
3	**5**	Ph_3MnLi	100
4	**5**	$Ph_3MnMgBr$	93
5	**6**	Bu_3MnLi	75
6	**6**	Ph_3MnLi	87

phosphates are less reactive, requiring the presence of a catalytic amount of $Pd(PPh_3)_4$ (equation 21).

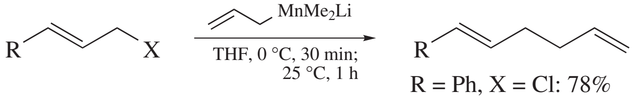


(**5**) 92% (20)



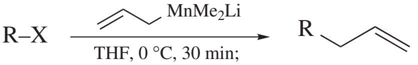
73% (21)

The reactions of allylic halides with lithium allyldimethylmanganate afford the 1,5-hexadienes without methyl transfer[42] (equation 22). The selective allylations of primary alkyl halides also take place (equation 23).



R = Ph, X = Cl: 78%
$R = C_{10}H_{21}$, X = Br: 81%

(22)



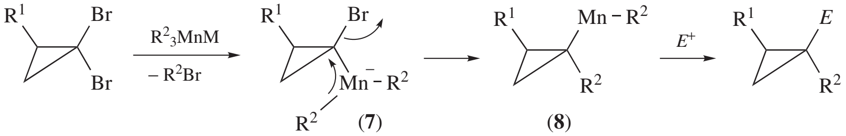
$R\text{–}X = C_8H_{17}\text{–}I$: 80%
$R\text{–}X = Ph(CH_2)_3\text{–}Br$: 82%

(23)

D. Halogen–Manganese Exchange and Related Reactions

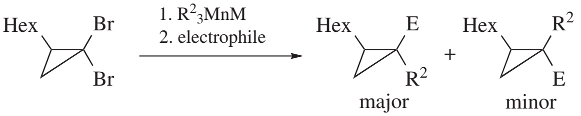
Halogen–metal exchange is a reliable method to prepare organometallic species. Organomanganates participate in the exchange with rather reactive organic halides and pseudohalides.

Organomanganates react with *gem*-dihalocyclopropanes with introduction of the organic moiety into the cyclopropane ring[50] (Table 8), in a similar fashion to organocuprates[51] and organozincates[52]. Instead of aqueous workup, an addition of electrophile leads to further functionalization of the cyclopropane. The reaction would proceed as follows (Scheme 3): (1) halogen–manganese exchange takes place to afford cyclopropylmanganate **7**, (2) alkyl migration (intramolecular S_N2 reaction) to form **8** and (3) reaction with electrophiles with retention of configuration. The initial



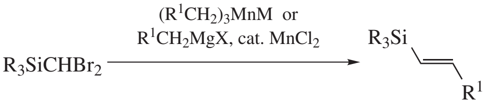
SCHEME 3

TABLE 8. Reactions of *gem*-dibromocyclopropane with manganates



Manganate	Electrophile	E	Yield (%)	Major/Minor
Me_3MnLi	H_2O	H	65	82/18
$Bu_3MnMgBr$	H_2O	H	89	71/29
$Bu_3MnMgBr$	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2$	77	89/11
$Bu_3MnMgBr$	MeI	Me	65	94/6
$Bu_3MnMgBr$	PhCOCl	PhCO	72	83/17

TABLE 9. Synthesis of vinylsilanes from (dibromomethyl)trialkylsilanes with manganates

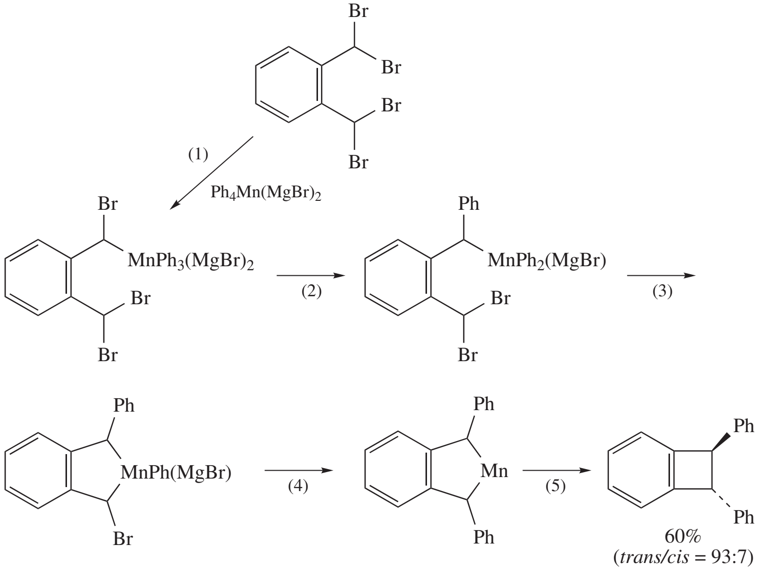


Entry	R_3Si	Reagent	Yield (%)
1	Ph_2MeSi	Me_3MnMgI	89
2	Ph_2MeSi	$Et_3MnMgBr$	76
3	Ph_2MeSi	Bu_3MnLi	95
4	Ph_2MeSi	$Bn_3MnMgBr$	88
5	$t\text{-}BuMe_2Si$	Bu_3MnLi	96
6	$(i\text{-}Pr)_3Si$	$Et_3MnMgBr$	79
7	Ph_2MeSi	BuMgBr, cat. $MnCl_2$	67
8	$(i\text{-}Pr)_3Si$	EtMgBr, cat. $MnCl_2$	88

halogen–manganese exchange occurs preferentially at the less hindered side, leading to the *trans* stereochemistry with regard to R^1 and R^2. The reaction also proceeds in the presence of a catalytic amount of manganese chloride, being slightly less efficient.

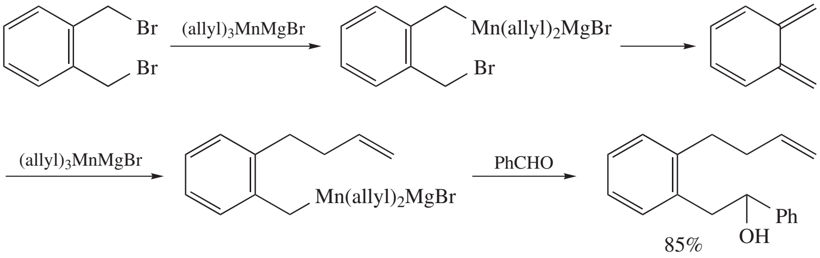
(Dibromomethyl)trialkylsilanes are good substrates for bromine–manganese exchange, which finally leads to (E)-(1-alkenyl)trialkylsilanes via β-elimination from the corresponding alkylmanganese intermediates[53] (Table 9). The reactions are highly stereoselective and thus useful. The reaction can proceed catalytically, and yields are comparable (entries 7 and 8).

The reaction of 1,2-bis(dibromomethyl)benzene with tri- or tetraarylmanganates provides strained diaryldihydrobenzocyclobutenes[50] (Scheme 4). Interestingly, *trans* isomers



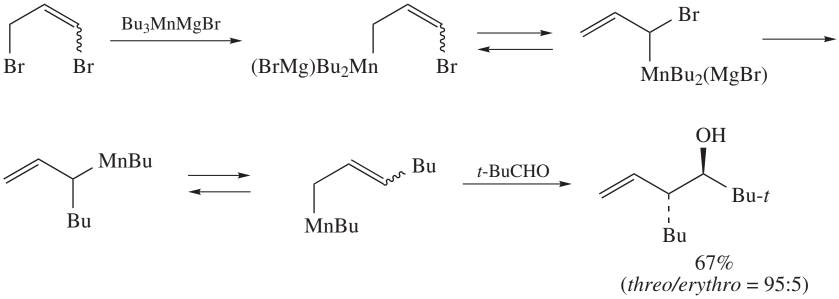
SCHEME 4

are obtained selectively. The reaction involves (1) bromine–manganese exchange, (2) phenyl migration, (3) intramolecular bromine–manganese exchange to yield manganacycle, (4) phenyl migration and (5) reductive elimination. Triallylmanganate reacts with 1,2-di(bromomethyl)benzene to yield 2-(3-butenyl)phenylmethylmanganese species, which is trapped with electrophiles such as benzaldehyde[53] (Scheme 5). The reaction is likely to proceed via *o*-quinodimethane.



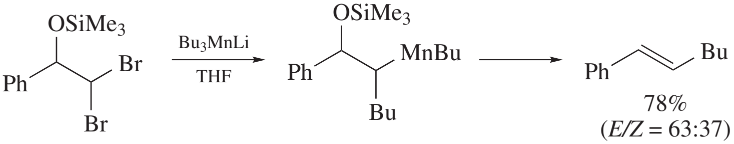
SCHEME 5

The scope of dihalo compounds is extended to 1,3-dihalopropene[54]. Treatment of 1,3-dibromopropene with tributylmanganate followed by an addition of pivalaldehyde affords the corresponding three-component coupling product (Scheme 6).



SCHEME 6

2-Siloxy-1,1-dibromoalkanes react with manganates[55] (equation 24). The organomanganese species that is formed through the initial bromine–manganese exchange and the subsequent alkyl migration undergoes β-siloxy elimination to afford the corresponding olefin regioselectively. Unfortunately, the olefination is not stereoselective. The reaction is applicable to the synthesis of tri- and tetrasubstituted olefins starting from 2,2,2-tribromoalkanol derivatives (equation 25).



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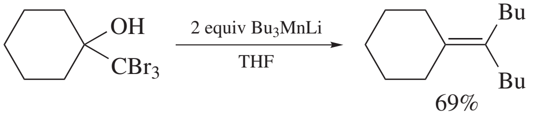
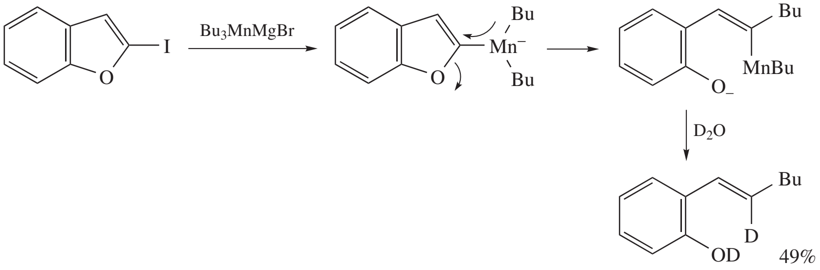


(25)

2-Iodobenzofuran undergoes iodine–manganese exchange followed by ring-opening to yield 2-(1-hexenyl)phenol with high *E*-selectivity[50] (Scheme 7).



SCHEME 7

The reactions of dibromoacetate or dibromoacetamide with trialkylmanganates provide the corresponding alkylated manganese enolates[56] (Table 10). The manganese enolates are trapped with a variety of electrophiles. The reaction is applied to the one-pot synthesis of α,β-unsaturated amide by using silylmanganate (Scheme 8). Difunctionalization of dibromo β-lactam proceeds without decomposition of the β-lactam ring (equation 26).

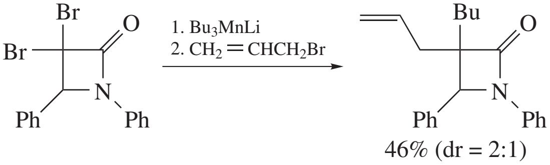


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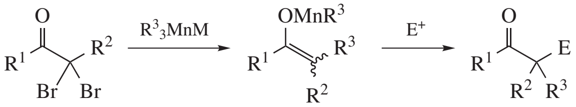
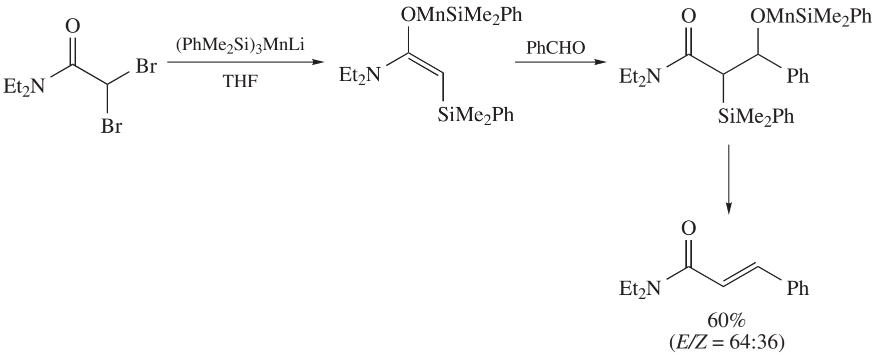
TABLE 10. Reactions of dibromoacetate or dibromoacetamide with trialkylmanganates

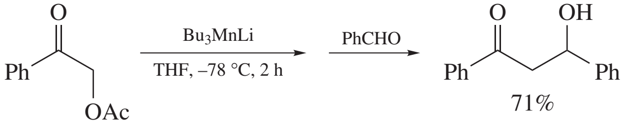


Entry	R^1	R^2	R^3_3MnM	E^+	Yield (%)
1	*t*-BuO	H	Bu_3MnLi	PhCHO	46
2	*t*-BuO	H	Bu_3MnLi	MeI	42
3	*t*-BuO	H	Bu_3MnLi	CH_2=$CHCH_2Br$	69
4	Et_2N	H	Bu_3MnLi	PhCHO	72
5	Et_2N	H	Bu_3MnLi	MeI	70
6	Et_2N	H	Bu_3MnLi	CH_2=$CHCH_2Br$	76
7	Et_2N	H	Ph_3MnLi	PhCHO	73
8	Et_2N	Me	Bu_3MnLi	H_2O	89
9	Et_2N	Me	Bu_3MnLi	PhCHO	90

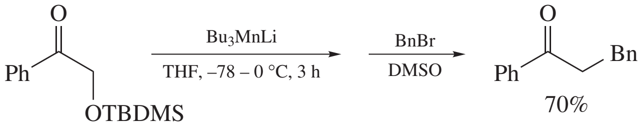


SCHEME 8

Hosomi and coworkers independently developed the use of manganates as reducing agents. They first demonstrated that manganates are useful for the regioselective generation of manganese enolates from α-acetoxy, siloxy and halo carbonyl compounds[57] (equations 27–29).



(27)



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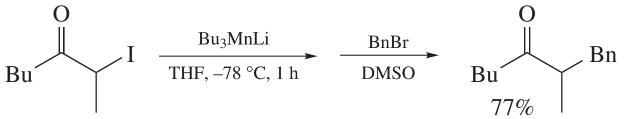
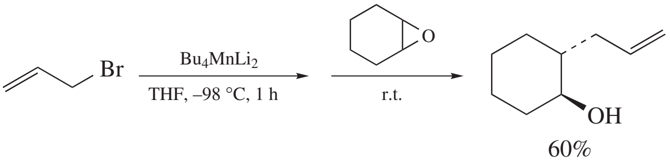
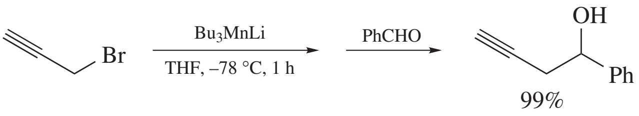


(29)

They also utilized manganate for reductive manganation of allyl bromide[58], propargyl bromide[58] and iodomethyl sulfide[59] (equations 30–32).



(30)



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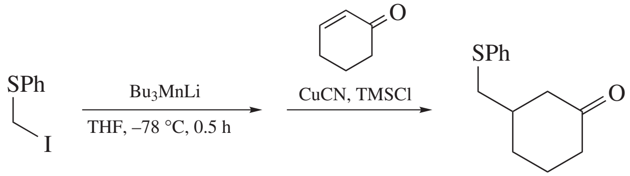
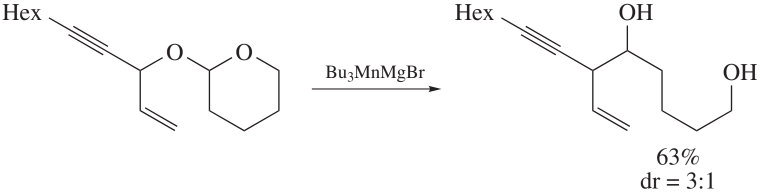


(32)

Allylic manganate is formed upon treatment of the THP ether of allyl alcohol with tributylmanganate[60] (Scheme 9). The allylic manganate reacts with magnesium lactolate to yield 7-octene-1,5-diol. Notably, the allylation of the lactolate predominates over conceivable butylation, and only a small amount of butylated product is obtained. Propargyl tetrahydropyranyl ethers also react to yield alkynediols (equation 33). These reactions can be catalytic in manganese.



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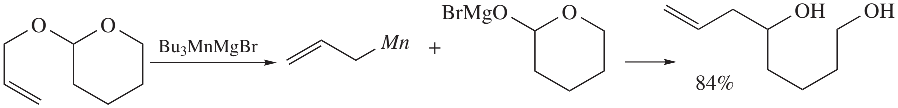


SCHEME 9

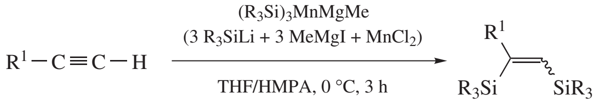
E. Carbometalation of Carbon–Carbon Multiple Bonds

Carbometalation of carbon–carbon multiple bonds is a useful reaction that forms a carbon–carbon bond and a carbon–metal bond in a single operation. The resulting organometallic species can react with other electrophiles to lead to complex molecules from rather simple alkenes and alkynes.

In 1985, silylmanganate, prepared from silyllithium, MeMgI and $MnCl_2$, proved to react with terminal alkynes to lead to disilylation[48, 61] (Table 11, entries 1–5). The reactions afford a mixture of stereoisomers while similar reactions with stannylmanganates proceed with high *Z* selectivity (entries 6 and 7). The use of MeMgI is essential: the formation of monosilylated product competes in the absence of MeMgI (equation 34). Disilylation of trimethylsilyl-substituted internal alkynes proceeds smoothly (Table 12), being applied to highly efficient synthesis of tetrakis(trimethylsilyl)ethene. Interestingly, selective monosilylation takes place when $Me_2PhSiMgMe$ reagent is used under $MnCl_2$ catalysis[62] (Equation 35).

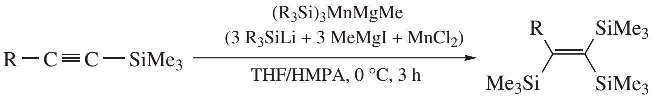
Silylmanganates also add to conjugated dienes[48, 63] (Table 13). The silylmanganation initially provides a silylmethyl-substituted allylmanganate, which eventually isomerizes into the corresponding silyl-substituted allylmetal at room temperature (Scheme 10). The allylic manganese species react with various electrophiles. While the reaction of methyl iodide proceeds preferentially at the silylated carbon, that of carbonyl compounds occurs exclusively at the γ-position from the silyl group. Similar silylmagnesiation reactions can proceed under manganese catalysis[62].

TABLE 11. Disilylation of terminal alkynes with silylmanganates (or stannylmanganates)

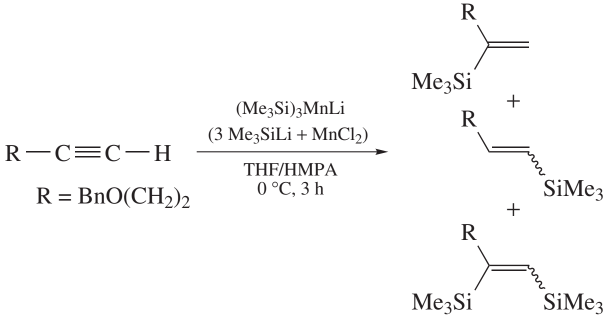


Entry	R^1	R^3Si	Yield (%)	E/Z
1	Me_3Si	Me_3Si	72	—
2	Bu	Me_3Si	66	67:33
3	Ph	Me_3Si	65	50:50
4	$THPO(CH_2)_2$	Me_3Si	63	35:65
5	$THPO(CH_2)_2$	$PhMe_2Si$	70	35:65
6	$THPO(CH_2)_2$	(Me_3Sn)	54	0:100
7	$THPO(CH_2)_2$	(Bu_3Sn)	48	10:90

TABLE 12. Disilylation of trimethylsilyl-substituted internal alkynes with silylmanganates

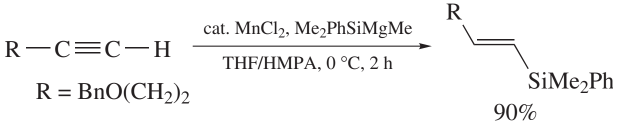


R	Yield (%)
Bu	80
$BnO(CH_2)_2$	59
$THPO(CH_2)_2$	83
Me_3Si	76



65% combined yield (1:1:1)

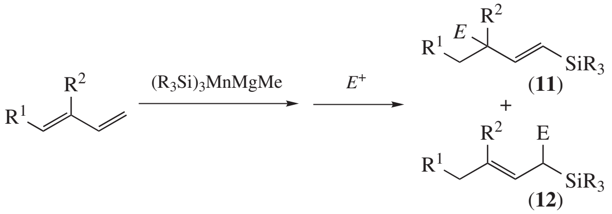
(34)



90%

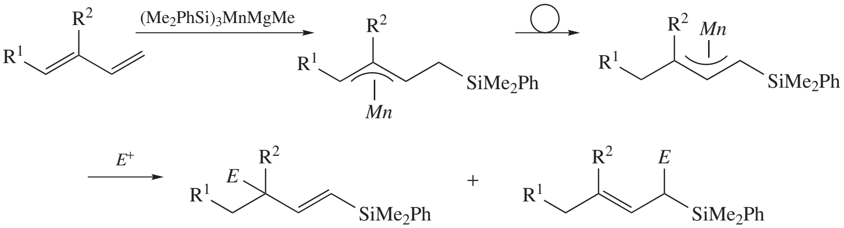
(35)

TABLE 13. Silylmanganation of conjugated dienes



R^1	R^2	R^3Si	Electrophile	*E*	**11** (%)	**12** (%)
H	H	Me_2PhSi	MeI	Me	11	69
H	H	Me_2PhSi	CH_3COCH_3	$C(CH_3)_2OH$	95	0
H	Me	Me_2PhSi	PhCHO	CH(Ph)OH	78	0
H	Me	Me_3Si	MeCH=CHCHO	CH(CH=CHMe)OH	75[a]	0
Me	H	Me_2PhSi	PhCHO	CH(Ph)OH	68[b]	0

[a] 1,2-Adduct.
[b] 1:1 Diastereomeric mixture.

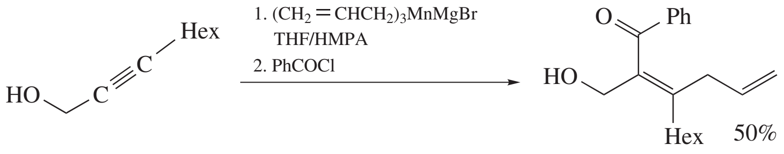


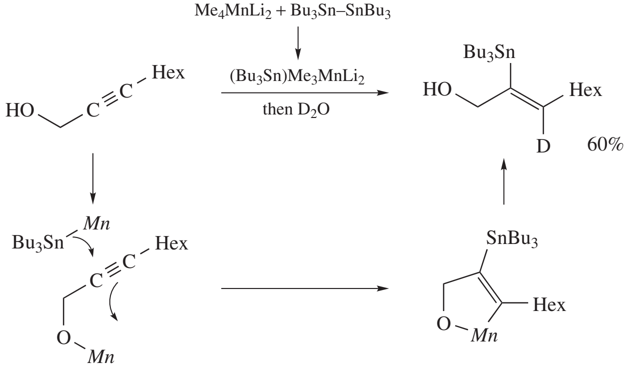
SCHEME 10

Dilithium trimethyl(tributylstannyl)manganate, prepared from dilithium tetramethylmanganate and hexabutylditin, reacts with propargylic alcohols to yield 2-tributylstannyl-2-alken-1-ol[64] (Scheme 11). Notably, the addition takes place in an *anti* fashion due to the directing effect of the hydroxy group.

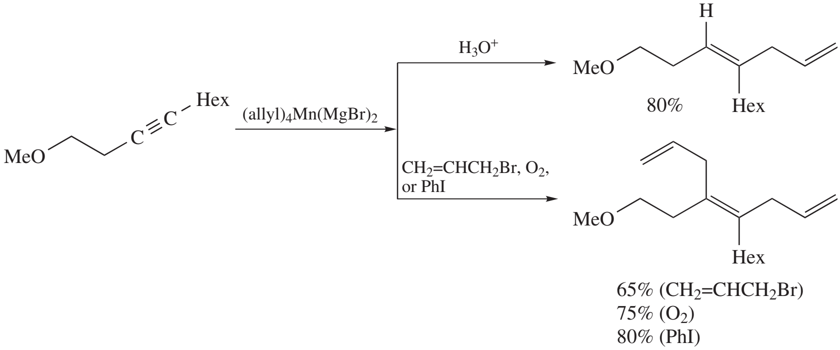
The first example of carbomanganation across apolar carbon–carbon multiple bonds is the allylmanganation of homopropargyl ethers[65] (Scheme 12). Several allylic manganese reagents were examined, and tetraallylmanganate of type $(allyl)_4Mn(MgBr)_2$ proved to be the best species. The resulting alkenylmanganese intermediate is readily trapped not only with water but also with allyl bromide to yield the diallylated product. Intriguingly, the diallylated product is also obtained when the alkenylmanganese intermediate is oxidized by air or iodobenzene. Probably, reductive elimination from allyl(alkenyl)manganese would occur upon the oxidative treatment.

A combination of triallylmanganate and HMPA is suitable for allylmanganation of propargylic alcohols (equations 36).

 (36)

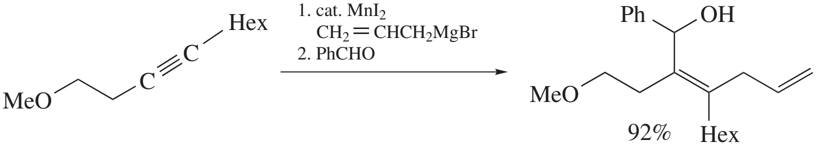


SCHEME 11

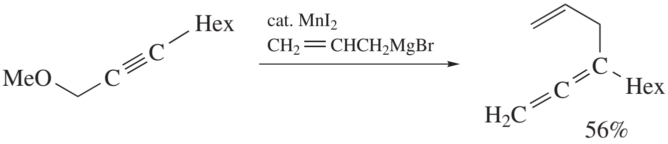


SCHEME 12

The allylmagnesiation is catalyzed by manganese salts, probably proceeding via tetraallylmanganate species (equation 37). The catalytic version generally affords higher yields of the products. The reactions of propargyl ethers afford allylallenes via β-alkoxy elimination from the vinylmanganese intermediate (equation 38). The vinyl ether of homopropargyl alcohol is converted to trienyl alcohol when being subjected to the manganese-catalyzed allylmetalation (Scheme 13). The reaction involves allylmanganation, intramolecular carbomanganation and ring-opening through a β-alkoxy elimination.



(37)



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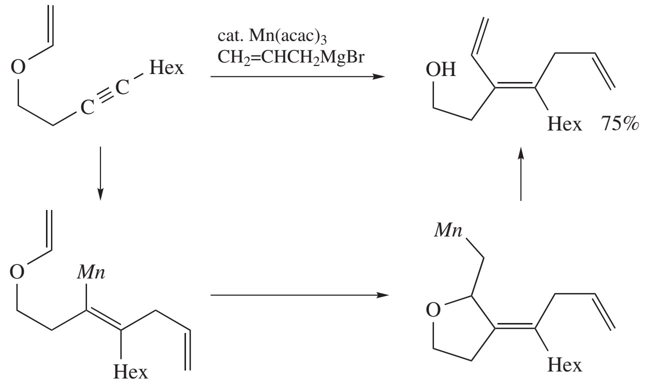
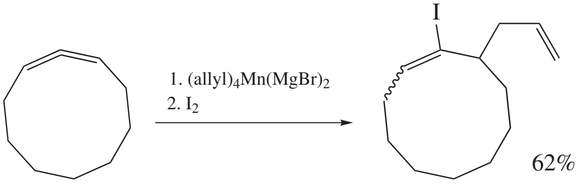


SCHEME 13

Tetraallylmanganate promotes regioselective allylmanganation of allenes, where a manganese–carbon bond formation takes place at the central carbon[66] (equation 39). A catalytic amount of $MnCl_2$ also promotes the allylmagnesiation of allene. When enallene **9** is subjected to the allylmanganation with tetraallylmanganate, regioselective allylation followed by cyclization yields cyclopentane derivative **10** in 46% yield (Scheme 14).



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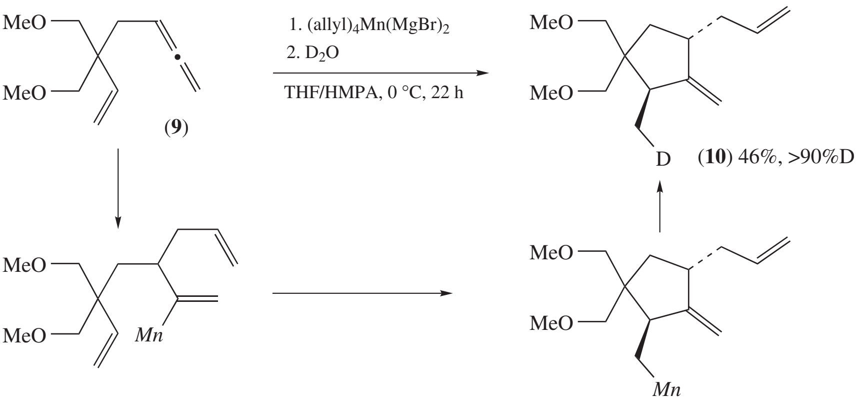
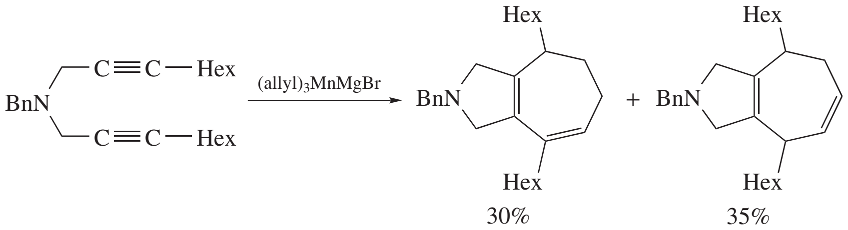


(**9**)

(**10**) 46%, >90%D

SCHEME 14

Treatment of benzyldi(2-nonynyl)amine with triallylmanganate affords unexpected azabicyclo[5.3.0]decadienes[67] (equation 40). Although the exact reaction mechanism is not clear, it is likely that the formation of azamanganacyclopentane occurs initially. In contrast, treatment of tris(3-phenyl-2-propynyl)amine or diallylbenzylamine leads to monocyclic product (equations 41 and 42). The reactions of oxygen-tethered or all-carbon enynes also proceed similarly[68].



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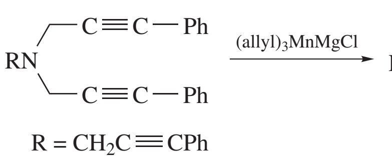

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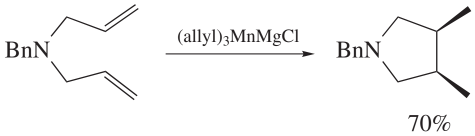
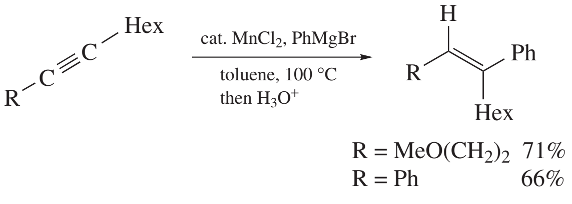


(42)

Not only allylic manganates but also other organomanganates participate in carbometalation reactions. Arylmagnesiation of homopropargyl ethers or 1-phenyl-1-alkynes proceeds with arylmagnesium bromides in the presence of $MnCl_2$, tri- or tetraphenylmanganate being involved[69] (equation 43). The reaction requires higher temperature such as 100 °C, compared to the allylmanganation at 25 °C. When the resulting alkenylmetal is trapped with electrophiles, tetrasubstituted alkenes are formed selectively (equation 44).



(43)

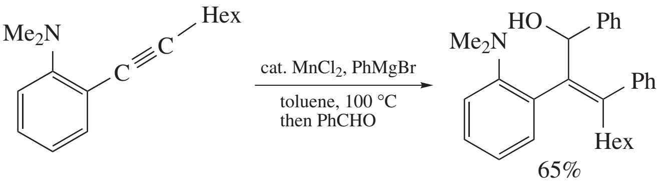


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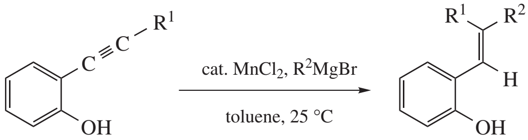
TABLE 14. Manganese-catalyzed alkylmagnesiation of 2-(alkynyl)phenols



R^1	R^2	Yield (%)	E/Z
Me	Bu	84	94:6
Me	$CH_2{=}CHCH_2$	52	90:10
Me	Ph	55[a]	95:5
Me	*i*-Pr	24[b]	79:21
Ph	Et	96	18:82

[a] At reflux.

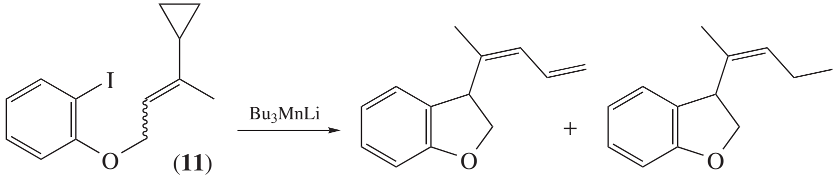
[b] (*Z*)-2-(1-Propenyl)phenol is obtained in 37% yield.

Alkylmetalation proceeds although substrates are limited to 2-(alkynyl)phenols and related alkynols[70] (Table 14). The reaction proceeds predominantly in a *syn* fashion. While butylation and ethylation proceed smoothly, the reaction with isopropylmagnesium bromide affords the reduced product mainly, along with the desired isopropylated product. The hydroxy group plays a critical role, and the methyl ether of 2-(1-propynyl)phenol affords the corresponding butylated product in only 19% yield.

F. Radical Reactions Promoted by Single Electron Transfer

In general, electron-rich organometallic reagents effect single electron transfer to organic halides. This is also the case for manganates[71]. The allylic ethers of 2-iodophenol react with lithium tributylmanganate to afford dihydrobenzofurans (Table 15, entries 1–3). Interestingly, a *trans* isomer is formed selectively when the allylic position has a substituent (entry 2). The cyclization is applicable to the synthesis of dihydroindoles (entries 4–6). Similar transformations occur upon treatment of 1-iodo-3-oxa-5-hexene derivatives with manganates (entries 7 and 8).

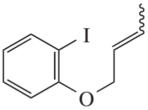
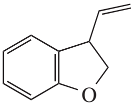
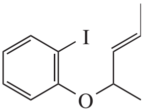
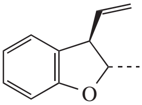
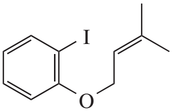
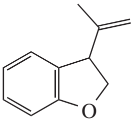
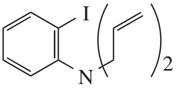
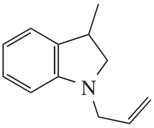
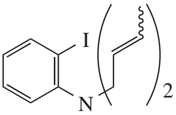
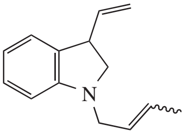
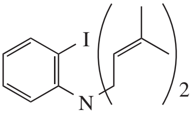
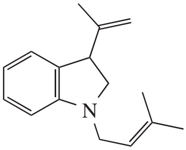
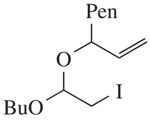
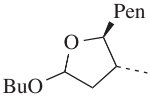
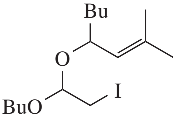
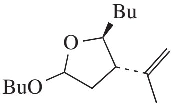
Treatment of allylic ether **11** having a cyclopropyl group with tributylmanganate provides a mixture of ring-opening products (equation 45). The ring-opening transformation suggests the intermediacy of radical species, and a plausible mechanism is proposed as shown in Scheme 15. Single electron transfer from the manganate affords firstly the radical anion and then the *5-exo-trig* radical cyclization proceeds to yield the corresponding tertiary radical, which should be trapped with BuMn. The following β-hydride elimination provides the product.

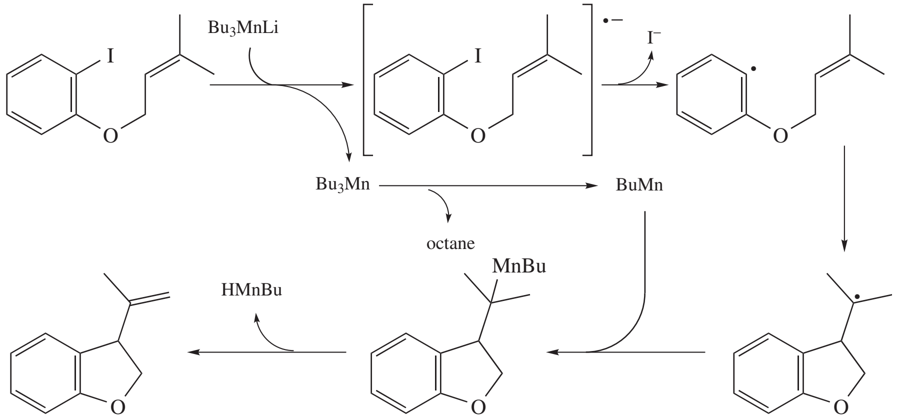


52%, 2:1

(45)

TABLE 15. Radical cyclization with lithium tributylmanganate

Entry	Substrate	Product	Yield (%)
1			63
2			70
3			88
4			72
5			74
6			92
7			68
8			70



SCHEME 15

G. Polymerization

There are several reports wherein manganates are used as initiators of polymerization of reactive olefins.

Ihara and coworkers reported the polymerization of methyl methacrylate initiated by lithium tributyl-, triphenyl- or trimethylmanganate[72]. In the presence of triisobutylaluminum and TMEDA, poly(methyl methacrylate)s of high molecular weights are prepared. The choice of alkyl groups of manganates can control the tacticity of the resulting poly(methyl methacrylate)s.

Forniés and coworkers reported that $[Mg(thf)_6][Mn(C_6F_5)_4]_2$ serves as an initiator by itself and as a weakly coordinating anion in palladium-catalyzed polymerization of norbornene-type olefins[19].

IV. SUMMARY

Even after 35 years since their appearance in the literature, the chemistry of organomanganates is still in its infancy. Because manganese can adopt a wide range of oxidation states, the future of the organometallic chemistry of manganates is expected to continue to expand and to be more fascinating than ever before. Although manganate reagents have exhibited a wide range of reactivity, including unique single electron transfer, in synthetic organic chemistry, they are still unexplored as compared to cuprates. Metallic manganese and manganese salts are inexpensive and ubiquitous. With more investigation, one will be able to find new and/or improved reactivities that will surely contribute to the development of organic synthesis.

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Structure and bonding of simple manganese-containing compounds

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I. INTRODUCTION AND HISTORICAL BACKGROUND

In the pure form, *elemental manganese* (Mn) is a silvery or gray white, very brittle and dense metal. Although Mn constitutes, by its abundance, the twelfth element in the Earth's crust, it does not occur as a free metal in nature, due to the fact that its concentrations are rarely high enough to form a pure ore deposit. Manganese mainly exists in different minerals. Among some 300 Mn-containing minerals available, only a dozen are however of mining significance. These include the oxides (pyrolusite, psimelane etc.), carbonates (rhodochrosite etc.) and silicates (thphroite etc.).

The Mn ores are found in locations all over the planet, and the actual reserves, that include rather low grade ores, reach several billion tons. Reserves of higher grade ores, having >40 % of Mn content, are currently estimated to be exploitable in the range of *ca* 700 million tons of ore, essentially located in China, Australia, Brazil, Gabon and South Africa. These countries are producing *ca* 80 % of the current international demand. In 2005, the global high grade manganese ore production attained an amount of *ca* 35 million tons. The world reserves are thus sufficient for just a few more decades to come. Large lumps of metallic ores are also known to lie in the form of polymetallic nodules, in thin layers, on the deep ocean floors (*ca* 5 km depth). These nodules contain, among other metals, a large amount of Mn as their main constituent, but the Mn quantities could not be accurately estimated. Although these nodules are regarded as potentially valuable resources for metals in future developments, their recovery and exploitation under ocean conditions are expected to be a challenging task[1].

Manganese does not have many common utilities, but where it can be used, it is important. Like other metals, the history of Mn usage dates back to ancient times, long before human civilization began. Thanks to the (green) color of manganese dioxide, it was presumably used by the nomads as a pigment for their decorations and cave paintings. It has also long been associated with glass-making. The Romans and Egyptians took manganese to color glass, yielding it a shade of purple. In modern times, it was used to decolorize glass in industries where glass impurities evolve due to iron, since Mn can return the glass back to its normal color. This type of applications was also used for text printing, ceramics, paints[2] etc.

In Ancient Greece, manganese was found in the iron ore used by Spartans. This probably gave them stronger swords and other weapons. As a matter of fact, we now know that the major use of Mn is as an alloy with other metals such as iron, aluminum and copper, and other elements such as silicon, titanium and zinc. At the beginning of the 19th century, both British and French industries started to use manganese in steelmaking (with British patents submitted in 1799 and 1808). When alloyed with Mn, the resulting steel becomes stronger, stiffer, tougher, harder and long-wearing. Mn is partly lost during the steelmaking processes simply by oxidation.

During the first half of the 19th century, different procedures were applied in Germany (1826) and England (1840) to produce ferromanganese containing a high Mn content (up to 80 % Mn). The major breakthrough in the use of manganese occurred in 1860, when Bessemer[3] developed a steelmaking process subsequently improved by Mushet[4]. Six years later, in 1866, Siemens[5] patented the use of ferromanganese in steelmaking to control the level of phosphorus and sulfur. In 1882, Hadfield[6] discovered the high-manganese steels which were named after him. Currently, the average unit consumption is *ca* 7.5 kg of Mn per ton of steel[1]. Changes in steel grade induce a significant effect on Mn demand, which thus follows the growth in steel production. In particular, its hardness makes it a strategic material in the production of equipment for war.

Apart from steel making and fabrication, Mn has been proved to be a critical metal in some civil and defense-related applications including improved fuel efficiency, welding, a vital and large component in batteries and other portable power sources. In 1868, Leclanché[7] developed the dry cell battery which uses manganese dioxide as a depolarizer in a simple but effective dry cell. The battery market today is the second largest Mn consumer.

Regarding the manganese-containing chemical compounds, potassium permanganate is perhaps one of the best known products used by consumers, for a long time. It is a powerful oxidizing agent with bactericidal and algicidal properties, which have been used in purifying drinking water and treating waste water. It is also used as deodorant, purifying odor from discharges in paint factories, fish-processing plants etc. In 1659, Glauber[8] fused a mixture of the mineral pyrolusite (MnO_2) and potassium carbonate (K_2CO_3) obtaining a material that, when dissolved in water, gave a green solution which slowly shifted to violet and then finally red. This report represented the first description of the preparation of potassium permanganate as antioxidant. Two centuries later, Condy[9] patented and marketed potassium permanganate named as Condy's Fluid or Condy's Crystals to be used as disinfectants. Let us note that aqueous solutions of $KMnO_4$ have more recently been used together with T-Stoff (i.e. *ca* 80 % hydrogen peroxide) as propellant for the rocket plane Messerschmitt (Me 163), known as Z-Stoff.

In 1774, Scheele[10] was the first to separate manganese by treating manganese dioxide with hot concentrated hydrochloric acid. Unfortunately, he thought that the produced metal was an oxygen-containing compound and did not recognize it as a pure element. He also did not recognize the produced reaction gas which for a long time was believed to be a complex moiety, until it was identified and named chlorine by Davy[11, 12]. Scheele's work however led to the discovery of the manganese element, later in 1774, by his friend

Gahn.[13] In fact, Gahn heated the same pyrolusite mineral (MnO_2) as Scheele used, but in a charcoal fire, and the resulting reaction was a reduction of manganese oxide by carbon. He obtained a small amount of grayish metal, thus becoming the first to identify Mn in its elemental metallic form. In this context, Gahn was considered as the discoverer of the elemental manganese. Note that from the middle of the 19th century, manganese oxide became the basis for the industrial manufacture of chlorine with metallic Mn as a byproduct. In 1937, Gilman and Bailie[14] reported the preparation of PhMnI and $MnPh_2$ that are the first known examples of organomanganese(II) compounds. Nevertheless, the chemistry of organomanganese reagents has rapidly developed only in the last 30 years[15]. In the 20th century, novel metallurgical and chemical applications were developed as diverse as beverage cans, agricultural pesticides and fungicides, and different electronic products. Manganese complexes are ubiquitous in the synthesis of molecular magnetic compounds and constitute the reaction centers of metalloenzymes. It is an important trace element for utilization of vitamin B. Overall, manganese remains an essential element contributing to the improvement of our daily fife.

II. THE ELEMENT

The name manganese came from the latin word '*magnes*' which means magnet, referring to the magnetic properties of pyrolusite (or probably due to a certain confusion with magnetic iron ores). Another interpretation which was put forward is that it came from the term '*magnesia nigri*' which means 'black magnesia', MnO_2 from Magnesia in ancient Greece. It is called manganèse in French, Mangan in German, mangaan in Dutch, manganeso in Spanish and manganese in Italian. The free element is a member of the transition metal series, located at group 7, period 4 of the Periodic Table. Table 1 lists the main basic properties of the elemental Mn.

The electronic structure of Mn is described by the orbital configuration [Ar] $4s^2 3d^5$. Its outer $4s$ shell is thus a closed shell, similar to alkaline earth atoms, and the $3d$ shell is only half filled with electrons. The five unpaired $3d$ electrons thus lead to its high spin $^6S_{5/2}$ ground state. Variable occupancies and removal of both $4s$ and $3d$ electrons play an important role for the electronic properties, and are sources for high spin and oxidation states in Mn compounds. This also determines the nature of Mn chemical bonding, and gives rise to various types of magnetism and open-shell electron reactivities. Such electronic properties usually lead to inherent difficulties for their treatments by traditional quantum chemical methods[16, 17].

Gas-phase atomic manganese has several lower-lying energy levels. The first excited state ^6D, which arises from an s–d orbital transition ($3d^6 4s^1$), is located at 2.114 eV (586.43 nm) above the ground state. Although this state has a relatively long lifetime ($\tau = 3.4$ s)[18], the $^6D \leftarrow {}^6S$ transition is formally forbidden in absorption spectra. Laser-induced excitation spectra for the electric-quadrupole $^6D \leftarrow {}^6S$ transition of Mn were however recorded[19], and allowed assignment of the red emission features observed in Mn/Ar,Kr,Xe matrices[20]. Within the $3d^6 4s^1$ configuration, a lower-spin state ^4D also exists.

Different excited states can be generated from s–p orbital transitions. Within the $3d^5 4s^1 4p^1$ configuration, the higher-spin state $z\ ^8P$ is located at 2.282 eV (543.4 nm, $\tau = 149\,\mu s$), but the $z\ ^8P \leftarrow {}^6S$ transition is also forbidden. The lower-spin state $z\ ^6P$ is higher in energy, being at 3.073 eV (403.42 nm, $\tau = 52$ ns), and the electric dipole transition $z\ ^6P \leftarrow {}^6S$ is allowed[19]. The luminescence spectra produced with excitations at lower energy than that of the latter were also observed and assigned. Details of the low energy

TABLE 1. Some basic properties of the manganese element

Property	Value
Symbol	Mn
Group/Period	Group 7, Period 4
Atomic number	25
Mass number	54.93805 amu
Isotope (stable)	55
Electron (orbital) configuration	$[Ar]3d^5 4s^2$
Magnetic moment (atomic)	$5\,\mu_B$
Local magnetic moment (solid, α-phase)	$2\,\mu_B$/atom
Heat of formation (gas, standard)	283.26 kJ mol^{-1}
Heat of formation (liquid, standard)	16.29 kJ mol^{-1}
Entropy (gas, 1 bar)	173.72 J mol^{-1} K^{-1}
Entropy (liquid, 1 bar)	43.49 J mol^{-1} K^{-1}
Entropy (solid)	32.01 J mol^{-1} K^{-1}
Excitation energy $3d^5 4s^2 \rightarrow 3d^6 4s^1$	2.114 eV
Ionization energy Mn $3d^5 4s^2 \rightarrow$ Mn$^+$ $3d^5 4s^1$	7.434 eV
Proton affinity (gas)	797.3 kJ mol^{-1}
Gas basicity (gas)	774.4 kJ mol^{-1}
Common oxidation states	+2, +3, +4, +7
Magic clusters (Site-selected $(\mathrm{Mn})_N$	$N = 13, 19, 57, \ldots$
Standard state	Solid at 298 K
Crystal structure	Complex lattice structure, 54 atoms per unit cell
Melting point	*ca* 1 245 °C
Boiling point	*ca* 1962 °C
Density	7.43 g cm^{-3} at 293 K
Color	Gray-white or silvery
CAS Registry ID	7 439-96-5

emission bands can be found in References 18 and 20. Thus, Mn exhibits exceptionally high s–d promotion energies, the largest within the series of first-row transition metals (Sc–Cu), and that makes its spin-polarized ground state ^{6}D stable, but also gives it a weak propensity to form covalent bonding.

The first ionization processes of the atomic Mn occur mainly upon removal of electrons from its 4s orbital. The ground state of the Mn$^+$ cation (or Mn(I)) is thus the septet state ^{7}S ($3d^5 4s^1$), and the corresponding ionization energy amounts to IE(Mn) = 7.43 eV[21]. It is known that this IE is higher than those of the Sc–Cr atoms, whereas it is smaller than those of Fe–Zn atoms. In the dication Mn^{2+} (or Mn(II)), the 4s orbital becomes vacant in its ground state ^{6}S ($3d^5 4s^0$). The charge state of a transition metal ion is often related to the oxidation state of its complexes[22]. In fact, the oxidation state of a central atom in a transition metal complex is defined as the charge remaining on it, when all the ligands are removed in their most stable form, along with the bonding electron pairs[23]. Due to the presence of seven removable electrons in the s–d shells, the highest achievable oxidation state of Mn is VII. The high oxidation state of Mn can be found in the various salts of the permanganate ion (MnO_4^-, VII), oxides (e.g. Mn_2O_7, VII) and oxyfluorides (e.g. MnO_3F, VII). The highest known manganese fluoride is MnF_4 (IV) and in some fluoromanganate salts of MnF_6^{2-} (IV).

III. THE DIMER AND CLUSTERS

The atomic Mn has a rather high magnetic moment of $5\,\mu_B$, whereas the local magnetic moments in the solid α-phase do not excess $2\,\mu_B$ per atom[24]. Mn displays an antiferromagnetic character in bulk states, and between these two limits the values vary in the nanoscale range $(Mn)_N$ clusters, with the pronounced minima at the magic clusters ($N = 13$, 19, 57, ...)[25]. The largest differences in the magnetic moment per atom of the Mn_N clusters, with respect to Mn_{N-1} and Mn_{N+1}, were observed at $N = 13$ and 19. While the dimer is a starting point for the study of fundamental properties of clusters, as in the case of Cr_2, Mn_2 was and remains a challenging molecular system for quantum chemical methods, in particular for density functional theory (DFT).

A. The Dimer

Experiments[26] suggested that Mn_2 is antiferromagnetic ($S = 0$) whereas Mn_4 and Mn_5 are ferromagnetic. Combined experimental results for Mn_2 determined in gas-phase and rare-gas matrices are as follows: (i) a ground ${}^1\Sigma_g{}^+$ state by ESR spectroscopy[26], (ii) an equilibrium distance r_e of *ca* 3.4 Å by resonance Raman spectrometry[27], (iii) a stretching frequency of $66.8\,\text{cm}^{-1}$ and (iv) a dissociation energy of *ca* 0.1 eV by high-temperature mass spectrometry[28]. Since 1964, extensive theoretical studies have been carried out on Mn_2[29–46]. Recent molecular orbital calculations at various levels[43–46] showed that the molecular states of Mn_2 are ${}^1\Sigma_g{}^+$, ${}^3\Sigma_u{}^+$, ${}^5\Sigma_g{}^+$, ${}^7\Sigma_u{}^+$, ${}^9\Sigma_g{}^+$ and ${}^{11}\Sigma_u{}^+(1)$ that correlate to $Mn({}^6S) + Mn({}^6S)$, and the undecet states include ${}^{11}\Pi_u$, ${}^{11}\Sigma_g{}^+$, ${}^{11}\Delta_g$, ${}^{11}\Delta_u$, ${}^{11}\Sigma_u{}^+(2)$ and ${}^{11}\Pi_g$, that connect an excited state asymptote $Mn({}^6S) + Mn({}^6D)$. The undecets correspond to the states of decaradicals each having ten unpaired electrons. Calculations pointed out that the interaction between both atomic ground states is not influenced by the total spin, and the six resulting dimeric states differ from each other by *ca* $70\,\text{cm}^{-1}$[43]. Due to the large s–d promotion energy of Mn as mentioned above, the hybridization, or spin exchange interactions, between the $4s$ and $3d$ AOs is not possible in Mn_2. The four outer $4s$ electrons thus occupy both σ-bonding and σ^*-antibonding MOs arising from interaction of two $4s$ AOs. The $3d$ electrons are not mixed in this bond formation, and as a consequence a covalent bond is not formed. This is similar to the situation of Be_2. The closed-shell singlet ${}^1\Sigma_g{}^+$ state was confirmed by high level MO calculations to be the electronic ground state of Mn_2[43–46]. The lowest state of the undecet manifold is the ${}^{11}\Pi_u$ state located at *ca* 1.3 eV above the $X\ {}^1\Sigma_g{}^+$ state, with a shorter bond distance of *ca* 2.5 Å and a stronger stretching frequency of *ca* $246\,\text{cm}^{-1}$[44]. In the latter manifold, the binding energies are consistently larger, ranging from 0.2 (${}^{11}\Pi_g$) to 1.1 (${}^{11}\Pi_u$) eV. This lies within the trend of transition metals in which the combination between ($4s^2\ 3d^{n-2}$) and ($4s^1\ 3d^{n-1}$) usually yields stronger bonds[47].

The long bond, low vibrational frequency and small bond energy confer on the bonding in Mn_2 a van der Waals character[48]. Note that most DFT methods predict a ${}^{11}\Pi_u$ ground state for Mn_2[42] due to their difficulties in treating very weak bonds. The high spin state is favored because of an s–d promotion occurred as the result of an artifact of DFT for Mn. Most DFT methods severely underestimate the $4s$–$3d$ promotion energy of atomic Mn. Only the popular hybrid B3LYP functional, which represents an exception, predicts a singlet ground state[42]. This suggests that a mixing of the exact (Hartree–Fock) exchange functional with pure exchange-correlation functionals leads to drastic improvement of the DFT results.

ESR study[26] suggested that Mn_2 represents a typical case of ‘exchange restriction’, in which the equilibrium distance is strongly dependent on the total spin S. Calculations tend to give support to a fact that r_e varies from 3.2 to 3. 6 Å, with S going from 0 to 5. Mn_2

thus differs much from Cr_2 which has 12 valence electrons and also a closed-shell singlet state, but exhibits a short distance of *ca* 1.7 Å and a dissociation energy of 1.47 eV[49].

As stated above, the Mn^+ cation is formed upon removal of one 4*s* electron of Mn. Thus the $Mn_2{}^+$ cation has three 4*s* valence electrons, of which two are distributed in one σ-bonding, and one electron in the σ^*-antibonding. The latter is delocalized on both atoms and the destabilization is reduced. Ar-matrice ESR[26] and photodissociation[50] experiments indicated a ferromagnetic $Mn_2{}^+$ ion with a total spin $S = 11/2$. Theoretical studies[38, 51] concurred with a high-spin $^{12}\Sigma_g{}^+$ ground state of $Mn_2{}^+$, which is consistent with its unusual magnetic properties. There has been a large discrepancy among the experimental dissociation energies of $Mn_2{}^+$, that range from 0.85 ± 0.3[52], >1.39[53] and 2.1 ± 0.3[54] eV. The value of *ca* 1.4 eV obtained form CASPT2 calculations[38] seems to support the medium experimental D_e result. The dimer cation has a bond distance of *ca* 2.94 Å and a stretching frequency of *ca* 214 cm^{-1}. The higher stability of the high spin state of $Mn_2{}^+$ arises from the fact that the intra-atomic 4*s*–3*d* ferromagnetic spin coupling (double exchange interaction) is much stronger than the interatomic 3*d*–3*d* antiferromagnetic coupling (Heisenberg exchange interaction)[38, 51]. The intra-atomic exchange energy was estimated to be *ca* 0.5 eV. The competition between both types of magnetic interactions can be classified as a case of ‘spin frustration’[55]. The double-exchange interaction, which is the result of the delocalization of the unpaired *s* electron, induces a large ferromagnetic effect and makes the energy level with the maximum spin to be the ground state[38]. The adiabatic ionization energy is estimated to be $IE(Mn_2) = 6.1 \pm 0.2$ eV.

B. Small Mn Clusters

For the Mn trimer, a 1988 Raman spectrometric study[27a] concluded that Mn_3 is a weakly Jahn–Teller-distorted equilateral triangle of possibly $^2E'$ or $^2E''$ electronic state. Matrix isolation studies[26] suggested a high-spin state ($S = 15/2$). Earlier DFT calculations suggested a sextet state[56]. More recent calculations[32, 33, 40, 57, 58] pointed out that Mn_3 possesses in fact a high symmetry (D_{3h}) and high-spin multiplicity. The orbital configuration of the ground state is as follows:

$$^{16}\boldsymbol{A}_2' : [\mathrm{core}](6\mathrm{a}_1')^2(8\mathrm{e}')^4(1\mathrm{a}_2'')^1(7\mathrm{a}'_1)^1(3\mathrm{e}_2'')^2(8\mathrm{a}'_1)^1(9\mathrm{e}')^2(10\mathrm{e}')^2(4\mathrm{e}_2'')^2(3\mathrm{a}_1'')^1(3\mathrm{a}'_2)^1(11\mathrm{e}')^2.$$

The distance in the neutral equilateral triangle is $r(\mathrm{Mn{-}Mn}) = 2.73$ Å. The vibrational frequencies of Mn_3 are located in the far IR region (130 and 197 cm^{-1}). Although the high-spin multiplicity of the ground state suggests that Mn_3 is basically a complex of three Mn (^6S) atoms, it has an atomization energy of $D_e = ca$ 2.3 eV, and a dissociation energy of *ca* 0.5 eV giving $Mn_2 + Mn$. The trimer is just thermodynamically more stable than the dimer. The identity of the excited state of Mn_3 is not well established yet. While the high-spin state $^{16}E''$ with a bond length of 2.76 Å and lying 0.24 eV above the ground state was derived[58], a sextet state (with unspecified spatial symmetry) was found to be nearly energetically degenerate with the higher-spin state[40].

The tetramer Mn_4 can exist in a tetrahedral shape with different total spins ($S = 0$, 10 and 20). The state having a spin multiplicity of 21 was found to be the ground state of Mn_4. On the contrary, a near-degeneracy occurs in the pentamer Mn_5, where the triangular bipyramid structures bearing the total spin of $S = 3/2$, 13/2 and 23/2 have a similar energy content. Mn_4 and Mn_5 were shown to be ferromagnetic by experiments[26]. A similar situation was found for the hexamer in which low- and high-spin states were found very close in energy[40]. Figure 1 displays the shape of the lowest-lying neutral Mn clusters together with their multiplicity. However, their electronic structure warrants further investigation.

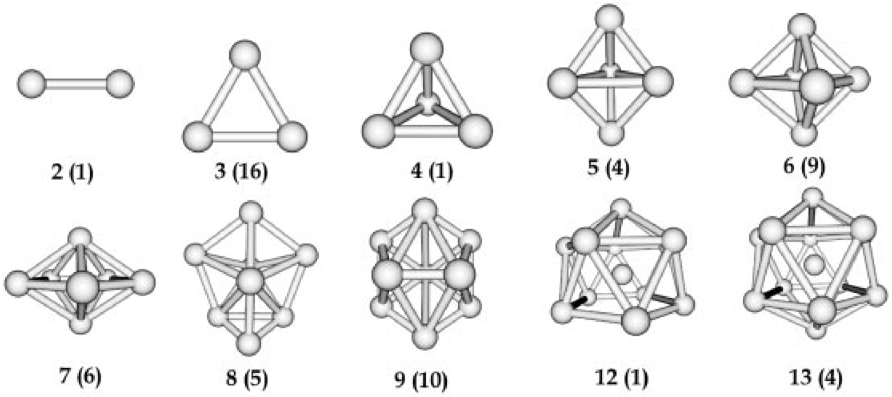


FIGURE 1. Shape and spin multiplicity of the lowest-lying isomers of small neutral Mn clusters. The numbers **n(M)** stand for: **n** = cluster size and **M** = multiplicity

The ionization energies of the clusters were also determined[25]. This energetic parameter tends to decrease as the cluster size increases. The value of Mn_{13} thus amounts to $IE(Mn_{13}) = 4.82\,eV$[25, 59, 60], as compared to that of *ca* 7.4 and *ca* 6.1 eV in the atom and dimer, respectively (see above). The binding energies of $Mn_N{}^+(N = 2–7)$ were also determined by the photodissociation experiments[50]. There is a gradual increase in the Mn-binding energy with the cluster size, due to an increasing contribution of nonbonding 3*d* orbitals to the bonding through a weak hybridization with the 4*s* orbitals. However, the binding energies per atom in the series of small cluster cations are nearly constant, being in the range of 1 eV per atom, which are much smaller than the cohesive energy of the Mn bulk (2.92 eV per atom). These results indicate the exceptionally weak metal–metal bonds in the small Mn clusters that are formed by 4*s*–4*s* covalent bonding with a minor participation of 3*d* electrons. Small-size Mn clusters exhibit peculiar magnetic properties due to the fact that each Mn atom retains a local spin almost as large as an atomic spin. While the lowest-energy states were found to have the atomic spin magnetic moments pointing in the same direction for Mn_2 and Mn_3, the noncollinear magnetism was found for Mn_N, $N = 4–6$[61]. The growth pattern of the Mn clusters can be summarized as follows: (i) small Mn_N clusters ($N = 2–4$) are ferromagnetic with the local magnetic moments as large as $5\,\mu_B$, (ii) binding energies increase with the size due to the increasing 4*s*–3*d* mixing and (iii) isomers having low-spin electronic state gain stability at larger size (Mn_{13} having a quartet ground state).

Let us mention that the anion photoelectron spectra were successfully recorded for the cluster anions $Mn_N{}^-$ [59, 62]. Again, the electron detachment energies of the anions increase with increasing size (N). As for a typical example, the adiabatic electron affinity was estimated to be $EA(Mn_{13}) = 1.9\,eV$[62–64].

C. Mn as a Dopant

It is well established that the physical and chemical properties of an atomic cluster are fundamentally modified following a doping by an impurity. The presence of a dopant tends to change not only the geometric structure of the host, but also its electronic distribution, and thereby its properties. Mn plays the role of a dopant in numerous clusters[65]. We now consider the behavior of the dopant Mn in the Si, Ge and Sn clusters. Similar to carbon whose clusters such as the class of fullerenes are well known, the higher congeners Si, Ge, Sn, ... also form stable clusters.

1. Si_7Mn^+

The silicon clusters Si_n can be doped by transition metal atoms[66], but the effects of dopants differ substantially from each other. Both the neutral Mn atom and Mn^+ ion can be doped into Si clusters. The cation Si_7Mn^+ presents a typical case. Using the DFT calculations at the B3LYP/6-311+G(d) level, a high-spin $^7A_1$ state of the capped pentagonal bipyramid (C_{2v}) turns out to be the ground state of Si_7Mn^+. Figure 2 gives a plot of the total and partial densities of states of its alpha orbital, and also the geometric shape of the cation. The (pink) dash line shows the contribution of $3d$(Mn) AOs to the MOs. They are localized in a narrow energy range and lie at the very low energy region as compared to the HOMO, which is mainly composed of the s(Mn)-orbital. Therefore, the six unpaired electrons of this state are mainly localized on the Mn center. The net charge on Mn is about +0.8 electron. Accordingly, this cluster cation can be regarded as a combination of the neutral Si_7 and the ion Mn^+, in which the metal holds its high-spin characteristic (see above). Thus the behavior of Mn^+ is similar to that of the Cu^+ ion, but differs significantly from that of the V^+ cation when they are doped into a Si host[66].

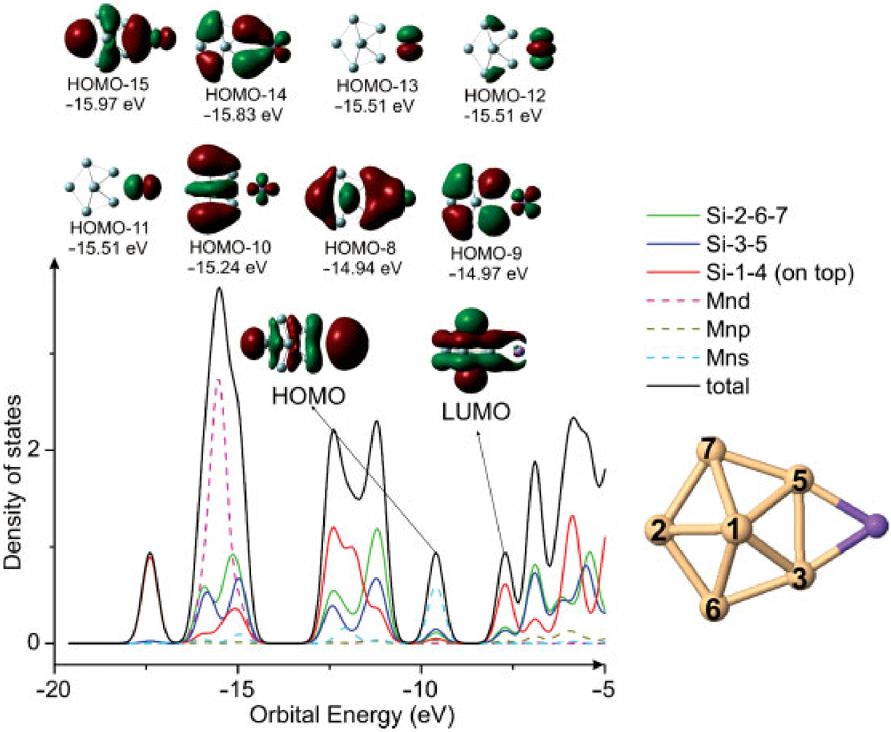
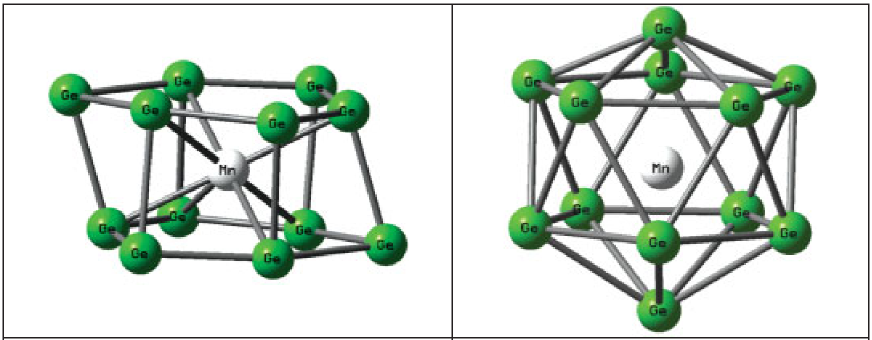


FIGURE 2. Total and partial densities of states (alpha orbitals) of the ground state of Si_7Mn^+. Shapes and energy levels of some valence orbitals are also given

2. $Ge_{12}Mn^+$ and $Sn_{12}Mn^+$

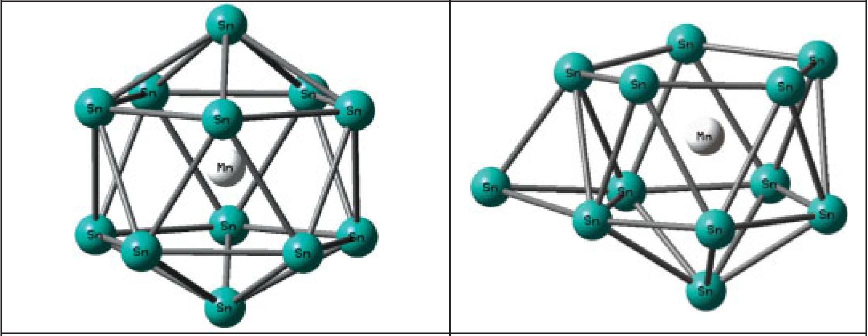
The Ge_{12} and Sn_{12} are interesting species as each features an icosahedral cage which can capture inside it other impurities[67]. Figure 3 displays for each system the geometrical shape and relative energies of the two lowest-lying isomers. According to DFT calculations, a Mn-doping modifies the shape of the host from the high icosahedral symmetry (I_h). The C_i **1.1** in which Mn is located at the center of a distorted hexagonal structure, is the most stable $Ge_{12}Mn^+$ isomer, and it is followed by the higher symmetry C_{5v} structure **1.2**.

The neutral $Sn_{12}Mn$ cluster is found to have a pseudo-icosahedron with an enhanced stability (high binding energy and large HOMO–LUMO gap) as compared to other derivatives ($M@Sn_{12}$, M = Ti, V, Cr, Fe, Co, Ni). For the cation $Sn_{12}Mn^+$, its global minimum is now the C_{5v} structure **2.1** that is slightly distorted from the ideal icosahedral form (I_h). A C_1 structure **2.2** that is formed from a prism pentagonal form with one Sn-atom capped at the top and one Sn-atom capped beside is the next isomer with a relative energy



1.1
C_i, ^5A_g
ΔE = 0

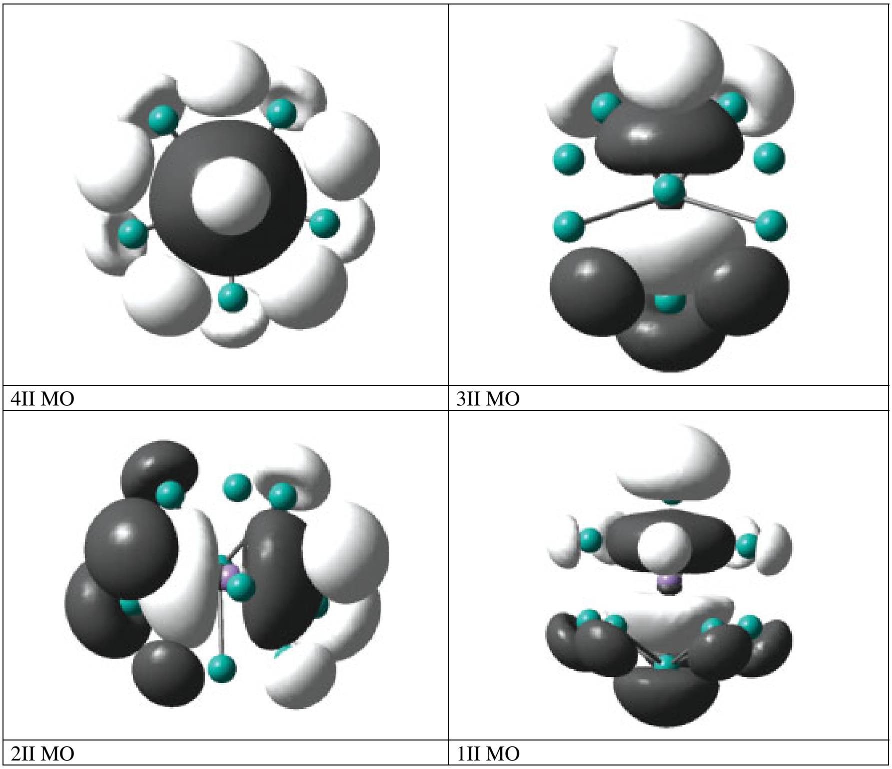
1.2
C_{5v}, $^5A_1$
ΔE = 35



2.1
C_{5v}, $^5A_1$
ΔE = 0

2.2
C_1, ^5A
ΔE = 25

FIGURE 3. Shape, symmetry and relative energies (ΔE in kJ mol^{-1}) of the two lowest-lying isomers of the cluster cations $X_{12}Mn^+$ (X = Ge and Sn) obtained using density functional theory computations at the B3LYP/LanL2DZ level


4II MO

3II MO

2II MO

1II MO

FIGURE 4. Shapes of the four π-MOs of the $Sn_{12}Mn^+$ cluster cation **2.1** (C_{5v})

of *ca* 25 kJ mol^{-1}. The HOMO–LUMO gap of 1.2 eV for the cation $Sn_{12}Mn^+$ (C_{5v}) is larger than the value of 1.0 eV of the neutral Mn@Sn_{12}. The high stability of the global minimum **2.1** (C_{5v}) can be rationalized on the basis of a spherical aromaticity[68]. It is assumed that the π-electron system of these species can approximately be considered as a spherical electron gas, which surrounds the surface of a sphere. The wavefunctions of this electron gas can be characterized by the angular momentum quantum numbers ($l = 0$, 1, 2, 3, ...) that are comparable to atomic s, p, d, f etc. orbitals. If a system having $2(N+1)^2\pi$-electrons fully fills all the π-shells, it then exhibits a spherical aromaticity. The MOs of **2.1** displayed in Figure 4 contains in fact eight valence π-electrons that satisfy the $2(N+1)^2$ electron counting rule.

IV. THE HYDRIDES AND METHYL DERIVATIVES

A key feature of transition metal coordination chemistry is the existence of homoleptic complexes (ML_n) in which all ligands L are the same. Beside carbonyl, fluoride, cyanide, nitrosyl etc., hydride represents another strong field ligand. Unlike the other ligands, the hydride (H^-) has only a single 1s orbital available for making a bond, and thus can take part in metal–ligand σ-bonding with no possibilities for π-bonding, either forward or backward[69]. It is known that the role of π-bonding is to destabilize some specific metal oxidation states. Due to the absence of π-orbitals, hydride anion can form complexes with the central atom M in a wide range of oxidation states. In this context, the bonding formation process in transition metal hydrides has been conceived as follows: (i) only s and d orbitals are used to form hybrid bond orbitals, (ii) the hybrid orbitals have maximal s character, (iii) lone pairs are placed in pure d-orbitals and (iv) three-center four-electron (3c–4e) bonds are used when the central metal atom has more than 12 valence electrons[69, 70].

A. MnH

The diatomic manganese hydride has been studied since the 1940s through a variety of spectrometric methods[71, 72]. Table 2 lists the main molecular constants of MnH obtained from various experiments[73, 74, 75]. A unanimous conclusion was long reached that $^7\Sigma^+$ is the ground state. It exhibits the orbital configuration $X\ ^7\Sigma^+$: core$[(6\sigma)^1(7\sigma)^2(8\sigma)^1(2\pi)^4(3\pi)^2(1\delta)^2]$. The ground $X\ ^7\Sigma^+$ state is dominated by a single configuration. The electronic process leading to formation of this state is as follows:

(i) the 4s orbital of the atomic ground state ^{6}S(Mn) needs first to hybridize with a $4p3d$ configuration prior to σ-bond formation,

(ii) when forming the MOs, the singly occupied 6σ MO is mainly of Mn(3d-4s, 3d main) in phase hybrid orbital with antibonding contribution of H(1s),

(iii) the doubly occupied 7σ MO is a bonding orbital between H(1s, main) and Mn(4s),

(iv) the singly occupied 8σ MO (a counterpart of 6σ) is an antibonding orbital between H(1s, minor) and Mn(3d-4s, 4s main), which is out-of-phase hybrid and largely polarized against H by Mn(4p), and

(v) promotion of the single electron in the 6σ MO to the empty 4π MO generates the excited state $A\ ^7\Pi \ldots [(7\sigma)^2(8\sigma)^1(2\pi)^4(3\pi)^2(4\pi)^1(1\delta)^2]$ with a transition energy of $T_e = 2.29$ eV. However, the lower spin $^5\Sigma^+$ state, which is formed by a spin flip, $a\ ^5\Sigma^+ : \ldots [(7\sigma)^2(8\sigma)^2(2\pi)^4(3\pi)^2(1\delta)^2]$ (main configuration of a multiconfigurational wavefunction), represents the lowest-lying excited state of MnH, being only 0.2 eV above the $X\ ^7\Sigma^+$ state.

The difference in the electron distribution in the low- and high-spin states arises from the fact that the relevant two electrons occupy the same orbital (low spin) or are distributed over two associated orbitals (high spin). This involves the occupancy of both 6σ and 8σ orbitals. The dipole moment of the $^7\Sigma^+$, $^7\Pi$ and $^5\Sigma^+$ amount to 1.1, 2.6 and 0.7 Debyes[76]. The lack of a large polarization of the 4s(Mn) by the 4p(Mn) in forming the 8σ orbital (which is fully occupied) does not induce a large dipole moment for the quintet state, as compared with the septet counterpart. The MnH molecule in the lower-spin state is bound through a single covalent bond, whereas it is partially ionic in the $^7\Pi$ state.

TABLE 2. Selected molecular constants of MnH species[a]

Species: State	r_0 (Å)	B_0 (cm^{-1})	ω (cm^{-1})	D_e (eV)	T_e (cm^{-1}) [eV]
MnH: X $^7\Sigma^+$	1.743	5.605608	1547	1.36	0
A $^7\Pi$	1.638	6.347840	(1653)		17 667 [2.19]
a $^5\Sigma^+$	1.625	-	1550		1725 ± 50 [0.214]
MnH$^-$: X $^6\Sigma^+$	1.722		(1 334)		−9 269[−1.15]

[a] Taken from References 73–75.

The Mn–H stretching frequency is affected by the presence of gas matrix, being observed at 1493, 1486 and 1478 $\mathrm{cm^{-1}}$ in Ne, H_2 and Ar, respectively. Let us note that the bond energy and electron affinity amount to $D_e(\mathrm{MnH}) = 132 \pm 18\,\mathrm{kJ\,mol^{-1}}$ (by mass spectrometry)[75], and $\mathrm{EA(MnH)} = 0.7–1.0\,\mathrm{eV}$ (by DFT calculations)[77].

B. MnH_2

The triatomic molecule was produced by co-condensing Mn and H atoms in solid Ar[78, 79], or Mn and H_2 followed by photolysis in rare gas solid matrices[77]. Irradiation at 285 nm, which is in the $^6\mathrm{P} \leftarrow {}^6\mathrm{S}$ resonance transition of Mn, formed MnH_2. The growth of MnH_2 was observed on annealing in solid Ar, and it was likely due to the successive combination reactions $\mathrm{Mn} + \mathrm{H} \rightarrow \mathrm{MnH}$ and $\mathrm{MnH} + \mathrm{H} \rightarrow \mathrm{MnH_2}$[77]. MnH_2 was identified by its asymmetric stretching mode centered at 1601 (Ne), 1598 (H_2) and 1592 (Ar) $\mathrm{cm^{-1}}$[77]. The bending mode frequency of 375 $\mathrm{cm^{-1}}$ was observed in Xe matrix[78]. The symmetric stretching frequency was not observed but predicted at *ca* 1647 $\mathrm{cm^{-1}}$. Figure 5 gives a summary of the shape, electronic states and energetic of MnH_2 in different charge states, including the IE and EA of the neutral.

High level CCSD(T) computations predicted that MnH_2 is linear in its sextet ground state. The orbital configuration with the unpaired electrons is $X\ {}^6\Sigma_g{}^+ : \ldots (1\pi_g)^2(1\delta_g)^2(5\sigma_g)^1$. The high-spin linear excited state is $A\ {}^6\Sigma_u{}^+ : \ldots (3\sigma_u)^1(1\pi_g)^2(1\delta_g)^2(5\sigma_g)^2$ and located at *ca* 3.6 eV above the ground state. The lower-spin and bent (C_{2v}) structure, $a\ {}^4B_2 : \ldots (b_2)^1(a_1)^1(a_1)^1$, turns out to be the first excited state, being at *ca* 2.6 eV (values from CCSD(T) computations) below the ground state (Figure 5). The H–Mn–H bond angle in the quartet state amounts to *ca* 106°. The singly occupied b_2 orbital results from a strong mixture of the $3d_{zx}$(Mn) with the $1s$(H).

Another property of MnH_2 obtained experimentally is the electron affinity determined from the laser photoelectron spectrum of the MnH_2 negative ion[80]. The anion is characterized by a stretching frequency centered at 1466 $\mathrm{cm^{-1}}$. The excess electron is added to the $5\sigma_g$ orbital of MnH_2 thus leading to the linear ground state of the $MnH_2{}^-$ anion:

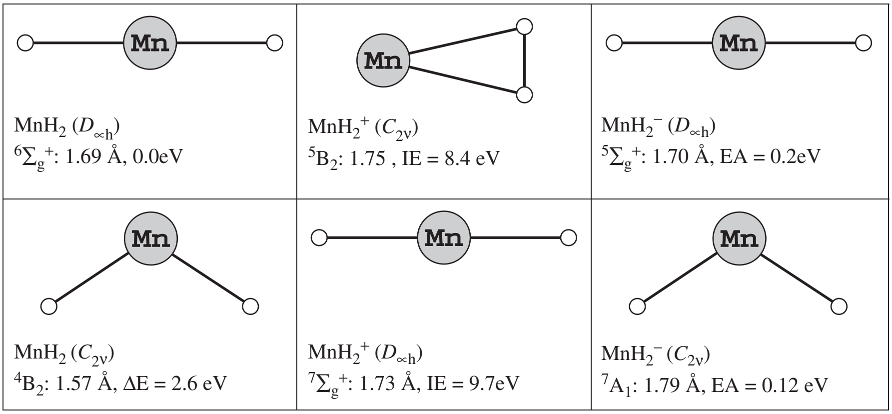


FIGURE 5. Calculated results obtained for MnH_2 species are at CCSD(T)/6-311++G(3df,2p) level. The entries are: (point group), electronic state, MnH bond distance in Å, relative energy in eV, IE (adiabatic ionization energy) and EA (electron affinity) of the neutral MnH_2

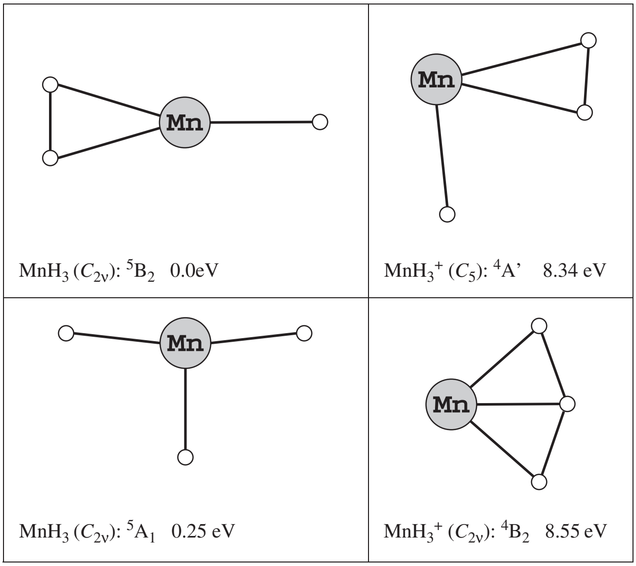


FIGURE 6. Calculated results obtained for MnH_3 and MnH_3^+ species are at B3LYP/6-311++G(3df,2p) level. The entries are: (point group), electronic state and relative energy with respect to the lowest-lying neutral (eV). The relative energy of the cation corresponds to IE(MnH_3)

$^5\Sigma^+{}_g \ldots (1\pi_g)^2(1\delta_g)^2(5\sigma_g)^2$. Most theoretical methods underestimated the EA(MnH_2) whose experimental value is $0.444 \pm 0.016\,eV$[80].

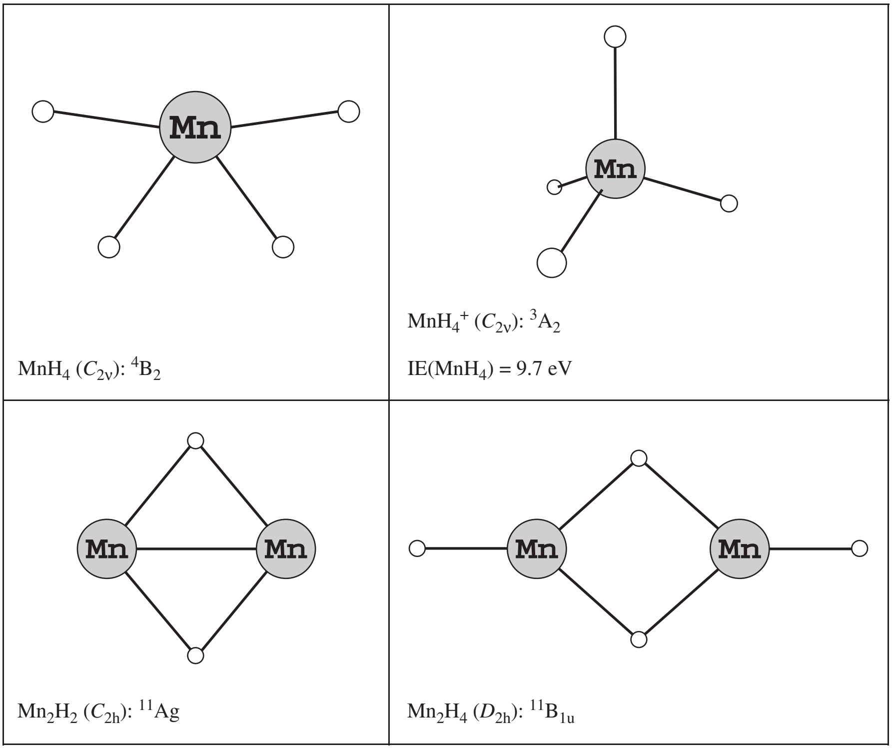
C. MnH_3

The existence of the manganese trihydride was proposed from a tentative assignment of the ESR spectra recorded for the $Mn + H_2$ reaction system[78]. Figure 6 gives a summary of the shape, electronic states and energetics of MnH_3 in different charge states. Starting from the high symmetry D_{3h} structure, the quintet $^5E'$, with the orbital configuration $(e'')^2(a_1')^1(e')^1$, turns out to be the lowest state, lying well below the corresponding triplets and singlets. However, the degenerate $^5E'$ state, which is the result of a conical intersection of two electronic states, is not stable upon Jahn–Teller distortions. Following geometry relaxation to lower symmetry, within a planar deformation, a T-shaped and a Y-shaped form can be obtained. Of the two forms, only the Y-shaped structure (C_{2v}, $^5B_2$) is characterized as a genuine energy minimum. The T-shaped (C_{2v}, $^5A_1$) is a first-order saddle point. The existence of a sharp Y-shaped equilibrium structure for MnH_3 represents a special case for a Jahn–Teller effect.

D. Other Hydrides

1. MnH_4 and MnH_4^{2-}

Optimized geometries for MnH_4 structure in both neutral and ionized states are displayed in Figure 7. They have distinct geometric shapes. MnH_4 is *ca* $40\,kJ\,mol^{-1}$ less



MnH_4 (C_{2v}): $^4B_2$

MnH_4^+ (C_{2v}): $^3A_2$

IE(MnH_4) = 9.7 eV

Mn_2H_2 (C_{2h}): ^{11}Ag

Mn_2H_4 (D_{2h}): $^{11}B_{1u}$

FIGURE 7. Geometrical shape of MnH_4, MnH_4^+, Mn_2H_2 and Mn_2H_4 species. The energy of the cation corresponds to IE(MnH_4)

stable than the limit $MnH_2 + H_2$, and has a relatively large ionization energy (Figure 7). Some other equilibrium structures also exist but lie much higher in energy. A dianion was found in the compounds $(M^+)_3(MnH_4{}^{2-})(H^-)$, where M = K, Rb, Cs[81]. The magnetic moment of K_3MnH_5 is found to be $6\,\mu_B$, in accord with the existence of five unpaired electrons of a Mn(II) cation in this species. The ion with five half-filled $3d^5$ electrons is thus particularly stable in a high-spin tetrahedral environment.

2. $MnH_6{}^{5-}$

The species Mg_3MnH_7 obtained by reaction of MgH_2 with Mn powder and H_2 was shown by neutron diffraction to have the form $(Mg^{2+})_3(MnH_6{}^{5-})(H^-)$[82]. The polyanion hydride $MnH_6{}^{5-}$ has an octahedral shape of a Mn(I) cation, similar to $Mn(CN)_6{}^{5-}$ or $Mn(CO)_6{}^+$.

3. Mn_2H_2 and Mn_2H_4

Some higher Mn hydrides have also been detected, but only the dimers $(MnH)_2$ and $(MnH_2)_2$ have been characterized by IR spectrometry. Figure 7 also shows their optimized shape. The dimer $(MnH)_2$ exhibits a C_{2h} head-to-tail structure with a high-spin $X\ ^{11}A_g$ ground state. The dimer is quite stable, with a dimerization energy of $-190\,\text{kJ mol}^{-1}$.

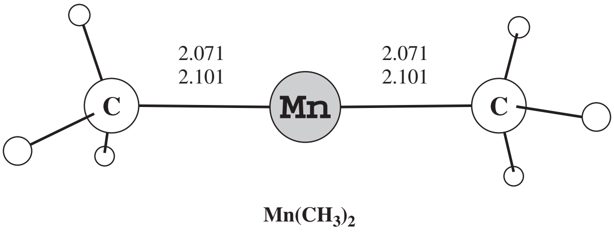
A dimer of MnH_2 is calculated to have a stable D_{2h} structure with a $^{11}B_{1u}$ ground state, in which both Mn atoms make a relatively short bond (*ca* 2.2 Å) and the two MnH_2 moieties are also bridged (Figure 7). The dimerization energy amounts to *ca* $-50\,\text{kJ mol}^{-1}$.

E. Methyl Derivatives

In many aspects, the structures of the methylated manganese are similar to those of the hydrides. Figure 8 displays the selected geometrical parameters of $Mn(CH_3)_2$ and $Mn(CH_3)_3$ in both neutral and cationic states. The neutral monomethyl species $Mn(CH_3)$ exhibits a septet ground state with a Mn−C bond distance of 2.10 Å. This distance is shortened to 1.99 Å in the sextet ground state of the cation $Mn(CH_3)^+$.

The dimethyl $Mn(CH_3)_2$ derivative is linear and characterized by a high-spin ground state in both neutral and cation forms. The neutral has a sextet state and the cation a septet ground state with comparable Mn−C distances (Figure 8).

The trimethyl $Mn(CH_3)_3$ derivative exhibits a T-shaped geometry and also a high-spin ground state, namely a quintet state for the neutral and a sextet state for the cation.



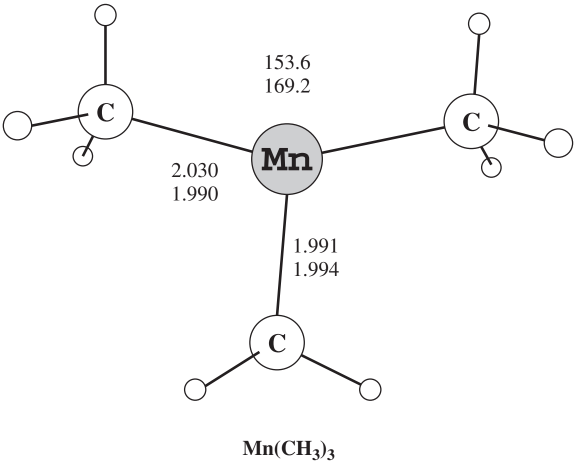


FIGURE 8. Geometrical shape of $Mn(CH_3)_2$ and $Mn(CH_3)_3$ in both neutral and cationic states. Bond distances are given in Å and bond angle in degrees: upper values for neutrals and lower values for cations

Following ionization, the T-shape is reinforced in which the C−Mn−C bond angle reaches near-linearity, in going from 154° in the neutral to 169° in the cation. The Mn−C bond distances are also compressed upon ionization (Figure 8).

The ionization energy of $Mn(CH_3)_n$ tends to be increased following poly-methylation, namely 7.1 eV in $Mn(CH_3)$, 8.5 eV in $Mn(CH_3)_2$ and 8.6 eV in $Mn(CH_3)_3$ (calculated values at the B3P86/6-311++G(3df,2p) level).

V. THE HALOGENIDES

A. MnX

Fluoride and other halogenide ligands (X) exhibit electron pairs and available *p*-orbitals for forward electron transfer to empty *d*-orbitals of the central metal atom $2p\pi(\mathrm{X}) \rightarrow 3d\pi^*(\mathrm{M})$, thereby stabilizing metal oxidation states, in particular the high oxidation states. The consequence of a π-donation of X ligands is a destabilization of low formal oxidation states. Table 3 lists the main parameters of the diatomic species MnF and its ions and MnCl selected from available experimental and theoretical studies[83–88].

All diatomic species possess high-spin states, either for the neutral or for the ions. As an example, let us consider MnF, which with six unpaired electrons has the following orbital configuration: MnF $X\ {}^7\Sigma^+$: $(\mathrm{core})(8\sigma)^2(1\delta)^2(9\sigma)^1(4\pi)^2(10\sigma)^1$. The 8σ MO corresponds to the bond between Mn and F. This orbital is likely polarized toward F giving rise to a Mn^+F^- bond. The 1δ, 4π and 9σ MOs are nonbonding as they come from 3d(Mn) AOs, and the 10σ MO is antibonding. Addition of an excess electron to the 9σ MO, or removal of an electron from the 10σ MO, both lead to the $X\ {}^6\Sigma^+$ of MnF^- or MnF^+, respectively. In MnF^+, the Mn^{2+} cation is characterized by its ${}^6S(3d^5)$ ground state. In the field of the F^- anion, formation of a sextet state can be expected giving rise to a highly ionic bond.

Experimental measurements of thermochemical parameters of Mn compounds are quite rare and, when available, they are not quite reliable. The experimental heats of formation of MnF thus range from −20 to −81 kJ mol^{-1} [89]. The ionization energy of MnF was re-evaluated to be IE(MnF) = 8.0 ± 0.1 eV by high level calculations[83], which differs substantially from the previous experimental result of 8.7 eV[87]. In this context, thermochemical parameters obtained from appropriate theoretical methods are expected to be more consistent and more reliable (Table 3).

An interesting property of high-spin species concerns their hyperfine parameters. The presence of multiple unpaired electrons results also in complicated hyperfine structures. In MnH, the hyperfine coupling is sufficiently strong that it competes with the spin interactions, inducing rotationally forbidden transitions[85]. Table 4 lists the isotropic hyperfine splitting constants (Fermi contact terms) and the anisotropic (dipolar) constants of a few diatomic Mn species. The values are taken from experimental studies[84–87]. The Fermi

TABLE 3. Selected molecular constants of MnX species[a]

Species:	State	r_0 (Å)	ω (cm^{-1})	D_e (eV)	T_e (cm^{-1})	μ (D)	ΔH_f (298 K) (kJ mol^{-1})
MnF:	$X\ {}^7\Sigma^+$	1.839	624	4.61		2.90	−76
MnF^+:	$X\ {}^6\Sigma^+$	1.750	730	3.99	0		
	$a\ {}^4\Delta$	1.683	800	3.06	21 755		
MnF^-:	$X\ {}^6\Sigma^+$	1.908	494	2.52			
MnCl:	$X\ {}^7\Sigma^+$	2.235	386	4.61			69

[a] Selected values taken from References 83–88.

TABLE 4. Hyperfine splitting constants of diatomic MnX species[a]

Diatomic	Ground state	A_{iso}(Fermi) (MHz)	$A_{dipolar}$ (MHz)
MnH	X $^7\Sigma^+$	279	36.0
MnF	X $^7\Sigma^+$	414	35.6
MnCl	X $^7\Sigma^+$	398	32.4
MnO	X $^6\Sigma^+$	480	−48.2
MnS	X $^6\Sigma^+$	206	−27.8

[a] Values taken from Reference 84.

contact interaction is the magnetic interaction between an electron around an atomic nucleus and that nucleus. It is established that the energy of the isotropic interaction is proportional to the nuclear magnetic moment (μ_N), the electron magnetic dipole moment (μ_e) and the value of the wavefunction at the nucleus. The Fermi contact terms of MnF, MnCl and MnO are relatively large, as compared to the corresponding value of 698 MHz in $Mn^+(^6S)$[90]. This suggests that Mn retains a large part of its original ionic character in the formation of diatomics. Within an atom, only *s* orbitals have nonzero electron density at the nucleus, so only *s*-electrons contribute to the Fermi contact interaction, which is responsible for the appearance of isotropic hyperfine coupling. Of the MOs having a 4*s* contribution, the antibonding lone pair $(\sigma)^1$ orbital in each diatomic species is expected to be the main source for Fermi contacts. The difference in the dipolar interactions between MnH, MnF and MnCl with MnO and MnS is due to the fact that there is no 4*s*3*d* mixture in the 9σ MO (in MnF, for example). This orbital remain a 3*d* orbital and does not contribute to the interactions. On the contrary, there is a certain 4*s*3*d* mixing in MnO and MnS, and this makes a significant contribution to their dipolar interactions[84].

B. MnX_2

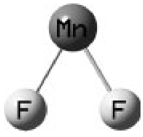
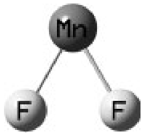
The transition metal dihalides are obtained experimentally as hot molecules (above 1000 K). Under these conditions, many vibrational and rotational levels are populated resulting in complex electronic spectra. Reliable results on MnX_2 are not available yet. Theoretical studies[89, 91] pointed out that MnX_2 possesses a high-spin linear $^6\Sigma_g{}^+$ ground state, for X = F, Cl and Br. Calculated results summarized in Tables 5 and 6 show that

TABLE 5. Vertical transition energies (eV) of some electronic states of MnX_2 species[a]

	Electronic state	Main orbital configuration	MnF_2	$MnCl_2$	$MnBr_2$
Neutral	$^6\Sigma_g{}^+$	$\delta^1\delta^1\pi^1\pi^1\sigma^1$	0.00	0.00	0.00
	$^4\Sigma_g{}^+$	$\pi^1\pi^1\sigma^1$	2.8	3.3	3.4
Cation	$^5\Sigma_g{}^+$	$\delta^1\delta^1\pi^1\pi^1$	12.6	12.3	12.8
	$^5\Pi$	$\delta^1\delta^1\pi^1\sigma^1$	12.2	—	—
Anion	$^5\Sigma_g{}^+$	$\delta^1\delta^1\pi^1\pi^1$	−0.9	−1.0	−1.8

[a] Values obtained using CASPT2/ANO-RCC calculations. The RAS2 active spaces include 20e for cation, 21e for neutral and 22e for anion within 14 valence orbitals. Vertical energies obtained at the geometries of the neutral linear MnX_2 ($^6\Sigma_g{}^+$).

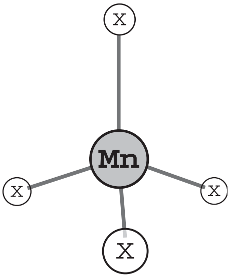
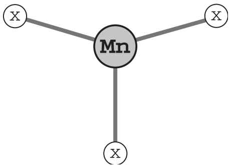
TABLE 6. Adiabatic transition energies (eV) of MnX_2 species[a]

	Electronic state	Geometric shape (F–Mn–F)	Main orbital configuration	Relative energy (eV)		
				MnF_2	$MnCl_2$	$MnBr_2$
Neutral	$^6\Sigma_g{}^+$		$\delta^1\delta^1\pi^1\pi^1\sigma^1$	0.00	0.00	0.00
	$^4\Sigma_g{}^+$		$\pi^1\pi^1\sigma^1$	2.7	—	—
	$^4B_2$		$(b_1)^1(a_1)^1(a_2)^1$	—	3.2	3.2
Cation	$^5B_2$		$\ldots(a_1)^1(a_1)^1(b_1)^1(a_2)^1$	11.5	11.7	14.5
	$^5A_2$		$\ldots(a_1)^1(a_1)^1(b_1)^1(b_2)^1$	12.5	11.9	14.5
	$^5A_1$		$\ldots(a_1)^1(b_1)^1(b_2)^1(a_2)^1$	15.0	14.2	11.8
	$^5B_1$		$\ldots(a_1)^1(a_1)^1(b_2)^1(a_2)^1$	15.3	13.8	14.3
Anion	$^5\Sigma_g{}^+$		$\delta^1\delta^1\pi^1\pi^1$	−1.0	−1.1	−1.9

[a] Values obtained using CASPT2/ANO-RCC calculations. The active spaces include 20e for cation, 21e for neutral and 22e for anion within 14 valence orbitals. Geometries are optimized.

the corresponding anions $MnX_2{}^-$ have also linear ground state $^5\Sigma_g{}^+$. The electron affinity of MnX_2 amounts to *ca* 1.0 eV. The excited states vary with respect to the nature of X. In MnF_2, the lowest-lying excited state is linear, whereas it is bent in $MnCl_2$ and $MnBr_2$. In the ionized states, all lower-lying states of the cations become bent (Table 7), even though the bending is a rather facile process, as the energy difference between vertical and adiabatic values are relatively small. The most remarkable result is that the XMnX bond angles vary strongly with X. It is wide open in F and Cl, but becomes closed in Br where a three-membered ring appears to be formed (Table 7). The first ionization energies are also large, in the range of 11.5 − 11.8 eV. The standard heats of formation of MnX_2 were tabulated at −534 and −253 kJ mol^{-1} for X = F and X = Cl, respectively[89].

TABLE 7. Electronic states and transition energies of MnX_3 and MnX_4 species

Geometrical shape	Species	State/Symmetry/Transition energy[a]								
		X = F			X = Cl			X = Br		
	**MnX_4**	$^4B_2$	C_{2v}	0.0	$^4A_2$	D_{2d}	0.0	$^4A_2$	D_{2d}	0.0
		$^2A_2$	D_{2d}	0.8	$^2B_1$	D_{2d}	0.9	$^2B_1$	D_{2d}	0.9
	MnX_4^+	$^3A_1$	T_d	12.1	$^3B_1$	T_d	10.1	$^3B_1$	T_d	9.4
		$^1A_1$	C_{2v}	13.7	$^1A_1$	D_{2d}	11.5	$^1A_1$	D_{2d}	10.9
	**MnX_3**	$^5A_1$	C_{2v}	0.0	$^5A_1$	C_{2v}	0.0	$^5A_1$	C_{2v}	0.0
		$^3B_2$	C_{2v}	1.6	$^7B_2$	C_{2v}	0.9	$^7B_2$	C_{2v}	0.5
	MnX_3^+	$^4A_1$	C_{2v}	11.8	$^4A_1$	C_{2v}	10.4	$^4A_1$	C_{2v}	9.9

[a] Transition energies given in eV are obtained from B3LYP/6-311++G(3df,2p) calculations. Energies of the cations are relative to the neutral ground state (0.0) that correspond to the adiabatic ionization energies (IE_a) of the neutrals.

C. MnX_3 and MnX_4

High valency metal fluorides are widely used as fluorinating agents in the synthesis of fluorinated organic compounds. Their thermal decomposition usually leads to the formation of the corresponding lower valency fluorides and a release of fluorine. Stable MnF_3 exists in a crystal form[92, 93], whereas MnF_4 could be generated in the gas phase by the reaction: $MnF_3(s) + TbF_4(s) \rightarrow MnF_4(gas) + TbF_3(s)$[94]. The IR spectrum of MnF_3 was recorded[95], and the spectroscopic pattern suggested a planar C_{2v} symmetry structure for MnF_3, with two longer and one shorter Mn−F bonds. A subsequent electron diffraction analysis provided support for this structure[96]. Calculated results recorded in Table 7 concur with this, and point out in addition that MnF_3, as well as $MnCl_3$ and $MnBr_3$, have a high-spin $^5A_1$ ground state. On the contrary, the lowest-lying excited state of MnF_3 is a triplet, whereas it is a septet for $MnCl_3$ and $MnBr_3$. In all cases, the transition energies are small. The cation MnX_3^+ is also characterized by a T-shaped form with a quartet $^4A_1$ ground state. The IE tends to decrease in going from F to Br (see Table 8 below).

The MnF_4 molecule was detected by matrix isolation IR spectroscopy[94]. The IR pattern suggested a T_d symmetry. Table 8 suggests the MnF_4 has a distorted tetrahedral C_{2v} form and a quartet $^4B_2$ ground state. $MnCl_4$ and $MnBr_4$ have a $^4A_2$ ground state. The lowest-lying excited state in all cases is a low-spin state, but with different spatial component. The corresponding cations MnX_3^+ exhibit a T_d point group, and a triplet ground state, but again with different spatial component. The closed-shell singlet state is an excited state having a distorted symmetry from T_d. The ionization energy is calculated to be

TABLE 8. Experimental and calculated transition energies (eV) of $MnO_4^{-\bullet}$

Electronic transition	Exptl.[111]	TD-DFT[110]	SAC-CI[108]	EOM-CCSD[109]
$1\ ^1T_2 \leftarrow {}^1A_1$	2.27	2.6 – 2.8	2.6	2.2
$2\ ^1T_2 \leftarrow {}^1A_1$	3.47	3.6 – 3.9	3.6	3.7
$3\ ^1T_2 \leftarrow {}^1A_1$	3.99	4.4 – 4.7	3.7	3.6
$4\ ^1T_2 \leftarrow {}^1A_1$	5.45	5.4 – 5.8	5.8	5.8

$IE_a(MnF_4) = 12.1$ eV (Table 8), which differs from the experimental result of 13.0 ± 0.7 eV determined from mass spectrometric measurements[94, 97]. No results are available for the higher congeners $MnCl_n$ and $MnBr_n$. Overall, further reliable theoretical studies are needed to address many spectroscopic and thermochemical issues of the MnX_n species.

VI. THE OXIDES

Structures and spectroscopic properties of small oxides have recently been reviewed[98].

A. MnO

The simplest oxide MnO has a high-spin ground state $^6\Sigma^+$: $(\text{core})(9\sigma)^2(4\pi)^2(1\delta)^2$ with the largest magnetic moment among the transition metal oxides. The bond energy and stretching frequency of MnO are consistently smaller than those of CrO[99].

Several experiments showed a ferromagnetic behavior of nanosized $(MnO)_N$ clusters, contrary to the antiferromagnetic phase of the bulk MnO[100]. The net magnetization of the latter was attributed to the spins at the surface of the particles. DFT calculations on $(MnO)_N$ pointed out that the small stoichiometric clusters may be ferromagnetic with a sizable magnetic moment per MnO[101]. The Mn_4O_4 cluster was shown to have a T_d structure rather than a cube[102].

B. MnO_2

In the gas phase, the symmetric OMnO form is by far the most stable dioxide, which is characterized by a bent configuration associated with a $^4B_1$ ground state[103]. The symmetric stretching frequency amounts to 816 cm^{-1}. The Mn atomic ground state is unreactive toward O_2[104].

C. MnO_3

Matrix isolation ESR experiments indicated that MnO_3 has a large Mn hyperfine coupling constant. This is due to the occupation of the unpaired electron in the $4s3d_{z^2}$ hybrid orbital, giving rise to a planar D_{3h} geometry ($^2A_1$ state)[105]. Subsequent calculations showed rather a pyramidal C_{3v} equilibrium structure ($^2A_1$) with a moderate inversion barrier[103]. The photoelectron spectrum of the anion MnO_3^- at 266 nm was recorded, and the electron affinity derived as $EA(MnO_3) = 3.335$ eV[103]. A vibrational frequency of 840 cm^{-1} was attributed to the symmetric Mn=O stretching mode.

D. MnO_4

As mentioned above, the potassium permanganate $KMnO_4$ has long been known and used in many concrete applications. Although the MnO_4^- anion is a prototype of transition metal compounds, a proper theoretical treatment of its electronic structure and its absorption spectrum has been a challenging problem for quantum chemists. The anion contains multiple metal–ligand bonds. Normally the transition metal 3*d* shell is comparable in size with the 3*s*/3*p* shell, although much higher in energy. Due to its size, an overlap of the metal 3*d* and ligand 2*p* AOs is not always effective. In addition, Pauli repulsion between O and metal 3s/3*p* orbitals also contributes to prevent the Mn–O distance becoming short enough for efficient 3*d*–2*p* overlap. The equilibrium distance is reached when the orbital interactions are not yet effective. Such a weak interaction is the cause for a considerable error in the description of the Mn–O bonds by Hartree–Fock wavefunctions. The errors are due to the nondynamical electron correlation[106]. The permanganate ion (MnO_4^-) has T_d symmetry and a $^1A_1$ ground state at the Hartree–Fock level. The metal–ligand bonding is described in terms of five electron-pair bonds between five 3*d* electrons on Mn^{2+} in d–t_2 and d–e AOs and five 2*p* electrons on O_4^{3-} in 2*p* combinations of t_2 and *e* symmetry. This is illustrated in Figure 9. In this case, high electron repulsion leads to a partial and unphysical localization of the five bonding orbitals, the *e* orbitals on the oxygens and the t_2 orbitals on the metal (without symmetry breaking). The covalent character of the bond is reduced and the ionic character is increased. Therefore, an appropriate theoretical treatment of MnO_4^- needs to include electrons that are delocalized in both *e* and t_2 orbitals, and thereby to restore the covalency. Configuration interaction (CI) and multiconfiguration self-consistent field (MCSCF) calculations including effects of correlation in the calculated energies were carried out to modify the wavefunctions and to get a better picture of the bonding characteristics[107–109]. The ground state still remains $^1A_1$

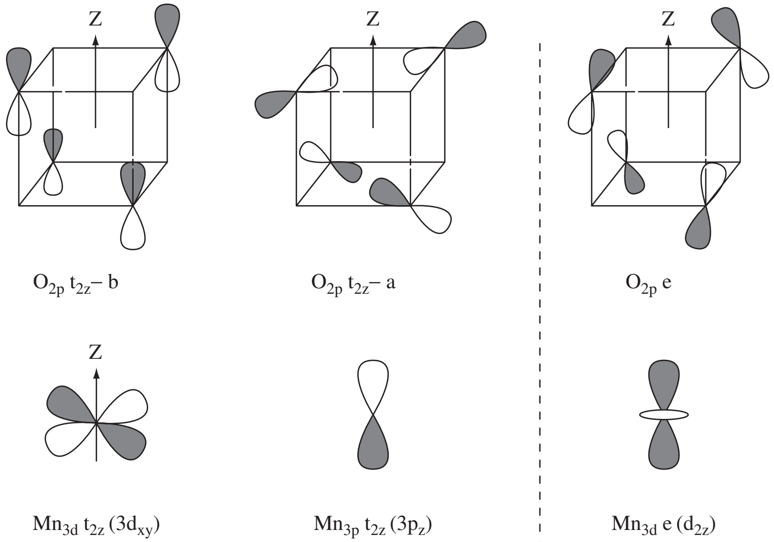


FIGURE 9. Schematic illustration of the orbital interactions in MnO_4^- (adapted from Reference 106)

in the advanced techniques, and thus it may be concluded that the ion does not have Jahn–Teller distortion. The CI wavefunction constructed in the space of bonding and antibonding orbitals delocalizes the electrons in e and t_2 symmetry and this delocalization results in considerable density changes in the metal 3d shell. Electron density is transferred from the oxygen to the metal in the e bonds and vice versa in the t_2 bonds. An optimum 3d occupation is found in MnO_4^- (5.4 electron) and it is independent of the state, geometry and total charge of the system. The MCSCF calculations also produce more or less similar bonding and charge transfer picture.

Similarly, in the treatment of electronic transitions, the low-lying transitions in MnO_4^- correspond to ligand–metal charge transfer processes, in which electrons from O lone pairs are delocalized to the Mn(3d)–O antibonding orbitals, and this causes a strong mixing between close-lying electron configurations. Bonding Mn–O orbitals lying below the O lone pairs also take part in the correlation. Table 8 lists the calculated[107–110] and experimental[111] vertical transition energies of MnO_4^-. The TD-DFT results vary with the functional used. All the theoretical methods considered reproduce the energies with a small over- or underestimation. In particular, they agree upon the assignment of the first band of MnO_4^- to the $1t_1 \rightarrow 2e$ excitation. The analysis of the upper part of the absorption spectrum was much debated, and their assignment remains open[112].

For the neutral radical MnO_4, its geometric structure has not been well assigned yet. Observations from the photoelectron spectrum of MnO_4^- suggested a transition from the T_d anion to the ground and excited states of a distorted neutral[113]. Available quantum chemical computations present disparate results for MnO_4[114].

The side-on bonded $(\eta^2\text{-}O_2)MnO_2$ structure was detected from matrix isolation experiments, and its structure was supported by calculations[114]. Similarly, the $(\eta^2\text{-}O_2)MnO_4$ species was assigned to be the MnO_6 species generated from a reaction of O_2 and $(\eta^2\text{-}O_2)MnO_2$ in solid argon. The $(\eta^2\text{-}O_2)MnO_4$ complex is characterized by a C_{2v} point group and a $^2A_2$ ground state, in which the O_2 molecule is interacting with two O atoms of the MnO_4 moiety[114]. The O_2-evolving complexes of MnO-containing compounds are of great interest in photosynthetic reactions at the active Mn site for the formation of O_2 from water[115, 116].

E. Mn_NO^+

The photodissociation of small Mn cluster oxide cations ($N = 2–5$) was investigated, and the analysis led to the bond dissociation energies giving Mn to be determined. It was found that MnO_2^+ does not dissociate, and the core ion Mn_2O^+ is only weakly bound with the rest of Mn atoms in Mn_NO^+[117].

VII. THE CARBONYLS

Interaction of carbon monoxide with transition metals is an important topic in organometallic compounds. Many industrial processes such as hydroformylation, Fischer–Tropsch synthesis and acetic acid synthesis employ CO as the reagent and transition metal compounds as heterogeneous or homogeneous catalysts. These processes usually involve transition metal carbonyl intermediates. The first Mn–carbonyl compound was obtained initially in 1954[118], and properly prepared in 1958[119] as $Mn_2(CO)_{10}$. Subsequently, the hydride derivative $HMn(CO)_5$ was prepared[120]. The carbonyl ligand has vacant π^*-orbitals in its C≡O bond, which can withdraw electron density from filled d-orbitals of the central metal through $d\pi \rightarrow p\pi^*$ transfer. This back-donation tends to stabilize low metal oxidation states. All these complexes exhibit a low-spin ground state.

A. $XMn(CO)_n$

The original X-ray study revealed that the H atom in $HMn(CO)_5$ is directly bonded to Mn, giving rise to a distorted octahedral coordination. A subsequent neutral diffraction study showed an Mn−H distance of 1.605 Å[121]. The FTIR spectra in the region of 400–4000 cm^{-1} of a series of vapor-phase Mn pentacarbonyl derivatives of the type $XMn(CO)_5$, where X = H, D, Cl, Br, I, CH_3, CD_3 and CF_3, were reported[122]. The relevant vibrational assignment pointed out that all these complexes exhibit C_{4v} symmetry. The gas-phase vibrational fundamentals do not differ much from the values in solution or in condensed phase. The Mn−C and M−CO frequencies remain almost unchanged in going from H to halide or methyl. There are also small changes from halide to halide. The Mn−X bond was found to be progressively weaker in both stretching and bending modes as X goes in the ordering Cl, Br to I.

The optimized geometry of $HMn(CO)_5$ has a C_{4v} point group and the Mn coordination is that of an octahedron. The spectroscopy of $HMn(CO)_5$ in the near-UV region was investigated in detail using MRCI and CASPT2 methods[123]. The transition $\sigma^*(\text{Mn}-\text{H}) \leftarrow \sigma(\text{Mn}-\text{H})$ is expected to occur at 198 nm, and this identifies the most likely photoinitiating states for the photochemistry of $HMn(CO)_5$. The lowest-lying triplet ($^3A_1$) was shown to have a valence character (not a Rydberg state) and lies about 7.2 eV above the singlet ground state[123].

For many metal complexes, the most common photoreaction is often a simple ligand dissociation. When the ligand is CO (or an alkene), the dissociation is also heterolytic, and with metal alkyls and halides, homolytic dissociation giving radicals is more frequent. In $R(Mn)(CO)_5$ with R = alkyl, the CO dissociation is often accompanied by a ‘migratory insertion’ into a metal–alkyl bond (equation 1)[124]. This is the key carbon–carbon bond formation pathway on catalytic carbonylations such as acetic acid synthesis from methanol, or alkene hydroformylations. Kinetic studies of the processes in alkane solution indicated a second-order over the ligand concentrations[125]. Theoretical studies based on DFT computations found that the migration-insertion process involves an intermediate (INT), and the latter is different in the thermal and photochemical pathways[126]. However, more detailed analyses suggested that this could be a concerted process[127]. The existence of intermediates is more likely in polar solvents, where the overall rates are much faster, consistent with the role of solvent in assisting alkyl migration[125, 127]. Overall, much ambiguity remains in the understanding of the mechanism of this process, which requires further appropriate studies.

$$\text{RMn(CO)}_5 + \text{L} \rightarrow \text{INT} \rightarrow \text{Mn(CO)}_4\text{L(CO}-\text{R)} \tag{1}$$

The smaller complexes $HMn(CO)_4$ and $HMn(CO)_3$ are also known. The lowest-lying C_s structure of $HMn(CO)_4$ has a singlet state and a form in which H and a CO group are in a *trans* configuration with respect to the $Mn(CO)_3$ framework. The C_{4v} form is however 8–10 kJ mol^{-1} higher in energy[128]. The triplet state of $HMn(CO)_4$ is a C_{4v} distorted trigonal bipyramid with H in the C_4 axis, and lies about 40 kJ mol^{-1} above the singlet C_s form[129].

The structures of $HMn(CO)_3$ can be generated from $HMn(CO)_5$ upon removal of different pairs of CO. The lowest-lying forms also have a singlet ground state. In general, the $HMn(CO)_n$ complexes having the longest Mn−H distances and the lowest Mn−H stretching frequencies correspond to structures in which a CO group is located in *trans* relation with respect to the Mn−H axis. This is the result of a *trans*-effect in which the back-donation mentioned above tends to weaken the metal–ligand bond in the *trans* configuration.

B. $Mn(CO)_3L_2$

The electronically unsaturated five-coordinate complexes $Mn(CO)_3L_2$, with $L_2 =$ chelating redox-active π-donor ligands that include the catecholates, dithiolates, amidothiolates, reduced diimines and biphosphinine types, have been investigated extensively. The related theoretical studies have been reviewed in much detail[130, 131]. The complexes often adopt a distorted square pyramidal geometry, even though the trigonal bipyramid also exists. Analysis of the electronic absorption in the visible region of these complexes showed that the lowest-energy absorption band always contains a dominant contribution from a $\pi^*(\text{LUMO}) \leftarrow \pi(\text{HOMO})$ transition within the MnL_2 metalacycle. The character of this optical transition thus depends on the composition of the frontier orbitals of the complex considered. These vary from a partial $Mn \leftarrow L_2$ charge transfer (LMCT), to a full $\pi^*(MnL_2) \leftarrow \pi(MnL_2)$ electron transfer, or a mixed $L_2 \leftarrow Mn(CO)$ charge transfer. The electronic absorption spectra tend to be more complex when the chelating ligand L_2 exhibit closely-lying vacant π^* orbitals[131]. In the case of $HMn(CO)_3(DAB)$ with $DAB = 1,4$-diaza-1,3-butadiene, the potential energy surfaces calculated using *ab initio* MO computations for the Mn−H bond homolysis and for the dissociation of an axial CO ligand, in both lowest-lying singlet and triplet states, pointed out the presence of significant energy barriers on the reaction paths of Mn−H bond cleavages. This is responsible for the low efficiency of this process in related complexes. The corresponding metal–ligand charge transfer excited state is responsible for a fast dissociation of the CO ligand[130]. In addition, the relative location of the MLCT states with respect to the $\pi^*(\text{DAB}) \leftarrow \sigma(\text{Mn}-\text{H})$ excited state apparently governs the photoreactivity of the complex[130].

C. $Mn_2(CO)$

Reactions of CO with metal dimers are the simplest models for the CO activation by metal clusters and surfaces. Matrix investigations of the reaction $Mn_2 + CO$ were reported[132, 133] and a theoretical study on this has also been performed[134]. Only in the septet state, a symmetrical bridged C_{2v} structure exists in which C binds to both Mn centers. Although the high spin linear $^9\Sigma^+$ form was found to be the lowest-lying structure, the other bent/semibridging and bridging structures are quite close in energy. In any case, the spin of Mn_2 (singlet state, see above) changes considerably upon interaction with CO. Relative to the singlet Mn_2, the Mn−Mn bond distance is stretched by 0.8 Å. The HOMO of Mn_2CO is nonbonding whereas the HOMO-1 comprises a certain back-bonding. The CO stretching frequencies were observed experimentally at around $1688\,\text{cm}^{-1}$, and this value has not been predicted by calculations. Therefore, the ground state of Mn_2CO remains to be established.

D. $Mn_2(CO)_n$

Several CO groups can also be attached to a Mn_2 framework. $Mn_2(CO)_6$ is of particular interest as the formal 18-electron rule predicts a formal metal–metal quintuple bond. However, the five components of the formal quintuple bond plus the three σ bonds to CO groups on each metal, leading to the full occupancy of eight valence MOs. As there are nine valence orbitals available (from 18 orbitals), one filled valence MO on each Mn atom is thus ready for $p\pi^* \leftarrow d\pi$ back-bonding to CO groups. Calculations showed that in $Mn_2(CO)_6$, two CO ligands form each with Mn_2 a [4-electron donor η^2-μ-CO] type of bonding. Such a carbonyl group is bonded to one metal atom through the usual $\sigma(\text{Mn}-\text{C})$ bond and to the other metal through a π-bond of CO[135].

Such four-electron donor bridging CO ligands are characterized by relatively short C−O distances and low stretching frequencies. This type of bonding has been found earlier in (μ-$Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) by X-ray diffraction experiment[136]. Overall, there is no quintuple Mn−Mn bond in $Mn_2(CO)_6$, but rather a triple bond, in its singlet ground state[135].

The binuclear $Mn_2(CO)_8$ complex is unbridged and has a formal quadruple bond[137]. The $Mn_2(CO)_{10}$ complex is a prototype for bimetallic transition metal complexes. It is characterized by a high-symmetry low-spin (singlet) ground state. Its photochemical reactivity leads to competitive primary reactions, including CO loss and homolytic cleavage of the Mn−Mn bond[138]. The two lowest bands of its absorption spectrum have been interpreted as follows: (i) an excitation ${}^1E_1 \leftarrow {}^1A_1$ corresponding to the orbital transition $\sigma^*(\text{Mn}-\text{Mn}) \leftarrow 3d_\pi$ is responsible for the poorly resolved shoulder centered at 3.31 eV, and (ii) an excitation ${}^1B_2 \leftarrow {}^1A_1$ is attributed to the intense band located at 3.69 eV. This excitation has an intrametallic character in which the electron moves from the bonding σ(MnMn) orbital to its counterpart antibonding σ^*(MnMn) orbital[139, 140]. The photodissociation of $Mn_2(CO)_{10}$ was studied in detail using DFT calculations[141]. Potential energy curves as functions of the Mn−Mn distances were constructed for many electronic states, and it turns out that the bond cleavage simply occurs in the two lower-lying excited states (mentioned above) giving two $Mn(CO)_5$ ground state fragments. In these lower-excited states, there is no dissociative character to the ionic species $Mn(CO)_n{}^+ + Mn(CO)_n{}^-$. The CO release mechanism from $Mn_2(CO)_{10}$ in the ground state was also probed using DFT computations[142]. The Mn−CO bond energy is an important factor governing the release of CO from the complexes. However, as the Mn−CO bond energy of $>175\,\text{kJ mol}^{-1}$ is relatively high, this bond cleavage is not competitive, unless some additional factors could help in the CO departure.

The hydrides $H_2Mn_2(CO)_n$ were predicted to have bridging Mn atoms in preference to bridging CO ligands. The latter can be regarded as generated from the bridged Mn_2H_2 (C_{2h}) species given in Figure 7 by adding the CO ligands around the two metal centers. This is clearly illustrated by the geometry of $H_2Mn_2(CO)_8$ which exhibits a ground state structure with the Mn(η-H)$_2$Mn core and four CO ligands attached to one Mn atom forming exclusively σ(Mn−C) bonds[129]. In this high-symmetry shape, the Mn−Mn distance amounts to 2.7 Å and the Mn(η-H)$_2$Mn core can be considered as a diprotonated double bond dimer having the favored 18-electron configuration. This type of structure is confirmed by the crystal structure of a similar derivative [$Mn_2(\mu$-$H_2)(CO)_6(\mu$-dppm)][143]. The more unsaturated derivatives $H_2Mn_2(CO)_6$ and $H_2Mn_2(CO)_7$ have similar structures with double-bridge Mn(η-H)$_2$Mn core and shortened Mn−Mn distances[129].

The trimetallic $Mn_3(CO)_n$ compounds have also been investigated[144]. In the carbonyl hydrid $H_3Mn_3(CO)_{12}$, all CO groups are terminal and each edge of a central Mn_3 equilateral triangle is bridged by a single H atom. The central [(μ-H)$_3$Mn$_3$] core unit is retained in the lowest-energy structure of $H_3Mn_3(CO)_{11}$. The structure of $H_3Mn_3(CO)_{10}$ turns out to be more complicated, but it seems that this species is favored by the 18-electron configuration with a relatively short Mn−Mn bond of 2.36 Å, which is characteristic for a formal MnMn triple bond[145, 146]. In the series of $H_3Mn_3(CO)_n$ with $n = 9$, 10 and 11, the closed-shell singlet structures are consistently lower than the corresponding triplet counterparts.

A trimetallic Mn−Mn−Au boride complex with a fluxional gold−boron bond has recently been prepared[147]. Theoretical analysis pointed out an unprecedented delocalized Mn−B−Au bond in which a facile rearrangement process occurs between both Mn centers rendering the two Mn-complex fragments equivalent on the NMR scale down to −90 °C. A number of [$Mn(CO)_nB$] and [$Mn_2(CO)_nB$] compounds have also been prepared with interesting properties[148].

An isoelectronic system of the $Mn(CO)_6{}^+$ complex is $[Mn(NO)(CN)_5]^{3-}$. Earlier experimental studies[149] suggested that its oxidation state is Mn(I), with the nitric oxide taken to be NO^+. Subsequent theoretical study demonstrated that $[Mn(NO)(CN)_5]^{3-}$ has a singlet ground state $(d_{xy})^2$, and it is more appropriate to describe the metal as having a Mn(V) state[150]. The $^1E \leftarrow {}^1A_1$ transition of $19\,380\,\text{cm}^{-1}$ of the trianion was well reproduced by DFT computations. The Mn−N distance of 1.65 Å in the nitric oxide complex confers a fractional Mn−N single bond character. The electronic properties of $[Mn(NO)(CN)_5]^{3-}$ was also found to be similar to that of $[Mn(N)(CN)_5]^{3-}$, which behaves electronically closer to a Mn(V) metal[150].

VIII. SANDWICH COMPLEXES

The metallocene or sandwich complexes of manganese have been known for quite a long time. This element like its other transition metal counterparts forms sandwich complexes with various ligands, and the 18-electron rule is not obeyed in such complexes. The more commonly known sandwich complexes of manganese are called half-sandwich complexes, where the second ligands are mainly carbonyls or various other ligands (apart from the aromatic ones). These complexes are mostly known for their diverse molecular properties, which include their magnetic behavior, ability to form inclusion complexes (e.g. cyclodextrins (CD))[151] and to form complexes with specific optical activities.

A. Sandwich Complexes

Figure 10 displays the different members of the manganocene family. The first representatives including $(C_5H_5)_2[MnCp]_2Mn$ and $(MeC_5H_4)_2Mn$ $[MeCp_2{-}Mn]$ (Figure 10a) have been known for around 55 years[152]. Their electronic properties, especially the high-spin/low-spin crossover, have attracted much attention and have been studied extensively by photoelectron[153] and EPR[154, 155] spectroscopy, by magnetic measurements in solution[154], by electron diffraction[156] and by NMR spectroscopy[154, 157]. The manganocenes have the longest M−C distances and exhibit the highest reactivity of all metallocenes of the 3*d* transition-metal series[156]. They are pyrophoric, hydrolyze instantaneously in contact with water and acids[158], undergo facile ring exchange reactions characteristic of ionic cyclopentadienide compounds[159] and allow substitution of one cyclopentadienyl ligand by three two-electron donors, e.g. L = CO[160] or $L = P(OR)_3$[161].

In the case of Cp_2Mn, the strong electron−electron repulsion and the exchange interaction between the five unpaired 3*d* electrons of the Mn^{2+} ion, this cation has a marked tendency to remain in the $S = 5/2$ spin state. In fact, in the complex, the two antibonding

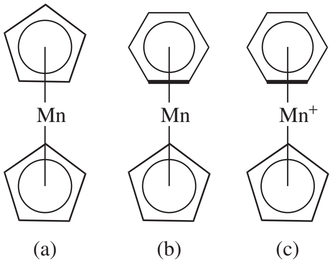


FIGURE 10. Structures of (a) Cp_2Mn, (b) $CpMn(C_6H_6)$ and (c) $(C_6H_6)Mn(C_6H_6)^+$ complexes

and three nonbonding MOs are singly occupied. The resulting electronic configuration of the D_{5h} structure is $^6A'_1 : \ldots (e_{2g})^2(a_{1g})^1(e_{1g})^2$ (5 unpaired electrons) and the 18-electron rule is not satisfied (1 electron short). This explains the paramagnetic behavior of the complex (magnetic moment $5.86\,\mu_B$). The low-spin (doublet) state also exists with a small amount in the gas phase. The transition energy between both states is tiny, being 2 kJ mol^{-1} [155]. In the gas phase at 100 °C, the methyl derivative has a 62:38 equilibrium mixture of high-spin and low-spin isomers. Such a mixture could be characterized by electron diffraction[156]. The Cp_2Mn complex has low dissociation energy (212 kJ mol^{-1})[162] and the presence of a high-spin Mn atom in the complex results in an absence of a strong covalent bond. The stability of the half-filled sub-shell ($3d^5$ configuration) is responsible for the anomaly of manganocene. DFT calculations (BP86/TZVP) reproduce quite well the geometric parameters of Cp_2Mn[163]. Figure 11 displays the corresponding MOs of Cp_2Mn. Experimental observation and DFT calculations indicate that delocalization of the positive spin density onto the ligand dominates over negative spin densities, due to spin polarization. Concerning the NMR parameters, downfield ^{13}C shifts are found[163]. The anomalous behavior disappears when methyl groups replace the hydrogen atoms of the ring. The $(MeCp)_2Mn$ and $(decaMeCp)_2Mn$ have low-spin ground state and have chemistry similar to the other metallocenes. Computed ^{13}C shifts for doublet states of the alkyl-substituted derivatives are small but positive, consistent with a preference of weak delocalization over spin polarization. There is a substantial difference in the ^{13}C isotropic chemical shifts between the low- and high-spin state of Cp_2Mn. These amount to 1701 and 82 ppm for the sextet and doublet states, respectively (using BP86/IGLO-II

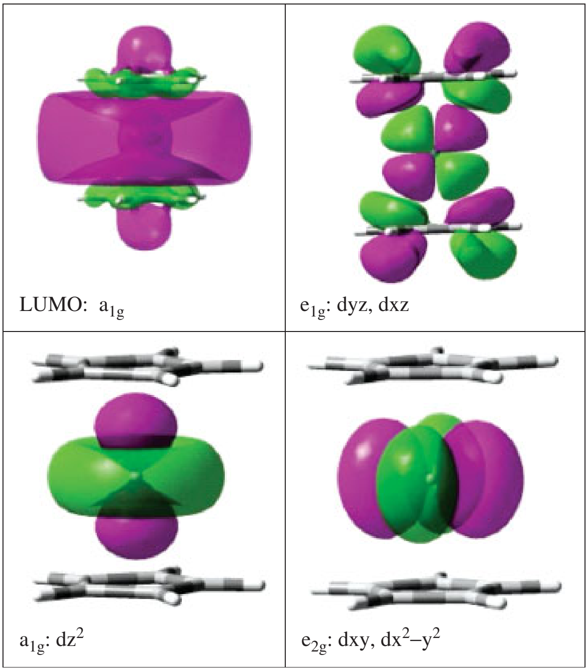


FIGURE 11. The shape of the frontier orbitals of manganocene $MnCp_2$ (D_{5h}, $^6A_1'$) from the ROHF wavefunction

calculations)[163]. The chemical shifts and g tensor of the manganocene are also computed and analyzed in terms of the Fermi-contact and spin–orbit contributions.

The first excited state of manganocene is located at around 4.2 eV, arising from a ${}^6A_2$ $(C_{2v}) \leftarrow {}^6A_1{}'$ transition. However, other states are also quite close in energy (${}^6B_1$ state at 4.5 eV and ${}^6B_2$ state at 4.6 eV)[164]. Calculations indicated that the negative ion state of manganocene Cp_2Mn^- is not stable with respect to electron detachment[165]. The vertical ionized state is nearly degenerate and located at around 6.7 eV (${}^5A_2$ and ${}^5B_1$ states under C_{2v} symmetry) with respect to the neutral ground state. The ${}^5A_1{}'$ state of the ion is higher at 8.9 eV. These values correspond to the experimental ionization energies of 7.01 and 8.85 eV obtained from photoelectron spectrometric experiment for manganocene[166].

The reactions of Cp_2Mn and $(MeCp)_2Mn$ with various ligands are well documented and their structures are also known through crystallographic analyses[167]. One typical example is the case where the MeCp rings are tilted due to adduct formation with the chelating agents. The chelating bis(phosphine) $Me_2PCH_2CH_2PMe_2$ (1,2-bis(dimethylphosphino)ethane, DMPE) even gives rise to adducts with such a structure of the MeCp (Figure 12)[168]. The electronic nature of this 19-valence-electron derivative could be explained from the basic electronic configuration of the Cp_2Mn complex as discussed above. The 1:1 adducts with the more electronegative donors 3,5-dichloropyridine[169] and tetrahydrofuran[170] are also known to have similar 'tilted' planar cyclopentadienyl rings in the solid state[171].

Other interesting derivatives of manganocene are those in which the carbon cycles are replaced by phosphorus rings. The complex $[Mn(\eta^4-P_4)_2]^-$ exhibits a Mn(III) $3d^4$ structure and adopts a sandwich-type D_{4h} eclipsed conformation as the lowest-energy conformer. The P_4 rings have both σ and π antiaromaticity[172].

The second class of manganocene complexes is of the type $Cp-Mn-C_6H_6$ (Figure 10b). A typical example of such a complex is methylethylcyclopentadienyl manganese benzene and was prepared by allowing phenylmagnesium bromide to react with methylcyclopentadienyl manganese chloride or bis(methylcyclopentadienyl)Mn in tetrahydrofuran and under an inert atmosphere[173]. The complex is ruby-red crystal (m.p. 116–118 °C) and is relatively stable in air. However, thermal degradation at higher temperatures (> m.p.) gave benzene and methylcyclopentadiene in good yield.

The sandwich complex of benzene (C_6H_6) and Mn is obtained in the ionic form $Mn(C_6H_6)_2{}^+$ (Figure 10c). The relative stability of this complex with respect to the other transition metal complexes (Ti, V, Cr, Fe, Co, Ni and Cu) was studied through collision-induced dissociation mass spectrometric experiments[174]. The characteristic metal–ligand vibrational modes of such complexes were also measured and the bonding characteristics

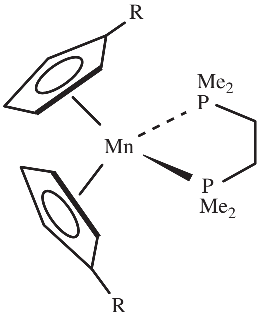


FIGURE 12. Schematic molecular structure of DMPE and $MeCp_2-Mn$ complex

analyzed (based on the earlier theoretical studies on $C_6H_6M^+$ complexes[175]) considering their structure in C_{6v} symmetry. In C_{6v} symmetry, the metal $3d$ orbitals in the $M(C_6H_6)^+$ complexes are energetically ordered as $3d\ e_2(\delta) < 3d\ a_1(\sigma) < 3d\ e_1(\pi)$. While occupying the $3d\ e_2(\delta)$ orbitals maximizes back-donation into the π^* orbitals on benzene and strengthens the metal–ligand interaction, the $3d\ e_1(\pi)$ orbitals overlap with the benzene π orbitals and are antibonding. The overlap of the compact $3d\ a_1(\sigma)$ with benzene should be small, because it points into the center of the aromatic ring[175]. Thus the binding energy (BDE) decrease going from $Ti(C_6H_6)^+$ to $V(C_6H_6)^+$ to $Cr(C_6H_6)^+$ (with three, four and five $3d$ electrons) as well as from $Co(C_6H_6)^+$ to $Ni(C_6H_6)^+$ and $Cu(C_6H_6)^+$ (with eight, nine and ten $3d$ electrons) reflects the filling of the energetically unfavorable $3d\ e_1(\pi)$ orbitals, which increases the repulsion with the benzene ligand. The BDE for $Mn(C_6H_6)^+$ is the smallest among the complexes studied, indicating that having an electron in the diffuse $4s$ orbital further increases the repulsion. The increase in BDE in going from $Cr(C_6H_6)^+$ to $Fe(C_6H_6)^+$ reflects addition of electrons to the bonding $3d\ e_2(\delta)$ orbitals. Another underlying effect should be the decreasing size of the metal ions as one move to heavier elements, which should increase the electrostatic binding by allowing a shorter metal–ligand bond distance. This effect can be observed in the calculated bond distances[175].

Assuming a 6-fold symmetry for both the mono- and bis-benzene metal ions, the relative ordering of the metal $3d$ orbitals is the same in both systems, but the splitting should approximately double such that spin pairing to form low-spin ground states is likely to occur in the case of the sandwich complexes. A $^2A_1(3d\ e_2{}^4\ 3d\ a_1{}^1)$ ground state of $Cr(C_6H_6)_2{}^+$ has been established by theory[176] and experiment[177]. Electron spin resonance and photoelectron studies[178] show that the ion ground states for the titanium and vanadium compounds are the $^2E_2(3d\ e_2{}^3)$ and $^3E_{2v}(3de_2{}^3\ 3d\ a_1{}^1)$ states, respectively. It is thus expected that the 18-electron complex, $Mn(C_6H_6)_2{}^+$, should be a singlet species, $^1A_1(3d\ e_2{}^4\ 3d\ a_1{}^2)$. Subsequent filling of the highest lying $3d\ e_1(\pi)$ metal orbitals should then result in a $^2E_1$ ground state for $Fe(C_6H_6)_2{}^+$ and $^3A_2$, $^2E_1$ and $^3A_1$ ground states for the cobalt, nickel and copper sandwich ions, respectively. DFT calculations[179] confirmed that $Mn(C_6H_6)_2{}^+$ exhibits indeed a high-symmetry singlet ground state.

A very different kind of Mn-sandwich complex was produced when the sandwiched paramagnetic species $\{[\eta^5\text{-1-Gd-2,3-(SiMe}_3)_2\text{-2,3-C}_2B_4H_4]_3[(\mu_2\text{-1-Li-2,3-(SiMe}_3)_2\text{-2,3-C}_2B_4H_4)_3(\mu_3\text{-OMe})][\mu_2\text{-Li(C}_4H_8O)]_3(\mu_3\text{-O})\}$ was reacted with $MnCl_2$ in benzene, followed by the addition of TMEDA. The newly generated dinuclear manganacarborane sandwich complex, 4,4′,5,5′-Mn(TMEDA)-1,1′-*commo*-$Mn[2,3\text{-(SiMe}_3)_2\text{-2,3-C}_2B_4H_4]_2$ (Figure 13), was characterized on the basis of its elemental analysis and IR spectrum and also by X-ray diffraction, and it is also paramagnetic in nature[180].

B. Half-sandwich Complexes

1. $(\eta^5\text{-Cp})Mn(CO)_3$

The half-sandwich complexes of Mn are more common and widely studied. The most commonly known complex in this class is $[(\eta^5\text{-Cp})\ Mn(CO)_3]$. The complex is a thermally stable (m.p. 77 °C) yellow solid. The standard electron count technique shows that it fulfills the 18-electron rule and accounts for its stability. An interesting point in this connection is that the elements in the first transition series with odd atomic number (V, Mn and Cr) form monomers, while the elements with even atomic number (Fe, Co and Ni) form dimeric species. This is in direct contrast to the behavior shown by their simple carbonyl complexes. The $[(\eta^5\text{-Cp})Mn(CO)_3]$ complex is the starting point of synthesizing various other half-sandwich complexes[181]. The electrochemical studies showed that (except for a few cases) they have high standard oxidation potential and thus are quite stable[181].

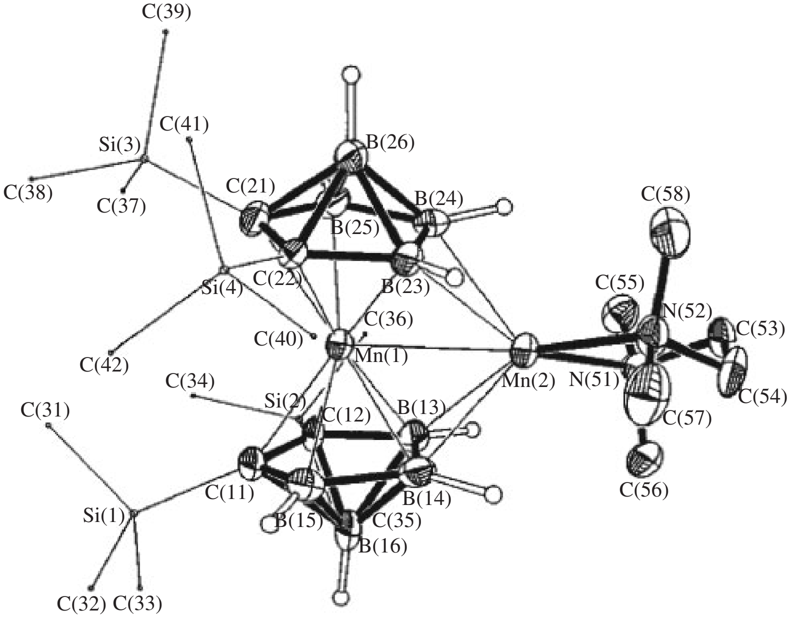


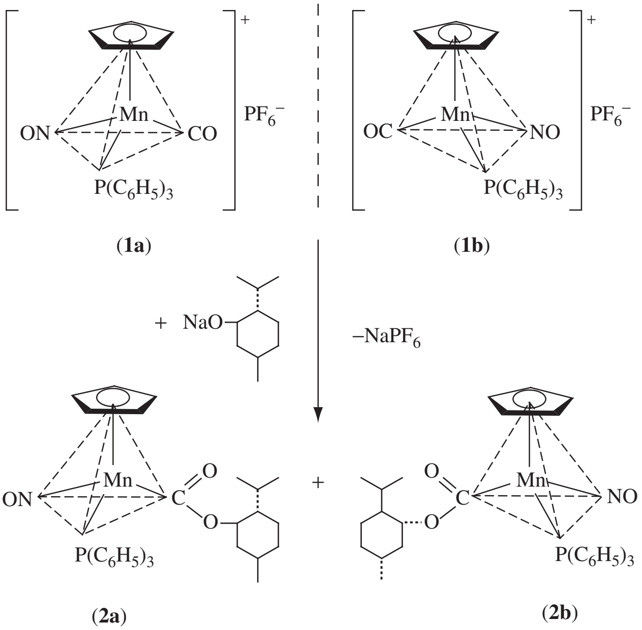
FIGURE 13. Perspective view of 4,4′, 5, 5′-Mn(TMEDA)-1,1′-*commo*-Mn[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ showing the atom numbering scheme with thermal ellipsoids drawn at the 40 % probability level. The methyl and methylene H's are not shown for clarity. The atoms of the silyl groups are drawn with circles of arbitrary radii (adapted from Reference 180)

The $[(\eta^5\text{-Cp})Mn(CO)_3]$ complex is used to design optically active half-sandwich complexes. Forty years ago, the first resolution of a transition metal complex with four different substituents was achieved with the manganese complex **1** (Scheme 1)[182]. In the cation of this complex the manganese atom is surrounded by a cyclopentadienyl, a carbonyl, a nitrosyl and a triphenylphosphane ligands. It can be obtained in two steps from the commercially available compound $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$, and is formed as the racemate (Scheme 1, **1a/1b**)[183, 184]. They are converted into a pair of diastereomers through reaction with the sodium derivative of the optically active alcohol (1*R*,3*R*,4*S*)-menthol. The mentholate ion adds to the carbon atom of the carbonyl ligand in the cationic starting material. The neutral esters **2a** and **2b** (Scheme 1) thus formed differ only in the configuration of the manganese atom. The formation of such complexes later led to the development of the optically active half-sandwich complexes of other transition metals[185].

The phosphorus derivative $[(\eta^5\text{-}P_5)Mn(CO)_3]$ in which the cyclic P_5 replaces the C_5H_5 ring was prepared in 1991, by heating the KP_5 salt with $Mn(CO)_5Br$ in DMF[186]. Nevertheless, this P-complex was not well characterized.

2. $Mn(CO)_3L$ (L = arene)

The cationic complex, which is isoelectronic with $(\eta^6\text{-arene})Cr(CO)_3$ can be synthesized with a wide variety of arenes. The positive charge of the Mn complex greatly enhances

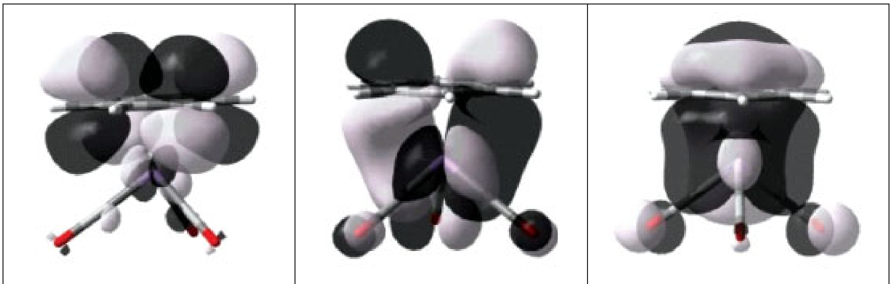


SCHEME 1. Complexes **2a** and **2b**, the first optically active transition metal complexes with four different ligands (adapted from Reference 185)

the electrophilic character of the ring, which is thereby suitable for reaction with nucleophiles[187]. They mainly function as effective Mn tricarbonyl transfer reagents, due to the facile $\eta^6 \rightarrow \eta^4$ slippage. Upon reduction or upon associative nucleophilic attack, the $Mn(CO)_3{}^+$ moiety can thus be migrated to generate new carbonyl-capped manganocenes. An easy and versatile functionalization of $Mn(CO)_3(\eta^5$-cyclohexadienyl) complexes by a lithiation/electrophilic quench sequence was also shown to be possible[188].

Figure 14 displays the frontier orbitals of $CpMn(CO)_3$. The species exhibits a singlet ground state. DFT computations showed the major role of the $Mn(CO)_3$ tripod on this regioreactivity is that it is mainly governed by the stability of the deprotonated species on the C^2 carbon center eclipsed by a Mn−CO bond. The regioselectivity of the related reactions can, however, not be explained by the sole thermodynamic properties of the deprotonated species[188]. The regioselectivity of nucleophilic attacks on this type of complex can better be understood from the influence of the CO group position on the strength of conjugation between the RCO function and the cyclohexadienyl ring, as evidenced by the vibrational frequencies of the CO bonds. Nevertheless, the carbonyl atom was shown to be the favored site for nucleophilic attack, irrespective of the position on which it is branched[189].

Theoretical studies, mostly using DFT methods, have been carried out on a number of disparate systems. We mention in particular the Mn enzymes that are the Mn superoxide dismutase for redox energetic[190]. Calculations on Mn-porphine (the simplest porphyrin) hydration and interaction with nitric oxide showed that the Mn(III) is on average coplanar with the porphine plane and forms a stable complex with two water molecules[191]. Hydroxo Mn(V) porphyrins were shown to undergo a C−H oxidation of toluene using both Mn(O) and Mn(OH) which are potent-atom abstractors[192]. Mn porphyrins could also be used in the



LUMO HOMO (dyz) HOMO-1 (dxy)

HOMO-2 (dxz) HOMO-3 (dx2-y2) HOMO-4 (dz2)

FIGURE 14. The shape of the frontier orbitals of $CpMn(CO)_3$ from the ROHF wavefunction

molecular junction for electron transport[193]. The adsorption of NO on Mn phthalocyanine is governed by the interaction between $3d\pi$(Mn) and the π^*(NO) orbitals[194]. Calculations on the prototype manganese carbide (MnC)[195], and the Mn(II)-glycine[196] and $Mn(CH_4)_n$[197] complexation processes in the gas phase have been reported.

IX. CONCLUDING REMARKS

Due to its half-filled electron shell $(4s)^2(3d)^5$, the Mn atom is highly magnetic and behaves quite differently from the other transition metals. The high-spin states and their multiconfigurational character make accurate calculations on Mn-containing compounds a great challenge for quantum chemists. While Cr_2 was a typical problem for molecular orbital methods, the Mn_2 dimer represents a difficult test case for density functional theory. Relative to the other transition metals, theoretical studies on Mn compounds are much less abundant and, when available, they are not quantitative. Let us hope that, using state-of-the-art first-principle methods, much effort will be invested in the near future in theoretical treatment of this important class of organometallic compounds.

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XI. REFERENCES AND NOTES

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2. Robert E. Krebs, *The History and Use of Our Earth's Chemical Elements: A Reference Guide*, Greenwood Publishing Group, CT, USA, 2006.
3. Sir Henry Bessemer (1813–1898) from England developed the first process for mass-producing steel inexpensively. The difficulty was the presence of an excess of residual oxygen and sulfur in the steel. The problems were overcome when a patent was granted to Robert Mushet in 1856. Mushet suggested adding ‘spiegeleisen’ after the blow to introduce both Mn and C and remove O. Thanks to this beneficial effect of Mn, the Bessemer process became possible, and thus paved the way for the modern steel industry. The current dominant steel manufacturing technology is an extension and refinement of those developed by Bessemer and Mushet.
4. Robert Forester Mushet (1811–1891) was a British metallurgist and businessperson. Whilst Bessemer and others made fortunes from his discoveries (see Reference 3), he failed to capitalize on his patents, and by 1866 was destitute and in ill health. Mary, his 16-year-old daughter, traveled alone to London to confront Henry Bessemer, arguing that his success was based on her father's work. Bessemer, whose own process for producing steel was not economically viable without Mushet's improvement techniques, decided to pay Mushet an annual pension of £300, a very considerable sum at that time, for over 20 years to keep the Mushets from legal action. Source: http://en.wikipedia.org/wiki/Robert_Forester_Mushet.
5. Carl Wilhelm Siemens (Charles William Siemens, later known as Sir William Siemens, 1823–1883) was a German born engineer, who worked in Britain and later became a British subject.
6. Robert Abbott Hadfield (1858–1940), an English metallurgist, was noted for his 1882 discovery of manganese steel, one of the first steel alloys. He also invented silicon steel, which was initially used thanks to its mechanical properties (1886), but became important in electrical applications for its magnetic behavior.
7. Georges Leclanché (1839–1882), a French electrical engineer, was chiefly remembered for his invention of the Leclanché cell, one of the first modern electrical batteries and the forerunner of the modern dry cell battery.
8. Johann Rudolf Glauber (1604–1668), a German-Dutch alchemist and chemist. Some historians of science have described him as one of the first chemical engineers. His discovery of sodium sulfate in 1625 led to the compound being named after him, ‘Glauber's salt’. The chemical garden (or silica garden), first observed and described by Glauber in 1649, involved the introduction of ferrous chloride ($FeCl_2$) crystals into a solution of potassium silicate (K_2SiO_3, water glass). He was the first to synthesize and isolate potassium permanganate, antimony trichloride, arsenic trichloride, tin tetrachloride and zinc chloride. He wrote *ca* 40 books. In *Dess Teutschlands Wohlfahrt* (Germany's Prosperity), he proposed the chemical industries as a means for Germany's economic recovery after the Thirty Years War. Source: http://en.wikipedia.org/wiki/Johann_Rudolf_Glauber.
9. Henry Bollmann Condy was a British chemist and industrialist best known for giving his name to the popular 19th and 20th century disinfectants Condy's Crystals and Condy's Fluid based on $KMnO_4$. He fused pyrolusite (MnO_2) with NaOH in water, producing a solution with disinfectant properties. He patented this solution and marketed it as Condy's Fluid. Later, he used KOH to make more stable and effective potassium permanganate crystals, which were known as Condy's crystals or Condy's powder. $KMnO_4$ was relatively easy to manufacture, therefore Condy was subsequently forced to spend considerable time in litigation in order to stop competitors from marketing similar products. Source: http://en.wikipedia.org/wiki/Henry_Bollmann_Condy.
10. Karl Wilhelm Scheele (1742–1786), a Swedish pharmacist, discovered many gases but he did not receive much credit for his findings. In fact, he discovered oxygen about two years before Joseph Priestly (1733–1804) and long before Antoine Lavoisier, but he did not publish

his work on time (see Reference 2). When reacting MnO_2 with HCl, Scheele did not regard the pungent green gas as an element. He referred to it as 'dephlogisticated marine acid'. To Scheele, phlogiston was practically synonymous with hydrogen. Such a view of chlorine was essentially correct, but in a curious context.

11. Sir Humphry Davy (1778–1829). Davy performed many experiments with 'oxymuriatic acid' (as Cl_2 was named at that time) with ammonia, and found only muriatic acid and nitrogen in the products: $3\ Cl_2 + 2\ NH_3 \rightarrow 6\ HCl + N_2$. He exposed the gas to white-hot carbon in attempts to remove the oxygen forming CO_2. Oxygen or any compound known to contain oxygen was not produced, and Davy finally concluded that the gas was an element. He called it 'chlorine' after the Greek 'chloros' meaning yellow-green, a similar color found in 'chlorophyll'. Davy also studied, among others, the oxides of nitrogen and discovered the physiological effects of nitrous oxide, which became known as the 'laughing gas' (see Reference 7).
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13. Johan Gottlieb Gahn (1745–1818), a Swedish chemist and mineralogist, studied in Uppsala and became acquainted with chemists Torbern Bergman and Carl Wilhelm Scheele. In 1770 he settled in Falun, where he introduced improvements in the copper smelting processes. He was the chemist for The Swedish Board of Mines Bergskollegium in 1773–1817. He also discovered phosphoric acid in bones with Karl Scheele and separated phosphorus from bones. Source: http://en.wikipedia.org/wiki/Johan_Gottilieb_Gahn.
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Mass spectrometry and gas-phase ion chemistry of organomanganese complexes

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I. ABBREVIATIONS

AP	appearance potential
BDE	bond dissociation energy
CI	chemical ionization
CID	collision-induced dissociation
Cp	cyclopentadienyl
cymantrene	cyclopentadienylmanganese tricarbonyl, $C_5H_5Mn(CO)_3$
DC/FT	dc discharge/flow tube (ion source)
EI	electron ionization
ESI	electrospray ionization
FAB	fast atom bombardment
FA-MS	flowing afterglow mass spectrometry
FD	field desorption
FT-ICR	Fourier transform-ion cyclotron resonance
FTR	flow-tube reactor
GC-MS	gas chromatography-mass spectrometry
GIB	guided ion beam (mass spectrometer)
HPMS	high-pressure mass spectrometry
ICP	inductively coupled plasma
IE	ionization energy
IP	ionization potential
IRMPD	infrared multiple-photon dissociation
LA	laser ablation
LD	laser desorption
LDI	laser desorption/ionization
LIAD	laser-induced acoustic desorption
LV	laser vaporization
M	neutral molecule
M^+	molecular ion
MALDI	matrix-assisted laser desorption/ionization
Me	methyl
Met	metal atom
MI	metastable ion
MPI	multiphoton ionization
MS	mass spectrometry
NR	neutralization–reionization
OMCVD	organometallic chemical vapor deposition
PES	photoelectron spectroscopy
r.a.	relative abundance
SI	surface ionization
SIFT	selected-ion flow tube (mass spectrometer)
SIMS	secondary-ion mass spectrometry
Solv	solvent molecule
SSMS	spark source mass spectrometer
TOF	time-of-flight (mass spectrometer)

II. INTRODUCTION

Manganese oxides are relatively abundant in nature, and, as attested by cave paintings, they were used in human activities as early as the Stone Age due to their chromogenic properties. Egyptian and Roman glassmakers used manganese compounds to add or modify glass color, or for bleaching glass. Manganese nodules and the mineral pyrolusite, the main ore of manganese, are rich in manganese dioxide (MnO_2). By reducing MnO_2 with carbon, chemist and mineralogist Johan Gottlieb Gahn was the first to isolate the manganese metal in 1774[1]. The chemistry of organomanganese compounds—species containing a manganese–carbon chemical bond—begins with the report by Henry Gilman and James Clyde Bailie on the synthesis of phenylmanganese iodide PhMnI **(1)** and diphenylmanganese Ph_2Mn **(2)** in 1937[2]. Since then, a multitude of new organometallic manganese-containing complexes have been synthesized and studied, as the current book *The Chemistry of Organomanganese Compounds* illustrates.

Most of the first synthesized organomanganese complexes were volatile in the vacuum and elevated temperature environment provided by classical mass spectrometers equipped with electron ionization (EI) ion sources. Consequently, EI mass spectrometry (MS) became the primary MS method for the analysis of this class of compounds. However, progress in organometallic synthesis furnished many species unstable under elevated temperatures or other harsh conditions. Therefore, an alternative analytical MS method with softer experimental conditions, fast atom bombardment (FAB) mass spectrometry, has also found extensive application for the analysis of organomanganese complexes. Electrospray ionization (ESI) mass spectrometry has successfully been used for the same purpose. The development of new MS techniques, such as ionization methods, and new concept spectrometers have made possible advancements in both analytical MS and in the field of gas-phase organometallic chemistry[3–10]. Generally, volatile organometallic species are ideal vehicles for the determination of isotopic abundances and accurate masses of the respective metal nuclides. Natural manganese is a monoisotopic element (^{55}Mn)[11], and consequently the interpretation methodology for isotope clusters of Mn-containing ions in mass spectra is atypical. In general, the mass spectra of the compounds containing polyisotopic elements are difficult to interpret if there is overlapping of isotope clusters of ions. On the other hand, if such overlapping does not occur, the presence of polyisotopic elements with their distinctive signature greatly facilitates the assignment of the isotope clusters in a mass spectrum[12]. As a monoisotopic element, manganese does not modify the isotopic distribution of the ligand(s) attached to it. Each ^{55}Mn atom in monocharged organometallic ions will only increase (or shift on m/z scale) the mass by 55 u without altering the isotopic distribution imposed by the rest of the elements in the species. This specific feature of manganese has to be taken into account for correct interpretation of ion composition in mass spectra, especially when examining polynuclear organometallic complexes. For example, the EI mass spectrum of decacarbonyldimanganese, $Mn_2(CO)_{10}$ **(3)** (Figure 1), illustrates how the presence of one or two Mn atoms in fragment ions does not alter the shape of the isotopic distribution of the coordinated carbonyl ligands (compare, for example, isotope cluster of $[Mn_2(CO)_5]^+$ (m/z 250 for basic peak) with that of $[Mn(CO)_5]^+$ (m/z 195 for basic peak))[13]. Another such example is the mass spectra of polynuclear species $[Mn_n(CO)_{14}]^+$, $[Mn_n(CO)_{15}]^+$ ($n = 3–6$) and $[Mn_n(CO)_{25}]^+$ ($n = 7, 8$) generated from **3** as a result of ion/molecule reactions[14]. Yet another, even more intriguing example, in which both a monoisotopic element (Mn) and a polyisotopic element (Re) form clusters, is illustrated by the mass spectra of $[Re_xMn_y(CO)_z]^+$ ($x = y = 3$; $z = 11–14, 17–19$. $x = y = 2$; $z = 6–8, 10–12, 15$. $x = 2$; $y = 1$; $z = 6, 10$. etc.) species generated from $ReMn(CO)_{10}$ **(4)** as a result of ion/molecule reactions[14]. In brief, the presence of a polyisotopic element (e.g. Re) in an ion modifies both the isotopic distribution and mass, whereas the presence of a monoisotopic element (e.g. Mn) contributes only to the ‘clean shift’ of the mass without altering the isotopic distribution imposed by the rest of the elements in the ion. The accuracy of isotopic distribution analysis and assignment of ion composition becomes even more important if operating with isotopically labeled species[13, 15–43], and the occurrence of isotope effects is under investigation.

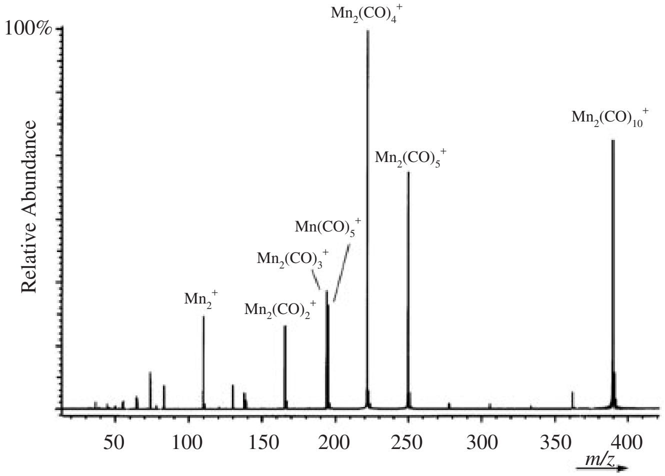


FIGURE 1. Electron ionization (70 eV) mass spectrum of $Mn_2(CO)_{10}$ as recorded with the Bruker Daltonics APEX II FT-ICR mass spectrometer. Reproduced by permission of Elsevier from Reference 13. Copyright (2005) Elsevier

Another manganese nuclide is the radioactive ^{53}Mn with a half-life of *ca* 3 × 10^6 years. This interval is too short for survival of a detectable amount of the primordial isotope[44]; in spite of this, ^{53}Mn has been identified on Earth as a cosmic-ray product and as a component of cosmic dust and iron meteorites[44, 45]. Therefore, ^{53}Mn turned out to be one of the most valuable natural radiogenic nuclides for meteorite chronology.

This review represents an up-to-date survey of literature on mass spectrometry of organomanganese species. Analytical applications of MS techniques to the characterization of compounds having a Mn−C bond will be discussed. This will include a number of relatively simple mononuclear complexes, polynuclear clusters, complexes incorporating organometallic units bridged with organic fragment(s), bifunctional compounds containing organometallic and classical coordination sites, fullerenes or planar polyaromatic hydrocarbons with a organomanganese fragment attached to them, manganospiralenes, manganoscorpionates, supramolecular entities, cymantrene-peptide bioconjugates, etc. Fundamental physico-chemical characteristics of organomanganese derivatives, as well as the gas-phase reactions resulting in the dissociation or formation of manganese−carbon bond(s), will also be reviewed.

III. MASS SPECTROMETRY OF ORGANOMANGANESE COMPOUNDS

A. Electron Ionization and Chemical Ionization Mass Spectrometry

Electron ionization mass spectrometry (EI MS) attested a large utilization in studies regarding MS behavior[15−21,46−168] of organomanganese species, as well as frequent use as a MS analytical tool[169−418] for analysis of this class of complexes. With a number of exceptions, most of the compounds subjected to MS examination are derivatives of manganese carbonyl complexes, manganocene and cymantrene (short for CYclopentadienylMANganese TRIcarbonyl[419]). Positive-ion mode EI mass spectra have been published for mononuclear manganese carbonyl derivatives (of the general formula $Mn(CO)_xL'_yL''_z$)[179–241], polynuclear manganese carbonyl compounds[176–178, 349] and their derivatives in which CO ligands were partially replaced with other monodentate or polydentate ligands[349–372], polynuclear carbonyl derivatives containing various metal atoms alongside manganese[373–404] (in some cases with metal–metal bonds), cubane-like manganese-containing clusters[409, 410], cymantrene-related complexes ($(RCp)Mn(CO)_nL_m$)[242–297], polynuclear mixed-metal compounds containing a cymantrene fragment linked through the organic ligand bridge or metal–metal bond[298–329], complexes incorporating two[330–342] or three[341] cymantrene fragments (including fulvalene based compounds[334, 343–348]), manganocene derivatives[36, 169–172], etc. A number of studies employed EI along with other ionization methods for the analysis of the organomanganese compounds: EI and chemical ionization (CI)[420–427], EI and FAB[428–446], EI and ESI[445–448] and EI and field desorption (FD)[449–455].

As the Mn^+–organic ligand bond is relatively weak, the EI mass spectra of the enumerated series of compounds consist of abundant fragment ion peaks and in many cases display a low or very low intensity molecular ion (M^+) peak. The abundance ratio of ions in the mass spectra depends on the energy of the ionizing electrons. As illustrated in Figure 2, at relatively low ionization energies (IEs), it is possible to detect a high-level ion current for M^+ of the examined analyte. Fragmentation of molecular ions of organomanganese complexes under EI conditions is dominated by a metal–ligand bond cleavage process. A classical example is fragmentation of the M^+ of cymantrene (**5**). The electron ionization mass spectrum of **5** ($CpMn(CO)_3$) at different IEs consists of the following ions: $[CpMn(CO)_3]^+$, $[CpMn(CO)_2]^+$, $[CpMn(CO)]^+$, $[CpMn]^+$ and Mn^+ (Figure 2)[103]. The observed competition between loss of CO and Cp in the precursor ion series is consistent with their respective bond dissociation energies. As metal–ligand bond cleavage represents a predominant fragmentation pathway under EI conditions, fragment assignment and interpretation of MS data for organomanganese species became to some extent undemanding. Generally, this makes the EI mass spectra of organomanganese complexes a good model for understanding experimental MS data. For these reasons EI MS data of organomanganese compounds were used as a key platform component in the development of computational tools for deciphering the MS spectra of organometallics[456–459].

It is noteworthy that under the action of EI, compounds resembling $(OC)_5MnC(O)R$ (**6–8**) generate predominantly the $[Mn(CO)_6]^+$ fragment ion instead of undergoing a stepwise loss of CO groups coordinated to the manganese atom[191, 207, 208]. This process involves C–C bond cleavage. Subsequently, the metal atom of the resulting ionic product $[Mn(CO)_6]^+$ remains in a coordinatively saturated state.

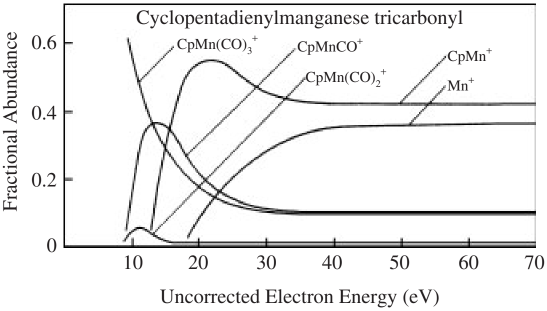
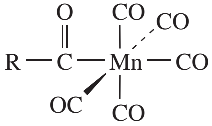
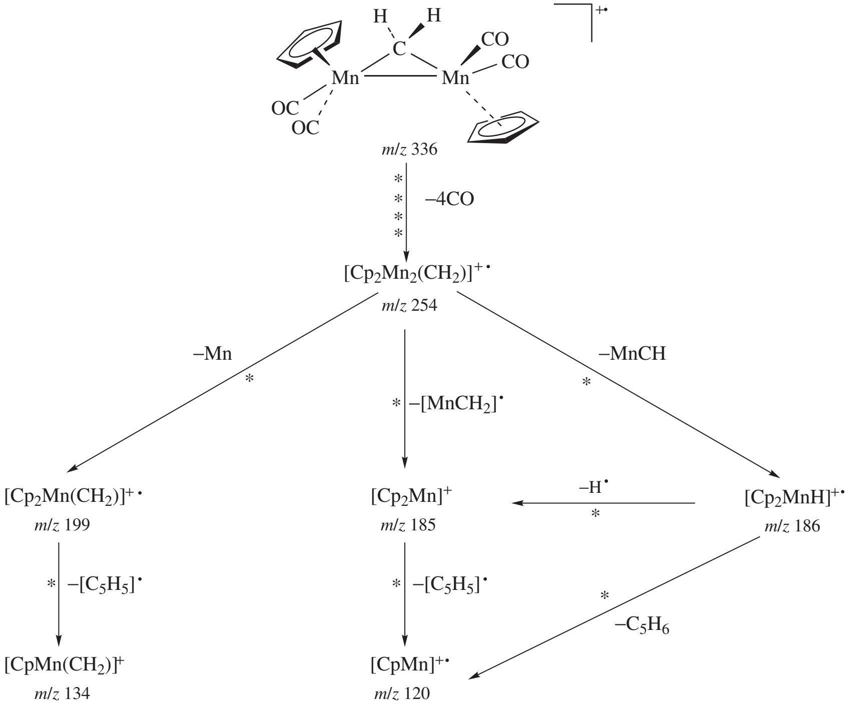


FIGURE 2. The fractional intensities of ions produced from cymantrene, $CpMn(CO)_3$, by EI as a function of the ionizing energy of electrons. Adapted from Reference 103 by permission of Elsevier

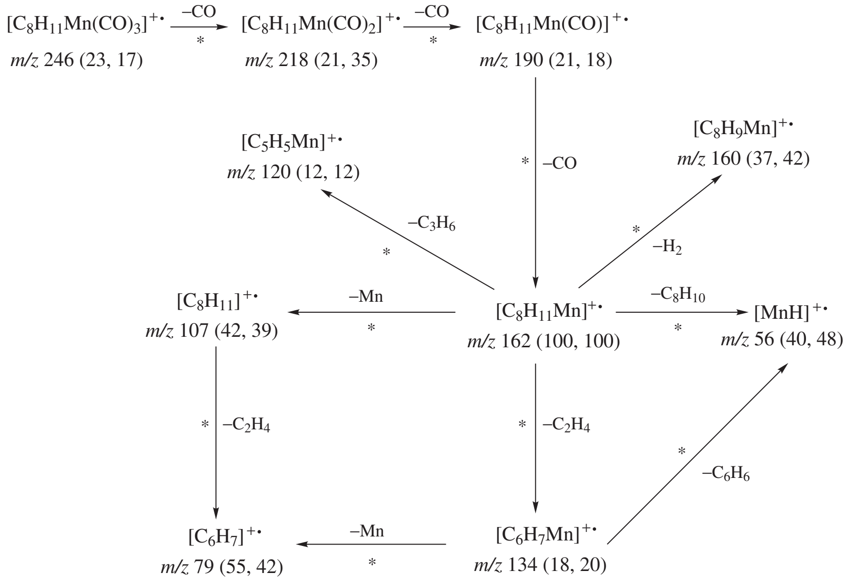


(**6**) R = $CH(CH_3)CH(CH_3)C_2H_5$
(**7**) R = $CH(n\text{-}C_3H_7)OSi(CH_3)_3$
(**8**) R = $CH(OCH_3)CH_2CH_2CH_2CH_2OSi(CH_3)_3$

Intramolecular rearrangement processes occurring during EI MS experiments have also been detected for some manganocene and cymantrene derivatives containing various functional groups in the cyclopentadienyl ligands (see, for example, References 37, 47, 65, 78, 96), as well as for some manganese carbonyl derivatives such as $RMn(CO)_5$ (where R = CH_3 **(9)**, CH_2CN **(10)**, SCN **(11)**, Ph_3Sn **(12)**, $PhBr_2Sn$ **(13)**, *o*-FC_6H_4 **(14a)**, *m*-FC_6H_4 **(14b)**, *p*-FC_6H_4 **(14c)**)[15] and other related compounds[121]. Typically, an increased complexity of the ligand coordinated to the manganese central atom represents a favorable structural premise and makes rearrangement processes more likely to occur.

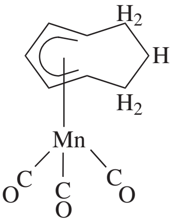


SCHEME 1. Fragmentation pathways of the binuclear compound $Cp_2Mn_2(CH_2)(CO)_4$ **(15)** under EI (70 eV). Metastable transitions are marked by asterisks. Adapted from Reference 94 by permission of Elsevier

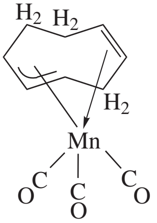


SCHEME 2. Fragmentation pathways of the isomer pair **16a** and **16b** (1,2,3,4,5- and 1,2,3,5,6-pentahaptocyclooctadienyltricarbonylmanganese of the general formula $C_8H_{11}Mn(CO)_3$) under EI (70 eV). The respective relative abundances of ions for each isomer are presented in brackets. Metastable transitions are marked by asterisks. Adapted from Reference 85 by permission of Wiley-Blackwell

Metastable transitions supportive of the determined formulations for fragment ions, as well as of the proposed fragmentation pathways, have also been reported[15, 16,73–100]. Schemes 1 and 2 show the fragmentation of the binuclear compound $Cp_2Mn_2(CH_2)(CO)_4$ **(15)**[94] and the isomer pair **16a** and **16b** (1,2,3,4,5- and 1,2,3,5,6-pentahaptocyclooctadienyltricarbonylmanganese of the general formula $C_8H_{11}Mn(CO)_3$)[85], with the metastable transitions marked by asterisks. Because the manganese–carbonyl bond is relatively weak, sequential loss of CO groups is a common event detected for all species containing such ligands coordinated to the Mn atom. Usually these processes precede other fragmentation reactions, as they are governed by the strength of the metal–ligand bonds. Bruce[76] reported the metastable transitions supportive of the loss of 56 u from the M^+ of the manganese pentacarbonyl derivatives



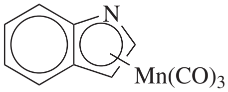
(**16a**)



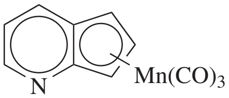
(**16b**)

of alicyclic fluorocarbons, $C_4F_5Mn(CO)_5$ **(17)** and $C_6F_9Mn(CO)_5$ **(18)**. The occurrence of such an event shows that a simultaneous detachment of two CO groups (56 u) is also possible during fragmentation reactions[76].

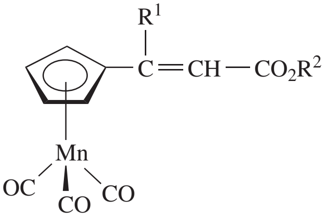
The respective relative abundances of ions in the positive-ion mode EI (70 eV) mass spectra of isomers **16a** and **16b**[85] are presented in brackets on Scheme 2. Notably, the slight differences in the detected ion abundances may prove beneficial for isomer differentiation. Mass spectra (70 eV) of isomers **14a, 14b** and **14c** show the $[FMn]^+$ ions resulting from intramolecular rearrangements. It is observed that for each examined isomer, fluorine transfer occurs at different rates[15]. These differences may also be used as a diagnostic tool for isomer differentiation. The structure of some isomeric organomanganese compounds (**19**[212], **20**[78], **21**[78], **22**[266], **23**[336], **24**[266], **25**[243], **26**[63], **27**[250], **28**[336], **29**[334], **30**[400], **31**[328], **32**[326], **33**[383], **34**[446]) for which a range of quantitative or occasionally even qualitative differences in EI mass spectra have been detected is shown below. It should be noted, however, that isomer differentiation remains a challenge for analytical MS studies of organometallic species.



(**19a**)

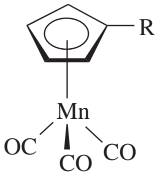


(**19b**)



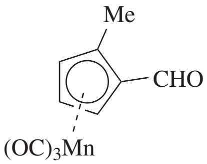
(**20a**) $R^1 = H$, $R^2 = Me$

(**20b**) $R^1 = Me$, $R^2 = H$

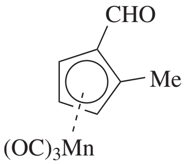


(**21a**) $R = (CH_2)_4CO_2H$

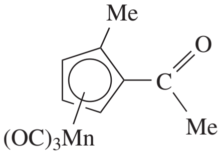
(**21b**) $R = CH(CH_3)CH_2CO_2CH_3$



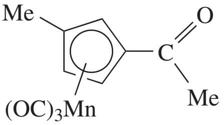
(**22a**)



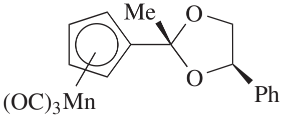
(**22b**)



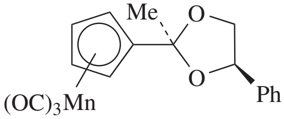
(**23a**)



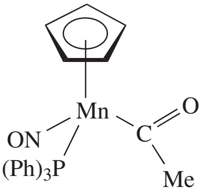
(**23b**)



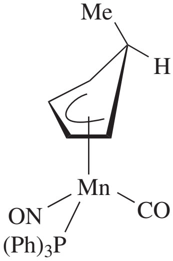
(**24a**)



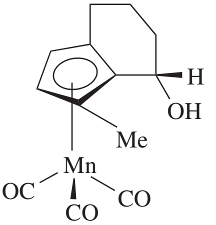
(**24b**)



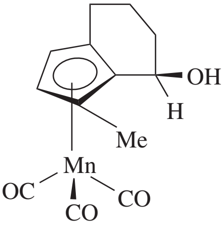
(**25a**)



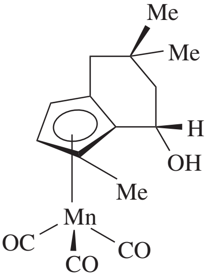
(**25b**)



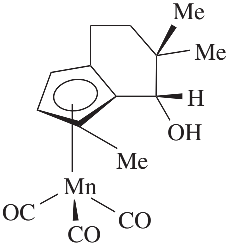
(**26a**)



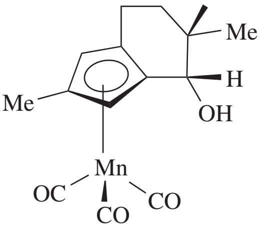
(**26b**)



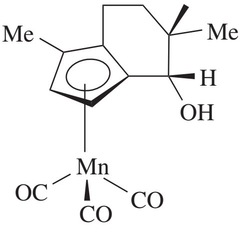
(**27a**)



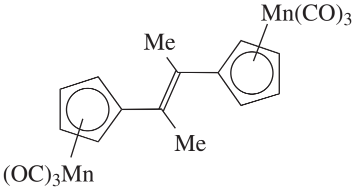
(**27b**)



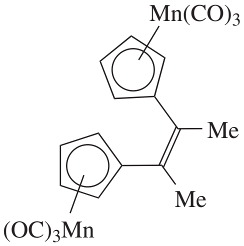
(**27c**)



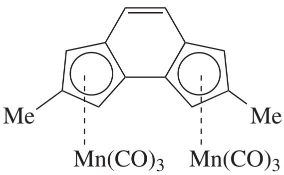
(**27d**)



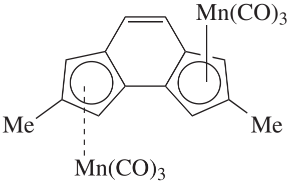
(**28a**)



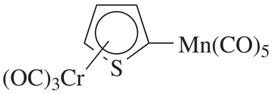
(**28b**)



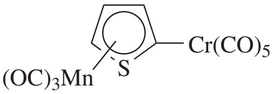
(**29a**)



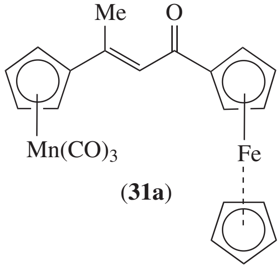
(**29b**)



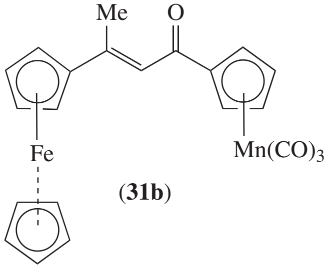
(**30a**)



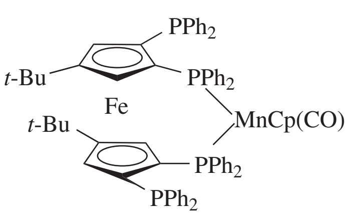
(**30b**)



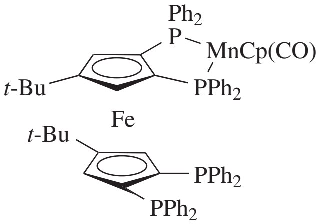
(**31a**)



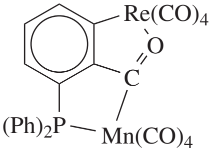
(**31b**)



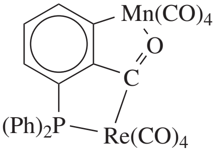
(**32a**)



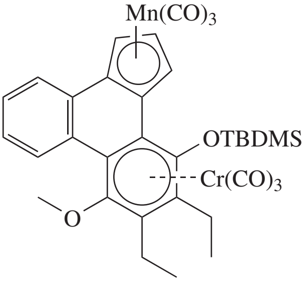
(**32b**)



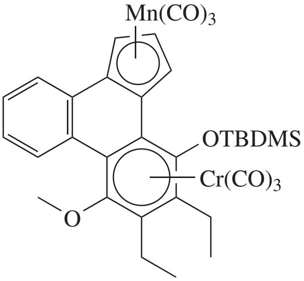
(**33a**)



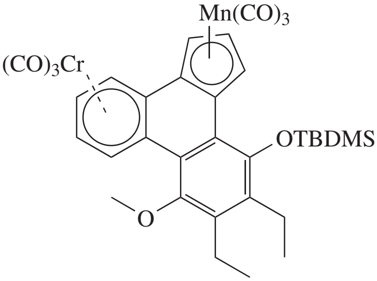
(**33b**)



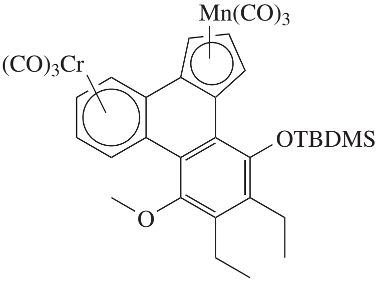
(**34a**)



(**34b**)



(**34c**)



(**34d**)

(TBDMS = *tert*-butyldimethylsilyl)

Operti and coauthors[71] studied doubly charged ions in the positive-ion mode EI mass spectra of mono- and binuclear metal carbonyl derivatives. In the mass spectrum of $Mn_2(CO)_{10}$, the total charge transported by doubly charged ions was less than 0.1%, when the IE was 40 eV. At 70 eV, the doubly charged ions showed a relative abundance (r.a.) of 1%. An IE increase to 100 eV led to a corresponding increase in the contribution of doubly charged ions to *ca* 3.5%. At IE = 100 eV, the following doubly charged ions were detected: $[M - 7CO]^{2+}$ (r.a. 1.5%), $[M - 8CO]^{2+}$ (r.a. 2%), as well as other species with r.a. lower than 0.5% ($[Mn(CO)_3]^{2+}$, $[Mn(CO)_2]^{2+}$ and $[MnCO]^{2+}$). In $Mn(CO)_5X$ **(35–37)** compounds (where X = Cl, Br and I), the presence of the halogen atom increases the stability of doubly charged ions. For instance, the mass spectrum of $Mn(CO)_5Cl$ recorded at 100 eV comprises twelve different manganese-containing doubly charged cations representing *ca* 8.8% of the total ion current[71].

The negative-ion mode EI MS behavior of a series of organomanganese complexes has been studied as well[64, 90, 104, 128,460–462]. Winters and Kiser[104] reported both negative-ion mode EI (85 eV) and positive-ion mode EI (70 eV) mass spectra of decacarbonyldimanganese, $Mn_2(CO)_{10}$, **3**. Meckstroth and Ridge[128] studied $Mn_2(CO)_{10}$ and decacarbonylmanganeserhenium, $ReMn(CO)_{10}$, **4**, at two different IEs (80 eV and 5 eV). Both laboratories concluded that under negative-ion mode EI MS conditions fragmentation of the metal carbonyls **3** and **4** occurs through the successive removal of CO ligands. In all reported mass spectra (IE = 85, 80 or 5 eV) of these two compounds, the peaks with the highest *m/z* were those of the $[M - CO]^-$ fragment ions. The negative-ion mass spectra at 70 eV of $Mn(CO)_5X$ **(36, 37)** (where X = Br or I) consist of the following ions: $[M - n\text{CO}]^-$ ($n = 1–5$)[64]. The binuclear complex $Mn_2(CO)_{10}Br_2$ **(38)** did not generate a negatively charged molecular ion (M^-) or $[M - CO]^-$ fragment at 70 eV. The peak with the highest *m/z* value in the mass spectrum of **38** was that of the $[M - 2CO]^-$ ion[64]. Blake and coauthors[90] examined cymantrene and its methyl derivative $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ **(39)** at 70 eV (negative-ion mode MS). The spectra are devoid of the negative molecular ion which, as discussed above, is usual for carbonyl-containing species. Interestingly, the peaks with the highest *m/z* value in the negative-ion mode mass spectra of cymantrene and its methyl derivative were those of $[M - H]^-$, not those of the fragment ions corresponding to the loss of CO groups as attested for other manganese carbonyl derivatives. The base peak in the mass spectra of these two compounds (**5** and **39**) was assigned to the $[M - CO]^-$ fragment ion. This anion arises from a reductive decarbonylation of the precursor molecule[90].

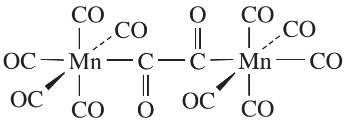
Mavrodiev and coauthors[462] studied the *resonance capture of electrons* by cymantrene derivatives $(RCp)Mn(CO)_3$ (for R = H (**40**), CN (**41**), CHO (**42**), C(O)Me (**43**), CH_2OH (**44**), C(O)OMe (**45**), $CH(Me)NH_2$ (**46**) and $n\text{-}C_5H_{11}$ (**47**)), $(1,3\text{-}CHO,(NMe_2)Cp)Mn(CO)_3$ **(48)** and $(Me_5C_5)Mn(CO)_3$ **(49)**. The presence of negatively charged molecular ions in the mass spectra of resonance capture of electrons depends on two competing factors: their stability relative to the autodetachment of an electron (which depends on the electron affinity and the number of vibrational degrees of freedom of the studied molecule) and their lifetime relative to dissociation (which is determined by the strength of the chemical bonds)[460–463]. Consequently, cymantrene derivatives containing both strong electron-withdrawing (**41, 42**) and electron-donating (**44, 46, 47, 49**) substituents do not form long-lived (on the mass spectral time scale of 1–10 ms) M^- species. On the other hand, the introduction of a dimethylamino group into the formylcymantrene molecule (**48**) results in the appearance of the negatively charged molecular ion peak in its mass spectrum. For compounds **43, 45** and **48**, the average lifetimes of the M^- relative to the autodetachment of an electron (τ_a) and to dissociation (τ_d) were measured. It was determined that electron-accepting substituents increase the τ_a value and decrease the τ_d value. The successive loss of CO groups is a primary fragmentation process for compounds **40–49** when examined under resonance capture of electrons conditions. The most abundant anion in all instances was $[M - CO]^-$. For the examined cymantrene derivatives, metastable transitions supportive of the sequential loss of CO groups were also detected. Compound **48** was the only one of the examined species for which the metastable transition $[M - CO]^- \rightarrow [M - 3CO]^-$ (loss of 56 u) was observed[462]. Some other negatively charged gaseous organomanganese species are discussed later in this chapter in the context of ion/molecule reactions and ion structures.

Chemical ionization mass spectrometry (CI MS) has been applied for the investigation of a number of organomanganese complexes[420–427,464–472], such as mono- and polynuclear derivatives of manganese carbonyl compounds, as well as of cymantrene and manganocene. Generally, these studies revealed that the positive-ion mode CI mass spectra of manganese-containing species comprise the $[M + H]^+$ peak and fragment ion peaks (usually produced via loss of the CO groups or other available monodentate ligands).

In some cases, they display the M^+ peak. The $[M + H]^+$ peak is generated as a result of the protonation reaction of the analyte by the CI reagent (typically in the $[\text{reagent} + H]^+$ form). M^+, on the other hand, is produced by a charge transfer process due to the relatively low ionization potentials of the metal complexes[420]. A variety of CI reagent gases were used for the analysis of organomanganese compounds, such as hydrogen[465], methane[420–423,465,470], ammonia[422,424,465] and isobutane[427,464,465,468]. Generation of $[M + H]^+$ and M^+ species depends primarily on the nature of the CI reagent used and the structure of the examined metal(s)–ligand(s) system, which may offer different sites of protonation. Experimental conditions such as ionization chamber pressure and temperature may also influence the yield of $[M + H]^+$ and M^+ ions[420,421,465]. In spite of the perception that CI MS is a soft ionization method, organomanganese complexes must be treated with caution during the MS experiment, because harsh experimental conditions may result in the absence of the $[M + H]^+$ (and if this is the case, of the M^+) ion peaks in the mass spectra. Under harsh MS conditions only the fragment ions have a chance to survive and be detected. In some conditions formation of the $[M + n(\text{CI reagent}) + H]^+$ species—products of the ion/molecule reactions—has been observed as well (e.g. $[M + NH_4]^+$ and $[M + 2NH_3 + H]^+$)[422,465]. By studying cymantrene and its derivatives $(RCp)Mn(CO)_2L$ (where $R = MeCO, L = CO$ for **(50)**, $R = H, L = NHMe_2$ for **(51)**, $R = H, L = SOMe_2$ for **(52)**, and $R = H, L = NCC_6H_{11}$ for **(53)**), Müller and Hänsch[421] observed that at elevated sample pressures ion/molecule reactions occur, generating secondary ions of di-, tri- and higher-nuclearity in considerable quantities. Gaseous ion/molecule reactions in which organomanganese species are involved are discussed later as a separate subject. The potential use of the manganese cation and $[ClMn(H_2O)]^+$ ion as soft CI reagents[473–475] is also addressed in the same context.

In what the negative-ion mode CI MS of organomanganese compounds is concerned, published information is scarce[426,464,466,467,471]. Mass spectra of most organomanganese complexes analyzed by this MS technique do not contain negatively charged molecular ion peaks[426,464,466,471]. For example, under negative-ion mode CI MS conditions, the ethane-1,2-dionyl compound $Mn_2(CO)_{12}$ **(54)** generated only fragment ions, $[Mn(CO)_n]^-$ ($n \leq 5$). No dimanganese fragments were detected[464]. When investigated using the same technique, carbonylpentamanganese cluster, $[(\mu\text{-H})Mn_5(CO)_{17}]^{2-}$ **(55)**, produced numerous fragment ions of the general formulae $[HMn_x(CO)_y]^-$ and $[Mn_x(CO)_y]^-$ (where $x = 1–5$ and $y = 2–15$ depending on the number of the metal atoms)[466]. Complex **56** generated several ions incorporating two manganese atoms, but lacked the molecular ion[471]. On the other hand, the dimer $[\{Mn(CO)_3\}_2\{\mu(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$ **(57)**, the result of the reductively induced dimerization of the ligated benzene in the monomer precursor, produced a strong negatively charged molecular ion (r.a. *ca* 30%), together with $[M - 2]^-$ species. The $[M - 2]^-$ arose from H_2 elimination (presumably across the bridgehead) since there are similar $[M - 3]^-$ and $[M - 4]^-$ peaks (from HD and D_2 elimination) below the molecular ion peaks of d_6-**57** and d_{12}-**57** in their respective mass spectra[467].

Overall, both the prevalence of the metal–ligand bond cleavage fragmentation pathway in organomanganese species under MS conditions and the monoisotopic nature of manganese significantly aid fragment ion assignment. They also facilitate the accurate determination of ion abundances when examining the presence/absence or addition/elimination of hydrogen(s) (H^+, $H^\bullet$ or H_2)[92,466,467,476]. From the same perspective, when working with isotopically labeled species[13,15–43], ion assignment is effectively accurate and, if applicable, the isotope effects may be determined with considerable precision. The presence of polyisotopic element(s) in the studied species increases the complexity of isotope clusters in the mass spectra. To avoid the misinterpretation of the MS data in such cases, some authors compare the experimental isotopic distribution patterns of the examined species to calculated ones[409,410,477–487], whereas others take the approach of transforming the experimental mass spectra to the monoisotopic form computationally[92].



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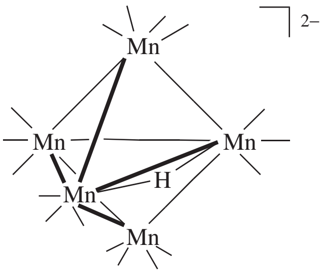
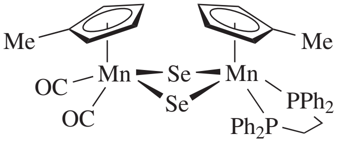


(**55**) $[(\mu\text{-H})Mn_5(CO)_{17}]^{2-}$



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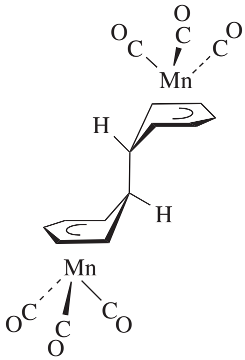
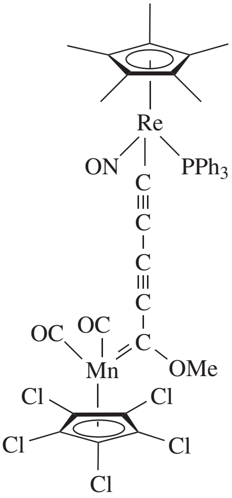


(**57**)

B. Fast Atom Bombardment and Electrospray Ionization Mass Spectrometry

Fast atom bombardment mass spectrometry (FAB MS) provides softer experimental conditions by comparison to EI MS, and for that reason it was the next analytical mass spectrometric method of choice for the analysis of organomanganese complexes (at least until the introduction of yet another soft ionization method, electrospray ionization mass spectrometry[488]). FAB MS has been used to investigate cyanometalate complexes[445, 489, 490], mono- and polynuclear derivatives of manganese carbonyl compounds and cymantrene[428–444,446, 481, 482, 484,490–536], including non-volatile, ionic and high-molecular weight complexes, such as *meso*-metallocenylporphyrins[435], wirelike cumulenic carbon chains that span two metallocenyl fragments (e.g. **58, 59**)[512], double helix mixed-metal cluster containing cymantrene units (**60**, $Cp' = C_5H_4Me$)[517], manganospiralenes[436, 439], manganoscorpionates[531], bifunctional compounds containing organometallic and Werner-type coordination sites (e.g. **61, 62**)[438, 441, 521].

Positive-ion mode FAB mass spectra of neutral organomanganese complexes usually contain $[M + H]^+$ and some fragment ion peaks. For example, such behavior was indeed displayed by the neutral molecule **63**, a synthetic precursor of the ionic compound **62**[441]. The peaks of $[M + Na]^+$ and $[M + K]^+$ may also be seen in the spectra along with the peak of the protonated analyte molecule, if sodium and/or potassium cations are present in the analyzed samples at the adequate concentrations. Jennings and coauthors[489] reported that under positive-ion mode FAB MS conditions even ionic complex $K^+{}_3[Mn(CN)_5(NO)]^{3-}$



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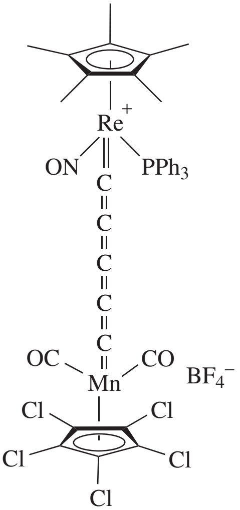

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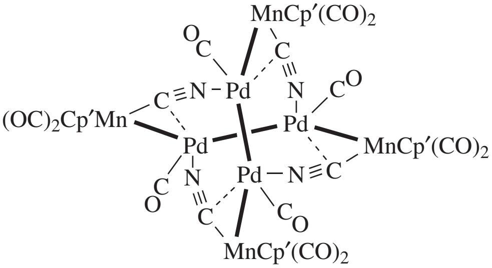

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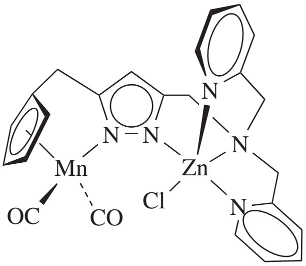

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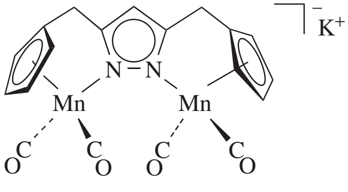

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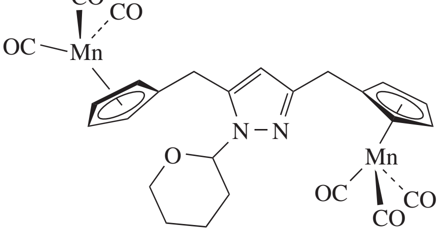
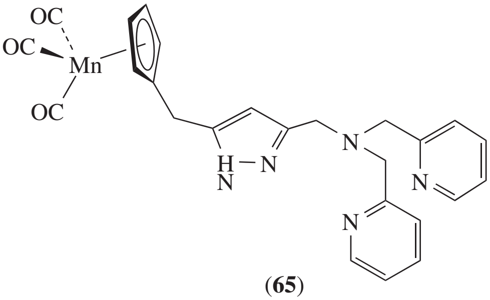


(**63**)



(**65**)

(**64**) generates [**64** + H]$^+$ (m/z 333, r.a. 75%) and [**64** + K]$^+$ (m/z 371, r.a. 100%) species, the latest ion [**64** + K]$^+$ incorporating a total of four potassium cations. Sporadically the [M + (solvent molecule) + H]$^+$ has been detected as well by the same method[429, 491]. Under FAB conditions the ionic compounds M$^+$A$^-$ (where A$^-$ is the counter ion) normally generate M$^+$ species in positive-ion mode detection. A good example is ionic complex **59** (produced from precursor **58** treated with excess BF_3 gas)[512]. In some circumstances redox reactions may also occur during the FAB MS experiment and, under such conditions, neutral organomanganese species may produce M$^+$ along with or instead of the expected [M + H]$^+$. For example, the neutral compound **61** generated M$^+$ (m/z 567, r.a. 15%), as demonstrated by means of high resolution MS and comparison of the experimental and simulated isotopic distribution patterns of the detected ion[438]. Interestingly, Röder and coauthors[441, 521] reported that the positive-ion mode FAB mass spectrum of the ionic complex **62** consists of the following ion peaks: M$^+$ (m/z 482), [M − K]$^+$ (m/z 443) and [M − K − 2CO]$^+$ (m/z 387) (where M = **62** = $C_{19}H_{13}KMn_2N_2O_4$). Evidently, formation of the enumerated ions can be rationalized by a change in the oxidation state of the manganese atoms in the analyte **62** during the FAB experiment.

Positive-ion mode FAB MS was also used to investigate the processes occurring in solutions of (arene)manganese dicarbonyl derivatives[495]. It was determined that relative abundances of some solution organometallic species are dependent on the sample age and storage temperature. As reported by Palii and coauthors[537], MS monitoring of processes occurring in solutions involving metal(s)/ligand(s) systems through recurrent sampling over a given interval of time may lead to the development of new synthetic methods or provide guidance for preparative studies. Such synthesis approaches are illustrated by the *aged solution strategy* and site-directed gradual replacement of terminal ligands via supramolecular assemblies, both developed for preparation of mixed-terminal-ligand polynuclear complexes[537].

Some organomanganese complexes have been analyzed by means of negative-ion mode FAB MS[438, 482, 492, 530, 532]. For neutral compounds, the formation of [M − H]$^-$ is anticipated, if the structure of the analyte favors it[438, 492] (e.g. complex **65**). For some neutral mixed-metal clusters, the detection of M$^-$ was also reported as a result of redox reactions[482, 530]. This MS method proved to be gentle indeed by allowing the detection of species like [M + (matrix molecule)]$^-$ along with M$^-$ ion[530]. As expected, ionic complexes of the general formulae Cat$^+$M$^-$ (where Cat$^+$ = positively charged counter ion, M$^-$ = negatively charged organomanganese complex) generate M$^-$ species under negative-ion mode FAB MS conditions[532].

Electrospray ionization mass spectrometry (ESI MS) is recognized as a soft ionization method, which allows for the transfer of ionic species preexisting in solution to the gas phase[488]. In the last two decades, this technique has become popular in MS studies of almost all classes of organic and metal-containing species. Organomanganese compounds are not an exception[445–448,469,483,485,486,490,532–536,538–570]. Under ESI (positive-ion mode) conditions neutral organomanganese complexes generate protonated and/or cationated (usually by Na^+ and/or K^+) analyte molecules, either alone or along with fragment ions, generally resulting from metal–ligand bond cleavage processes. In the negative-ion mode of detection, $[M - H]^-$ is expected for neutral organomanganese compounds containing acidic hydrogen atoms. Depending on the polarity of the apparatus, the ESI environment predisposes the redox active neutral organomanganese species to also generate M^+ or M^-. Finally, the charged constituents of the ionic organomanganese complexes are normally transferred intact by the ESI device from solution to gas phase, in conformity with the operated instrument polarity. For example, the ionic supramolecular tetranuclear compound $[L\{Mn(CO)_3\}_4]^{4+}(BF_4{}^-)_4$ **(66)** (where L represents multitopic ligand prepared by linking tripodal tris(pyrazolyl)methane units in a single molecule, $C_6H_2[CH_2OCH_2C(pz)_3]_4$) generated $[L\{Mn(CO)_3\}_4(BF_4)_3]^+$ (*m/z* 1919) and fragment ions $[L\{Mn(CO)_3\}_3(BF_4)_2]^+$ (*m/z* 1693), $[L\{Mn(CO)_3\}_2(BF_4)]^+$ (*m/z* 1467) and $[L\{Mn(CO)_3\}]^+$ (*m/z* 1241) in positive-ion mode ESI MS[550]. The negative-ion mode ESI mass spectrum of the ionic fullerene-60 complex $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-Na^+$ **(67)** (Figure 3) consists of a $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ (*m/z* 887) base peak[486,544,547]. Under identical MS conditions, higher fullerene complexes $[Mn(CO)_4(\eta^2\text{-}C_n)]^-Cat^+$ **(68–79)** (where Cat^+ is a positively charged counter ion, $n = 70$, 76, 78, 80, 82, 84, 86, 88, 90, 92, 96 and 98) generated M^- species[547,551], in a manner similar to the fullerene-60 complex **67**[486,544,547]. In general, this soft ionization method has been successfully applied for the investigation of neutral, ionic, high-molecular weight manganese-containing (mono- and polynuclear) compounds and even complex mixtures of molecular species[445–448,469,483,485,486,490,532–536,538–570].

Bioconjugates of cymantrene derivatives with biotin[570] and most recently of cymantrene or $[Mn(CO)_3\{tris(pyrazolyl)methane\}]^+$-based derivatives with peptides (enkephalin, neurotensin, pseudoneurotensin, HIV transactivator of transcription protein, etc.)[566–569] have also been analyzed using ESI MS. The labeling of physiologically active molecules with metal complexes for applications in the diagnosis and therapy of human diseases is of

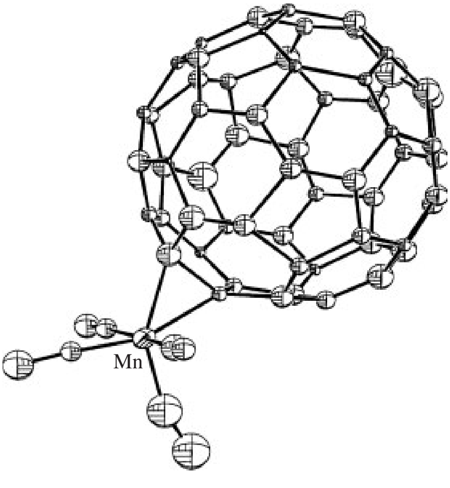


FIGURE 3. Molecular structure of the anion of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-Na^+$ **(67)** complex. Adapted from Reference 544 with permission from the American Chemical Society

ongoing interest, and from this standpoint mass spectrometry is an ideal analytical method for structure determination, purity control and trace detection of newly synthesized conjugates. Under ESI conditions neutral cymantrene-peptide bioconjugates behave not unlike other neutral organomanganese complexes described above, but with one significant difference: the mass spectra of labeled peptides recorded in the positive-ion mode also include peaks for multicharged species $[M + nH]^{n+}$ ($n = 2$–6)[566–568].

Multicharged species may also be detected in the negative-ion mode, provided that such anions preexist in solution. Some ionic organomanganese clusters containing M^{2-} polynuclear cores subjected to ESI MS analysis generated intact M^{2-} entities[539, 548]. Fullerenes larger than C_{60} containing two manganesetetracarbonyl units, $[\{Mn(CO)_4\}_2(C_n)]^{2-}2Cat^+$ ($n = 76, 78, 84, 92$) also produced the intact M^{2-} species under negative-ion mode ESI[551].

ESI MS analysis of neutral organomanganese complexes by derivatization with alkoxide ions has been described in a series of publications[540, 554, 561,571–573]. Derivatization of analyte molecules by OR^- in ROH solvents (usually a NaOMe/MeOH system) allows for their ESI MS characterization by producing stable $[M + OR]^-$ species. The NaOR/ROH systems (where R stands for Et or *i*-Pr) were tested under the same MS conditions for a variety of organometallic compounds, including Mn-containing ones[571].

ESI MS detection of adduct species such as $[M + Solv + H]^+$ (where Solv is a solvent molecule) and $[M + NH_4]^+$ (where NH_4^+ acts as ionization agent) has been reported for some neutral organomanganese compounds[447, 574, 575]. Generally, ESI MS data must be analyzed with caution, because ions like $[M + x\mathrm{Solv} \pm y\mathrm{H}]^{z+/-}$, which are sometimes produced under soft ionization conditions, may lead to misinterpretation of analyte structure.

Additional MS structural information can be obtained by dissociation techniques. ESI MS allows for an exclusive dissociation method—in-source CID. For example, this method was used for characterization of the fullerene derivative $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ by varying cone voltages[544]. Matching data were obtained by traditional CID MS/MS (using Ar as the target gas) by the same authors[486]. Furthermore, comparison of the energy-resolved CID MS/MS data for $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ with similar data for $[Mn(CO)_5]^-$ suggests that fullerene complex **67** contains weaker Mn–CO bonds[486].

C. Other MS Ionization Methods

Field desorption mass spectrometry (FD MS) is another valuable method for obtaining detailed information about the composition and molecular weight of unstable or nonvolatile organometallic species[576–579]. A series of neutral organomanganese compounds has been investigated with this method for analytical purposes[449–455,480, 481, 530, 531,576–580]. In most cases, only the molecular ions were generated, although in some cases fragment ions could be observed as well. In this way, for $Mn_2(CO)_{10}$, the molecular ion dominated the FD mass spectrum, with $[Mn(CO)_5]^+$ (r.a. 1.5%) as the only other ion of significance[576]. Positive-ion mode FD mass spectra of cationic organomanganese species, M^+A^- (where A^- is the counter ion), consist of M^+ peaks. Occasionally, the M^+ base peak in the mass spectra of such complexes is accompanied by low abundance peaks of the $(M^+A^-)_nM^+$ associate ions[449, 578, 579].

Laser desorption/ionization (LDI) is an alternative method for generating ionic species to investigate their gas-phase structure and reactivity in ion/molecule reactions by MS. Additionally, it was observed that under LDI conditions the analyte is able to produce ions with masses higher than its own. Some manganese-containing organometallic species studied with LDI MS[274, 581–583] behaved in the described manner. Dyson and coauthors[583] reported positive- and negative-ion mode UV laser-induced desorption/ionization mass spectra for the trinuclear cluster $Mn_3H_3(CO)_{12}$ **(80)**. Besides the peak corresponding to the molecular ion of trinuclear cluster **80**, the mass spectra also contain peaks in the higher mass range, corresponding to a series of condensed products. For example, in the negative-ion mode, clusters with the general formulae $[Mn_xH_{x-1}(CO)_{4x}]^-$ (where $x = 4-9$) have been detected. It was proposed that such new clusters have cyclic structures formed by the stepwise insertion of $[MnH(CO)_4]$ units into a metal–metal bond. The largest cluster detected in the positive-ion mode was $[Mn_7H_7(CO)_{29}]^+$ (*m/z* 1204)[583]. Suzuki and coauthors[581] investigated the formation and stability of MnC_n clusters with the same technique. Barrow and coauthors[274] reported a remarkable result for penta(cyclopentadienyl)-η^5-cyclopentadienylmanganesetricarbonyl, $(Cp_5Cp)Mn(CO)_3$ **(81)**: it was shown that under LDI MS experimental conditions, complex **81** undergoes dissociative coalescence to fullerene-C_{60} and other carbon clusters. This is just another example demonstrating the value and predictive ability of MS techniques in the search for new synthetic methods.

Multiphoton ionization (MPI) and dissociation (MPD) of organomanganese species[584–610] are discussed later in the context of photodissociation studies.

IV. ORGANOMANGANESE ION STRUCTURE AND ENERGETICS

A. Energetics and Photodissociation Studies

Gas-phase studies involving organometallic species have generated a wealth of valuable thermodynamic data, such as homolytic and heterolytic metal–element (Met–H, Met–C, Met–O, etc.) bond strengths, relative ligand binding energies for coordinated and atomic metal ions, gas-phase basicities, hydride affinities, electron affinities, and ionization potentials for neutral metal complexes[3–12]. In conjunction with experimental findings and theoretical calculations, the thermodynamic data greatly facilitate assessment of reaction pathways and understanding of the mechanisms of chemical reactions. An elegant example of a study concerning a Mn^+-mediated reaction in the gas phase is represented in Figure 4. It was by BEBE configuration four-sector mass spectrometer

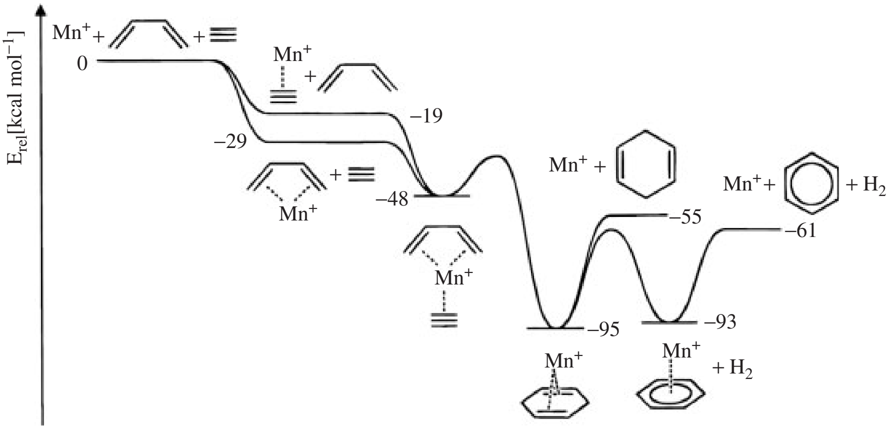


FIGURE 4. Qualitative potential-energy surface for the Mn^+-mediated [4 + 2] cycloaddition of butadiene and acetylene in the gas phase. Reprinted with permission from Reference 611. Copyright 1997 American Chemical Society

(B, E, for magnetic and electric sectors, respectively) and FT-ICR MS instrument that this comprehensive research was performed[611].

The manganese–ligand bond dissociation energies were measured experimentally and estimated theoretically for a series of Mn-containing gas-phase ions using different methods. Bond dissociation energy (BDE), appearance potential (AP) and ionization potential (IP) (adiabatic and vertical) are the primary data measured by MS equipment[17, 20, 21, 74, 93, 95, 96, 100–168, 612, 613], photodissociation (PD) techniques[584–610] and photoelectron spectroscopy (PES)[612–657] in studies involving organomanganese species. Literature analysis shows that early publications regarding the BDEs of manganese-containing entities are subject to some controversy, as evidenced by a number of reports[131, 133, 168, 613]. The attested differences may well be due to the specifics or limitations of the utilized methods. For example, photodissociation occurs from excited-state surfaces, but CID experiments may well be sampling ground-state surfaces or excited states of the examined species. Starting in the early 1990s, high resolution (*ca* 0.1 eV) photoelectron spectroscopy was applied to organometallic (including organomanganese)[646] compounds instead of the low resolution (> 1 eV) or medium resolution (*ca* 0.5 eV) PES used largely until that time. Use of high resolution PES much improved measurements and informativeness of the data, especially if employing tunable monochromatized radiation. Critical discussion of the reports concerning particular BDEs is beyond the scope of this review. Uppal and Staley[658] reported relative ligand binding energies for Mn^+ with 33 organic molecules. Larsen and coauthors[141] also estimated experimentally the relative strength order of bonds to Mn^+ for several ligands: $D°(Mn^+{-}H_2S)$, $D°(Mn^+{-}H_2O)$, $D°(Mn^+{-}CH_3SH) < D°(Mn^+{-}Mn)$, $D°(Mn^+{-}CH_2O)$, $D°(Mn^+{-}CH_3OH) < D°(Mn^+{-}C_2H_5OH)$, $D°(Mn^+{-}n\text{-}C_3H_7OH)$, $D°(Mn^+{-}t\text{-}C_4H_9OH)$, $D°(Mn^+{-}\text{acetone})$. Armentrout[659] reviewed guided ion beam studies of transition metal–ligand thermochemistry and reported the following values for Mn-containing gas-phase ions: $D°(Mn^+{-}H) = 199(14)\,kJ\,mol^{-1}$, $D°(Mn^+{-}CH_3) = 205(4)\,kJ\,mol^{-1}$, $D°(Mn^+{-}CH_2) = 286(9)\,kJ\,mol^{-1}$, $D°(Mn^+{-}O) = 285(13)\,kJ\,mol^{-1}$ and $D°(Mn^+{-}S) = 243(23)\,kJ\,mol^{-1}$. Rodgers and coauthors[660] summarized the periodic trends in the metal ion–ligand BDEs determined by energy-resolved CID (for the ligands: carbonyl, ethene, water, benzene, ammonia, pyridine). As can be seen in Figure 5, the largest deviations in behavior are observed for Mn^+. For all examined ligands, the Mn^+–ligand bond dissociation energy is the lowest measured of all transition-metal cations. The ligand bond to Mn^+ is the weakest bond due to the fact that the ^7S ground electronic state (Table 1) has no empty orbitals for accepting electron density. It should be noted, however, that water does not show a highly pronounced dip for manganese cation, as other ligands do (Figure 5)[660].

B. IRMPD Spectroscopy

Infrared multiple-photon dissociation (IRMPD) spectroscopy is a highly sensitive technique which has been successfully employed to obtain detailed binding information on metal ion-organic ligand complexes. This method offers the opportunity to directly probe the 3D structural features of gas-phase ions. MacAleese and Maître[663], Eyler[664], Polfer and Oomens[665] and Fridgen[666] have reviewed the application of this technique to the study of metal-containing species.

IRMPD occurs through non-coherent absorption of tens to hundreds of IR photons when the laser frequency matches a vibrational mode of the gas-phase ion. The energy is distributed over all vibrational modes by intramolecular vibrational redistribution, which allows the energy of each photon to be ‘relaxed’ prior to the absorption of the next photon, and thus allows promotion of the ion’s internal energy to the dissociation threshold[667].

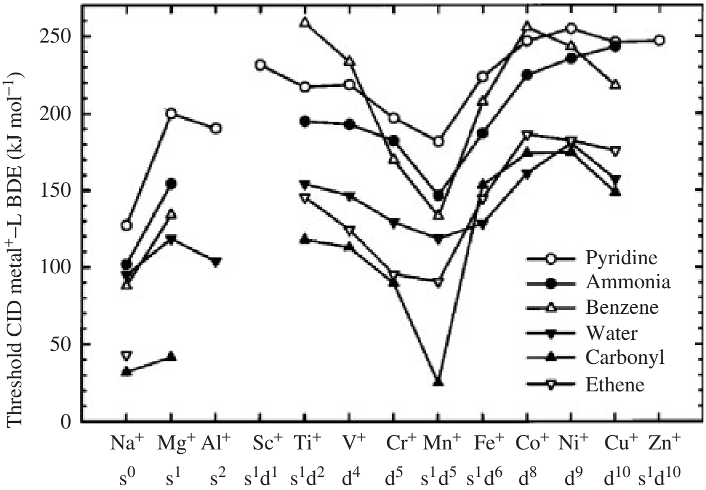


FIGURE 5. Comparison of the periodic trends in the metal$^+$–L bond dissociation energies determined by collision-induced dissociation. Ligands, L, include pyridine, ammonia, benzene, carbonyl, ethene and water. Ground-state electron configurations are provided for each metal ion. Reprinted with permission from Reference 660. Copyright 2000 American Chemical Society

TABLE 1. Some electronic states of Mn^+ and their distributions at different ion source operational parameters of the mass spectrometer

State[a]	Electron configuration	Energy (eV)[b]	Distribution (%)			
			SI[c]	EI (25 eV)[d]	EI (30 eV)[d]	EI (50 eV)[d,e]
^7S	$3d^5 4s^1$	0.0	99.72	90	70	50
^5S	$3d^5 4s^1$	1.175	0.22	3	5	10
^5D	$3d^6$	1.808	0.05	0.6	1.7	3.4

[a] Ionization potential for ^7S state is 7.44 eV, for ^5S state is 8.61 eV and for ^5D state is 9.22 eV; values are from References 148 and 661.
[b] Energy is a statistical average over the J levels; values are from Reference 662.
[c] Maxwell–Boltzmann distribution at 2375 K of the SI ion source filament[147].
[d] Distributions estimated for Mn^+ generated by EI of $Mn_2(CO)_{10}$ complex[143].
[e] EI ion source generates a non-Boltzmann distribution of electronic states with more excited ions.

This method has been employed to investigate $[Mn(CO)_n(CF_3)]^-$ ($n = 2$–5), $[Mn(CO)_3(CF_3)(NO)]^-$, $[Mn(CO)_4(CF_3)(I)]^-$, $[Mn(CO)_3(\eta^5\text{-}C_5H_4R)]^+$ (R = H, CH_3), $[Mn(CO)_n]^+$ ($n = 6$–9), $[Mn(CO)(Ar)_3]^+$ (Ar = argon), $[Mn(CO)_2(Ar)_2]^+$, $[Mn(CO)_n(Ar)]^+$ ($n = 3$–6) and $[Mn(tryptophan)_2]^{2+}$ organomanganese species[28, 668–672]. To date, Shin and Beauchamp[28, 668, 669] reported the most detailed IRMPD spectra of selected organomanganese anions and proposed the CF_3 group as an ideal infrared chromophore for investigating the IR photochemistry of coordinatively unsaturated organometallic intermediates containing metal-bonded CF_3 groups. The trifluoromethyl migratory decarbonylation reaction in the gas phase was studied in detail for $[Mn(CO)_n(CF_3)]^-$ ($n = 2$–4) species. Additionally, IRMPD and CID were used to identify two pairs of structural isomers with the general formula $[Mn(CO)_n(CF_3)]^-$ (where $n = 5$ for the first pair and $n = 4$ for the second). These isomers have been generated from different precursors, $(CF_3CO)Mn(CO)_5$ **(82)** and $(CF_3)Mn(CO)_5$ **(83)**[28]. Majima[670] examined cymantrene and its methyl derivative by several methods. It was shown that in short-pulsed IRMPD, the initial process is the dissociation of the Mn$-$(η^5-C_5H_4R) bond, rather than the Mn$-$carbonyl bond, as in UV photolysis and thermolysis. It was suggested that under IRMPD conditions the Mn$-$(η^5-C_5H_4R) dissociation occurs through effective IR multiple-photon excitation of molecules to high vibrational states. Reed and Duncan[671] investigated the geometries and electronic states of $[Mn(CO)_n]^+$ ($n = 6$–9), $[Mn(CO)(Ar)_3]^+$ (Ar = argon), $[Mn(CO)_2(Ar)_2]^+$ and $[Mn(CO)_n(Ar)]^+$ ($n = 3$–6) species by comparing their infrared spectra to the theoretically predicted ones. It was concluded that the spin multiplicity of $[Mn(CO)_n]^+$ complexes gradually decreases with progressive ligand addition. Dunbar and coauthors[672] investigated the $[Mn(tryptophan)_2]^{2+}$ complex along with analogs of other doubly charged metal ions by IRMPD spectroscopy and supported the experimental findings by theoretical calculations. This study showed that in the gas phase the investigated metal complexes can adopt different geometries. The spectra indicated a mixed charge-solvated (CS)/zwitterionic (ZW) conformation for the manganese analog.

C. Gas-phase Ion/Molecule Reactions

In spite of the prevailing opinion that gas-phase ion chemistry of manganese with predilection to ion/molecule reactions is relatively scarcely described compared to that of other transition metals, literature analysis reveals *ca* 300 examples of such reactions characterizing the reactivity of various Mn-containing species. Table 2 summarizes the majority of reports to date on ion/molecule reactions in which Mn^+, positively or negatively charged manganese clusters, as well as cations, anions and neutrals of manganese-containing species have been investigated. Studies of multicoordinatively unsaturated metal-containing particles are possible only in the gas phase or in nonreactive matrices, where conventional solvents are absent. Therefore, a large variety of MS techniques has been employed to investigate those reactions, as well as the structure and reactivity of the involved reactants. The primary ionization methods applied for ion generation to be examined herein are EI, CI, SI, FAB, ICP, DC/FT, LD/LI and MPI (Table 2).

The ground-state manganese cation has relatively poor reactivity, in particular with respect to C$-$H and C$-$C bond activations when compared to other transition-metal ions[6,7,145]. This inertness of Mn^+ has been attributed to its very stable high-spin half-filled 3*d* shell[730]. In contrast to the ground electronic state of Mn^+ (^7S), the excited states (^5S and ^5D) react with alkanes, including C$-$C bond cleavage of ethane[731]. For the ground-state manganese cation (^7S), exothermic reactions have only been observed with unsaturated hydrocarbons as large as 4-octyne[26,146,699], the latter exhibiting much larger complexation energies than alkanes[4,6]. Therefore, studying the state-specific reactions of Mn^+ or Mn-containing ions with neutrals may indeed elucidate intrinsic properties of this charged species. The proper choice of ionization method, MS apparatus, as well as precursor compound are all crucial to the success of such experiments. Some electronic states of Mn^+, along with their distributions at different ion source operational parameters, are listed in Table 1. Elkind and Armentrout[143] estimated electronic state populations in the Mn^+ beams generated by SI and EI (at 25, 30 and 50 eV). Rue and coauthors[165] estimated electronic state populations in the beams of Mn^+ produced from $MnCl_2$ at various temperatures (2050, 2200 and 2350 K) of the SI ion source filament.

TABLE 2. Gas-phase ion/molecule reactions involving Mn-containing and C-containing species[a]

Ionization (MS)[b]	Ion	Reagent	Major product ion(s)	Other product ions[c]	Reference
ICP (SIFT-MS)	Mn^+	CH_4	–	–	673
ICP (SIFT-MS)	Mn^+	CH_3F	$[Mn(CH_3F)]^+$	$[Mn(CH_3F)_2]^+$	674
DC/FT (GIB)	Mn^+	C_2H_4	$[Mn(C_2H_4)_{1,2}]^+$	–	162
EI (GIB)	Mn^+	C_2H_6	$[MnCH_3]^+$, $[MnH]^+$	–	145, 147
SSMS	Mn^+	C_3H_6	$[MnCH_3]^+$	–	675
SSMS	Mn^+	C_3H_8	$[MnCH_3]^+$	–	675
EI (FT-ICR)	Mn^+	c-C_3H_6	$[MnCH_2]^+$	–	17
EI or SI (GIB)	Mn^+	c-C_3H_6	$[MnCH_2]^+$	$[MnH]^+$	149
EI or SI (GIB)	Mn^+	i-C_4H_{10}	$[MnCH_3]^+$, $[MnH]^+$	$[C_4H_7]^+$, $[C_4H_9]^+$	149
FAB (HPMS)	Mn^+	i-C_4H_{10}	$[C_4H_9]^+$	$[C_4H_{10}Mn]^+$, $[C_4H_{11}Mn]^+$	676
FAB (MS/MS)	Mn^+	1-pentyne	$[Mn(C_5H_8)_{1,2}]^+$	$[C_{10}H_{15}]^+$, $[C_7H_{11}]^+$, $[C_6H_9]^+$	677
FAB (MS/MS)	Mn^+	2-pentyne	$[Mn(C_5H_8)_{1,2}]^+$	$[C_5H_7]^+$	677
FAB (MS/MS)	Mn^+	1,3-pentadiene	$[Mn(C_5H_8)_2]^+$	$[Mn(C_5H_8)]^+$	677
FAB (MS/MS)	Mn^+	1,4-pentadiene	$[Mn(C_5H_8)_2]^+$	–	677
FAB (MS/MS)	Mn^+	2-methyl-1,3-butadiene	$[Mn(C_5H_8)_2]^+$	$[Mn(C_5H_8)]^+$, $[C_6H_9]^+$	677
FAB (MS/MS)	Mn^+	3-methyl-1,2-butadiene	$[Mn(C_5H_8)]^+$, $[C_{10}H_{17}]^+$	$[C_7H_{11}]^+$, $[Mn(C_5H_8)_2]^+$, $[Mn(C_5H_8)(C_5H_6)]^+$, $[MnC_7H_9]^+$	677
FAB (MS/MS)	Mn^+	c-C_5H_8	Mn^+	$[Mn(C_5H_8)_{1,2}]^+$, $[Mn(C_5H_8)(C_5H_5)]^+$, $[Mn(C_5H_5)]^+$	678
EI or SI (GIB)	Mn^+	neo-C_5H_{12}	$[MnCH_3]^+$, $[MnH]^+$	$[C_4H_9]^+$	149
LD/LI (FT-ICR)	Mn^+	C_6H_6	$[Mn(C_6H_6)]^+$	–	160
DC/FT (GIB)	Mn^+	C_6H_6	$[Mn(C_6H_6)_{1,2}]^+$	–	158
ICP (SIFT-MS)	Mn^+	C_6H_6	$[Mn(C_6H_6)_{1,2}]^+$	–	679
LA (TOF)	$[Mn_x]^{+d}$	C_6H_6	$[Mn(C_6H_6)_2]^+$	$[Mn(C_6H_6)]^+$, $[Mn_2(C_6H_6)_2]^+$	680
LD/LI (FT-ICR)	Mn^+	C_6H_5F	–	–	681
LD/LI (FT-ICR)	Mn^+	C_6H_5Cl	–	–	681
LD/LI (FT-ICR)	Mn^+	C_6H_5Br	$[C_6H_5]^+$	–	681
LD/LI (FT-ICR)	Mn^+	C_6H_5I	$[Mn(C_6H_5I)]^+$	–	681

(*continued overleaf*)

TABLE 2. (*continued*)

Ionization (MS)[b]	Ion	Reagent	Major product ion(s)	Other product ions[c]	Reference
ICP (SIFT-MS)	Mn^+	C_6F_6	$[Mn(C_6F_6)]^+$	$[MnF]^+$	682
LD/LI (FT-ICR)	Mn^+	1,4-cyclohexadiene	$[Mn(C_6H_6)]^+$	–	611
LD/LI (FT-ICR)	Mn^+	c-C_6H_{10}	–	–	41
EI (MS/MS)	Mn^+	4-octyne	$[C_8H_{14}Mn]^+$	–	146
EI or FAB (MS/MS)	$[MnL_n]^{+e}$	4-octyne	$[C_8H_{14}Mn]^+$	–	26
LD/LI (FT-ICR)	Mn^+	$C_{24}H_{12}$ (coronene)	$[Mn(C_{24}H_{12})]^+$	$[Mn(C_{24}H_{12})_2]^+$	161
LD/LI (FT-ICR)	Mn^+	$C_{24}H_{12}$ (TBC)[f]	$[Mn(C_{24}H_{12})]^+$	$[Mn(C_{24}H_{12})_2]^+$	683
LD/LI (TOF)	Mn^+	$C_{28}H_{58}$ (octacosane)	$[Mn(C_{28}H_{58})]^+$	$[Mn(C_{28}H_{56})]^+$, $[Mn(C_{28}H_{54})]^+$	684
LD/LI (TOF)	Mn^+	$C_{36}H_{74}$ (hexatriacontane)	$[Mn(C_{36}H_{74})]^+$	$[Mn(C_{36}H_{72})]^+$, $[Mn(C_{36}H_{70})]^+$	684
EI (GIB)	Mn^+	C_{60}	$[C_{60}]^+$, $[MnC_{60}]^+$	$[C_{60-2n}]^+$	156, 163
EI (GIB)	$[Mn_2]^+$	C_{60}	$[MnC_{60}]^+$, $[C_{60}]^+$	$[C_{60-2n}]^+$	156
FAB (HPMS)	Mn^+	$CH_3(CH_2)_2CN$	$[CH_3(CH_2)_2CNMn]^+$	–	685
FAB (HPMS)	Mn^+	$(CH_3)_2CHCH_2CN$	$[(CH_3)_2CHCH_2CNMn]^+$	–	685
FAB (HPMS)	Mn^+	$CH_3(CH_2)_3CN$	$[CH_3(CH_2)_3CNMn]^+$	–	685
FAB (HPMS)	Mn^+	$(CH_3)_2CH(CH_2)_2CN$	$[(CH_3)_2CH(CH_2)_2CNMn]^+$	–	685
FAB (HPMS)	Mn^+	$CH_3(CH_2)_4CN$	$[CH_3(CH_2)_4CNMn]^+$	–	685
FAB (HPMS)	Mn^+	PhCN	$[PhCN]^{+\bullet}$	$[PhCNMn]^+$	686
FAB (HPMS)	Mn^+	$PhCH_2CN$	$[C_7H_7]^+$	$[PhCH_2CN]^{+\bullet}$, $[PhCH_2CNMn]^+$	686
FAB (HPMS)	Mn^+	$Ph(CH_2)_2CN$	$[C_7H_7]^+$	$[C_8H_9]^+$, $[Ph(CH_2)_2CNMn]^+$, $[Ph(CH_2)_2CN]^{+\bullet}$	686
FAB (HPMS)	Mn^+	$Ph(CH_2)_3CN$	$[C_7H_7]^+$	$[C_8H_9]^+$, $[Ph(CH_2)_3CNMn]^+$, $[Ph(CH_2)_3CN]^{+\bullet}$	686
FAB (HPMS)	Mn^+	o-$MeC_6H_4CH_2CN$	$[C_8H_9]^+$	$[o\text{-}MeC_6H_4CH_2CNMn]^+$, $[o\text{-}MeC_6H_4CH_2CN]^{+\bullet}$, $[o\text{-}MeC_6H_4CH_2CNMn - HCN]^+$	686
FAB (HPMS)	Mn^+	$CH_2{=}CHCN$	$[C_3H_3NMn]^+$	–	687
FAB (HPMS)	Mn^+	$CH_3CH{=}CHCN$	$[C_4H_5NMn]^+$	–	687
FAB (HPMS)	Mn^+	$CH_3CH_2CH{=}CHCN$	$[C_5H_7NMn]^+$	–	687
FAB (HPMS)	Mn^+	$CH_3CH{=}CHCH_2CN$	$[C_5H_7NMn]^+$	–	687
LD/LI (FT-ICR)	Mn^+	2-ethylbutanenitrile	$[C_6H_{11}NMn]^+$	–	35

FAB (HPMS)	Mn^+	cyclohexylamine	$[C_6H_{13}NMn]^+$	$[C_6H_{11}NMn]^+$, $[C_6H_7NMn]^+$, $[C_6H_6Mn]^+$	688
LD (FT-ICR)	Mn^+	*n*-BuNCS	$[MnC_3H_5NS]^+$, $[MnC_2H_3NS]^+$	$[MnC_5H_7NS]^+$, $[MnC_5H_7N]^+$, $[MnC_3H_4NS]^+$	30
LD/LI (FT-ICR)	Mn^+	chloroalkyl sulfide[g]	[chloroalkyl sulfide - Cl]$^+$	–	473
LD/LI (FT-ICR)	Mn^+	C_4H_5N (pyrrole)	$[Mn(C_4H_5N)]^+$	$[Mn(C_4H_5N)_2]^+$	164
DC/FT (GIB)	Mn^+	C_5H_5N (pyridine)	$[Mn(C_5H_5N)]^+$	–	660
LD/LI (FT-ICR)	Mn^+	C_4H_4O (furan)	–	–	167
EI (FT-ICR)	Mn^+	c-C_2H_4O	$[MnO]^+$	$[MnCH_2]^+$	17
EI or SI (GIB)	Mn^+	c-C_2H_4O	$[MnCH_2]^+$, $[MnO]^+$	$[MnH]^+$, $[C_2H_{3,4}]^+$, $[CHO]^+$	149
EI (GIB)	Mn^+	$(CH_3)_2CO$	$[MnCH_3]^+$, $[MnH]^+$	$[MnO]^+$, $[CH_3CO]^+$	149
SI (GIB)	Mn^+	$(CH_3)_2CO$	$[MnCH_3]^+$	$[MnO]^+$, $[CH_3CO]^+$	149
LD/LI (FT-ICR)	Mn^+	CH_3OOCH_3	$[Mn(OCH_3)]^+$	–	42
CI (MS/MS)	$[MnL_x]^{+h}$	CH_3OOCH_3	$[Mn(CH_3OOCH_3)]^+$	–	42
LA (FT-ICR)	Mn^+	$CH{\equiv}CCH_2OH$	$[C_3H_3O]^+$, $[C_3H_5O]^+$	$[MnC_3H_{2,4}]^+$, $[C_5H_{5,7}]^+$, $[C_6H_{5,7}]^+$, $[Mn(CHCCH_2OH)]^+$	689
ICP (SIFT-MS)	Mn^+	CO_2	$[Mn(CO_2)]^+$	$[Mn(CO_2)_2]^+$	690
DC/FT or SI (GIB)	Mn^+	COS	$[MnS]^+$	–	165
DC/FT or SI (GIB)	Mn^+	CS_2	$[MnS]^+$	$[MnCS]^+$	165
ICP (SIFT-MS)	Mn^+	CS_2	$[Mn(CS_2)]^+$	$[Mn(CS_2)_{2,3}]^+$	691
ICP (SIFT-MS)	Mn^+	O_2	–	–	692
ICP (SIFT-MS)	Mn^+	$^{\bullet}NO$	$[NO]^+$	$[MnO]^+$	693
ICP (SIFT-MS)	Mn^+	N_2O	$[Mn(N_2O)]^+$	–	694, 695
LD/LI (FT-ICR)	Mn^+	NO_2	$[MnO]^+$	–	157
EI (FT-ICR)	Mn^+	NO_2	$[MnO]^+$	–	17
FAB (HPMS)	Mn^+	BrCN	$[MnBr]^+$, $[MnCN]^+$	–	154
FAB (HPMS)	Mn^+	ICN	$[MnI]^+$, $[MnCN]^+$	$[MnCNI_2]^+$, $[I]^+$	154
EI or SI (FT-ICR)	Mn^+	ICl	$[MnCl]^+$	$[MnI]^+$	148
EI (FT-ICR)	$[MnCH_2]^+$	C_2D_4	Mn^+, $[MnCD_2]^+$	–	17
LD/LI (FT-ICR)	$[Mn(C_2H_4)]^+$	O_2	$[MnO_2]^+$	$[MnOH]^+$	696
LD/LI (FT-ICR)	$[Mn(C_4H_6)]^+$	C_2H_2	Mn^+	–	611

(*continued overleaf*)

TABLE 2. (*continued*)

Ionization (MS)[b]	Ion	Reagent	Major product ion(s)	Other product ions[c]	Reference
ICP (SIFT-MS)	$[Mn(C_6H_6)]^+$	O_2	$[MnC_6H_6O_2]^+$	–	679
LV (FTR)	$[Mn_xC]^+$	H_2	$[Mn_xCH_y]^+$ ($x > 6$, $y = 2, 3$)	$[Mn_xCH_y]^+$ ($x > 15$, $y > 3$)	159
EI (FT-ICR)	$[Mn_2]^+$	CH_3OH	$[Mn(CH_3OH)]^+$	–	141
EI (FT-ICR)	$[Mn_2]^+$	C_2H_5OH	$[Mn(C_2H_5OH)]^+$	$[Mn_2OH]^+$	141
EI (FT-ICR)	$[Mn_2]^+$	n-C_3H_7OH	$[Mn(C_3H_7OH)]^+$	$[Mn_2OH]^+$	141
EI (FT-ICR)	$[Mn_2]^+$	i-C_4H_9OH	$[Mn(C_4H_9OH)]^+$	$[Mn_2OH]^+$, $[Mn(H_2O)]^+$	141
EI (FT-ICR)	Mn^+	$Cr(CO)_6$	$[Cr(CO)_6]^+$	$[MnCr(CO)_{5,6}]^+$	148
MPI (TOF)	Mn^+	$Mn_2(CO)_{10}$	$[Mn_3(CO)_{8,10}]^+$	–	586
MPI (TOF)	Mn^+	$Re_2(CO)_{10}$	$[MnRe_2(CO)_{8-10}]^+$	–	586
LA (HPMS)	Cu^+	$Mn_2(CO)_{10}$	$[CuMn(CO)_{0-10}]^+$	$[CuMn_2(CO)_{0-10}]^+$, $[CuCO]^+$	697
LA (HPMS)	Nb^+	$Mn_2(CO)_{10}$	$[NbMn(CO)_{0-8}]^+$	$[NbMn_2(CO)_{0-6}]^+$, $[NbCO]^+$	697
EI (FT-ICR)	$[Mn(CO)_3]^+$	H_2O	$[Mn(CO)(H_2O)]^+$	$[Mn(CO)_2(H_2O)]^+$	698
EI (MS/MS)	$[Mn(CO)_x]^{+i}$	alkynes[i]	$[Mn(alkyne)]^+$	$[Mn(alkyne) - C_nH_m]^+$	699
CI (FT-ICR)	$[Mn(CO)_5]^+$	CH_4	$[(CH_4)Mn(CO)_5]^+$	–	700
EI (FT-ICR)	$[Mn(CO)_{2,3,4}]^+$	Me_3TACN[j]	$[Me_3TACN]^+$	$[Mn(Me_3TACN)]^+$	698
EI (FT-ICR)	$[Mn(CO)_5]^+$	Me_3TACN	$[Me_3TACN]^+$	$[Mn(Me_3TACN)]^+$, $[Mn(CO)(Me_3TACN)]^+$	698
EI (FT-ICR)	$[Mn_2(CO)_2]^+$	Me_3TACN	$[Mn(Me_3TACN)]^+$	–	698
EI (FT-ICR)	$[Mn_2(CO)_4]^+$	Me_3TACN	$[Mn(Me_3TACN)]^+$	$[Mn(CO)(Me_3TACN)]^+$	698
EI (FT-ICR)	$[Mn_2(CO)_5]^+$	Me_3TACN	$[Mn_2(CO)_3(Me_3TACN)]^+$	$[Mn_2(CO)_{1,2,4}(Me_3TACN)]^+$, $[Mn_2(CO)_{0,1,2}(Me_3TACN)_2]^+$, $[Mn(CO)_4(Me_3TACN)]^+$	698
EI (FT-ICR)	$[Mn_2(CO)(Me_3TACN)_2]^+$	O_2	$[Mn_2(O_2)(CO)(Me_3TACN)_2]^+$	–	698
EI (FT-ICR)	$[Mn_2(CO)_2(Me_3TACN)_2]^+$	O_2	$[Mn_2(O_2)(CO)_2(Me_3TACN)_2]^+$	–	698
EI (FT-ICR)	$[Mn_2(CO)]^+$	aliphatic alcohol[k]	$[Mn_2(ROH)]^+$	–	13
EI (FT-ICR)	$[Mn_2(CO)_2]^+$	aliphatic alcohol[k]	$[Mn_2(ROH)]^+$	$[Mn(ROH)_2]^+$	13
EI (FT-ICR)	$[Mn_2(CO)_3]^+$	aliphatic alcohol[k]	$[Mn_2(CO)_{1,2}(ROH)]^+$	$[Mn_2(ROH)_2]^+$, $[Mn(ROH)_2]^+$	13
EI (FT-ICR)	$[Mn_2(CO)_4]^+$	aliphatic alcohol[k]	$[Mn_2(CO)_3(ROH)]^+$	$[Mn_2(CO)_n(ROH)_m]^+$, $[Mn(CO)_x(ROH)_y]^+$	13

EI (FT-ICR)	$[Mn_2(CO)_5]^+$	aliphatic alcohol[k]	$[Mn_2(CO)_5(ROH)]^+$	$[Mn_2(CO)_5(ROH)_2]^+$	13
EI (FT-ICR)	$[Mn_x(CO)_y]^{+l}$	$Mn_2(CO)_{10}$	$[Mn_{4,5}(CO)_{15}]^+$, $[Mn_2(CO)_{10}]^+$	$[Mn_3(CO)_{10,14,15}]^+$, $[Mn_4(CO)_{8,9,14}]^+$, $[Mn_5(CO)_{14}]^+$, $[Mn_6(CO)_{14-16,18-20}]^+$, $[Mn_{7,8}(CO)_{25}]^+$, $[Mn_4(CO)_8(H_2O)_{1,2}]^+$, $[Mn_4(CO)_9(H_2O)]^+$, $[Mn_5(CO)_{15}(H_2O)]^+$, $[Mn_6(CO)_{14,18}(H_2O)]^+$	14
EI (FT-ICR)	$[Re_xMn_y(CO)_z]^{+m}$	$ReMn(CO)_{10}$	$[ReMn(CO)_{5,10}]^+$, $[Re(CO)_6]^+$	$[ReMn]^+$, $[ReMn(CO)_{1-4}]^+$, $[ReMn_2(CO)_4]^+$, $[HReMn(CO)_{9,10}]^+$, $[Re_2Mn(CO)_{6,10}]^+$, $[Re_2Mn_2(CO)_{6-8,10-12,15}]^+$, $[ReMn_3(CO)_{15}]^+$, $[Re_3Mn_3(CO)_{11-14,17-19}]^+$, $[ReMn(CO)_5(H_2O)]^+$, $[Re_2Mn_2(CO)_8(H_2O)_{1,2}]^+$, $[Re_2Mn_2(CO)_{10}(H_2O)]^+$	14
EI (FT-ICR)	$[(CO)_5MnCH_2]^+$	*i*-C_4H_8	$[(CO)_5Mn]^+$	–	17
EI (FT-ICR)	$[(CO)_5MnCH_2]^+$	*cis*-2-C_4H_8	$[(CO)_5Mn]^+$	–	17
EI (HPMS)	$[CpMn(CO)_3]^+$	C_4H_6	$[CpMnC_4H_6]^+$	–	701
EI (HPMS)	$[CpMn(CO)_3]^+$	C_6H_6	$[CpMnC_6H_6]^+$	$[CpMn(CO)C_6H_6]^+$, $[CpMnC_6H_5]^+$, $[MnC_6H_6]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	1,3-cyclohexadiene	$[CpMnC_6H_8]^+$	$[CpMn(CO)C_6H_8]^+$, $[CpMnC_6H_6]^+$, $[CpMnC_6H_5]^+$, $[CpMnC_3H_4]^+$, $[MnC_6H_6]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	*c*-C_6H_{10}	$[CpMnC_6H_{10}]^+$	–	701
EI (HPMS)	$[CpMn(CO)_3]^+$	cyclooctatetraene	$[CpMnC_8H_8]^+$, $[MnC_6H_6]^+$	$[CpMnC_6H_6]^+$, $[CpMnC_6H_5]^+$, $[MnC_8H_8]^+$, $[MnC_8H_7]^+$, $[CpMnC_2H_2]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	1,3,5-cyclooctatriene	$[CpMnC_8H_{10}]^+$	$[CpMnC_6H_6]^+$, $[CpMnC_6H_5]^+$, $[MnC_8H_9]^+$, $[CpMnC_2H_2]^+$, $[MnC_6H_6]^+$	701

(*continued overleaf*)

TABLE 2. (*continued*)

Ionization (MS)[b]	Ion	Reagent	Major product ion(s)	Other product ions[c]	Reference
EI (HPMS)	$[CpMn(CO)_3]^+$	1,5-cyclooctadiene	$[CpMnC_8H_{12}]^+$	$[CpMnC_4H_6]^+$, $[MnC_8H_{12}]^+$, $[CpMnC_2H_2]^+$, $[MnC_6H_6]^+$, $[MnC_5H_9]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	cyclooctene	$[CpMnC_8H_{14}]^+$	$[MnC_8H_{14}]^+$, $[CpMnC_2H_2]^+$, $[MnC_5H_9]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	NH_3	$[CpMnNH_3]^+$	–	701
EI (HPMS)	$[CpMn(CO)_3]^+$	$NH(C_2H_5)_2$	$[CpMnNH(C_2H_5)_2]^+$	$[MnNH(C_2H_5)_2]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	NF_3	–	–	140
EI (HPMS)	$[CpMn(CO)_3]^+$	PF_3	$[CpMnPF_3]^+$	$[CpMn(CO)PF_3]^+$	140, 701
EI (HPMS)	$[CpMn(CO)_3]^+$	AsF_3	$[CpMnAsF_3]^+$	$[CpMn(CO)AsF_3]^+$	140
EI (HPMS)	$[CpMn(CO)_3]^+$	SbF_3	$[CpMnSbF_3]^+$	–	140
EI (HPMS)	$[CpMn(CO)_3]^+$	SF_4	$[CpMnSF_4]^+$	–	140
EI (HPMS)	$[CpMn(CO)_3]^+$	H_2O	$[CpMnOH_2]^+$	$[CpMn(CO)OH_2]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	H_2S	$[CpMnSH_2]^+$	–	701
EI (HPMS)	$[CpMn(CO)_3]^+$	$O(C_2H_5)_2$	$[CpMnO(C_2H_5)_2]^+$	$[MnO(C_2H_5)_2]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	$H_3COCH_2CH_2OCH_3$	$[CpMnC_2H_4(OCH_3)_2]^+$	$[CpMnCH_2OCH_3]^+$, $[CpMnC_2H_2]^+$, $[MnC_2H_4(OCH_3)_2]^+$, $[CpMnCH_3]^+$	701
EI (HPMS)	$[CpMn(CO)_3]^+$	$CpMn(CO)_3$	$[Cp_2Mn_2]^+$, $[Cp_2Mn_2(CO)_3]^+$, $[CpMn_2(CO)_2]^+$	$[Cp_2Mn_2(CO)_2]^+$, $[Cp_2Mn_2(CO)]^+$, $[CpMn_2C_3H_2(CO)_3]^+$, $[CpMn_2C_3H_2]^+$, $[CpMn_2C_3H]^+$, $[CpMn_2(CO)_3]^+$	702
EI (HPMS)	$[(RCp)Mn(CO)_3]^{+n}$	$c\text{-}C_4H_4X^n$	$[(RCp)Mn(c\text{-}C_4H_4X)]^+$	–	703
EI (HPMS)	$[MnCp_2]^+$	18-crown-6	$[CpMn(18\text{-crown-6})]^+$	–	24
EI (HPMS)	$[BrMn(CO)_x]^+$	crown ether	$[BrMn(\text{crown ether})]^+$	–	24, 704
EI (HPMS)	$[CpMn(CO)_{0-2}]^+$	crown ether	$[CpMn(\text{crown ether})]^+$	–	24
EI (HPMS)	$[Mn(C_5H_4XOH)]^{+o}$	18-crown-6	$[HOMn(18\text{-crown-6})]^+$	–	24
EI (HPMS)	$[Mn(C_5H_4XR)]^{+p}$	18-crown-6	$[(C_5H_4XR)Mn(18\text{-crown-6})]^+$	$[RMn(18\text{-crown-6})]^+$,	24, 704

				$[(C_5H_4R)Mn(18\text{-crown-}6)]^+$	
EI (HPMS)	$[CpMn]^+$	crown ether^q	$[CpMn(\text{crown ether})]^{+q}$	$[Mn(\text{crown ether - H})]^{+q}$	704
EI (FT-ICR)	$[MnCp_2]^+$	$^*MnCp_2$	$[^*MnCp_2]^+$	–	705, 706
EI (FT-ICR)	$[Mn(MeCp)_2]^+$	$^*Mn(MeCp)_2$	$[^*Mn(MeCp)_2]^+$	–	706
EI (FT-ICR)	$[Mn(Me_5Cp)_2]^+$	$^*Mn(Me_5Cp)_2$	$[^*Mn(Me_5Cp)_2]^+$	–	706
EI (FT-ICR)	$[Mn(Me_5Cp)_2]^+$	$Ni(Me_5Cp)_2$	$[Ni(Me_5Cp)_2]^+$	–	153
EI (FT-ICR)	$[MnCp_2]^{2+}$	$^*MnCp_2$	$[MnCp_2]^+$, $[^*MnCp_2]^+$	–	142
EI (FT-ICR)	$[MnCp_2]^+$	$NiCp_2$	$[NiCp_2]^+$	–	706
EI (FT-ICR)	$[FeCp_2]^+$	$MnCp_2$	$[MnCp_2]^+$	–	706
EI (FT-ICR)	$[CoCp_2]^+$	$Mn(Me_5Cp)_2$	$[Mn(Me_5Cp)_2]^+$	–	153
EI (FT-ICR)	$[NiCp_2]^+$	$MnCp_2$	$[MnCp_2]^+$	–	152, 706
EI (FT-ICR)	$[RuCp_2]^+$	$Mn(Me_5Cp)_2$	$[Mn(Me_5Cp)_2]^+$	–	706
EI (FT-ICR)	$[Cr(C_6H_6)_2]^+$	$Mn(Me_5Cp)_2$	$[Mn(Me_5Cp)_2]^+$	–	153
LD/LI (FT-ICR)	$[MnO]^+$	H_2	$[MnOH]^+$	Mn^+	157
LD/LI (FT-ICR)	$[MnO]^+$	CH_4	$[MnOH]^+$	–	157
EI (FT-ICR)	$[MnO]^+$	C_2H_4	Mn^+, $[MnCH_2]^+$	–	17
LD/LI (FT-ICR)	$[MnO]^+$	C_2H_6	Mn^+	$[MnOH]^+$, $[Mn(H_2O)]^+$	157
LD/LI (FT-ICR)	$[MnO]^+$	C_3H_8	Mn^+	$[MnOH]^+$, $[Mn(H_2O)]^+$, $[(C_2H_4)MnOH]^+$	157
LD/LI (FT-ICR)	$[MnO]^+$	n-C_4H_{10}	Mn^+, $[Mn(H_2O)]^+$	$[MnOH]^+$, $[(C_3H_6)MnOH]^+$, $[(C_2H_4)MnOH]^+$	157
LD/LI (FT-ICR)	$[MnO]^+$	i-C_4H_{10}	Mn^+	$[MnOH]^+$, $[(C_3H_6)MnOH]^+$, $[Mn(H_2O)]^+$	157
LD/LI (FT-ICR)	$[MnO]^+$	n-C_5H_{12}	Mn^+, $[Mn(H_2O)]^+$	$[MnOH]^+$, $[(C_3H_6)MnOH]^+$, $[(C_4H_8)MnOH]^+$, $[(C_2H_4)MnOH]^+$	157
LD/LI (FT-ICR)	$[MnO]^+$	i-C_5H_{12}	$[MnOH]^+$, Mn^+	$[(C_4H_8)MnOH]^+$, $[Mn(H_2O)]^+$	157
LD/LI (FT-ICR)	$[MnO]^+$	*neo*-C_5H_{12}	$[(C_4H_8)MnOH]^+$	$[MnOH]^+$, Mn^+	157
LD/LI (FT-ICR)	$[MnO]^+$	C_6H_6	Mn^+	$[Mn(C_6H_4)]^+$, $[MnOH]^+$	707
LD/LI (FT-ICR)	$[MnO]^+$	n-C_6H_{14}	$[Mn(H_2O)]^+$	Mn^+, $[MnOH]^+$, $[(C_2H_4)MnOH]^+$, $[(C_3H_6)MnOH]^+$, $[(C_4H_8)MnOH]^+$, $[(C_5H_{10})MnOH]^+$	157
CI (FT-ICR)	$[Mn_2O]^+$	C_2H_2	Mn^+	$[Mn_2]^+$, $[MnOH]^+$	708

(*continued overleaf*)

TABLE 2. (*continued*)

Ionization (MS)[b]	Ion	Reagent	Major product ion(s)	Other product ions[c]	Reference
CI (FT-ICR)	$[Mn_2O]^+$	C_3H_4	Mn^+	$[Mn_2O(C_3H_4)]^+$	708
CI (FT-ICR)	$[Mn_2O]^+$	C_6H_6	Mn^+	$[Mn_2]^+$, $[Mn_2O(C_6H_6)]^+$	708
CI (FT-ICR)	$[Mn_2O]^+$	CH_3OH	Mn^+	$[Mn_2]^+$, $[Mn_2OH_2]^+$	708
CI (FT-ICR)	$[Mn_2O]^+$	CH_3CHO	Mn^+	$[MnOH]^+$	708
CI (FT-ICR)	$[Mn_2O]^+$	$H_2^{18}O$	Mn^+	$[Mn_2]^+$, $[Mn_2OH_2]^+$, $[Mn_2^{18}O]^+$	708
CI (FT-ICR)	$[Mn_2O]^+$	H_2S	Mn^+	$[Mn_2]^+$, $[Mn_2OH_2]^+$, $[Mn_2S]^+$, $[Mn_2S_2]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	H_2	–	–	708
CI (FT-ICR)	$[Mn_2O_2]^+$	C_2H_2	Mn^+	$[Mn_2O]^+$, $[Mn_2]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	C_2H_4	Mn^+	$[Mn_2]^+$, $[Mn_2O]^+$, $[Mn_2OH_2]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	C_3H_4	$[Mn_2C_6H_4]^+$, $[Mn_2OC_3H_2]^+$	Mn^+, $[Mn_2O]^+$, $[Mn_2O_2H]^+$, $[Mn_2O_2H_2]^+$, $[Mn_2OC_2H_2]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	C_3H_6	Mn^+, $[Mn_2O_2H]^+$	$[Mn_2]^+$, $[Mn_2O]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	i-C_4H_{10}	–	–	708
CI (FT-ICR)	$[Mn_2O_2]^+$	C_6H_6	Mn^+, $[Mn(C_6H_6)_{1,2}]^+$	$[Mn_2O_2C_6H_6]^+$, $[Mn_2O]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	CH_3OH	Mn^+, $[Mn(CH_3OH)_{1,2}]^+$	$[Mn_2O_2H_2]^+$, $[Mn_2O_2CH_4]^+$, $[Mn_2O_2C_2H_6]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	CH_3CHO	Mn^+, $[Mn(C_2H_4O)_{1,2}]^+$	$[Mn_2O_2H_2]^+$, $[Mn_2O_2C_2H_2]^+$, $[Mn_2O_2(C_2H_4O)]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	NH_3	Mn^+, $[Mn(NH_3)_{1,2}]^+$	$[Mn_2O_2(NH_3)_{1,2}]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	$H_2^{18}O$	$[Mn_2O^{18}O]^+$, $[Mn_2^{18}O_2]^+$	$[Mn_2{*}O_2H_2]^{+r}$, $[Mn_2{*}O_2(H_2{*}O)_{1,2}]^{+r}$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	H_2S	$[Mn_2OS]^+$, $[Mn_2S_2]^+$	$[Mn_2S_2H_2]^+$	708
CI (FT-ICR)	$[Mn_2O_2]^+$	HCl	–	–	708
LV (FT-ICR)	$[Mn_2O_4N_2]^+$	CO_2	$[Mn_2O_4(CO_2)]^+$	–	709
LV (FT-ICR)	$[Mn_2O_6]^+$	CO_2	$[Mn_2O_4(CO_2)]^+$	–	709
LV (FT-ICR)	$[Mn_2O_6]^+$	N_2	$[Mn_2O_4N_2]^+$	–	709
EI (FT-ICR)	$[MnCl]^+$	C_3H_8	$[Mn(C_3H_8)]^+$	–	144
EI (FT-ICR)	$[MnCl]^+$	n-C_4H_{10}	$[Mn(C_4H_{10})]^+$	–	144
EI (FT-ICR)	$[MnCl]^+$	i-C_4H_{10}	$[Mn(C_4H_{10})]^+$	–	144

EI (FT-ICR)	$[\mathrm{MnCl}]^+$	*neo*-$\mathrm{C_5H_{12}}$	$[\mathrm{Mn(C_5H_{12})}]^+$	–	144
EI (FT-ICR)	$[\mathrm{ClMn(CO)}_x]^+$	$\mathrm{H_2O}$	$[\mathrm{ClMn(H_2O)}]^+$	–	474, 475
EI (FT-ICR)	$[\mathrm{ClMn(H_2O)}]^+$	L^s	$[\mathrm{ClMn(L)}]^+$	–	474
EI (FT-ICR)	$[\mathrm{ClMn(H_2O)}]^+$	base oils	$[\mathrm{ClMn(base\ oils)}]^+$	–	475
EI (FT-ICR)	$[\mathrm{CH_5}]^+$	$\mathrm{(CO)_5MnCH_2F}$	$[\mathrm{(CO)_5MnCH_2}]^+$	$[\mathrm{(CO)_4MnCH_2}]^+$	17
CI (HPMS)	$[\mathrm{CH_5}]^+$	$(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Mn(CO)_4}$	$[\mathrm{H(C_3H_5)Mn(CO)_{1-4}}]^+$	$[\mathrm{(C_3H_5)Mn(CO)_4}]^+$	423
CI (HPMS)	$[\mathrm{CH_5}]^+$	$(\sigma\text{-}\mathrm{C_3H_5})\mathrm{Mn(CO)_5}$	$[\mathrm{H(C_3H_5)Mn(CO)_{1-5}}]^+$	$[\mathrm{(C_3H_5)Mn(CO)_{0-5}}]^+$, $[\mathrm{Mn(CO)_{1-5}}]^+$	423
CI (HPMS)	$[\mathrm{CH_5}]^+$	$\mathrm{CpMn(CO)_3}$	$[\mathrm{HMn(Cp)(CO)_{2,3}}]^+$, $[\mathrm{CpMn(CO)_3}]^+$	$[\mathrm{Cp_2Mn_2(CO)_3}]^+$, $[\mathrm{Cp_2Mn_3(CO)_5}]^+$, $[\mathrm{Cp_3Mn_3(CO)_{2,6}}]^+$, $[\mathrm{Cp_3Mn_4(CO)_8}]^+$, $[\mathrm{Cp_4Mn_5(CO)_{11}}]^+$	421^t
CI (HPMS)	$[i\text{-}\mathrm{C_4H_{10}}+\mathrm{H}]^+$	$\mathrm{(CO)_5MnC(O)C(O)\text{-}Mn(CO)_5}$	$[\mathrm{Mn_2C_{12}O_{12}H}]^+$	–	464
CI (HPMS)	$[\mathrm{NH_4}]^+$	$\mathrm{(CO)_5MnSiPh_3}$	$[\mathrm{(CO)_5MnSiPh_3}+\mathrm{NH_4}]^+$	fragment ions	465
CI (HPMS)	$[\mathrm{NH_4}]^+$	$\mathrm{(CO)_5MnGePh_3}$	$[\mathrm{(CO)_5MnGePh_3}+\mathrm{(NH_3)_{1,2}}+\mathrm{H}]^+$	fragment ions	465
CI (HPMS)	$[\mathrm{NH_4}]^+$	$\mathrm{(CO)_5MnSnPh_3}$	$[\mathrm{(CO)_{5,4}MnSnPh_3}+\mathrm{NH_4}]^+$	fragment ions	465
CI (HPMS)	$[\mathrm{TCNE}]^{+u}$	$(\eta^1\text{-}\mathrm{C_3H_5})\mathrm{Mn(CO)_5}$	$[\mathrm{C_{14}H_5N_4O_5Mn}]^+$	–	710
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{H_2}$	$[\mathrm{(CO)_3Mn(H_2)}]^-$	–	711
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{NH_3}$	$[\mathrm{(CO)_3Mn(NH_3)}]^-$	–	711
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{PH_3}$	$[\mathrm{(CO)_3Mn(PH)}]^-$	$[\mathrm{(CO)_3Mn(H)(PH_2)}]^-$	711
EI (FT-ICR)	$[\mathrm{Mn(CO)}]^-$	$\mathrm{H_2O}$	–	–	38
EI (FT-ICR)	$[\mathrm{Mn(CO)_2}]^-$	$\mathrm{H_2O}$	$[\mathrm{HMn(OH)}]^-$	$[\mathrm{HMn(CO)(OH)}]^-$	38
EI (FT-ICR)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{H_2O}$	$[\mathrm{(CO)_2Mn(H)(OH)}]^-$	–	38
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{H_2O}$	$[\mathrm{(CO)_2Mn(H)(OH)}]^-$	–	711
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{H_2S}$	$[\mathrm{(CO)_2MnS}]^-$	$[\mathrm{(CO)_3MnS}]^-$	711
EI (FT-ICR)	$[\mathrm{Mn(CO)}]^-$	$\mathrm{N_2O}$	$[\mathrm{MnO}]^-$	$[\mathrm{MnO_2}]^-$	40
EI (FT-ICR)	$[\mathrm{Mn(CO)_2}]^-$	$\mathrm{N_2O}$	$[\mathrm{MnO}]^-$	$[\mathrm{MnO_2}]^-$, $[\mathrm{(O)Mn(CO)}]^-$	40
EI (FT-ICR)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{N_2O}$	$[\mathrm{(O)Mn(CO)}]^-$	$[\mathrm{(O)Mn(CO)_2}]^-$, $[\mathrm{(N_2O)Mn(CO)_2}]^-$	40
EI (FT-ICR)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{N_2O}$	$[\mathrm{(N_2O)Mn(CO)_3}]^-$	$[\mathrm{MnO_2}]^-$, $[\mathrm{(O)Mn(CO)}]^-$, $[\mathrm{(O)Mn(CO)_2}]^-$, $[\mathrm{(O)Mn(CO)_3}]^-$	40

(*continued overleaf*)

TABLE 2. (*continued*)

Ionization (MS)^b	Ion	Reagent	Major product ion(s)	Other product ions^c	Reference
EI (FT-ICR)	$[Mn(CO)_2]^-$	O_2	$[MnO_2]^-$	$[MnO]^-$	40
EI (FT-ICR)	$[Mn(CO)_3]^-$	O_2	$[MnO_2]^-$	$[MnO]^-$, $[MnO_3]^-$	40
EI (FT-ICR)	$[Mn(CO)_4]^-$	O_2	$[(O)Mn(O)(CO)_2]^-$	$[MnO_2]^-$, $[MnO_3]^-$, $[MnO_4]^-$, $[(O)Mn(O)(CO)]^-$, $[(O)Mn(CO)_2]^-$, $[(O)Mn(CO)_3]^-$	40
EI (FT-ICR)	$[Mn(CO)_3]^-$	$^{13}CO_2$	$[(^{13}CO_2)Mn(CO)_2]^-$	$[(^{13}CO_2)Mn(CO)]^-$, $[(O)Mn(O)(CO)_3]^-$, $[(O)Mn(CO)_2]^-$	33
EI (FA-MS)	$[Mn(CO)_4]^-$	^{13}CO	$[(^{13}CO)Mn(CO)_4]^-$	$[(^{13}CO)Mn(CO)_3]^-$	32
EI (FA-MS)	$[Mn(CO)_3]^-$	CH_4	–	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	$(CH_3)_4C$	–	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	C_2H_6	$[(CO)_3Mn(C_2H_4)]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	C_2D_6	$[(CO)_3Mn(C_2D_4)]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	C_3H_8	$[(CO)_3Mn(H)(C_3H_5)]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	$CH_3CD_2CH_3$	$[(CO)_3Mn(D)(C_3H_4D)]^-$	$[(CO)_3Mn(H)(C_3H_4D)]^-$	29
EI (FA-MS)	$[Mn(CO)_3]^-$	$(CH_3)_3CH$	$[(CO)_3Mn(H)(C_4H_7)]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	$(CD_3)_3CH$	$[(CO)_3Mn(D)(C_4D_7)]^-$	$[(CO)_3Mn(H)(C_4D_7)]^-$	29
EI (FA-MS)	$[Mn(CO)_3]^-$	n-C_4H_{10}	$[(CO)_3Mn(H)(C_4H_7)]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	n-C_5H_{12}	$[(CO)_3Mn(H)(C_5H_9)]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	n-C_6H_{14}	$[(CO)_3Mn(H)(C_6H_{11})]^-$	–	29
EI (FA-MS)	$[Mn(CO)_3]^-$	n-C_7H_{16}	$[(CO)_3Mn(H)(C_7H_{13})]^-$	–	29
EI (FT-ICR)	$[Mn(CO)_3]^-$	n-C_7H_{16}	$[C_7H_{14}Mn(CO)_3]^-$	–	38
EI (FA-MS)	$[Mn(CO)_3]^-$	c-C_3H_6	$[(CO)_3Mn(H)_2(c\text{-}C_3H_4)]^-$	$[(CO)_3Mn(c\text{-}C_3H_4)]^-$	31
EI (FA-MS)	$[Mn(CO)_3]^-$	c-C_3D_6	$[(CO)_3Mn(D)_2(c\text{-}C_3D_4)]^-$	$[(CO)_3Mn(D)(c\text{-}C_3D_5)]^-$	31

EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	c-$\mathrm{C_5H_6}$	$[\mathrm{(CO)_2Mn(H)}(\eta^5\text{-}\mathrm{C_5H_5})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	c-$\mathrm{C_5H_6}$	$[\mathrm{(CO)_4Mn(H)}(\eta^2\text{-}c\text{-}\mathrm{C_5H_6})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	c-$\mathrm{C_5H_{10}}$	$[\mathrm{(CO)_2Mn(H)}(c\text{-}\mathrm{C_5H_7})]^-$	–	29
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{C_6H_6}$	$[\mathrm{(CO)_3Mn}(\eta^4\text{-}\mathrm{C_6H_6})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{C_6H_6}$	$[\mathrm{(CO)_4Mn}(\eta^2\text{-}\mathrm{C_6H_6})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	c-$\mathrm{C_6H_{12}}$	$[\mathrm{(CO)_2Mn(H)}(c\text{-}\mathrm{C_6H_9})]^-$	–	29
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	c-$\mathrm{C_6D_{12}}$	$[\mathrm{(CO)_2Mn(D)}(c\text{-}\mathrm{C_6D_9})]^-$	–	29
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH{\equiv}CH}$	$[\mathrm{(CO)_2Mn(C_2H_2)}]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{CH{\equiv}CH}$	$[\mathrm{(CO)_4Mn(C_2H_2)}]^-$	$[\mathrm{(CO)_3Mn(C_2H_2)}]^-$	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH_2{=}CH_2}$	$[\mathrm{(CO)_3Mn(C_2H_4)}]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{CH_2{=}CH_2}$	$[\mathrm{(CO)_4Mn}(\eta^2\text{-}\mathrm{C_2H_4})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{CH_2{=}C{=}CH_2}$	$[\mathrm{(CO)_4Mn(C_3H_4)}]^-$	$[\mathrm{(CO)_3Mn(C_3H_4)}]^-$	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH_3CH{=}CH_2}$	$[\mathrm{(CO)_3Mn(H)}(\eta^3\text{-}\mathrm{C_3H_5})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CD_3CD{=}CD_2}$	$[\mathrm{(CO)_3Mn(D)}(\eta^3\text{-}\mathrm{C_3D_5})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CD_3CH{=}CH_2}$	$[\mathrm{(CO)_3Mn(D)}(\eta^3\text{-}\mathrm{C_3H_3D_2})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{CH_3CH{=}CH_2}$	$[\mathrm{(CO)_4Mn}(\eta^2\text{-}\mathrm{C_3H_6})]^-$	–	34
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH_2{=}CHCH{=}CH_2}$	$[\mathrm{(CO)_2Mn}(\eta^4\text{-}\mathrm{C_4H_6})]^-$	$[\mathrm{(CO)_3Mn}(\eta^4\text{-}\mathrm{C_4H_6})]^-$	34
EI (FA-MS)	$[\mathrm{Mn(CO)_4}]^-$	$\mathrm{CH_2{=}CHCH{=}CH_2}$	$[\mathrm{(CO)_4Mn}(\eta^2\text{-}\mathrm{C_4H_6})]^-$	–	34
EI (FT-ICR)	$[\mathrm{Mn(CO)}]^-$	$\mathrm{CH_3OH}$	–	–	38
EI (FT-ICR)	$[\mathrm{Mn(CO)_2}]^-$	$\mathrm{CH_3OH}$	–	–	38
EI (FT-ICR)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH_3OH}$	$[\mathrm{Mn(CO)_4}]^-$	$[\mathrm{HMn(CO)_2(OCH_3)}]^-$, $[\mathrm{(CH_2O)Mn(CO)_3}]^-$	38
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH_3OH}$	$[\mathrm{(CH_2O)Mn(CO)_3}]^-$	$[\mathrm{HMn(CO)_2(OCH_3)}]^-$	25
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CH_3OD}$	$[\mathrm{(CH_2O)Mn(CO)_3}]^-$	$[\mathrm{DMn(CO)_2(OCH_3)}]^-$	25
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CD_3OH}$	$[\mathrm{(CD_2O)Mn(CO)_3}]^-$	$[\mathrm{HMn(CO)_2(OCD_3)}]^-$	25
EI (FT-ICR)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CD_3OH}$	$[\mathrm{Mn(CO)_4}]^-$, $[\mathrm{HMn(CO)_2(OCD_3)}]^-$	$[\mathrm{(CD_2O)Mn(CO)_3}]^-$	38
EI (FA-MS)	$[\mathrm{Mn(CO)_3}]^-$	$\mathrm{CD_3OD}$	$[\mathrm{(CD_2O)Mn(CO)_3}]^-$	$[\mathrm{DMn(CO)_2(OCD_3)}]^-$	25

(*continued overleaf*)

TABLE 2. (*continued*)

Ionization (MS)[b]	Ion	Reagent	Major product ion(s)	Other product ions[c]	Reference
EI (FT-ICR)	$[Mn(CO)]^-$	$HCOOCH_3$	–	–	39
EI (FT-ICR)	$[Mn(CO)_2]^-$	$HCOOCH_3$	$[HMn(CO)(OCH_3)]^-$	$[HMn(OCH_3)]^-$	39
EI (FT-ICR)	$[Mn(CO)_3]^-$	$HCOOCH_3$	$[HMn(CO)_2(OCH_3)]^-$, $[(CH_2O)Mn(CO)_3]^-$	$[Mn(CO)_4]^-$	39
EI (FT-ICR)	$[Mn(CO)_2]^-$	$H^{13}COOCH_3$	$[HMn(CO)(OCH_3)]^-$, $[HMn(^{13}CO)(OCH_3)]^-$	$[HMn(OCH_3)]^-$	39
EI (FT-ICR)	$[Mn(CO)_3]^-$	$H^{13}COOCH_3$	$[(CH_2O)Mn(^{13}CO)(CO)_2]^-$	$[HMn(CO)(^{13}CO)(OCH_3)]^-$, $[HMn(CO)_2(OCH_3)]^-$, $[(CH_2O)Mn(CO)_3]^-$, $[Mn(^{13}CO)(CO)_3]^-$	39
EI (FA-MS)	$[(CO)_3Mn(c\text{-}C_3H_4)]^-$	SO_2	$[(CO)_3Mn(SO_2)]^-$	–	31
EI (FA-MS)	$[(CO)_3Mn(H)_2(c\text{-}C_3H_4)]^-$	SO_2	$[(CO)_3Mn(SO_2)]^-$	–	31
EI (FT-ICR)	$[CF_3Mn(CO)(NO)]^-$	$^{\bullet}NO$	$[CF_3Mn(NO)_2]^-$	–	668
EI (FT-ICR)	$[CF_3Mn(CO)_4]^-$	$^{\bullet}NO$	$[CF_3Mn(CO)_3(NO)]^-$	–	28, 668
EI (FT-ICR)	$[CF_3Mn(CO)_4]^-$	^{13}CO	–	–	28
EI (FT-ICR)	$[CF_3Mn(CO)_4]^-$	PF_3	–	–	28
LD/LI (FT-ICR)	$[MnO_2]^-$	CH_3OH	$[MnO_2H_2]^-$	$[MnO_3]^-$	712
LD/LI (FT-ICR)	$[Mn_2O_3]^-$	CH_3OH	$[Mn_2O_3H_2]^-$	$[CH_3O]^-$	712
LD/LI (FT-ICR)	$[Mn_2O_4]^-$	CH_3OH	$[Mn_2O_4H_2]^-$	$[Mn_2O_4CH_4]^-$, $[Mn_2O_4C_2H_6]^-$	712
LA (TOF)	$[Mn_x]^{-v}$	C_6H_6	$[Mn_{1,2,3,4,5}(C_6H_5)]^-$	$[Mn_{1,2,3}(C_6H_5)(C_6H_6)]^-$	680
EI (FT-ICR)	NH_2^-	$MeCpMn(CO)_3$	$[(C_6H_6)Mn(CO)_3]^-$	–	713

EI (FT-ICR)	$O^{-\bullet}$	$MeCpMn(CO)_3$	$[MeCpMn(CO)_2]^-$	–	713
EI (FT-ICR)	F^-	$MeCpMn(CO)_3$	$[(C_6H_6)Mn(CO)_3]^-$	–	713
EI (FT-ICR)	Cl^-	$MeCpMn(CO)_3$	–	–	713

---

[a] For other reports describing gas-phase ion/molecule reactions involving Mn-containing species which are not included in this table, refer to References 13, 17, 21, 22, 43, 69, 124, 143, 150, 151, 155, 166, 168, 421, 473, 663, 671, 704, 708, 714–729.

[b] See Abbreviation section for meaning of acronyms.

[c] Dash = no observed ions.

[d] $[Mn_x]^+$ = metal clusters produced by laser ablation[680].

[e] $[MnL_n]^+$ = ions generated from the $Mn_2(CO)_{10}$ in a EI source or from the $Mn(NO_3)_2$ in a FAB source[26].

[f] TBC = tribenzocyclotriyne.

[g] Chloroalkyl sulfide = 2-chloroethyl ethyl sulfide (CEES) or chloromethyl methyl sulfide (CMMS).

[h] $[MnL_x]^+$ = ions generated from the $Mn_2(CO)_{10}$ in a CI source[42].

[i] $[Mn(CO)_x]^+$ = ions generated from the $Mn_2(CO)_{10}$ or $Mn(CO)_3(CH_3\text{-}C_5H_4\text{-}c)$ under EI[699]; alkynes = $C_3H_7C{\equiv}CR$ (where R = H, CH_3, C_2H_5, C_3H_7).

[j] Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane.

[k] Aliphatic alcohol = MeOH, EtOH, *n*-PrOH, CD_3OH, C_2D_5OH or *n*-C_3D_7OH.

[l] $[Mn_x(CO)_y]^+$ = ions generated from the $Mn_2(CO)_{10}$ under EI[14].

[m] $[Re_xMn_y(CO)_z]^+$ = ions generated from the $ReMn(CO)_{10}$ under EI[14].

[n] R = H, Cl, Br, $COCH_3$; X = NH, CHN, S[703].

[o] XOH = CH_2OH, $CH(OH)CH_3$, $CH(OH)C_6H_5$[24].

[p] Product ions are generated depending on XR nature (for details see References 24 and 704; compounds with XR = CN, CHO, $COCH_3$, COPh, CH_2Ph, $CH_2N(CH_3)_2$, $CH(CH_3)NHCH_3$, CH_2OH, $CH(OH)CH_3$, CH(OH)Ph, COOH, and $(CH_2)_3COOH$ have been studied).

[q] Product ions are formed depending on the nature of the crown ether (for details see reference 704); $[Mn(\text{crown ether - H})]^+$ was generated for crown ethers containing -OH or -NH- groups[704].

[r] *O stands for either ^{16}O or ^{18}O.

[s] L = a variety of volatile and nonvolatile, saturated and unsaturated hydrocarbons: 2,2,4,4-tetramethylpentane (a branched alkane), 2,3-dimethylpentane (a branched alkane), 1-octene (a linear alkene), *c*-hexene (a cyclic alkene), benzene (aromatic hydrocarbon), tetrahydrothiophene (thiophene), and tetrahydrofuran (furan), all introduced via an adjustable leak valve; **or** a five-component mixture containing tetracosane (a linear alkane), 5-α-cholestane (a cyclic alkane), squalane (a branched alkane), coronene (a polyaromatic hydrocarbon), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (a N-heteroaromatic compound), evaporated by laser-induced acoustic desorption (LIAD) and allowed to react with the $[ClMn(H_2O)]^+$ ion[474].

[t] In Reference 421, $(CH_3COC_5H_4)Mn(CO)_3$ and $CpMn(CO)_2L$ complexes (L = $NHMe_2$, $SOMe_2$, CNC_6H_{11}, norbornene, norbornadiene) have also been subjected to CI (CH_4), and at elevated sample pressures ion/molecule reactions occur, yielding secondary ions of di-, tri- and higher-nuclearity in considerable quantities.

[u] TCNE = tetracyanoethylene.

[v] $[Mn_x]^-$ = metal clusters produced by laser ablation[680].

Lower temperatures resulted in low total ion intensities, dictated by the poor volatility of the precursor. Strobel and Ridge[148] used $MeCpMn(CO)_3$ as precursor for ground-state Mn^+ generation by SI in FT-ICR MS experiments. Armentrout and Li[166] have also used a DC/FT source in combination with a guided ion beam (GIB) tandem mass spectrometer to examine the kinetic energy dependence of some ion/molecule reactions. Koyanagi and coauthors[692] estimated the state distribution for 29 transition-metal ions (including Mn^+) produced in an inductively coupled plasma (ICP) ion source of a selected-ion flow tube (SIFT) tandem mass spectrometer. Characterization of the periodic trends in the reactivity of the metal-containing ions across and down the periodic table represents yet another approach for understanding intrinsic properties of the studied species[21, 26, 30, 35, 41, 42, 145, 154, 158, 161–164, 167, 660, 673, 674, 677–679, 681–684, 689–696, 729].

Several studies[17, 157, 708, 709, 712] have focused on investigating the reactivity of $[MnO]^+$, $[Mn_2O]^+$, $[Mn_2O_2]^+$, $[Mn_2O_4N_2]^+$, $[Mn_2O_6]^+$, $[MnO_2]^-$, $[Mn_2O_3]^-$ and $[Mn_2O_4]^-$ toward various neutral molecules (Table 2). Stevens and Beauchamp[17] reported that $[MnO]^+$ reacts with ethene to form bare manganese cation and $[MnCH_2]^+$ with concomitant eliminations of C_2H_4O and CH_2O, respectively. In the reaction of $[MnO]^+$ with ethane, the neutral products water and ethene are eliminated as the result of β-hydrogen transfer[157]. The same cation, $[MnO]^+$, when reacting with alkanes larger than ethane, also produces $[(\text{olefin})MnOH]^+$ (Table 2). The latter event is suggested to occur through an initial hydrogen-abstraction process followed by Mn-induced C–C bond cleavage. As mentioned above, compared to the other first-row transition metals, the manganese cation is the least reactive toward alkanes, whereas $[MnO]^+$ is the most reactive metal oxide cation[157]. The reactivity of the binuclear manganese oxide cations $[Mn_2O]^+$ and $[Mn_2O_2]^+$ toward selected neutrals has been investigated by FT-ICR MS after their gas-phase generation from the reaction of O_2 with $[Mn_2(CO)_4]^+$ (formed in the external ion source by CI of $Mn_2(CO)_{10}$)[708]. Therefore, oxidative features are displayed in the ion/molecule reactions of cluster ions $[Mn_2O]^+$ and $[Mn_2O_2]^+$ with model organic molecules such as methanol, acetaldehyde and unsaturated hydrocarbons. Accordingly, dehydrogenation, oxygen-atom transfer and homolytic cleavage processes have been identified[708]. The oxygen-rich manganese cation $[Mn_2O_6]^+$ displays an easy exchange of the O_2 ligand against carbon dioxide and dinitrogen. In the reaction with CO_2, $[Mn_2O_4N_2]^+$ showed an easy exchange of the N_2 ligand against the reactant molecule, generating the $[Mn_2O_4(CO_2)]^+$ product ion[709]. Data on gas-phase reactivity of some anions of transition-metal oxides, including $[MnO_2]^-$, $[Mn_2O_3]^-$ and $[Mn_2O_4]^-$, have also been reported[712]. It was shown that in the $[Met_xO_y]^-$/methanol system (for Met = Mn, Fe, Co, Ni, Cu), the $[MetO_2]^-$ and $[Met_2O_3]^-$ anions react more efficiently than $[Met_2O_4]^-$. At the same time, the relative reaction efficiencies decrease when the metal atom varies from Mn to Cu. The latter observation suggests that the number of electrons in the *d* shell of the metal atom appears to be an important factor influencing the reactivity in the described system[712].

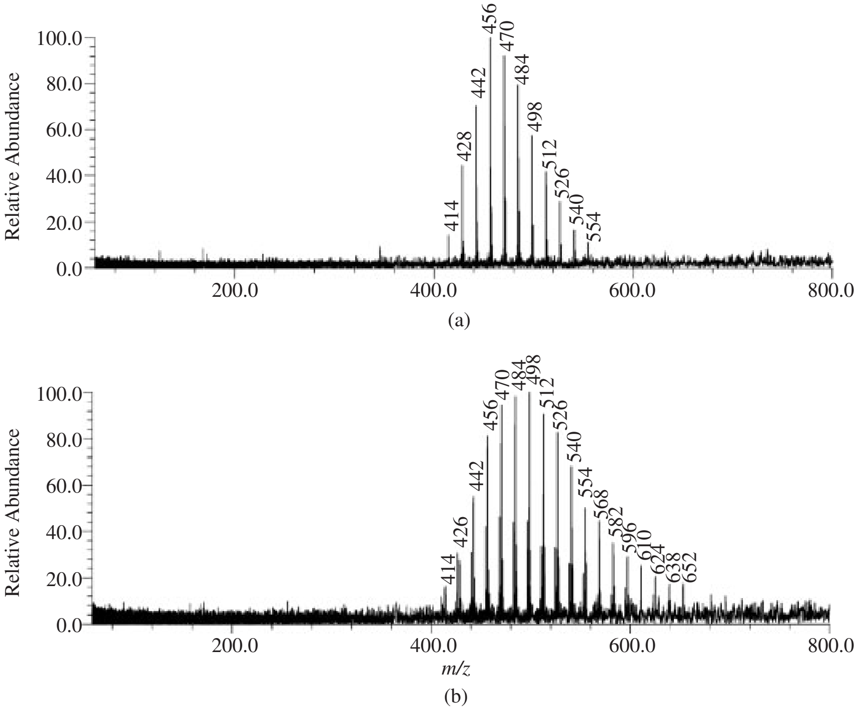
The gas-phase ion/molecule reactions involving organomanganese complexes (ionic or neutral), as well as coordinatively unsaturated organomanganese fragment ions and electronically unsaturated organomanganese anions, were also investigated in recent decades. Ligand substitution or addition, electron transfer, insertion of the metal ion into a bond of the organic molecule with formation of insertion intermediates, metal-induced rearrangement, and fragmentation of the ligand are among the processes occurring during ion/molecule reactions in which organomanganese species participate (Table 2). Eyler and Richardson[705] studied thermal self-exchange and cross reactions of organometallic molecules and ions (including Mn-containing species). Equations 1 and 2 represent investigated electron transfer processes with participation of organomanganese complexes[142, 152, 153, 705, 706].

$$[\mathrm{Met}'\mathrm{L}'_2]^+ + [\mathrm{Met}''\mathrm{L}''_2]^0 \rightarrow [\mathrm{Met}'\mathrm{L}'_2]^0 + [\mathrm{Met}''\mathrm{L}''_2]^+ \tag{1}$$

(Met′ = Met″ = Mn; L′ = L″ = Cp, MeCp, *Cp. Met′ = Mn; Met″ = Ni;
L′ = L″ = Cp, *Cp. Met′ = Fe, Ni; Met″ = Mn; L′ = L″ = Cp. Met′ = Co, Ru;
Met″ = Mn; L′ = Cp; L″ = *Cp. Met′ = Cr; Met″ = Mn; L′ = C_6H_6; L″ = *Cp.)

$$[\mathrm{MnCp}_2]^{2+} + [{}^*\mathrm{MnCp}_2]^0 \rightarrow [\mathrm{MnCp}_2]^+ + [{}^*\mathrm{MnCp}_2]^+ \tag{2}$$

From the analytical chemistry point of view, the study of ion/molecule electron transfer kinetics is important for method development emphasizing sensitivity and specificity enhancement of charge-transfer chemical ionization mass spectrometry (charge-transfer CI MS). The manganese cation[473] and more recently $[\mathrm{ClMn(H_2O)}]^+$ ion[474, 475] have been probed as soft chemical ionization reagents in order to expand analytical capabilities of CI MS and make possible the simultaneous analysis of a variety of saturated and unsaturated hydrocarbons[474], including base oil samples[475] (Table 2 and Figure 6). Ni and Harrison[677] investigated the possibility of the differentiation of C_5H_8 isomers 1-pentyne, 2-pentyne, l,3-pentadiene, 1,4-pentadiene, 2-methyl-1,3-butadiene and 3-methyl-1,2-butadiene by gas-phase reactions with Mn^+ and some other metal ions. MS differentiation and



(a)

(b)

FIGURE 6. LIAD/$[\mathrm{ClMn(H_2O)}]^+$/FT-ICR mass spectra of two base oil samples: (a) G1F1 (single scan); (b) G1F2 (single scan). Reprinted with permission from Reference 475. Copyright 2008 American Chemical Society

identification of isomers (organic or organometallic) by reactions with metal cations or organometallic ions represents another challenge for analytical mass spectrometry.

Long-chain alkanes[684], polyaromatic hydrocarbons[161, 474], fullerene[156, 163], polyazamacrocyclic compounds[698, 704] and crown ethers[24, 704, 728] have also been subjected to ion/molecule reaction studies with Mn-containing ions. Zagorevskii and Nekrasov[24, 704] revealed two major reactions in the $[(RXC_5H_4)Mn(CO)_n]^+$/crown ether system: adduct formation and substitution of a metal atom ligand by a crown ether. A rearrangement process in $[RXC_5H_4Mn]^+$, namely the migration of R to the Mn atom, was detected as well. The degree of isomerization was discussed in terms of the nature of R and X groups[704].

Reactivity of dimanganese $[Mn_2(CO)_n]^+$ ions toward polyazamacrocyclic compounds[698] or aliphatic alcohols[13], as well as polynuclear species $[Mn_x(CO)_n]^+$ and $[Re_xMn_y(CO)_n]^+$ toward their binuclear neutral precursors $Mn_2(CO)_{10}$ and $ReMn(CO)_{10}$, respectively[14], were also studied in the FT-ICR MS apparatus (Table 2). According to van Beelen and Ingemann[13], the predominant reaction of the $[Mn_2(CO)_n]^+$ (where $n = 1-4$) involves the coordination of one methanol molecule and the loss of one or more carbonyl ligands, whereas the $n = 5$ reaction occurs by the successive addition of two alcohol molecules. For the series of ions with $n = 2-5$, the efficiency of the reaction with MeOH decreases as n increases. On the other hand, the efficiency of the reactions of the $[Mn_2(CO)_4]^+$ ion with alcohols decreases in the series MeOH, EtOH and n-PrOH. Remarkably, the efficiency of the reaction of the same $[Mn_2(CO)_4]^+$ ion with CD_3OH, C_2D_5OH or n-C_3D_7OH is much lower than that of the reaction with the corresponding unlabelled alcohols, revealing the occurrence of a significant isotope effect. The H−O and C−O bond activation were also detected during this study[13].

Finally, multicoordinatively and multielectronically unsaturated organomanganese anions, $[Mn(CO)_n]^-$ ($n = 1-4$), were also investigated by several groups: by McDonald and coauthors[25, 29, 31, 32, 34, 711], Gregor and Gregor[33], as well as by van den Berg and coauthors[38−40] (Table 2). In these studies, substitution or addition of the ligand has been observed; competitive H−O and H−C bond activation in the $[Mn(CO)_3]^-$/methanol system, as well as cyclopropane and alkane C−H bond activation with $[Mn(CO)_3]^-$, have been examined in addition to the reactivity of $[Mn(CO)_{3,4}]^-$ toward the alkenes, dienes, acetylene, benzene, etc. Apparently, in most of the enumerated reactions (except

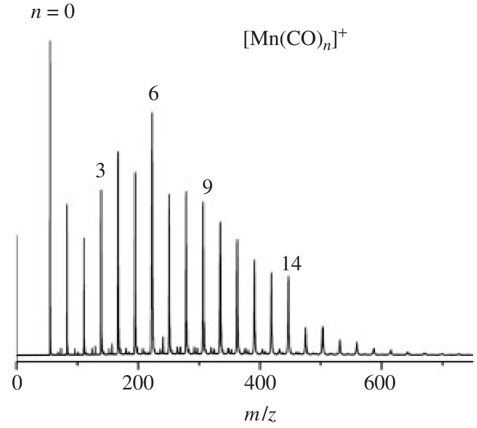


FIGURE 7. The mass spectrum of $[Mn(CO)_n]^+$ clusters produced by cluster source. Reproduced by permission of Elsevier from Reference 671. Copyright (2010) Elsevier

ligand substitution or addition), $[Mn(CO)_3]^-$ participates in C–H bond insertion. Quite the opposite in fact: insertion into a C–C bond does not appear to be a common process for the investigated organomanganese anions.

Recently, a remarkable experiment was performed by Reed and Duncan[671], generating manganese carbonyl cations, $[Mn(CO)_n]^+$ ($n > 6$), in a molecular beam by laser vaporization (LV) in a pulsed nozzle source (Figure 7). Six carbonyl ligands satisfy the coordinative needs of the central manganese atom. The addition of extra CO ligands to the coordinatively saturated $[Mn(CO)_6]^+$ ion results in 'external' COs coordinated to other carbonyls through weaker electrostatic forces. As a result, monocharged cation clusters with *ca* 20 carbonyls have been detected (Figure 7). The clusterization process occurs due to the cold supersonic expansion in the apparatus. The generation of the $[Mn(CO)_n(Ar)_m]^+$ (Ar = argon; $n = 1$; $m = 3$. $n = 2$; $m = 2$. $n = 3–6$; $m = 1$) ions was achieved as well, using the same apparatus. The structure and reactivity of the $[Mn(CO)_n]^+$ ($n = 1–9$) and enumerated $[Mn(CO)_n(Ar)_m]^+$ species were investigated by IRMPD spectroscopy and experimental findings were supported by theoretical calculations[671].

D. Organomanganese Ion Structures Studied by Computational Methods

Ions with a Mn–C bond which were studied by computational methods are listed in Table 3. Computational data with reference to the geometry and thermochemistry of gas-phase ions are often used to support experimental findings or predict new ones. The simplest ionic organomanganese species studied by theoretical methods were $Mn^{(I)}$-carbene systems, i.e. $[MnCH]^+$, $[MnCH_2]^+$ and $[MnCH_3]^+$. Geometries, electronic states and strengths of the manganese–carbon bonds in the enumerated cations were calculated at different levels of theory[732–738]. For the manganese dicarbide cation ($[MnC_2]^+$), Rayón and coauthors[139] suggested the existence of two structures, *cyclic* and *linear*. The isomerization barrier between them was estimated to be very small, lower than 2 kcal mol^{-1}. The negatively charged species $[MnC_2]^-$ and $[MnC_3]^-$ were investigated as well[139, 652, 653].

Recently, the mechanism of ethylene production from acetone complexes of metal dications, along with quantum chemical calculations of the geometry of the species and intermediates involved in the process, have been reported[743]. It was suggested that the Mn–C bond is present in two ions, namely $[Mn(acetone)(CH_3)]^+$ and $[Mn(acetone - H)]^+$, generated by CID of $[Mn(acetone)_2]^{2+}$ in the ESI triple-quadrupole mass spectrometer. The first ion consists of an acetone molecule coordinated to the Mn-carbene system, $[H_3C–Mn–OC(CH_3)_2]^+$. For the $[Mn(acetone - H)]^+$ ion, two isomeric structures, one *cyclic* and one *linear* (shown in Table 3), were postulated. The CID pathways at different collision energies (E_{lab}) and product species derived from the manganese dication coordinated with five ligands, $[Mn(acetone\text{-}d_6)_5]^{2+}$, were also examined[743].

Large organomanganese ions studied by computational methods were represented by various carbonyl-containing (including mixed-ligand) species and coordinatively unsaturated or saturated compounds with some combinations of π-ligands such as cyclopentadienyl, benzene, cycloheptatrienyl, furan and pyrrole (sandwich and mixed sandwich complexes) (Table 3). Even though the furan[167] and pyrrole[164] molecules have structural similarities with pyridine to some extent, the optimized geometry of the $[Mn(pyridine)]^+$ points out that there is no π-complex type of coordination in this ion, contrary to the fact that such coordination is characteristic for furan and pyrrole. Calculations performed by Rodgers and coauthors[660] showed that the starting π-complex geometry of pyridine with selected metal ions always converted to the energetically more favorable planar structure with a metal–nitrogen bond. Gaseous neutral manganocene is presumed to exist as a mixture of both *eclipsed* conformation (D_{5h}) and *staggered* conformation (D_{5d}), with only a small energy difference[606, 755–757]. Manganocene, with its low stability and five

TABLE 3. Mn−C bond-containing ions studied by computational methods

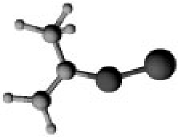
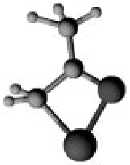
No.	Ion	Mn bonding environment	Reference
	Cation		
1	$[Mn(CH)]^+$	$[Mn-CH]^+$	732
2	$[Mn(CH_2)]^+$	$[Mn-CH_2]^+$	732–735
3	$[Mn(CH_3)]^+$	$[Mn-CH_3]^+$	732, 736–738
4	$[MnC_2]^+$	$[MnC_2]^+$ (linear isomer)	139
5	$[MnC_2]^+$	$[MnC_2]^+$ (cyclic isomer)	139
6	$[Mn(CO)_{1-3}]^+$	$[Mn(CO)_{1-3}]^+$	671
7	$[Mn(CO)_{4,5}]^+$	$[Mn(CO)_{4,5}]^+$	671, 739
8	$[Mn(CO)_6]^+$	$[Mn(CO)_6]^+$	671, 739–742
9	$[Mn(CO)_7]^+$	$[Mn(CO)_7]^+$	671
10	$[Mn(CO)_{1-6}(Ar)]^+$	$[Mn(CO)_{1-6}(Ar)]^+$	671
11	$[Mn(CO)_4(PH_3)]^+$	$[Mn(CO)_4(PH_3)]^+$	739
12	$[Mn(CO)_5(PH_3)]^+$	$[Mn(CO)_5(PH_3)]^+$	739, 742
13	[Mn(acetone − H)]$^+$	 (linear isomer)	743
14	[Mn(acetone − H)]$^+$	 (cyclic isomer)	743
15	$[Mn(acetone)CH_3]^+$	$[H_3C-Mn-OC(CH_3)_2]^+$	743
16	$[Mn(furan)]^+$	$[Mn(\pi\text{-}C_4H_4O)]^+$	167
17	$[Mn(pyrrole)]^+$	$[Mn(\pi\text{-}C_4H_5N)]^+$	164
18	$[Mn(pyrrole)_2]^+$	$[Mn(\pi\text{-}C_4H_5N)_2]^+$	164
19	$[Mn(C_5H_5)]^+$	$[Mn(\eta^5\text{-}C_5H_5)]^+$	605
20	$[Mn(C_5H_5)(CO)]^+$	$[Mn(\eta^5\text{-}C_5H_5)(CO)]^+$	605
21	$[Mn(C_5H_5)(CO)_2]^+$	$[Mn(\eta^5\text{-}C_5H_5)(CO)_2]^+$	605, 609
22	$[Mn(C_5H_5)(CO)_3]^+$	$[Mn(\eta^5\text{-}C_5H_5)(CO)_3]^+$	605, 609
23	$[Mn(C_5H_5)_2]^+$	$[Mn(\eta^5\text{-}C_5H_5)_2]^+$	606, 657, 744, 745
24	$[Mn(C_5H_5)(C_6H_6)]^+$	$[Mn(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)]^+$	746
25	$[Mn(C_5H_5)(C_7H_7)]^+$	$[Mn(\pi\text{-}C_5H_5)(\pi\text{-}C_7H_7)]^+$	746
26	$[Mn(C_6H_6)]^+$	$[Mn(C_6H_6)]^{+a}$	160, 663, 747–749
27	$[OMn(C_6H_6)]^+$	various structures	749
28	$[Mn(C_6H_6)(N_2O)]^+$	various structures	749
29	$[Mn(C_6H_6)_2]^+$	$[Mn(\pi\text{-}C_6H_6)_2]^+$	663, 746–748
30	$[Mn(C_6H_6)(CO)_3]^+$	$[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$	663, 750
31	$[Mn(C_6H_6)(CO)_4]^+$	$[Mn(\eta^4\text{-}C_6H_6)(CO)_4]^+$	663
32	$[Mn(arene)(CO)_3]^{+b}$	$[Mn(\eta^6\text{-arene})(CO)_3]^+$	750
33	$[\{Mn(CO)_2(PH_3)_3\}_2(CN)]^+$	$[(CO)_2(PH_3)_3Mn-CN-Mn(CO)_2(PH_3)_3]^+$	751
34	$[Mn(tryptophan)_2]^{2+}$	mixed CS/ZW conformations^c	672

TABLE 3. (*continued*)

No.	Ion	Mn bonding environment	Reference
	Anion		
35	$[MnC_2]^-$	$[MnC_2]^-$	652, 653
36	$[MnC_3]^-$	$[MnC_3]^-$	653
37	$[Mn(CO)_5]^-$	$[Mn(CO)_5]^-$	739, 740, 752
38	$[Mn(CO)_{4,5}(Cl)]^-$	$[Mn(CO)_{4,5}(Cl)]^-$	753
39	$[Mn(CO)_4]^{3-}$	$[Mn(CO)_4]^{3-}$	752
40	$[Mn^{(II)}(CN)_5(CO)]^{3-}$	$[Mn^{(II)}(CN)_5(CO)]^{3-}$	754
41	$[Mn^{(I)}(CN)_5(CO)]^{4-}$	$[Mn^{(I)}(CN)_5(CO)]^{4-}$	754
42	$[Mn^{(0)}(CN)_5(CO)]^{5-}$	$[Mn^{(0)}(CN)_5(CO)]^{5-}$	754
43	$[Mn(CO)_3]^{5-}$	$[Mn(CO)_3]^{5-}$	752
44	$[Mn(C_5H_5)(C_6H_6)]^-$	$[Mn(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)]^-$	746
45	$[Mn(C_6H_6)(CO)_3]^-$	$[Mn(\pi\text{-}C_6H_6)(CO)_3]^-$	750
46	$[Mn(\text{naphthalene})(CO)_3]^-$	$[Mn(\eta^4\text{-naphthalene})(CO)_3]^-$	750
47	$[Mn(\text{acenaphthene})(CO)_3]^-$	$[Mn(\pi\text{-acenaphthene})(CO)_3]^-$	750

[a] Different authors[160, 663,747–749] suggested that $[Mn(\text{benzene})]^+$ adopts one or two of the following three conformations: C_{6v}, C_{2v}, C_s. The most stable is the C_{6v} structure. See text for details.
[b] Arene = benzene, naphthalene, acenaphthene.
[c] CS = ligand in the charge-solvated configuration; ZW = ligand in the zwitterionic form.

unpaired electrons (reminiscent of the Mn^{2+} ion), is considered to possess significant ionic character[756, 758, 759]. The $[Mn(\eta^5\text{-}C_5H_5)_{1,2}]^+$ species were studied by computational methods as well[606, 657, 744, 745].

Analysis of $[Mn(C_6H_6)_2]^+$ suggested the D_{6h} conformation[747, 748]. According to the same studies, the monomer $[Mn(C_6H_6)]^+$ exhibits two structures (C_{6v} and C_{2v}) with different spin states. The most stable one is the C_{6v} conformation, in which Mn^+ is over the center of the C_6H_6 ring. In the C_{2v} structure, the benzene ring has two carbon atoms distorted slightly toward the metal. Recently, Zhao and coauthors[749] proposed that $[Mn(C_6H_6)]^+$ adopts C_{6v} and C_s conformations. In the C_s structure the metal ion is located nearly above three adjacent carbon atoms of benzene.

The quantum chemistry-based geometry of the cymantrene cation, $[(C_5H_5)Mn(CO)_3]^+$, is the *three-legged piano-stool* structure[603, 605, 609]. The C_5 and C_3 axes of the η^5-C_5H_5 and manganese tricarbonyl groups are coincident, and the cyclopentadienyl ring is nearly symmetrical and lies parallel to the plane formed by the three O atoms of the carbonyl ligands. The geometries of the coordinatively unsaturated species $[(C_5H_5)Mn(CO)_2]^+$ and $[(C_5H_5)Mn(CO)]^+$ were fully optimized at several levels of theory as well. It was proposed that the $Mn(CO)_n$ symmetries of the $[(C_5H_5)Mn(CO)_n]^+$ ions ($n = 3 \rightarrow 1$) are C_{3v}, C_{2v} and $C_{\infty v}$, respectively[605]. The last symmetry assumes that the MnCO group of the $[(\eta^5\text{-}C_5H_5)Mn(CO)]^+$ ion is linear.

Density functional theory calculations were performed for the cationic, neutral and anionic species $[(\text{arene})Mn(CO)_3]^z$ (where arene = benzene, naphthalene, acenaphthene)[750]. It was shown that cationic complexes prefer the η^6-bound structure. These results agree with X-ray crystallographic data. For the anionic naphthalene derivative, $[(\text{naphthalene})Mn(CO)_3]^-$, the η^4-bound structure was suggested[750]. The geometries of some other ionic manganese carbonyl derivatives have also been calculated and are summarized in Table 3.

Interesting experimental and theoretical data on the structure of the gas-phase dimeric complexes of tryptophan with a series of doubly charged metal ions were reported recently by Dunbar and coauthors[672]. It was proposed that the $[Mn(tryptophan)_2]^{2+}$ gaseous species exist in mixed charge-solvated (CS)/zwitterionic (ZW) conformations. Several other conformations have been calculated as well.

E. Neutralization–Reionization Mass Spectrometry

Manganese-containing ions generated in the gas phase during MS experiments have been used for non-traditional goals, and one such example is provided by *neutralization–reionization mass spectrometry* (NR MS) studies[760–762]. The unique objective of this technique is the generation of neutrals that cannot be produced by other methods, and NR MS is acting as a prediction/detection tool for new, elusive species. Another purpose of NR MS is to confirm the existence of molecules (or radicals) that are presumed intermediate particles of chemical reactions, consequently contributing to the deciphering of reaction mechanisms. In NR MS experiments, ions of interest are produced in the ion source of a mass spectrometer, mass-selected, and transferred into the first collision cell where they are neutralized by collisions. The remaining ions are deflected, so that only neutral particles are allowed to enter the second collision cell. In this cell, some neutrals are collisionally reionized allowing their detection as charged species. The observation of a ‘recovery signal’ at the same mass-to-charge ratio as the m/z of precursor ions selected for neutralization–reionization provides evidence for the existence of the corresponding neutrals and their stability throughout the experimental time-frame. The NR MS method has been applied to the investigation of various organometallic systems[760–762]. Zagorevskii and coauthors[37, 761, 762] have used this method to generate neutral coordinatively unsaturated manganese derivatives of the MnR type. The investigated $[MnR]^+$ species were generated by electron ionization of Mn-containing complexes and used as precursors for neutral analogs. By this method, a variety of neutral σ- and π-derivatives of $Mn^{(I)}$ complexes, MnR (where $R = H$, OH, CH_3, Ph, C_5H_5, C_5H_4CN, C_5H_4CHO, $C_5H_4COCH_3$, C_5H_4COPh, C_5H_4COOH and $C_5H_4CH_2OH$), was generated in the gas phase.

Another application of metal-containing ions is the generation of unusual organic species. In organometallic cations, the metal atom is a common site for charge localization and it often plays an ‘internal’ catalyst role, causing ligand transformations that are otherwise impossible. One such example is the generation of $[C_6,H_5,O]^+$ from a $[Mn(C_5H_4CHO)]^+$ precursor. The dissociation of the latter is very unusual because manganese-containing ions mainly produce neutral organic products and charged metal-containing species[37]. In this case, the reverse was observed: a neutral metal atom and an organic ion were formed. Tandem mass spectrometry studies and appearance energy measurements showed that the structure of $[C_6,H_5,O]^+$ was different from that of phenoxy and hydroxyphenyl ions[763]. Consequently, the $[(C_5H_5)CO]^+$ structure was assigned to a product of the general formula $[C_6,H_5,O]^+$ derived from a $[Mn(C_5H_4CHO)]^+$ coordinatively unsaturated precursor.

V. OTHER STUDIES INVOLVING MASS SPECTROMETRY

Manganese-containing complexes have extensive use in many fields. Quality and compound purity control, as well as monitoring of reagent modification or degradation during different processes, are often required for practical applications. Naturally, mass spectrometric techniques have become a standard practice for express analysis of a large variety of species, including organometallics.

Organometallic chemical vapor deposition (OMCVD) is a common way of creating materials for use in the electronics industry. Deposition may be induced by pyrolysis, photolysis or plasma processes. Some authors investigated derivatives of manganese carbonyl complexes $[Mn(CO)_4(\mu\text{-TeR})]_2$ (where R = Me **(84)**, Et **(85)**, *i*-Pr **(86)**, CH_2SiMe_3 **(87)**, Ph **(88)**), $[Mn(CO)_5]_2(\mu\text{-SiH}_2)$ **(89)** and cymantrene-based compounds for OMCVD and applied mass spectrometry to monitor this modus operandi[132, 764–766].

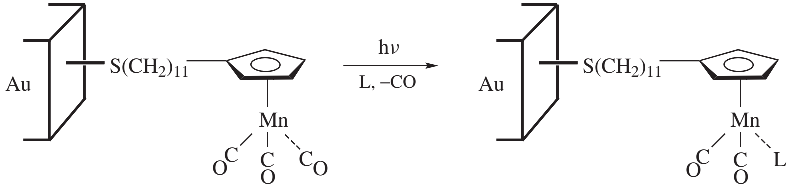
The thermal chemistry of decacarbonyldimanganese deposited on MgO thin films[767], the pyrolysis of this binuclear complex[768], and its thermal dissociation on the heated Re surface[769] were studied by mass spectrometry as well. Similarities and differences of cymantrene fragmentation in low-temperature plasma versus fragmentation under EI revealed the mechanisms of dissociation channels[770]. The flash vacuum pyrolysis technique in combination with EI MS is another way of generating reactive intermediates and elucidating the reaction mechanisms. This apparatus was employed to study organomanganese pentacarbonyl compounds $PhCH_2Mn(CO)_5$ **(90)** and binuclear derivative $(CO)_5MnCH_2(p\text{-}C_6H_4)CH_2Mn(CO)_5$ **(91)**[771].

According to a few reports, ions containing a Mn–C bond can be generated by MS methods even from classical Werner-type coordination compounds[772–774]. It was shown that CID of doubly charged complexes of manganese with dimethyl sulfoxide[773] or acetamide molecules[774] resulted in formation of $[MnCH_3]^+$ along with other fragment ions. The studied doubly charged precursors have been produced by the ESI source. The same type of complex with acetonitrile was transferred from solution to the gas phase by the ESI interface and subjected to CID as well[772]. In this case, the fragmentation of doubly charged precursor resulted in the formation of $[MnCN(CH_3CN)_{0-2}]^+$ species.

Wollman and coauthors[775] examined a photosensitive self-assembled monolayer of 11-mercaptoundecylcyclopentadienylmanganese tricarbonyl on polycrystalline gold **(92)** by means of secondary-ion mass spectrometry (SIMS). It was shown that the tricarbonyl moiety in this type of substrate undergoes efficient photoinduced CO substitution with a variety of phosphor-containing ligands (Figure 8). Positive-ion mode SIMS spectra of **92** treated with several $RPPh_2$ molecules in the dark and irradiated in the presence of the same species were discussed in detail[775].

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry is a soft ionization technique which was used for the analysis of only a few cymantrene-based species[472] including cymantrene-peptide bioconjugates[567] and metallofullerenes $Mn@C_n$ ($n = 80, 82$)[776].

The use of methylcyclopentadienyl-manganese tricarbonyl, $(MeCp)Mn(CO)_3$, as a gasoline fuel additive raised environment contamination concerns, particularly due to manganese neurotoxicity. Consequently, EI MS and GC-MS analytical methods for the analysis of this compound in soil[174] and water samples[777], respectively, have been developed and described.



(**92**)

FIGURE 8. Photochemistry of photosensitive self-assembled monolayer of 11-mercaptoundecylcyclopentadienylmanganese tricarbonyl on polycrystalline gold **(92)**. The process involves surface photoattachment of functionalized phosphines, L. Reprinted with permission from Reference 775. Copyright 1994 American Chemical Society

VI. CONCLUSIONS

A survey of literature on mass spectrometry and gas-phase ion chemistry of organomanganese species illustrates the importance and wide application of MS and related techniques to the organometallic chemistry of manganese. The most common use of MS is molecular weight determination and structural characterization of compounds having a Mn−C bond: polynuclear clusters, complexes incorporating organometallic units bridged with organic fragment(s), bifunctional compounds containing organometallic and classical Werner-type coordination sites, fullerenes or planar polyaromatic hydrocarbons with an organomanganese fragment attached to them, manganospiralenes, manganoscorpionates, self-assembled monolayers of cymantrene derivatives on metals, cymantrene-peptide bioconjugates, etc. To achieve these goals, a variety of ionization methods has been applied. In addition to molecular weight measurements, in some cases mass spectrometry was successfully applied for differentiation of isomeric organometallic complexes. Early studies could only be performed on volatile compounds using EI MS and CI MS methods. The development of ionization techniques such as FD, LDI, FAB and ESI allowed the MS investigation of more complex non-volatile or unstable molecules, including ionic ones. It is expected that MALDI MS will contribute to the characterization of this type of compounds in the future. Also, qualitative and quantitative methods based on mass spectrometry are likely to be improved in sensitivity and optimized for metallomics studies, as well as other bioscience fields. Another important area where new high-performance MS techniques are sure to be employed is environmental toxicology, as manganese neurotoxicity concerns and pollutant monitoring are addressed. Use of the manganese cation or $[ClMn(H_2O)]^+$ ion as soft chemical ionization reagents will expand analytical capabilities of CI mass spectrometry and make possible the simultaneous analysis of a large variety of saturated and unsaturated hydrocarbons, thus potentially facilitating petroleomics studies[778–780].

Mass spectrometry methods have been widely used for the measurement of fundamental physico-chemical parameters such as IEs, APs and BDEs of organomanganese species. The gas-phase reactions resulting in the dissociation or formation of Mn−C bond(s) have been investigated as well. Experimental data demonstrated that manganese−carbon bonds in various species are rather weak and easily cleaved during MS experiments. Characterization of the periodic trends in the reactivity of metal-containing ions across and down the periodic table represents a cognitive approach for understanding intrinsic properties of the investigated particles.

It is worth mentioning that mass spectrometry provides a variety of choices for the generation of manganese-containing complexes of unusual structure, whose detection under ‘regular’ conditions of chemical reactions is simply impossible. Some unimolecular dissociation reactions involve atypical transformations of ligands. Ion/molecule reactions have been used to obtain previously unknown manganese-containing ionic species. The latter gas-phase ions can be subjected to neutralization−reionization in order to produce their neutral analogs and consequently predict the existence of new elusive neutral species or confirm the existence of molecules (or radicals) that are presumed intermediates of chemical reactions. IRMPD spectroscopy was used to directly probe the 3D structural features of several gas-phase manganese-containing anions and cations. Overall, MS dissociation techniques, neutralization−reionization mass spectrometry and IRMPD spectroscopy have great potential for gas-phase studies (see, for example, reviews authored by Jennings[781], Holmes[760, 761, 782] and Eyler[664] dedicated to these areas) and are far from being fully exploited for the field of gas-phase ion chemistry of organomanganese species. Theoretical calculations have also contributed to the 3D characterization of Mn-containing ion structures and understanding of the reaction mechanisms in which such species are involved.

The constantly growing potential of mass spectrometry is certain to positively impact both analytical and research aspects of studies on organomanganese species in the future.

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s-Block-metal-mediated manganation reactions

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I. INTRODUCTION

The selective functionalization of C−H bonds remains one of the most important and exacting tasks in modern organic synthesis. The ability to substitute hydrogens for functional groups provides a powerful method for constructing complex organic molecules from simple starting materials, and new and improved approaches to the task are constantly sought. Amongst the most successful strategies for removing unwanted hydrogens from target carbon atoms are metal-mediated reactions in which the role of the metal can either be catalytic or stoichiometric. In catalytic functionalizations, often referred

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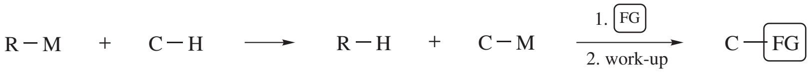
to as C–H activations, softer, low-polarity organotransition metal catalysts undoubtedly dominate[1]. Stoichiometric activations of C–H bonds are more commonly effected by organometallic compounds of the main group metals, with lithium, magnesium, aluminium and zinc organometallics playing prominent roles[2]. The unifying property of main group organometallics is the higher polarity of their metal–carbon bonds, stemming from the presence of hard 'cations', such that these compounds may be referred to as 'hard' organometallics[3]. Although the applications of main group organometallics in the functionalization of C–H bonds have reached an advanced stage, we can in the majority of cases still rationalize their reactivity in terms of kinetic and thermodynamic Brønsted acidities and the simplified reaction shown in Scheme 1:



M = electropositive main group metal; R = alkyl, amido; FG = functional group

SCHEME 1

If all deprotonative metallations proceeded as trivially as Scheme 1 suggests they might, the life of the synthetic chemist would be considerably less interesting. However, the nature of organometallic reagents and of organic substrates presents us with stimulating challenges, namely *reactivity* and *selectivity*. Sometimes, main group organometallics are too reactive, and sometimes they are not reactive enough. Organometallics that are too reactive will attack C–H bonds and other functional groups indiscriminately, resulting in poor regioselectivity in some instances or decomposition of the substrate to useless by-products in others. Low reactivity organometallics can offer greater functional group tolerance but they can also require forcing conditions in order to obtain satisfactory yields.

Fortunately, considerable success has been achieved in developing hard organometallic reagents that meet the reactivity and selectivity requirements without having to resort to extensive use of protecting groups and, hence, long, linear synthetic sequences[2,4]. Firstly, main group organometallic Brønsted bases of a particular carbanion can have their reactivity tuned simply by varying the metal. Secondly, reactivity can be further modified through the addition of complexing agents (ligands) to reaction mixtures, an effect that derives from the ability of Lewis bases to deaggregate organometallic clusters. Thirdly, amongst the most significant recent additions to the arsenal of the synthetic chemist are mixed-metal bimetallic and trimetallic 'superbases' that bring about remarkable reactivity that cannot be achieved with analogous monometallic systems: the classic example of a mixed-metal superbase is the Lochmann–Schlosser BuLi/*t*-BuOK or 'LICKOR' reagent[5]. The development of new 'turbo-charged' superbases consisting of various permutations of highly polar and less polar main group organometallics remains the subject of intense activity, and the reader is directed to excellent recent review articles on the subject[6].

A. Manganese(II): A Transition Metal Masquerading as a Main Group Element

In the ongoing search for new bimetallic reagents for C–H deprotonations, however, synthetic chemists have paid increasing attention to combinations of hard main group organometallics with a *transition metal*, and one notable for its unusual organometallic chemistry: manganese(II). Although it can be argued that all individual transition metal ions possess some unique characteristics, manganese(II) is distinguished from its neighbours in the d-block owing to its high-spin $3d^5$ electronic configuration (or ^6A ground state, in spectroscopic parlance), which results in a crystal field stabilization energy of zero and confers manganese(II) with harder character than is found for other first-row M(II) species[7]. As such, manganese(II) has 'main-group-like' character, making it an excellent partner for s-block metals in the development of new superbases. Manganese(II) also offers potential redox reactivity that is inaccessible to main group organometallics, which could expand the range of transformations achievable to bimetallic superbase reagents. As this chapter shows, many C−H deprotonation reactions of mixed alkali metal−manganese(II) reagents, recently dubbed 'alkali-metal-mediated manganation'[6], are truly eye-catching.

The first applications of bimetallic s-block metal/manganese(II) reagents were reported by Normant and Cahiez in the 1970s[8]. Three general types of organomanganese(II) reagent were reported in these pioneering studies: organomanganese halides, RMnX, dialkyl manganese, MnR_2, and trialkyl manganates, $[R_3Mn][M]$ ($M = Li, MgCl$). The greater thermal stability of the trialkyl manganates has meant that reagents of this type are typically more popular than the other two, which often decompose at $T < 0\,^{\circ}C$. Trialkylmanganates were initially used in alkylation and 'carbomanganation' reactions, and this chemistry has been reviewed by Cahiez, Duplais and Buendia[9], and by Oshima[10]. More recently, organomanganates and the closely related amidomanganates, $[(R_2N)_3Mn][M]$, have been developed for new C−H metallation chemistry, and as such the area has recently undergone something of a renaissance. This new chemistry has not previously been reviewed, and hence it is the subject of this chapter.

II. MANGANATION REACTIONS

Before discussing alkali-metal-mediated manganations with manganese(II), it is informative to look at other forms of manganation by manganese organometallics so that the reactivities can be compared.

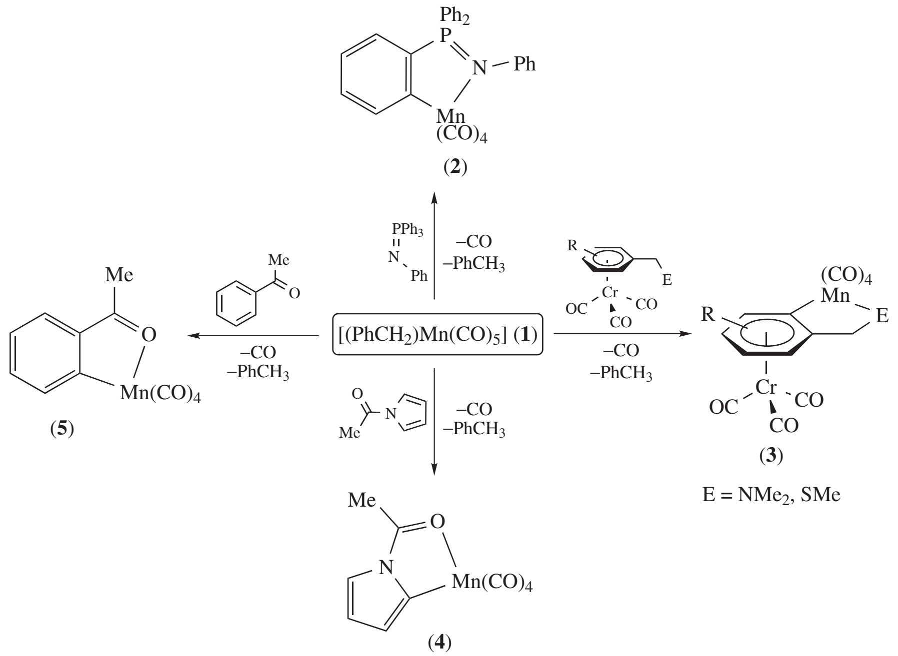
A. *ortho*-Manganation by Manganese(I)

The *ortho*-functionalization of aromatic ketones using stoichiometric amounts of benzyl(pentacarbonyl)manganese(I) $[(PhCH_2)Mn(CO)_5]$ (**1**) is a versatile reaction that has been known for many years, and the cyclomanganated species are of interest because they can be partners in palladium-catalysed cross-coupling reactions[11]. The functional group tolerance of the reaction is high, and it can be extended to manganations of: iminophosphoranes to give complexes such as **2**[12]; η^6-arene complexes of chromium tricarbonyl, $[(\eta^6\text{-arene})Cr(CO)_3]$ (to give **3**)[13]; arylhydrazones[14]; azobenzenes[15]; triphenylphosphine chalcogenides[16]; podocarpic acid derivatives[17]; *N*-acyl heteroaromatics (**4**), benzamides, ketones (**5**) and substituted aldehydes[18] (selected examples are shown in Scheme 2).

In these *ortho*-metallation reactions, the manganese(I) centre in **1** is thought to be directed to the *ortho* C−H bond by the Lewis base functionality in the arene, and the reaction is driven by entropy (the chelate effect). The intermolecular version of the reactions shown in Scheme 2 are not known: the manganese−benzyl bond contains the soft and kinetically inert metal species manganese(I) (low-spin $3d^6$ valence configuration), which is not sufficiently reactive to deprotonate sp^2 C−H bonds without the directing influence of a coordinating substituent.

B. Manganations with Manganese(II)

As with main group metals, the essence of the synthetic organometallic chemistry of manganese(II) is *diversity*[7,9,10]. The focus of this chapter is on reactions that introduce



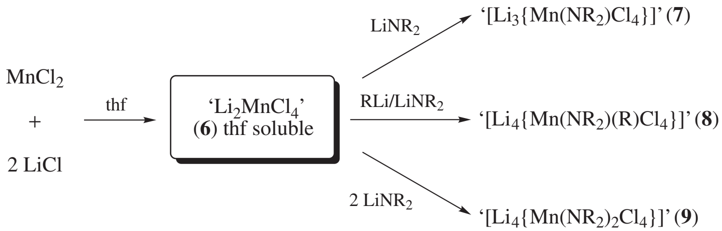
SCHEME 2

manganese(II) into the framework of an organic substrate via s-block metal manganate reagents, i.e. via s-block-metal-mediated manganations. Although chemistry of this type has been known for some time, exciting developments are happening at the time of writing, and the literature up to mid-2010 is surveyed here.

1. Enolates from alkali metal amido manganates: manganation by deprotonation

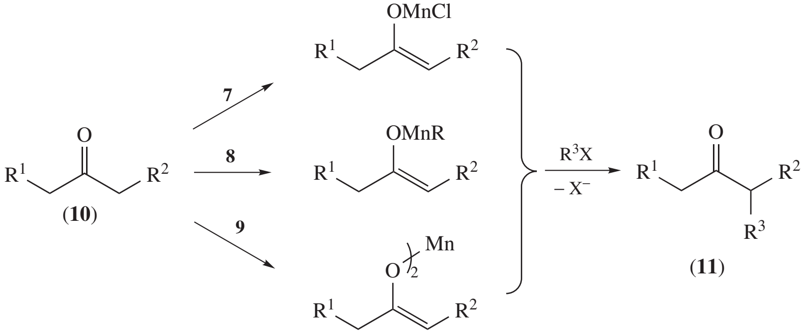
Enolates are amongst the most important synthons in organic synthesis, and α-alkylation of metal enolates has been a standard reaction for many years[19]. Lithium enolates are perennially popular in this context, but they suffer from the drawback of being prone to polyalkylation. Methods are available to avoid the formation of polyalkylated products, but arguably one of the most simple and accessible involves the use of manganese(II) amides as precursors to manganese(II) enolates. The detailed chemistry of manganese enolates is described by Concellon in Chapter X of this book, so only aspects specifically relevant to s-block-metal-mediated reactions will be covered here. First reported by Cahiez and coworkers in a series of patents prior to publication[20], lithium−manganese(II) enolates can be prepared from the manganese(II) amido precursors **7**−**9**, which themselves are synthesized according to Scheme 3.

The synthesis of lithium−manganese(II) amides **7**−**9** is achieved by reacting the THF-soluble salt of composition ‘Li_2MnCl_4’ (**6**) with lithium complexes of secondary amides. Unlike their monometallic lithium amide counterparts, the mixed metal amides can be stored conveniently as THF solutions at room temperature for several months without visible signs of decomposition[21]. The exact compositions of **7**−**9** are currently unknown,



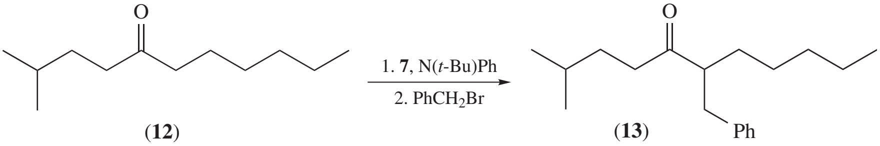
SCHEME 3

but the common feature of a manganese amido functionality, {Mn−NR$_2$}, is presumed to be responsible for their observed Brønsted basicity. The manganese enolates themselves can be synthesized by the reactions of **7**−**9** with ketones (**10**), and subsequently reacted with organic halides to selectively form the mono-substituted products **11** (Scheme 4). An interesting dependence of enolization regioselectivity on the nature of the amido ligand was observed, which is thought to be steric in origin. High selectivity for the kinetic enol can be achieved with both cyclic and acyclic ketones, and particularly good selectivities were obtained with NR$_2$ = N(*t*-Bu)Ph, as illustrated with the synthesis of **13** from the unsymmetrical ketone **12** (Scheme 5)[22].



10 = Bu$_2$CO, Pr$_2$CO, *i*-PrC(O)Hex, PhCH$_2$EtCHC(O)Pr; **11** R^3 = alkyl, benzyl, allyl; X = Br, Cl

SCHEME 4

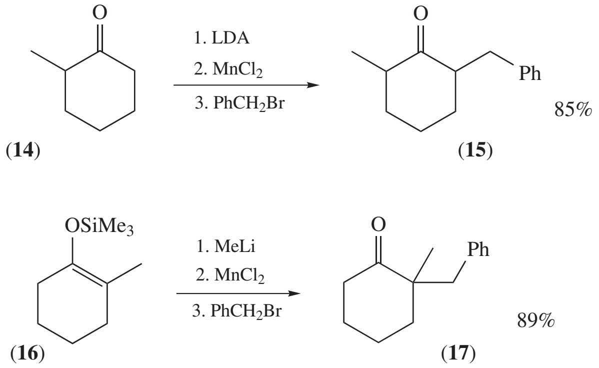


85% yield
97% regioselective

SCHEME 5

By varying the reaction conditions through the use of highly polar co-solvents, a wide range of alkylating reagents can be used to produce monoalkylated ketones in high yields and with excellent selectivity; the S_N2 substitution reaction with allylic halides is also stereospecific. In these reactions, polyalkylated products were almost never obtained[23, 24].

The results obtained in Cahiez's original study of alkali-metal-mediated manganation of ketones were a significant improvement on analogous reactions that used lithium-only enolates. Thus, this work by Cahiez may be the first documented example of alkali-metal-mediated metallation. A related study that described the synthesis of manganese enolates by reacting lithium enolates with manganese(II) bromide also revealed that alkylation of the enolate proceeded in high yields and was selective for the monoalkylation product. A comparison of the reaction of the manganese enolate derived from 2-methylcyclohexanone (**14**) and benzyl bromide with the analogous reaction of the lithium enolate found that the manganese(II) version is clearly superior in terms of both regioselectivity and monoalkylation to form the 2,6-dialkylated product **15** (Scheme 6)[25].



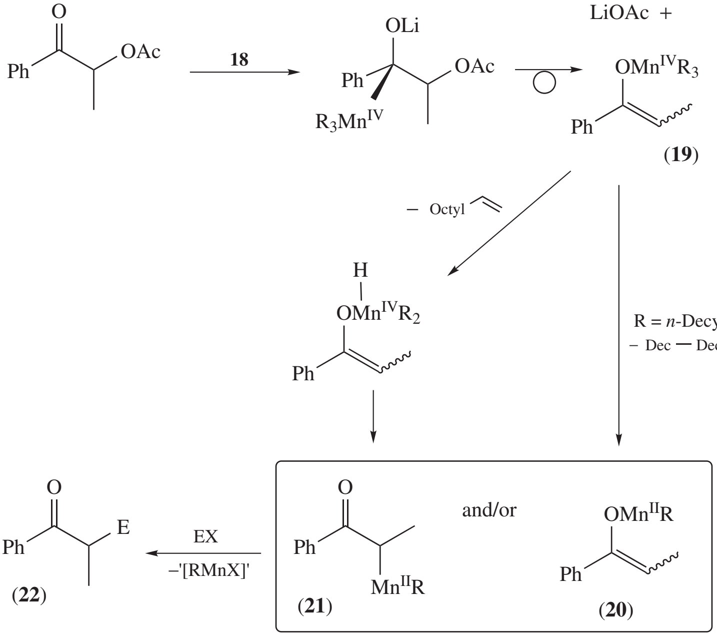
SCHEME 6

The 2,2-dialkylated product **17** can be obtained with 95% regioisomeric purity in a yield of 89% by generating the manganese enolate from the silyl enol ether (**16**) according to Scheme 6. The crucial observation in this work that explains the superiority of bimetallic manganese/lithium enolates is that the equilibrium responsible for the formation of unwanted by-products in the lithium-only enolate reactions does not occur in the presence of manganese(II).

2. Enolates from alkali metal alkyl manganates by reductive manganation

Alkali metal manganates such as $[R_3Mn][Li]$ (R = Bu **18a**, *n*-Dec **18b**) are able to generate manganese enolates such as **19** with a degree of regiocontrol *directly* from ketones bearing a leaving group in the α-position by acting as formal 2-electron reducing agents (Scheme 7)[26].

A mechanism was proposed to account for the generation of **19** by oxidative addition of the ketone to **18b** followed by reductive elimination to afford a manganese(II) enolate (**20** or **21**), which can then be used in aldol reactions and alkylations (**22**), the latter being specific for the monoalkylation product.

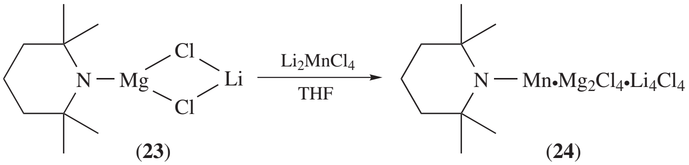


R = Bu, *n*-decyl; EX = alkyl halide

SCHEME 7

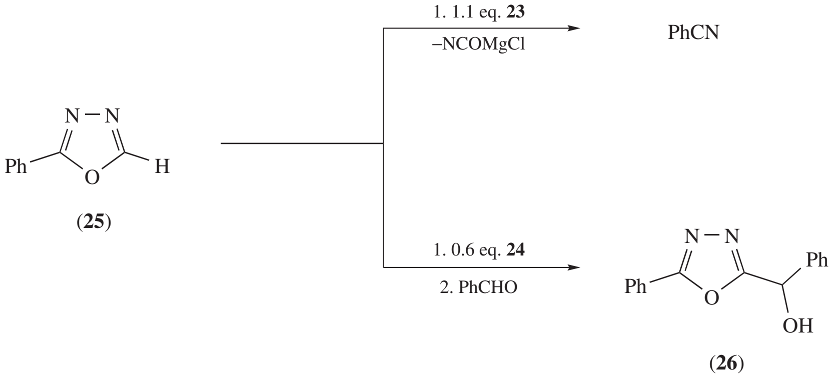
C. A Trimetallic Manganese(II)-containing Superbase

Although the *ortho* (or intramolecular) manganation of arenes by phenylmanganese(I) pentacarbonyl (discussed in Section II.A) is well established, its scope is somewhat limited. The report in 2009 by Knochel and coworkers of the powerful trimetallic manganese(II)−magnesium−lithium metallating reagent $[(TMP)_2Mn{\bullet}2MgCl_2{\bullet}4LiCl]$ (TMP = 2,2,6,6-tetramethylpiperidide) (**24**) was a significant addition to the arsenal of 'ate-type metallating agents, and even showed reactivity superior to that of the mixed lithium−magnesium amide metallating reagent $[(TMP)MgCl{\bullet}LiCl]$ (**23**).[27] The addition of **23** to solutions of Li_2MnCl_4 leads to the formation of THF solutions of **24** that are stable for several weeks without showing signs of decomposition (Scheme 8).



SCHEME 8

The reactivities of **23** and **24** clearly contrast: for example, whereas **23** reacts with 2-phenyl-1,3,4-oxadiazole (**25**) to result in fragmentation (decomposition products), compound **24** smoothly metallates **25**, allowing the subsequent reaction with benzaldehyde to produce **26** in a yield of 77% (Scheme 9).



(**25**)

(**26**)

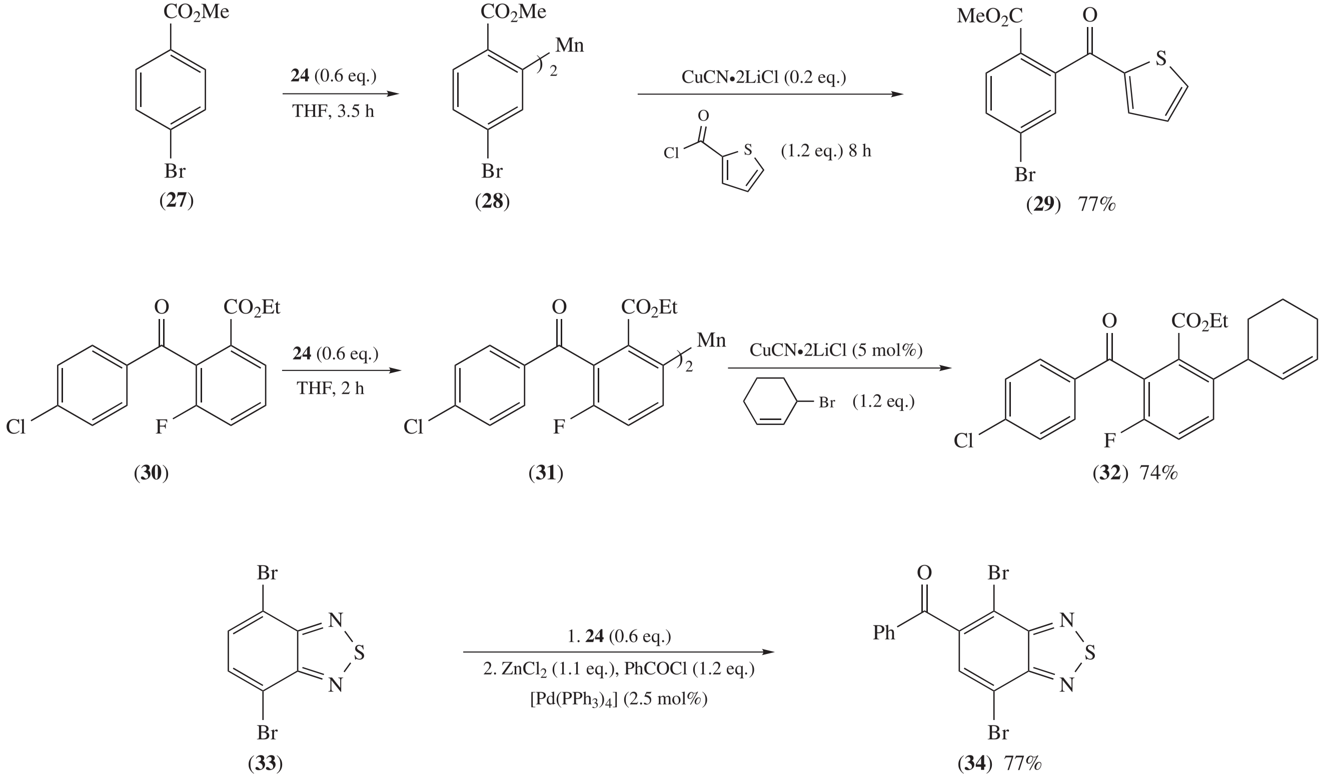
SCHEME 9

In general, the manganation reactions of **24** proceed under convenient conditions at temperatures in the range 0–25 °C. Many functionalized aromatic compounds are readily manganated by **24** without the formation of unwanted by-products, enabling a broad range of subsequent reactions that includes: palladium-catalysed arylations; addition to aldehydes and acid chlorides; substitution of allylic bromides; and oxidative aminations of arenes and heterocycles. Selected examples of arenes that have been efficiently functionalized via **24** are **27**, **30** and **33** (Scheme 10).

The sensitive methyl ester functional group in **27** is not attacked by **24**, allowing the intermediate species **28** to be formed and subsequently reacted with 2-thienoyl chloride to produce **29** in 77% yield. Similarly, the highly functionalized benzophenone derivative **30** was selectively deprotonated ortho to the ethyl ester group to generate the manganated intermediate **31**, which was subsequently reacted with cyclohexene-3-yl bromide to give **32** in a yield of 74%. An interesting reaction of 3,6-dibromobenzothiadiazole (**33**) with **24** results in functionalization in the 4-position, and the subsequent reaction with benzoyl chloride gives **34** in 77% yield.

III. STRUCTURAL STUDIES OF ORGANOMANGANESE REAGENTS

From a pragmatic point of view, it can be said that bimetallic manganating reagents are often superior in terms of reactivity and selectivity to monometallic s-block metal analogues in a range of settings. However, it is more than an intellectual exercise to ask *why* this is so: an understanding of the nature of the manganating reagents themselves could allow chemists to modify or to enhance their unusual reactivity. Such studies are inspired by the long tradition of structural studies on organo-lithium and -magnesium reagents that has led to their ubiquitous applications in a diverse range of synthetic settings[28]. One drawback with manganese(II) reagents is that characterization in the solution phase by NMR

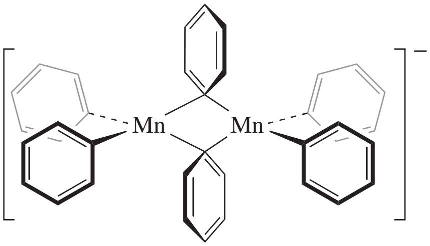

CO2Me
Br
(27)
24 (0.6 eq.)
THF, 3.5 h
CO2Me
Mn
2
Br
(28)
CuCN•2LiCl (0.2 eq.)
O
Cl
S
(1.2 eq.) 8 h
MeO2C
O
S
Br
(29) 77%
O
CO2Et
Cl
F
(30)
24 (0.6 eq.)
THF, 2 h
O
CO2Et
Mn
2
Cl
F
(31)
CuCN•2LiCl (5 mol%)
Br
(1.2 eq.)
O
CO2Et
Cl
F
(32) 74%
Br
N
S
N
Br
(33)
1. 24 (0.6 eq.)
2. ZnCl2 (1.1 eq.), PhCOCl (1.2 eq.)
[Pd(PPh3)4] (2.5 mol%)
O
Br
Ph
N
S
N
Br
(34) 77%

SCHEME 10

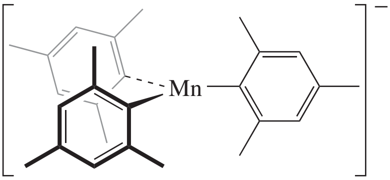
spectroscopy is severely hampered by the paramagnetism of the transition metal. Thus, X-ray crystallography is a vital analytical tool for studying manganese(II) organometallics.

A. Structure-directing Influences in s-Block Manganates

Many examples of manganese(II) organometallics containing formally anionic alkyl and aryl ligands have been reported and their structural properties described in detail[7]. Observations on the structures of compounds of general formula $[MnR_2]_n$, determined mainly by X-ray crystallography, support the assertion that highly polar or ionic manganese(II)−carbon bonds are present. For example, the empirical observation that ionic coordination compounds tend to maximize metal−ligand interactions as far as steric constraints permit is reflected in the oligomeric or polymeric structures found in instances where alkyl or aryl ligands are not very sterically demanding, such as $[Mn_2Ph_6]^{2-}$ (**35**), whereas lower-coordinate complexes are found in the presence of bulkier ligands such as $[MnMes_3]^-$ (Mes = mesityl, 2,4,6- $Me_3C_6H_2$) (**36**)[29].



$[Mn_2Ph_6]^-$ (**35**)



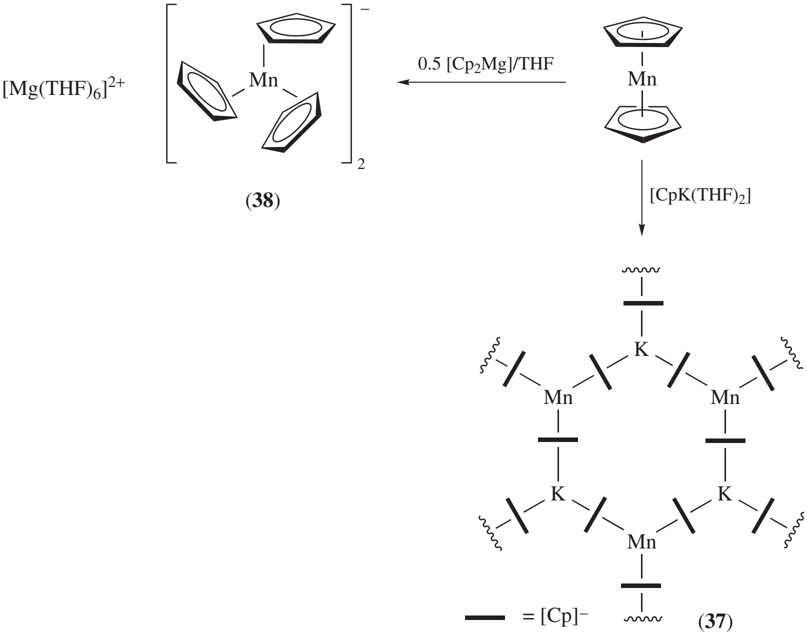
$[Mn(Mes)_3]^-$ (**36**)

It has also been observed that different s-block metal cations can have profound effects on the structures of alkali metal manganates. For example, whereas the crystalline product arising from the addition of potassium cyclopentadienide, $[CpK(THF)_2]$, to manganocene, $[Cp_2Mn]$, is the polymeric ion-contacted complex **37**, an ion-separated complex **38** is obtained from the reaction of magnesocene $[Cp_2Mg]$ with manganocene[30−32] (Scheme 11).

Although the structures of s-block metal manganates in solution may differ from those in the solid state, there are important lessons to be learned from observations such as those on **35**−**38**: the structures of manganating reagents may be complicated, and knowledge of them can only assist in their development for applications in synthesis. Structural studies on reagents for alkali-metal-mediated manganations specifically relevant to synthesis, although rare, can provide powerful insight, and are considered in Section III.B.

B. Alkali-metal-mediated Manganation: Insight from Structural and Reactivity Studies

The concept of alkali-metal-mediated metallation as a targeted synthetic strategy was introduced through the work of Mulvey and coworkers, who have described the potent reactivity of a family of mixed-metal co-complexes formed between alkali metal organometallics or amides in conjunction with an organometallic of a lower polarity metal: this work has recently been reviewed[6]. These bimetallic compounds are often capable of reactivity that cannot be achieved with their monometallic counterparts. In the



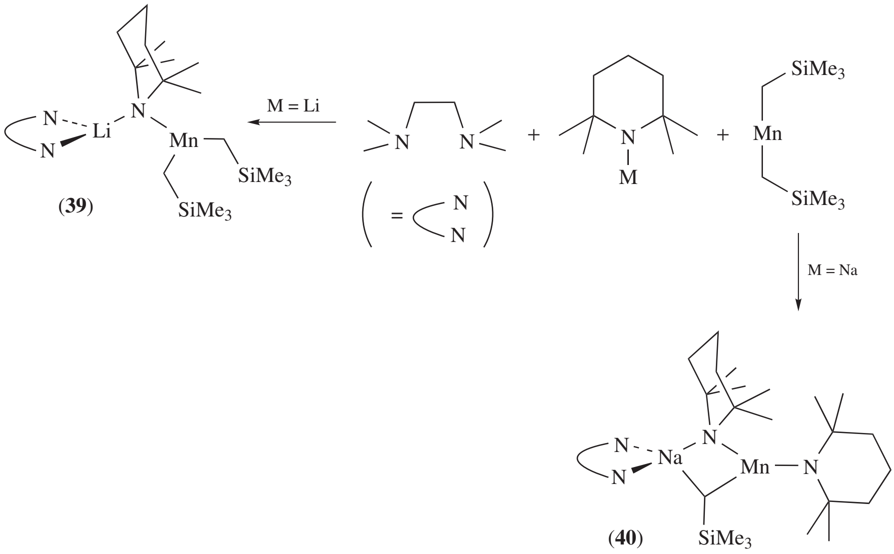
SCHEME 11

case of the lower polarity metal ion being manganese(II), the molecular design process is shown in Scheme 12.

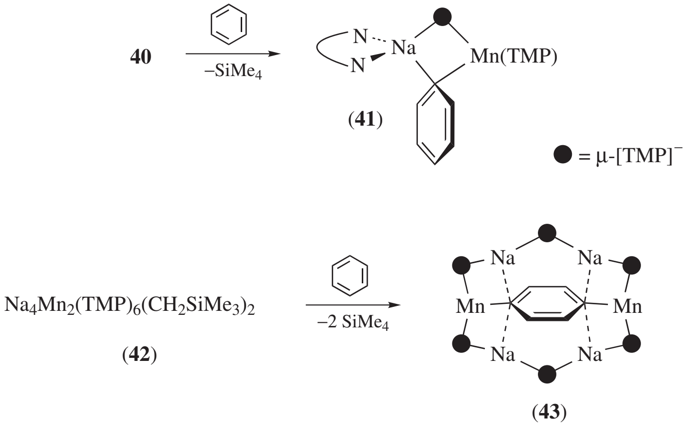
In contrast to essentially all previous work in the field of alkali-metal-mediated manganation, the organometallic reagents **39**, **40** and many of the intermediate manganated species have had their structures fully elucidated. The structures of Mulvey's manganating superbases **39** and **40** reveal the presence of low-coordinate metals owing to the presence of sterically demanding $[Me_3SiCH_2]^-$ and $[TMP]^-$ ligands, a key combination of structural properties that results in high reactivity. The ratio of alkali metal to manganese(II) in **39** and **40** is 1:1, and the presence of three reactive anionic ligands introduces the possibility of individual molecules being capable of three-fold Brønsted basic reactivity: such accurate structural information cannot be inferred unambiguously in the organomanganate reagents discussed in the preceding sections.

Preparing **40** *in situ* followed by the addition of one equivalent of benzene results in the formation of **41** as the only product, in which a phenyl anion has been formed from the deprotonation of benzene by the $[Me_3SiCH_2]^-$ ligand in **40**. In contrast, the reaction of '$[Na_4Mn_2(TMP)_6(CH_2SiMe_3)_2]$' (**42**) with benzene, i.e. in the absence of the bidentate ligand TMEDA (*N*,*N'*-tetramethylethylenediamine), produces **43** in which benzene has been doubly deprotonated with 1,4-regioselectivity (Scheme 13)[33].

The combined effect of the two metal ions is truly synergic, since neither Na(TMP) nor $Mn(CH_2SiMe_3)_2$ is capable of deprotonating benzene on its own. The structures of **41** and **43** were also determined by X-ray crystallography and gave crucial insight into the contrasting reactivities of **40** and **41** towards benzene. The presence of the TMEDA co-ligand in **40** serves to reduce the aggregation state of the system, thus the [NaNMnC] 4-membered ring is preserved throughout the reaction, the $[Me_3SiCH_2]^-$ ligand simply being



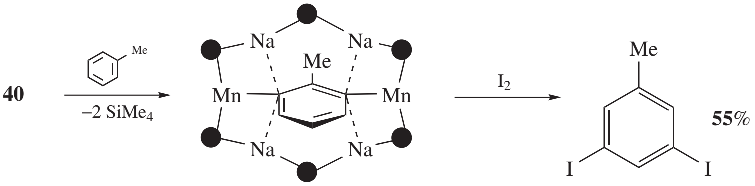
SCHEME 12



SCHEME 13

replaced by $[Ph]^{-}$. In the absence of TMEDA coordination, the sodium cations in **42** seek to increase their coordination number as far as steric constraints permit: this could result in the formation of highly aggregated structures. It can be seen in the structure of **43**[33] that the Na^{+} cations interact with the π-system of the aromatic ring, whereas the Mn(II) cations occupy the bonding sites where the removed protons were previously located. For this arrangement to occur, the $[C_6H_4]^{2-}$ must place two mutually *para* carbons within the cavity of a so-called inverse crown ligand (so-called because the Lewis base donor atoms are in the cavity and the metals in the crown). The formation of **43** is notable also because of the reaction requiring one equivalent of benzene: the analogous reaction in which manganese is replaced by magnesium requires a large excess of benzene to proceed.

Another reaction of **40** has been observed in which the thermodynamically most acidic benzylic proton of toluene is untouched and 3,5-regioselective double deprotonation occurs (Scheme 14)[34].



● = μ–[TMP]⁻

(**44**)

(**45**) 55%

SCHEME 14

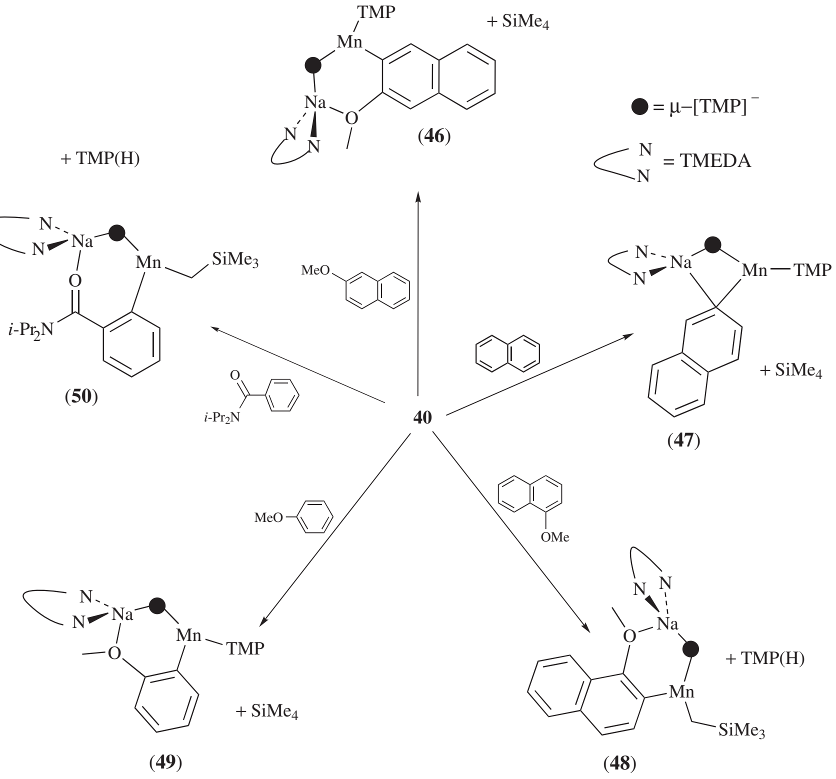
Again, the formation of an inverse crown ether is believed to be responsible for the observed chemo- (non-benzylic) and regio-selectivity. A crystallographic study of **44** revealed that the two manganese(II) centres sit almost co-planar with the arene plane, resulting in Mn−C distances of 2.220(6) Å, which are quite typical. Thus, the two *meta* carbons ‘just fit’ into the inverse crown; any other regiochemistry would give poorer size-fits. The electrophilic quenching reaction of **44** with iodine forms 3,5-diiodotoluene (**45**) in a yield of 55%.

The manganation of naphthalene and its 1- and 2-methoxy derivatives by **40** proceed regioselectively to give the corresponding bimetallic manganates **46**−**48** in good to excellent isolated yields (Scheme 15)[35].

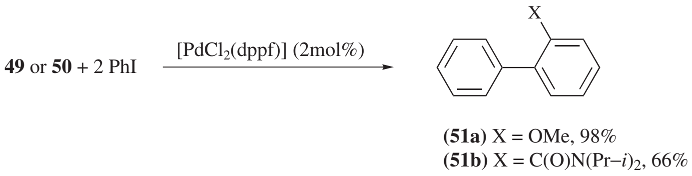
The structures of **46**−**48**, as determined by X-ray crystallography, are closely related to that of **40**, although it is interesting that in the reaction of **40** with 1-methoxynaphthalene a $[TMP]^-$ ligand acts as the base, whereas in the other two reactions the $[Me_3SiCH_2]^-$ ligand performs the deprotonation. In the cases of the methoxy-substituted naphthalenes, the selectivity for only one regioisomer in each case is impressive in light of the number of potential sites available for metallation, and these bimetallic manganating reagents offer good alternatives to other ‘conventional’ reagents that might be used for this reaction. Quenching **46**−**48** with elemental iodine gives the corresponding iodonaphthalenes in yields of 45, 38 and 51%, respectively.

Whether **40** acts as an alkyl base or an amido base appears to be dependent on the nature of the substrate, as mentioned above: a similar difference was observed in the reaction of **40** with anisole and with *N*,*N*-diisopropylbenzamide (Scheme 15). As an extension of the synthetic utility of the synergic manganating reagent **40**, the manganated functionalized arenes **49** and **50**, which were also structurally characterized by X-ray crystallography, can be cross-coupled with iodobenzene under palladium catalysis to give **51a** and **51b**. An interesting observation was that these cross-coupling reactions also occur in the absence of a palladium catalyst, albeit with reduced yields in each case (Scheme 16)[36].

Complex **39** is an effective reagent for the direct manganation of ferrocene to give the 1,1′-dimetallated ferrocenophane $[\{Fe(C_5H_4)_2Fe\}(Li(TMEDA)Mn\}_2]$ (**52**) in a yield of 83%. In the formation of **52**, the lithium manganate **39** provides the first example of tribasic behaviour by an alkali metal ate complex (Scheme 17)[37, 38].



SCHEME 15

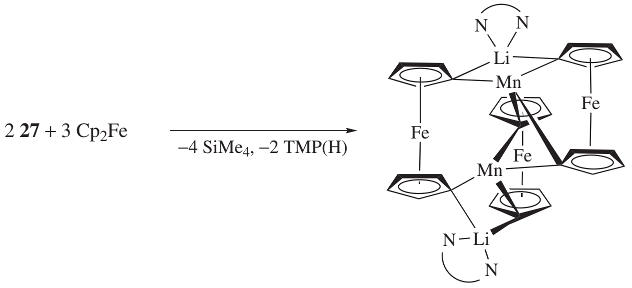


dppf = 1, 1'-bis(diphenylphosphino)ferrocene

SCHEME 16

Mixed-metal synergy is again evident in these metallations because ferrocene is unreactive towards Mn(CH$_2$SiMe$_3$)$_2$.

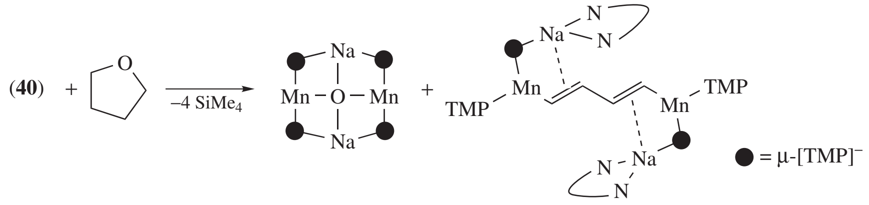
In addition to the unusual reactivity of the manganese(II)–sodium and manganese(II)–lithium bases **39** and **40**, compound **40** also has the remarkable ability to effect the decomposition of THF and to trap the nascent products of this decomposition.[39] The



(**52**)

SCHEME 17

fragments of the ring-opening decomposition reaction of **40** with THF were identified as being the oxide anion, $[O]^{2-}$, and butadienediide, $[C_4H_4]^{2-}$, each of which was captured as the bimetallic complexes **53** and **54** (Scheme 18).



(**53**) (**54**)

SCHEME 18

Complexes **53** and **54** were characterized by X-ray crystallography. Complex **53** reveals that the THF oxygen atom is captured within a so-called inverse crown, whereas the structure of **54** shows that the carbon skeleton of THF ends up as the *s-trans* conformation of the dianion of butadiene. This insight into the decomposition of THF, a very common side-reaction in organometallic chemistry, highlights the power of using mixed metal reagents in synthesis since it is not possible for such reactivity to occur using single metal organometallic chemistry.

IV. THE IMPORTANCE OF BEING SYNERGIC

Organometallic chemistry should, in principle, transcend the traditional barriers between ‘inorganic’ and ‘organic’ chemistry: by studying the chemistry of metal–carbon bonds we are all coordination chemists and we are all synthetic organic chemists. By applying a truly unified approach to organometallic chemistry more will be achieved than if a single organic or inorganic approach is followed. A great deal remains unknown about the precise role of alkali metal manganate reagents in synthesis, from the nature of the manganating reagent itself, through the manganated intermediates to the organic products they generate. The challenge to organometallic chemists is to accelerate the development of our understanding of the structures of manganese organometallics in their own right: this will surely lead to more effective applications of existing organomanganese reagents and to the development of new reagents for previously unseen transformations.

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Cationic (η^6-arene)- and neutral (η^5-cyclohexadienyl)-tricarbonylmanganese complexes: Synthesis and reactivity

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I. INTRODUCTION

The tricarbonyl-chromium and -manganese groups are known to easily coordinate arene rings to form η^6-arene complexes. The electrophilic nature of the tricarbonyl metal fragments makes the arene electron-deficient and renders it susceptible to nucleophilic attack. The (η^6-arene)$Cr(CO)_3$ complexes[1–10] have been extensively studied and their applications widely investigated, in contrast to the isoelectronic cationic manganese counterparts[11–15] which are far more electrophilic than the neutral chromium analogues. For example, these manganese complexes react cleanly and rapidly with a variety of nucleophiles, including Grignard reagents and ketone enolates[1] which give little or no product with chromium complexes[16]. Despite these interesting features they have received much less attention for the following reasons: (i) The synthetic routes to functionalized η^6-Mn complexes are not as obvious as those for analogous Cr–arene complexes. For example, the preparation of cationic (η^6-arene)$Mn(CO)_3$ complexes, bearing electron-withdrawing sustituents or conjugated aryl or vinyl groups by direct complexation of the arenes to the $Mn(CO)_3$ entity is almost impossible. Furthermore, one direct functionalization method is known involving *ipso* nucleophilic substitution but it is limited to oxygen-, sulfur- and nitrogen-containing nucleophiles[17–19]. (ii) The lack of solubility of these cationic complexes in common organic solvents and the fact that they cannot be purified by column chromatography strongly limits their use and the subsequent development of their applications. It is for these reasons that in the last few years a new trend has emerged, the study of the chemistry of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes which are easily obtained by addition of a nucleophile to the arene ring. They are neutral, stable, soluble in most commonly used organic solvents and easily purified by silica gel chromatography columns. In the last ten years, the discovery of new methods of functionalization involving Pd cross-coupling and lithiation reactions has greatly expanded the scope of the (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes and consequently represents a key step in the development of the arene manganese chemistry since $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes can be easily obtained from rearomatization of the corresponding (η^5-cyclohexadienyl)Mn derivatives. The present review aims to describe the situation for the synthesis and the reactivity of η^6-arene–Mn complexes as well as that of η^5-cyclohexadienyl–Mn complexes to highlight the recent breakthrough in their chemistry. When relevant, some comparisons with the isoelectronic analogous Cr complexes will be presented, especially for the study of the tricarbonyl–metal tripod conformation in the solid state.

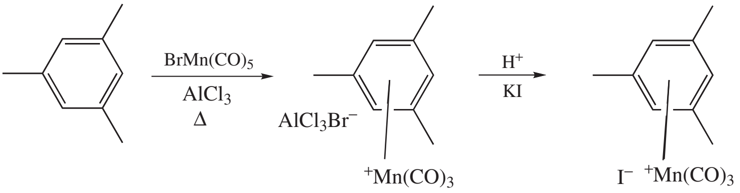
II. CATIONIC (η^6-ARENE)TRICARBONYLMANGANESE COMPLEXES

A. Preparation of (η^6-Arene)tricarbonylmanganese Complexes

There is no general method of preparation of η^6-Mn complexes. The principle of complexation of free arenes involves very often an exchange of ligands, usually with $BrMn^{I}(CO)_5$, without change of the oxidation state of the Mn. There is no general rule to predict if a free arene can be coordinated to a $Mn(CO)_3{}^+$ tripod or not. However, the preparations described in the literature can be organized into different classes depending on the source of the reactive intermediate $[Mn(CO)_3]^+$.

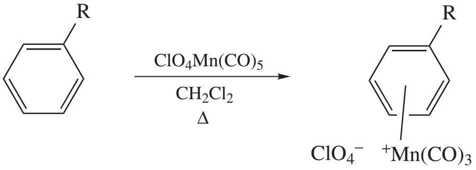
1. Complexation with $Mn(CO)_5{}^+$

(a) *Complexation with* $BrMn(CO)_5/AlCl_3$. The first (η^6-arene)$Mn(CO)_3{}^+$ complex was described in 1957 by heating $BrMn(CO)_5$ and $AlCl_3$ in mesitylene[20]. The η^6-arene complex is obtained in 90% yield (Scheme 1). This method is still used to prepare complexes of benzene, or arenes substituted by alkyl groups or by a heteroatom such as a chloride or an oxygen atom. Thus hexamethylbenzene[21], chlorobenzene, bromobenzene, anisole[19], *para*-dimethoxybenzene[22], 9,10-dihydroanthracene and tetraline complexes[23, 24] are obtained. Unfortunately, this method is not general: arenes substituted by a nitrogen, a sulfur atom or by a hydroxy group do not coordinate, and in some cases secondary reactions such as rearrangements[23] or reductions[24] can occur. It is noteworthy that the use of microwaves can reduce the time to prepare the complexes but the yields are not as good as those obtained without irradiation[25].



SCHEME 1

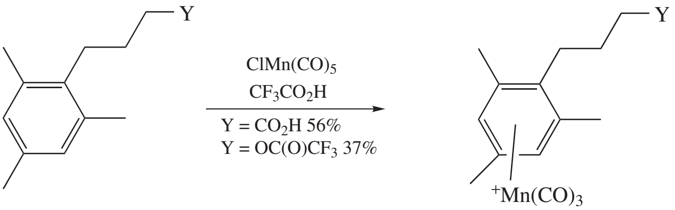
(b) *Complexation with BrMn(CO)*$_5$*/AgClO*$_4$. By mixing BrMn(CO)$_5$ and AgClO$_4$ in CH$_2$Cl$_2$, Pauson and coworkers[26] obtained the perchlorate of pentacarbonylmanganese[27] which can coordinate benzene and chlorobenzene (Scheme 2). Even complexes of *tert*-butylbenzene and arenes sensitive to AlCl$_3$ can be obtained without rearrangement by-products[28]. In this way the complex of phenylsilatrane is obtained in 90% yield[29]. However, even if the yields are usually good, even if the experimental conditions are milder in refluxing CH$_2$Cl$_2$ and even if this preparation does not require a Lewis acid because the ClO_4^- anion is very weakly bound to the metal, this method is too dangerous due to the explosive nature of AgClO$_4$.



SCHEME 2

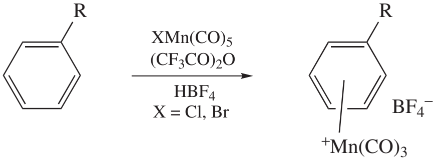
(c) *Complexation with* $BrMn(CO)_5/AgBF_4$. The use of AgBF$_4$ instead of AgClO$_4$ avoids the danger of perchlorate and permits the preparation of previously unprepared complexes: substituted arenes such as bromoanisole, 4-bromoveratrole[30], phenol[31] or naphthalene[32] can be coordinated with this methodology.

(d) *Complexation with* $XMn(CO)_5/CF_3CO_2H/(CF_3CO)_2O$. Refluxing an arene with XMn(CO)$_5$ (X = Cl, Br) in CF$_3$CO$_2$H affords many known complexes (benzene, mesitylene, etc.), but also new ones starting from arenes bearing functional groups at the terminus of an alkyl chain, such as an acid and a trifluoroacetate function (Scheme 3)[33].



SCHEME 3

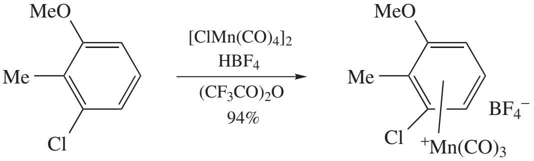
(e) An alternative has been described using $(CF_3CO)_2O/HBF_4$, and it is suggested that $[XMn(CO)_4]_2$ is the active species instead of $XMn(CO)_5$ because a suspension of $ClMn(CO)_5$ in the medium can yield $[ClMn(CO)_4]_2$ at 45 °C (Scheme 4)[34].



SCHEME 4

Pike and coworkers investigated the scope of η^6-Mn synthesis using different methods of preparation from $Mn(CO)_5Br$ and $AlCl_3$ or Ag^+, or alternatively from oxidation of $Mn_2(CO)_{10}$ by strong acid[35]. The TFA anhydride method usually results in the highest product yields.

(f) *Complexation with* $[ClMn(CO)_4]_2$. Pearson and coworkers succeeded in preparing in 94% yield the Mn complex of 2-methyl-3-chloroanisole using $[ClMn(CO)_4]_2$[36]. This example clearly shows how important are the experimental conditions, the nature of the Mn derivative and the substituents of the arene, because this synthesis is unsuccessful with $BrMn(CO)_5/AlCl_3$ and gives with the $BF_4Mn(CO)_5$ methodology a very low yield (8%) (Scheme 5)[37].



SCHEME 5

2. Complexation with $Mn_2(CO)_{10}$

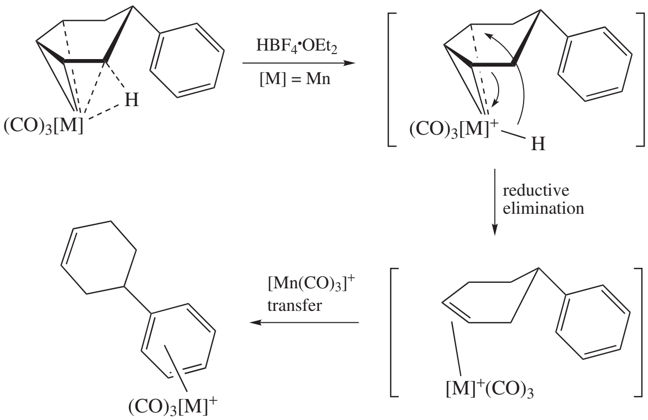
The direct synthesis of a complex starting from an arene and $Mn_2(CO)_{10}$ is very attractive because it avoids the oxidation step affording $BrMn(CO)_5$. Unfortunately, only the complex of mesitylene has been obtained in this way by refluxing CF_3CO_2H in 62% yield. The acid may play the role of an oxidant[33] transforming $Mn_2(CO)_{10}$ into $[Mn(CO)_5]^+$.

3. Complexation with ligand exchange

(a) *Complexation using* $[(CH_3C_5H_5)Mn(CO)_3]$. Benzene and methyl-substituted arenes, such as toluene, xylene or mesitylene, can also be complexed by using the inexpensive (η^5-methylcyclopentadienyl)manganesetricarbonyl in the presence of $AlBr_3$. But in this ligand exchange reaction, yields are widespread and hardly predictable[38, 39].

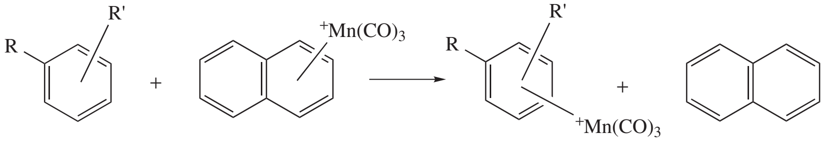
(b) *Unusual preparation of η^6-areneMn complexes*. Sheridan and coworkers described a synthesis of an areneMn complex by treatment of the agostic compound [Mn($\eta^{3:CH}$-

$C_6H_8Ph)(CO)_3]$ with $HBF_4{\bullet}Et_2O$, which gives the arene complex via a migration of the metal from the cyclohexadienyl unit to the aryl substituent (Scheme 6)[40].



SCHEME 6

(c) *Complexation with* $[(\eta^6\text{-}naphthalene)Mn(CO)_3]^+$. ($\eta^6$-Polyarene) Cr and Mn complexes are excellent chromium and manganese tricarbonyl transfer reagents. Because those complexes are *ortho* disubstituted, the metal entity is weakly linked to the cycle junction, facilitating an η^6/η^4 hapticity change. Thus the naphthalenic ligand appears to be very labile and can be easily substituted by another arenic ligand (Scheme 7)[32, 41].



SCHEME 7

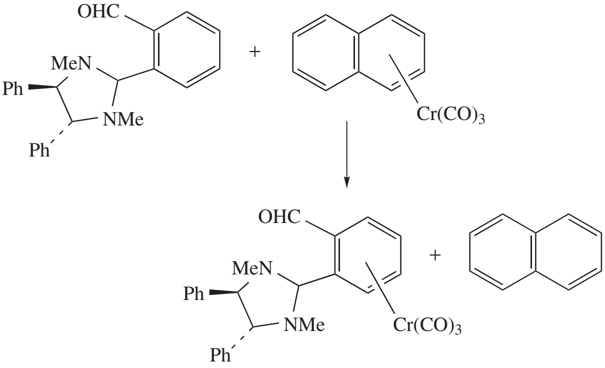
The experimental conditions are mild and the $[Mn(CO)_3]^+$ transfer occurs in refluxing CH_2Cl_2. Thus the Mn complexes of dibenzothiophenes and benzothiophenes[41], hydroquinone, catechol[42], biphenylene[43] and steroids[44] can be easily obtained. It is noteworthy that this intermolecular exchange is well precedented for Cr complexes, e.g. the aminal of benzaldehyde complexes have been metallated with naphthalene–$Cr(CO)_3$ (Scheme 8)[45].

Many polyaromatic complexes have proved to be efficient tools for manganesetricarbonyl transfer, but naphthalene manganese complex is the most commonly used, certainly for cost reasons.

B. Physical Properties of (η^6-Arene)tricarbonylmanganese Complexes

1. Structure of (η^6-arene)tricarbonylmanganese complexes

(a) *Cr complexes*. The structures of isoelectronic analogous η^6-chromium complexes have been extensively described in the literature and have been shown to adopt a



SCHEME 8

‘piano-stool’ conformation, whose Cr−CO feet are oriented according to steric and electronic effects of the arene substituents[46, 47]. It is interesting to briefly mention some typical conformations. For example, (η^6-benzene)$Cr(CO)_3$ and (η^6-hexamethylbenzene)$Cr(CO)_3$ show a staggered conformation **SC** of the $Cr(CO)_3$ tripod with respect to the arenic carbon atoms.

If the arene is substituted by an electron donor group D, the complex adopts an eclipsed conformation **EC** with respect to this donor group, such as a methoxy or a dimethylamino group. Finally, if the arene is substituted by an electron-withdrawing group Σ, the complex exhibits an anti-eclipsed conformation **AEC** with respect to this group, such as a ketone or an ester group (Figure 1).

The interactions beween the orbitals of the $Cr(CO)_3$ tripod and those of the substituted arene mainly govern the orientation of the chromium−carbon bonds toward the electrophilic arenic carbons (Figure 2)[48, 49].

To illustrate the variety of structures, Figure 3 catalogs some examples studied by Rose-Munch, Rose and coworkers of almost staggered conformations of Cr complexes. Almost anti-eclipsed conformations with respect to a bulky or electron-withdrawing substituent are shown in Figure 4, while almost eclipsed conformations of Cr complexes are shown in Figure 5.

(b) *Mn complexes*. For Mn complexes, the conformations of the tripod $Mn(CO)_3$ behave similarly to the chromium tripods. A selection of structures studied by Rose-Munch, Rose and coworkers is presented in Figure 6. For structure a, external methoxy groups attached to the C1 and C3 carbons lie in the plane of the arene ring whereas the central methoxy group points out toward the $Mn(CO)_3$ entity. The longest Mn−C bonds are metal to C1 and C3 distances 2.283 and 2.287 Å and the shortest one is Mn−C5 distance 2.146 Å. Structure b has dihedral angle Mn−CO/Mn−C_{Ar} 12 and 13°. Structure c, unpublished results,

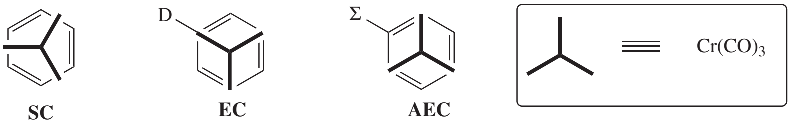


FIGURE 1

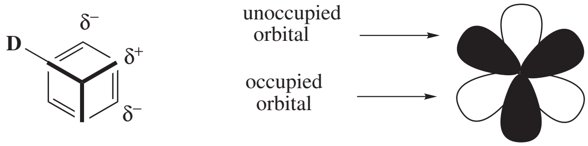


FIGURE 2

has staggered conformation dihedral of angle Mn−CO/Mn−C_{Ar}29°. For structure d, the asymmetric unit consists of two independent molecular cations. The conformations of the two $Mn(CO)_3$ tripods are not identical. In one molecule, the structure shows an expected eclipsed tripod conformation with respect to the methoxy group whereas a slightly more deviated conformation is observed for the other molecule, the Mn−CO being rotated by 5 and 17°. Structure e shows eclipsed conformations. Two independent molecular cations are observed: in one of these complexes, the structures show an anti-eclipsed conformation with respect to the keto group, whereas in the other one, a slightly deviated conformation is found. Structure f has slightly eclipsed dihedral of angles Mn−CO/Mn−C_{Ar}17° and 18°. Structure g has dihedral of angles Mn−CO/Mn−C_{Ar}37°, 38° and 39°. Structure i has dihedral of angles Mn−CO/Mn−C_{Ar}37°, 39° and 38°.

2. Spectroscopic properties of (η^6-arene)tricarbonylmanganese complexes

(a) *IR spectroscopy*. IR of (η^6-arene)$Mn(CO)_3^+$ complexes exhibit two CO stretching bands around 2000 cm^{-1} and 2100 cm^{-1}, since the local symmetry of the $Mn(CO)_3$ group is C_{3v}[79]. For methylated or permethylated $(CH_3)_nC_6H_{6-n}Mn(CO)_3^+$ complexes, it has been concluded that the electron density changes on the metal are transmitted in a corresponding fashion to the CO groups with ring substitution $n = 0$–6 because the carbonyl IR frequencies show a linear correlation with ring substitution[80].

(b) *NMR spectroscopy*. NMR data of substituted complexes of the type (η^6-arene)$Mn(CO)_3^+$ show a small shielding of the ring nuclei compared to the free arenes. This is ascribed to magnetic anisotropy of the ring caused by the metal. By comparison to the isoelectronic Cr^0 derivatives, much more ring-to-metal electron migration occurs with Mn^I than the Cr^0 complexes[17, 18]. Thus a smaller shielding of 0 to 1.5 ppm is usually observed for the protons by ^1H NMR and of 10 to 30 ppm for the carbons by ^{13}C NMR spectroscopy. Very often, the chemical shifts of the arenic protons of the Mn complex are more differentiated than those of the free arene. The carbons of the $Mn(CO)_3$ tripod resonate at around 215 ppm whereas those of the Cr analogs are more deshielded at around 230 ppm. ^1H NMR spectra of cationic $(\eta^6\text{-}C_6H_6)MnL_{3-n}(CO)_n^+, L = P(OEt)_3$ complexes have been studied according to the n value. Indeed, chemical shifts for the benzene ring C_6H_6 coordinated to the $Mn(CO)_3^+$, $Mn(CO)_2[P(OEt)_3]^+$ and $Mn(CO)[P(OEt)_3]_2^+$ tripods resonate at 6.92, 6.49 and 5.90 ppm, respectively. Thus displacement of 2 CO ligands by 2 phosphito ligands modifies by more than one ppm the chemical shift of the hydrogen of the benzene ring attached to the $Mn(CO)[P(OEt)_3]_2^+$ entity which reaches a value comparable with that of (η^6-benzene)$Cr(CO)_3$ complex (Figure 7a). Indeed, the protons of (η^6-benzene)$Cr(CO)_3$ complex present a signal at 5.62 ppm.

^{13}C NMR data for the carbons of the carbonyl of these benzene derivatives are reported in Figure 7b. The carbons of the CrCO and MnCO entities resonate respectively at 234.4 and 216.3 ppm for the complexes whose metal atom is substituted by 3 CO ligands,

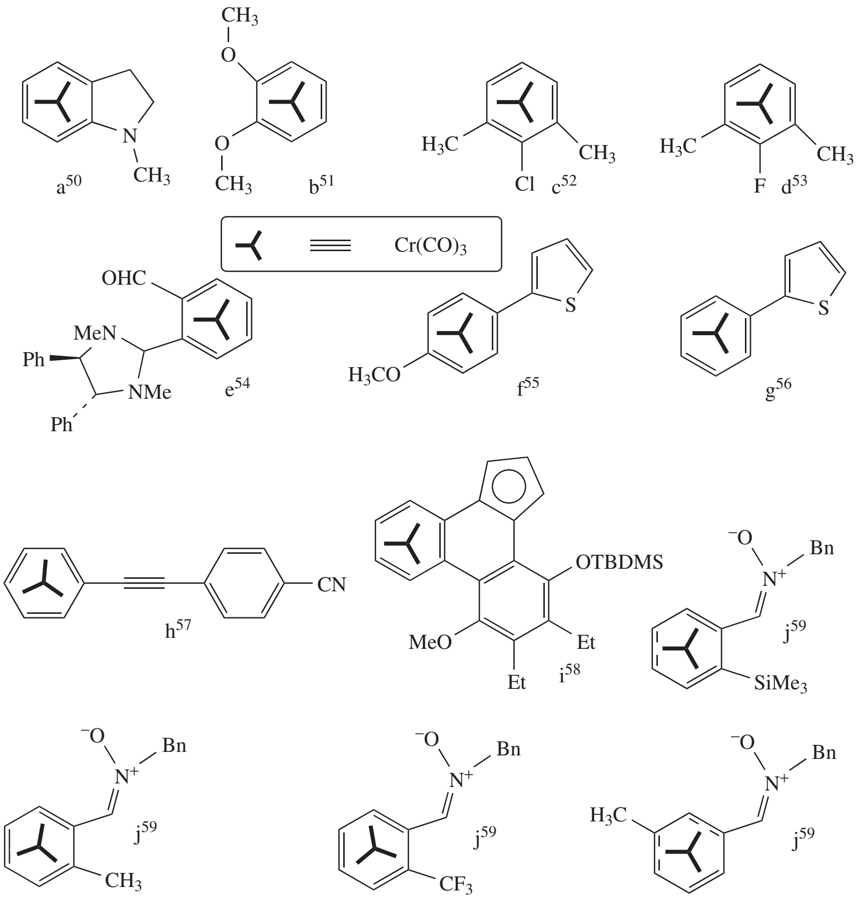


FIGURE 3

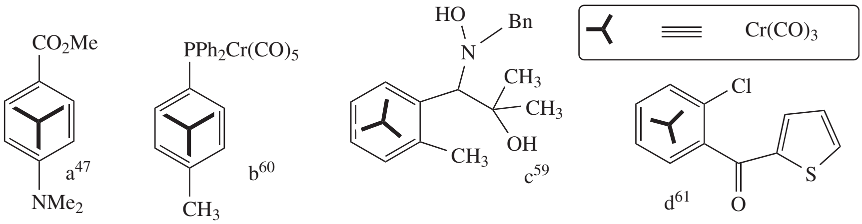


FIGURE 4

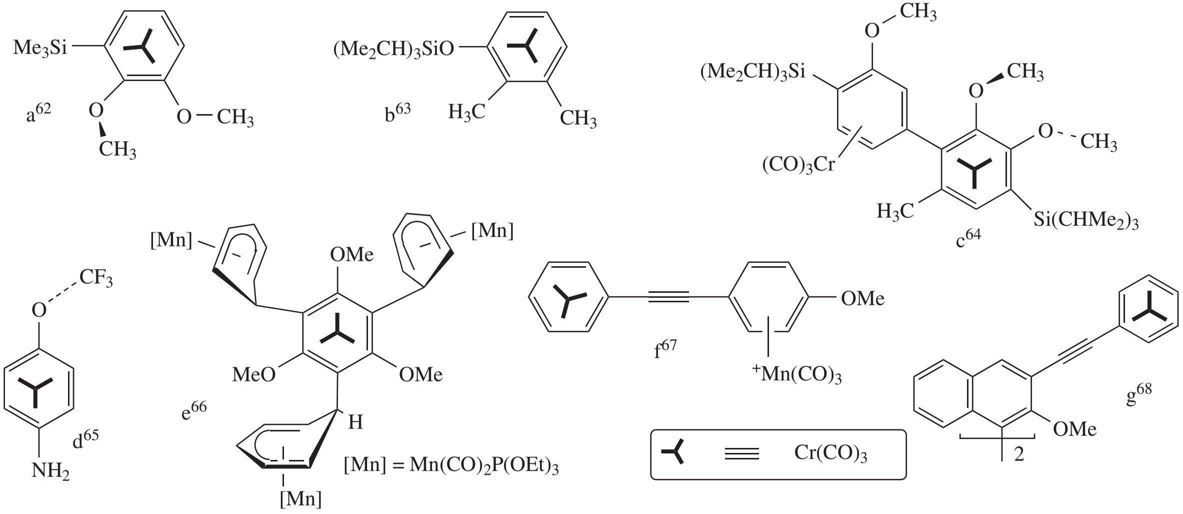

Me$_3$Si
a^{62}
(Me$_2$CH)$_3$SiO
b^{63}
H$_3$C
CH$_3$
(Me$_2$CH)$_3$Si
(CO)$_3$Cr
Si(CHMe$_2$)$_3$
c^{64}
CF$_3$
d^{65}
NH$_2$
[Mn]
OMe
MeO
H
e^{66}
[Mn] = Mn(CO)$_2$P(OEt)$_3$
f^{67}
$^+$Mn(CO)$_3$
Cr(CO)$_3$
2
g^{68}

FIGURE 5

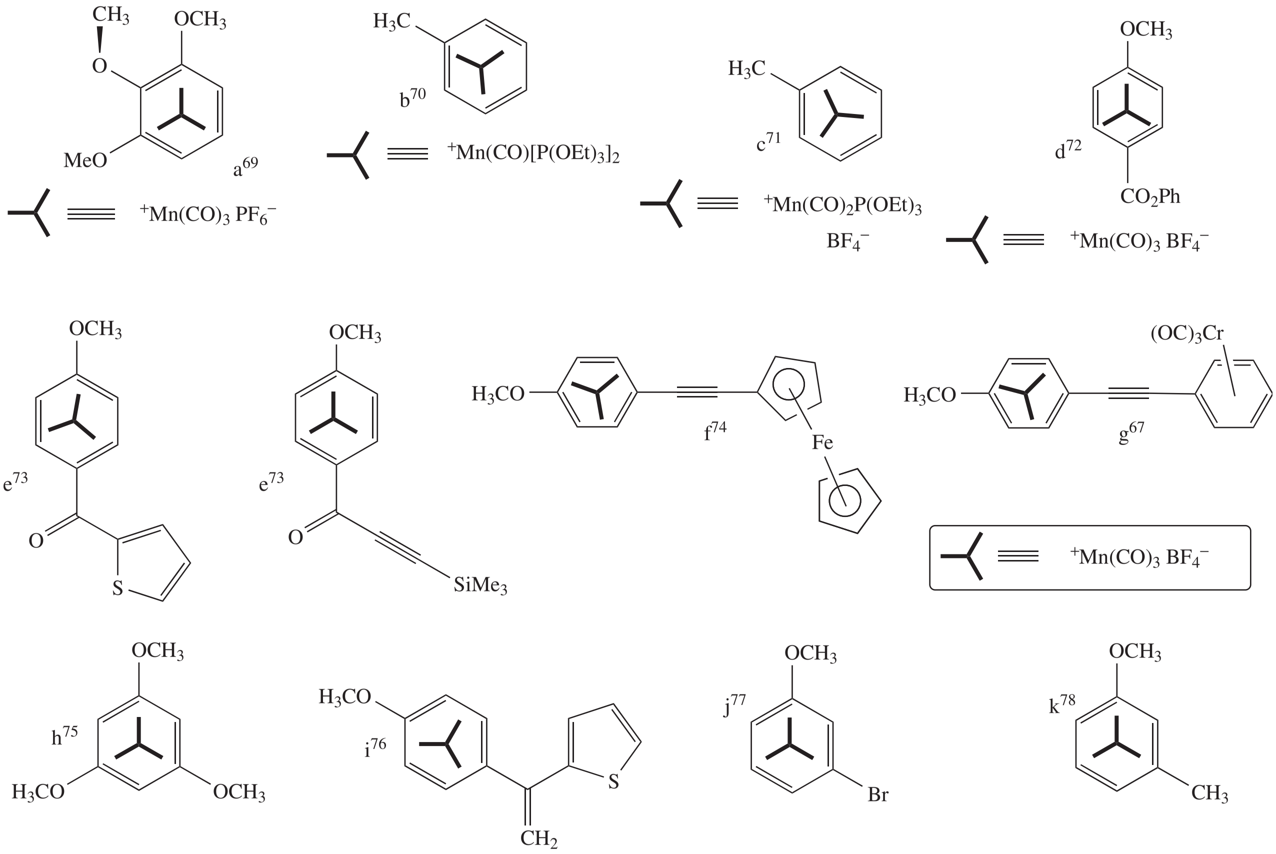

CH3
OCH3
O
MeO
a69
+Mn(CO)3 PF6−
H3C
b70
+Mn(CO)[P(OEt)3]2
H3C
c71
+Mn(CO)2P(OEt)3
BF4−
OCH3
d72
CO2Ph
+Mn(CO)3 BF4−
OCH3
e73
O
S
OCH3
e73
O
SiMe3
H3CO
f74
Fe
(OC)3Cr
H3CO
g67
+Mn(CO)3 BF4−
OCH3
h75
H3CO
OCH3
H3CO
i76
S
CH2
OCH3
j77
Br
OCH3
k78
CH3

FIGURE 6

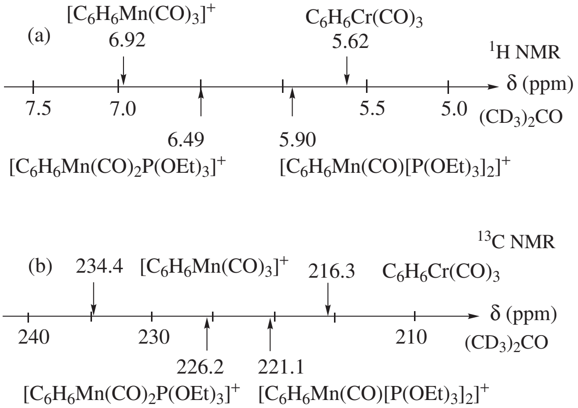


FIGURE 7

whereas those of (η^6-benzene)Mn(CO)[P(OEt)$_3$]$_2{}^+$ and (η^6-benzene)Mn(CO)[P(OEt)$_3$]$_2{}^+$ show signals respectively at 226.2 and 221.1 ppm.

Two applications of NMR spectroscopy have been recently reported. The determination of the enantiomeric purity of Mn(CO)$_3$ complexes of anisole and toluene derivatives with planar chirality can be carried out by ^{1}H NMR analysis after anion exchange with TRISPHAT (tris(tetrachlorobenzenediolato)phosphate(V) anion), the chiral anion behaving as a diamagnetic chiral shift reagent[81, 82]. Another application concerns ^{1}H and ^{19}F pulsed gradient spin-echo (PGSE) NMR diffusion studies on cationic η^6-arene Mn complexes, which prove to be one of the most useful tools for elucidating how ions interact in solution. For example, tetraphenylborate complex of anisole shows strong ion pairing in CH_2Cl_2 solution, whereas the (BArF=B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) salts do not. ^{1}H and ^{1}H NOESY data support this anion selectivity[75].

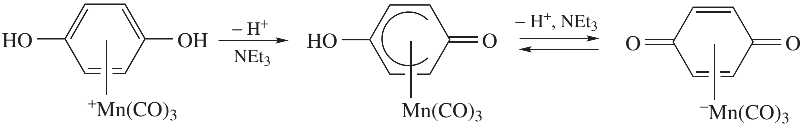
C. Chemical Reactivity of (η^6-Arene)tricarbonylmanganese Complexes

1. Acidity of the benzylic protons

The description of the metal–ring bond of (η^6-arene)tricarbonylchromium complexes suggests the dominance of ring (π) to metal electron migration over the back-bonding effect. Thus, the electronic density of the arene ring is diminished and induces the acidic character of arenic and benzylic protons. A stronger acidity of $C_6H_5CO_2HCr(CO)_3$ compared to $C_6H_5CO_2H$ has been reported and a weaker basicity of $C_6H_5NH_2Cr(CO)_3$ compared to $C_6H_5NH_2$. This is true also for Mn complexes. Thus, phenol and diphenylamine complexes of Mn, treated with a base, give neutral η^5-Mn complexes with an exocyclic double bond[17, 27].

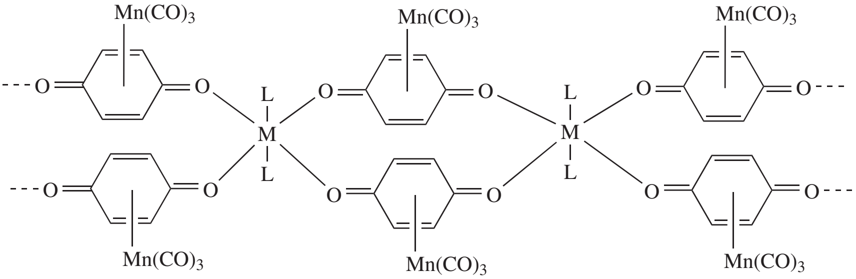
η^6-Hydroquinone, catechol and resorcinol complexes are reversibly mono- and dideprotonated by NEt$_3$ to afford the corresponding η^5-semiquinone and η^4-quinone complexes (Scheme 9). The semiquinone complexes derived from hydroquinone and catechol participate in strong intermolecular hydrogen bonding that persists in solution as well as in the solid state.

These specific properties were applied by Sweigart and coworkers[83] in the field of supramolecular chemistry. They described supramolecular networks based on metal nodes



SCHEME 9

connected by organometallic spacers to give MOMNs (metal-organometallic networks), the driving force being the development of functional materials. The organometalloligand utilized is the stable anionic complex (η^4-benzoquinone)Mn(CO)$_3{}^-$ which is the base to form, for example, crystaline polymers with incorporation of Mn, Co, Ni or Cd, L = DMSO, Py (Scheme 10)[84].



SCHEME 10

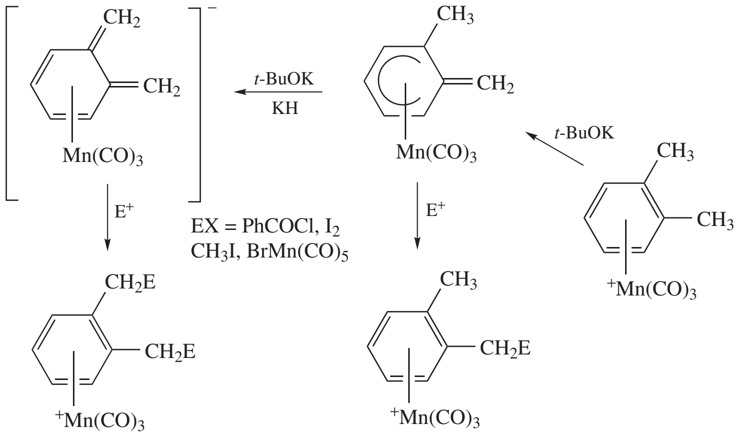
Thus, (η^4-quinone)Mn(CO)$_3{}^-$ binds to metals through the quinone oxygen atoms to afford 1D, 2D and 3D coordination polymers[85–87]. Furthermore, with a modified quinonoid tricarbonylmanganese system, the same group reported the formation of 2D metal-organic systems on a highly ordered pyrolitic graphite surface[84]. This concept should apply to a variety of catalytic active metals and thereby provide new opportunities in catalysis.

Similarly, the acidity of benzylic protons is enhanced and *t*-BuOK or KH easily deprotonate these positions affording neutral η^5-Mn complexes with an exocyclic double bond. They can be trapped with different electrophiles such as a methyl group, for example, yielding new η^6-Mn complexes substituted at the benzylic position (Scheme 11)[88, 89].

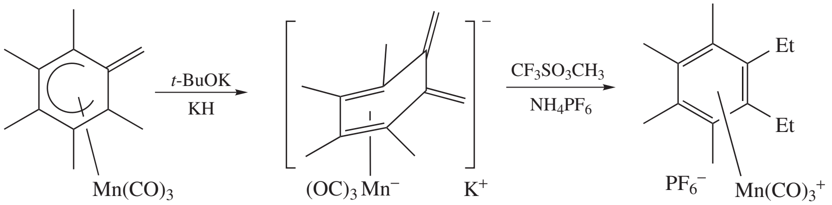
Deprotonation of the Mn complex of hexamethylbenzene with *t*-BuOK gives the exomethylene cyclohexadienyl complex which is stable only in solution at rt. A second deprotonation using the dual base system *t*-BuOK/KH in THF affords an anionic η^4-cyclohexadiene *o*-xylylene Mn complex as a stable solid which is alkylated at the exomethylene positions with an excess of $CF_3SO_3CH_3$ to afford the diethyl arene complex (Scheme 12)[90].

(η^6-Dibenzosuberane)Mn(CO)$_3$ BF$_4$ suffers deprotonation at a benzylic site with *t*-BuOK in THF and gives the orange elimination product with an exocyclic double bond which has been characterized by an X-ray diffraction[87]. The metal tripod is coordinated in an η^5-fashion to one of the outer six-membered rings, such that the manganese is located 1.718 Å below the ring (Scheme 13)[91].

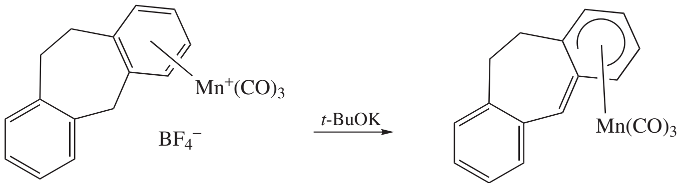
The yellow permethylated Mn complex of fluorene treated with *t*-BuOK in CH$_2$Cl$_2$ gives a dark orange η^5-cyclohexadienyl–Mn complex with an exocyclic double bond, in good agreement with a deprotonation of one of the methyls of the ring (Scheme 14).



SCHEME 11



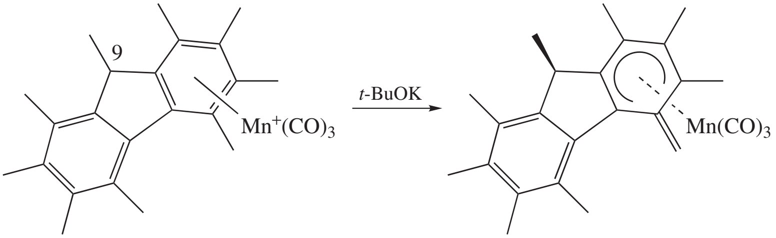
SCHEME 12



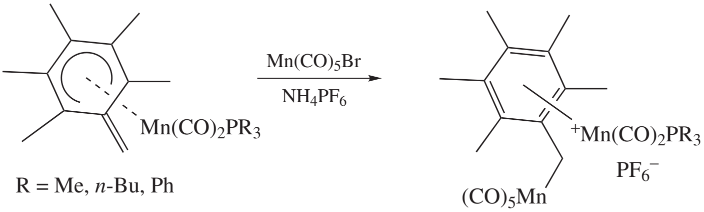
SCHEME 13

Deprotonation of the corresponding $9H$-fluorene was known to occur at the C9 carbon, and the kinetics and mechanism of the subsequent equilibrium between the η^6-bound and the η^5-bound $Mn(CO)_3{}^+$ fragment have been reported[92, 93] (Scheme 14).

A series of (η^5-pentamethylcyclohexadienyl-*exo*-ene)$Mn(CO)_2PR_3$ complexes has been synthesized. Phosphine ligand substitution increases the electron density on the manganese and enhances the nucleophilicity of the exocyclic methylene. Nucleophilic reaction forms a C−C bond with CH_3I and even the metal−halogen bonds of organometallic complexes such as $BrMn(CO)_5$ and $FeCp(CO)_2Cl$ are cleaved to give bimetallic species (Scheme 15)[90].



SCHEME 14

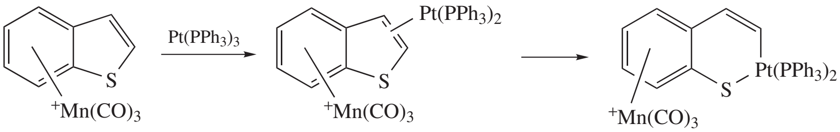


SCHEME 15

2. Remote activation of chemical bonds

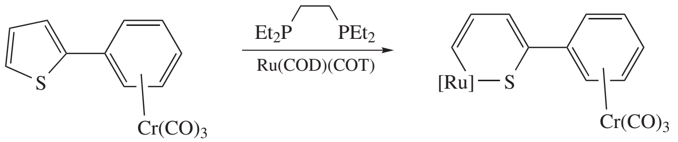
The coordination of the $Mn(CO)_3$ tripod to a part of a molecule activates covalent bonds adjacent or near to the coordinated arene, so that appropriate metal nucleophile can cleave the bonds. This leads to unprecedented levels of activation for the C−C bond in biphenylene, the C−O bond in benzofuran, the C−S bond in benzothiophene, the C−Se bond in benzoselenophene and the N−H bond in indole, the ultimate goal being to make these activations catalytic[94–98].

Taking benzothiophene as an example, a weak nucleophile such as $Pt(PPh_3)_3$ can insert into the C(vinyl)−S bond via coordination of Pt to the thiophenic double bond (Scheme 16)[99].



SCHEME 16

With arenetricarbonylchromium derivatives, heterobimetallic Ru/Cr complexes had been obtained by completely regioselective 1,2- or 1,5-C−S bond insertion of a [Ru] fragment into the thienyl ring of 2- or 3-thienyl-arene$(CO)_3$ residues. The D-enantiomer has been differentiated from the L-enantiomer by using chiral shift reagent TRISPHAT (Scheme 17)[100].



COD = 1,5-cyclooctadiene
COT = 1,3,5-cyclooctatriene

SCHEME 17

3. Nucleophilic addition to the arene ring

Nucleophiles can react with η^6-arene–Mn complexes by several pathways which depend on the nature of the nucleophile, but also on many other parameters such as the solvent and the reaction temperature. The attack can occur at the metal with arene or CO displacement, at a carbonyl carbon, or at the ring. The latter is the most attractive reaction in terms of its applications in organic as well as organometallic chemistry and we will focus only on this aspect of the nucleophilic addition. Indeed, the electronic density of the arene ring is so much reduced by the coordination of the $Mn(CO)_3$ tripod that addition of a nucleophile to the arene ring is easy. Thus, addition/elimination giving *ipso* chloride substitution allows nucleophile introduction without changing the hapticity of the Mn complex, but such a strategy is restricted to amino, oxo and thio nucleophiles, limiting its scope[17–19]. It is noteworthy that only chloride substitution is known, since high-yield direct syntheses of bromo- and iodo-substituted η^6-arene—Mn complexes have been reported only in 2009[77]. For non-halogenated arene–Mn complexes, a wide range of nucleophiles react with $(\eta^6\text{-arene})Mn(CO)_3{}^+$ complexes to give stable neutral $(\eta^5\text{-cyclohexadienyl})Mn(CO)_3$ complexes whose properties are described in Section III.

III. NEUTRAL (η^5-CYCLOHEXADIENYL)TRICARBONYLMANGANESE COMPLEXES

A. Preparation of (η^5-Cyclohexadienyl)tricarbonylmanganese Complexes

We will focus mainly on nucleophilic additions to $(\eta^6\text{-arene})Mn(CO)_3{}^+$ complexes which is the general method of preparation of $(\eta^5\text{-cyclohexadienyl})Mn(CO)_3$ complexes, the nucleophile Nu being located *anti* to the metal entity. The five sp^2 carbons of the π-system are coplanar, while the remaining sp^3 carbon atom is located 35–45° above this plane due to an antibonding interaction between the *endo* hydrogen orbital of the sp^3 carbon and one orbital of the tricarbonylmanganese tripod which is minimized by the remoteness of the sp^3 carbon (Figure 8)[101].

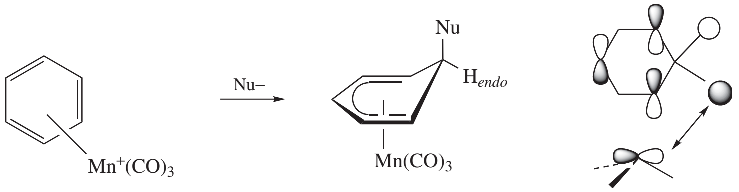


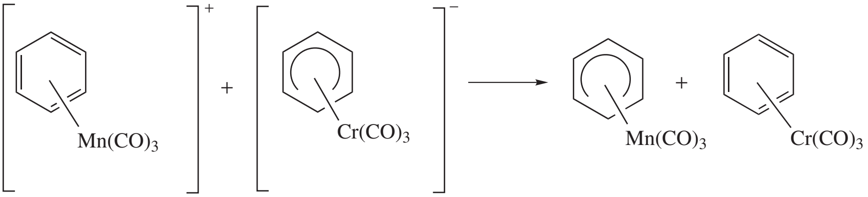
FIGURE 8

A large variety of neutral or charged nucleophiles, the nature of which is detailed in the following subsection, has been used. Other methods of preparation of η^5-Mn complexes reported in the literature involve (i) complexation of 1,3-cyclohexadienes[102], (ii) trapping the anionic $[(\eta^4\text{-benzene})\text{Mn(CO)}_3]^-$[103–107] with varied electrophiles, and (iii) radical addition to an η^6-Mn complex[108–110].

1. Nature of the nucleophile

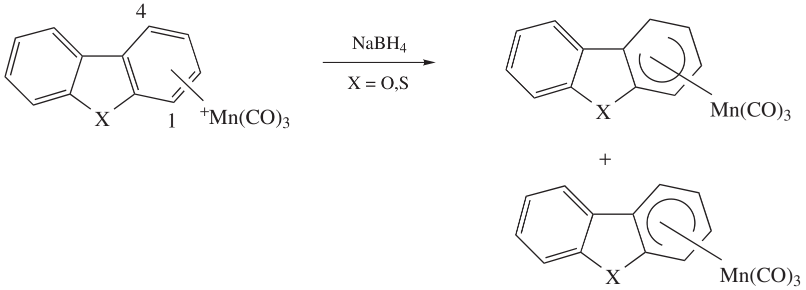
a. Addition of hydride. The first hydride addition was reported in 1960 and involves the reaction of $NaBH_4$ to $(\eta^6\text{-benzene})\text{Mn(CO)}_3^+$ in aqueous solution[111]. Since then, numerous other hydride sources were shown to be efficient: $LiAlH_4$[17, 22, 111], $LiBEt_3H$[112], $KBEt_3H$, $KB(i\text{-PrO})_3H$, $LiB(i\text{-PrO})_3H$[103], $LiB(CH(CH_3)C_2H_5)_3H$[103], KBH_4[112], $NaBH_3CN$[25] and KH[113, 114].

The anionic (η^5-cyclohexadienyl)Cr(CO)_3 complex obtained by hydride addition to (η^6-benzene)Cr(CO)_3, represents an original source of hydride which can react with the cationic (η^6-arene)Mn(CO)_3^+. Two neutral (η^6-benzene)Cr(CO)_3 and (η^5-cyclohexadienyl)Mn(CO)_3 complexes are quantitatively recovered after trapping of the *exo*-hydride of the anionic η^5-Cr complex by the cationic η^6-Mn complex. This reaction highlights the reversibility of the hydride addition to η^6-Cr complexes (Scheme 18)[115].



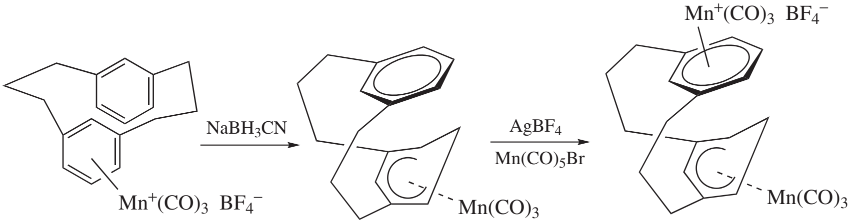
SCHEME 18

The yellow dibenzofuran and dibenzothiophen complexes of Mn react with hydride to give the corresponding cyclohexadienyl complexes substituted at the C1 and C4 carbons. The C1 regioisomer predominates in a 14:1 ratio for X = O whereas this ratio is 2:1 for X = S (Scheme 19)[116].



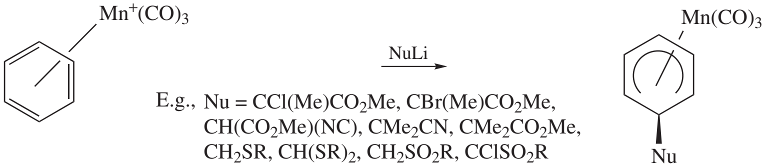
SCHEME 19

Nucleophilic addition of $NaBH_3CN$, a mild hydride nucleophile, to the manganese cyclophane complex $[(\eta^6\text{-}[3_2](1,3)\text{cyclophane})\text{Mn(CO)}_3][BF_4]$ yields the cyclohexadienyl manganese [(η^5-6*H*-[3_2](1,3)cyclophane)Mn(CO)$_3$]. Treatment of this neutral complex with Mn(CO)$_5$BF$_4$ gives the yellow bis-manganese $\eta^6 : \eta^5$ complex after complexation of the cationic tripod [Mn(CO)$_3$]$^+$ to the free arene ring (Scheme 20)[117].



SCHEME 20

b. Addition of stabilized carbanions and organometallic nucleophiles. A wide range of nucleophiles such as carbanions α to a ketone[16, 30, 112, 118, 119], an ester[118–120], a chloroester[121, 122], a bromoester[122, 123], a nitrile[23, 116], a trimethylsilylnitrile, a sulfonyl group[70, 123], an iminoester or iminonitrile[70, 123], a nitro group[70, 123], an isonitrile[117, 71], a diazo[124], a sulfur atom[28], a sulfinyl[125], a dithiane[126], Schöllkopf's carbanions[36] and *N*-acyl oxazolidinone carbanions[127] add to [(η^6-arene)Mn(CO)$_3$][BF$_4$] complexes (Scheme 21).



E.g., Nu = CCl(Me)CO$_2$Me, CBr(Me)CO$_2$Me,
CH(CO$_2$Me)(NC), CMe$_2$CN, CMe$_2$CO$_2$Me,
CH$_2$SR, CH(SR)$_2$, CH$_2$SO$_2$R, CClSO$_2$R

SCHEME 21

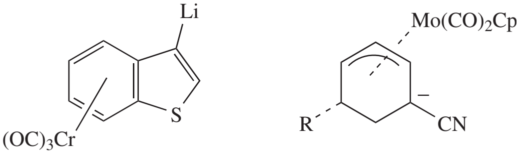
These reactions, which occur in good to excellent yields, lead to neutral cyclohexadienyl Mn complexes which usually easily afford crystals suitable for X-ray structure determinations[128–133].

The reaction of non-stabilized ylides, such as CHR=PPh$_3$ (R = H, Me, OMe, Et, OCH$_2$Ph), with (η^6-benzene)Mn(CO)$_3{}^+$ complex delivers the corresponding organometallic-substituted ylide in yields ranging from 38 to 86%, in contrast to the reactions of stabilized ylides such as Ph$_3$P=C(COR)H (R = H, Me, OMe, OEt, Ph) which are inert toward this complex[134].

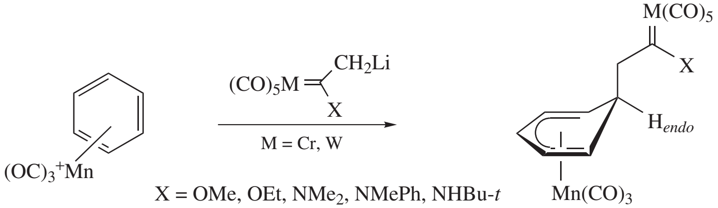
Reaction with organometallic nucleophiles is also possible. Thus, addition of 3-lithio benzothiophene–Cr(CO)$_3$[135] shown in Scheme 22 and of a carbanion of a π-allyl-Mo complex[136] readily occurs to form dinuclear η^5-Mn complexes.

The synthesis of heterodimetallic complexes upon addition of anionic Fischer-type carbenes of W and Cr to (η^6-benzene)Mn(CO)$_3{}^+$ complex is achieved with yields reaching 70% in the case of the aminocarbenes (X = NMe$_2$, NMePh) (Scheme 23)[137, 138].

A dinuclear complex has been obtained by adding LiCH(SiMe$_3$)CN to (η^6-1,2,3-trimethoxybenzene)tricarbonylmanganese complex[69]. Thus, the neutral mononuclear Mn

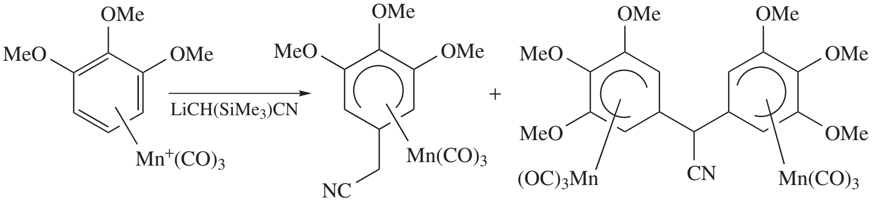


SCHEME 22



SCHEME 23

complex corresponding to the major addition of the nucleophile to the C5 carbon is recovered with cleavage of the C−Si bond by silica gel chromatography. However, deprotonation of this compound also occurs and the corresponding anion reacts with (η^6-1,2,3-trimethoxybenzene)tricarbonylmanganese complex to yield a dinuclear Mn complex (Scheme 24).



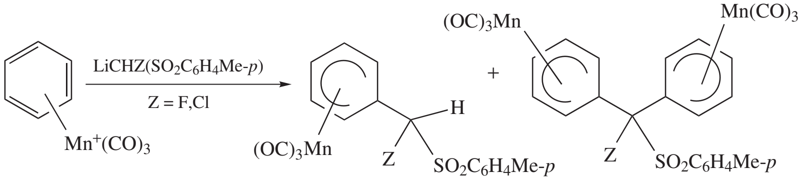
SCHEME 24

Similarly, the following sulfonyl mono- and dinuclear Mn complexes are obtained by addition of α-fluorosulfonyl or α-chlorosulfonyl carbanions to the Mn complex of benzene in a 9:1 ratio for $Z = F$ and in a 1:1 ratio for $Z = Cl$ (Scheme 25)[139].

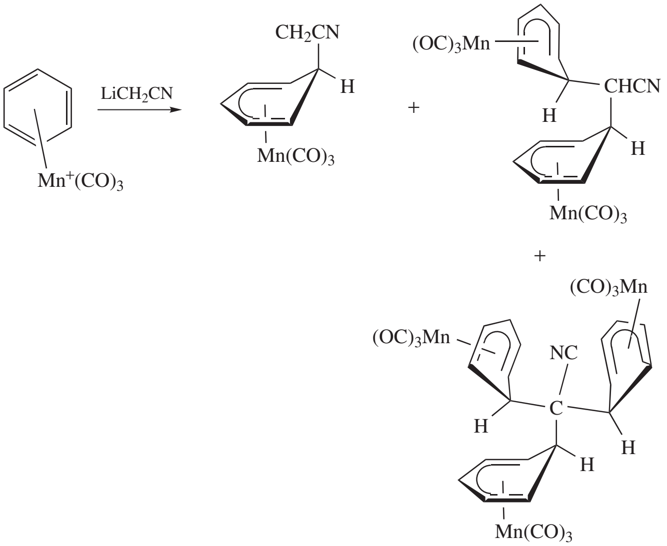
Formation of polymetallic complexes is also observed when stabilized carbanions, α to cyano or sulfonyl groups, are added to the (η^6-benzene)$Mn(CO)_3^+$ complex, and the formation of the corresponding neutral η^5 complex as well as of the di- and even of the ‘carousel’ trinuclear complex occurs in the case of acetonitrile carbanion (Scheme 26)[139].

The addition of the benzylic carbanion of bis(tricarbonylchromium) diphenylmethane complex to (η^6-benzene)$Mn(CO)_3^+$ affords in good yield a yellow trinuclear complex (Scheme 27)[135, 140, 141].

Another example of polymetallic complexes comprising a (η^6-Cr)–(η^5-Mn) pattern is achieved by reacting lithiated arenetricarbonylchromium complexes with cationic η^6-Mn complexes. Thus by using a manganese complex where one CO ligand is replaced by a



SCHEME 25

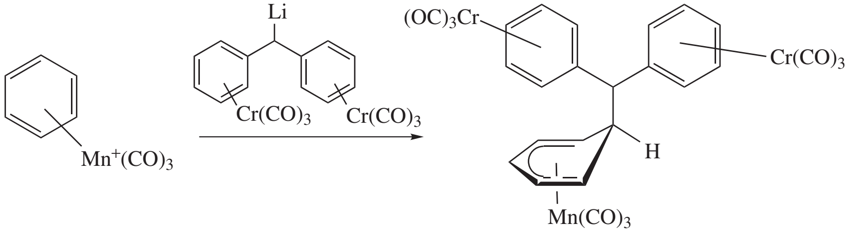


SCHEME 26

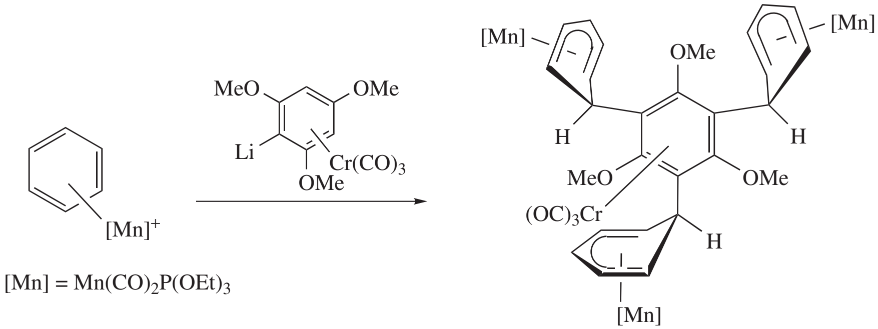
phosphito ligand in order to avoid by-product formation and the lithiated Cr complex of 1,3,5-trimethoxybenzene, a one-pot synthesis of a tetranuclear carousel-like complex is realized (Scheme 28)[66].

Addition of $Re(CO)_5^-$ or $Os(CO)_4^{2-}$ anionic complexes to (η^6-benzene)$Mn(CO)_3^+$ complex leads to the neutral hetero-di- or trimetallic corresponding complexes, where the metal atom of the organometallic nucleophile is directly linked to the sp^3 carbon atom of the η^5-cyclohexadienyl ring (Scheme 29)[142–144].

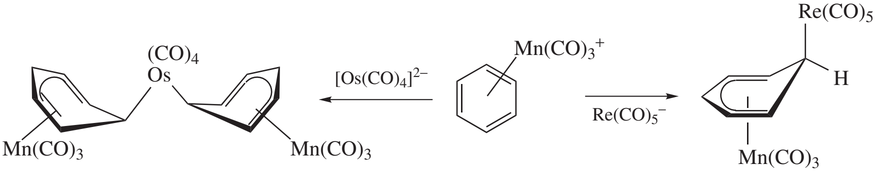
c. Addition of non-stabilized carbanions. The organolithium reagents RLi (R = Ph, Me) add to the ring of (arene)$Mn(CO)_3^+$ to give the corresponding η^5-cyclohexadienyl complexes in good yields[126, 145, 146]. In contrast to neutral (η^6-arene)$Cr(CO)_3$ complexes, Grignard reagents RMgX (R = Me, Ph, CH=CH$_2$) react with (η^6-arene)$Mn(CO)_3^+$ complexes to form the addition compounds, and the yields are generally better than with the corresponding lithium reagents[126, 147–149]. More recently, it has been shown that addition of allylic and benzylic zinc reagents to (η^6-arene)$Mn(CO)_3^+$ form η^5 neutral complexes substituted at the sp^3 carbon by an allylic and benzylic group in good to excellent yields (Scheme 30)[150].



SCHEME 27



SCHEME 28

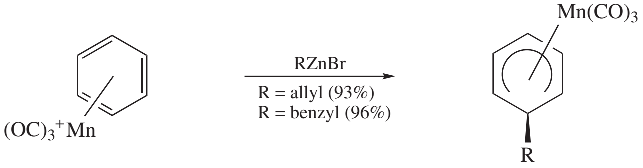


SCHEME 29

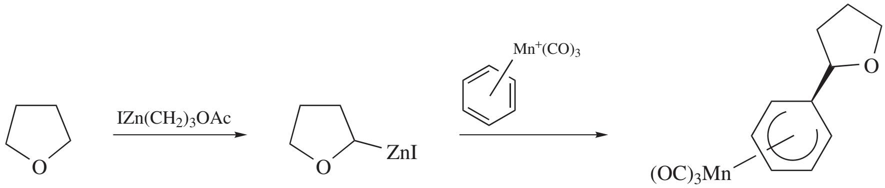
Treatment in THF of an organozinc reagent containing an acetoxy group results in the formation of a Zn(II) enolate which can alkylate the cationic organometallic Mn complex (Scheme 31)[150].

Reaction of less reactive primary organozinc reagents bearing an ester or a cyano group $Zn(CH_2)_2CO_2Et$ or $Zn(CH_2)_2CN$ affords α-alkylated products. According to the authors, deprotonation of the α-proton may proceed to give a zinc-enolate which reacts with the benzene complex to provide the neutral 2-cyclohexadienyl-Mn propionic ester (Scheme 32)[150].

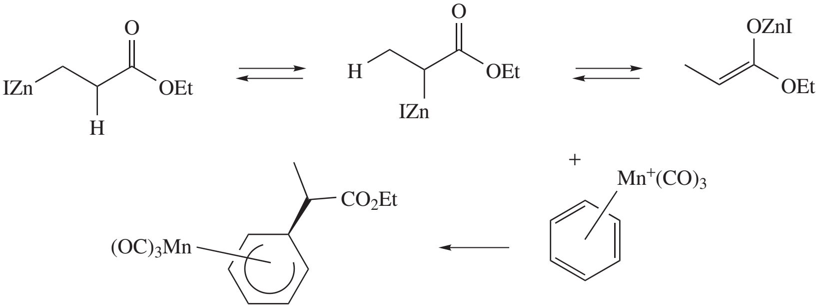
Addition of NaCp to $(C_6H_6)Mn(CO)_3{}^+$ gives (*exo*-cyclopentadienyl)tricarbonylmanganese in 91% yield, which reacts with *n*-BuLi to produce a cyclopentadienyl compound which, after complexation to $Mn(CO)_5Br$, delivers a dinuclear η^5-cyclohexadienyl/η^5-cyclopentadienyl Mn complex (Scheme 33)[151].



SCHEME 30



SCHEME 31

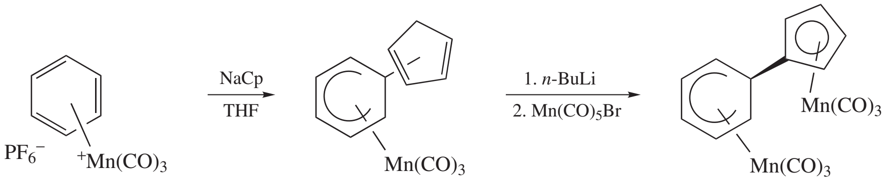


SCHEME 32

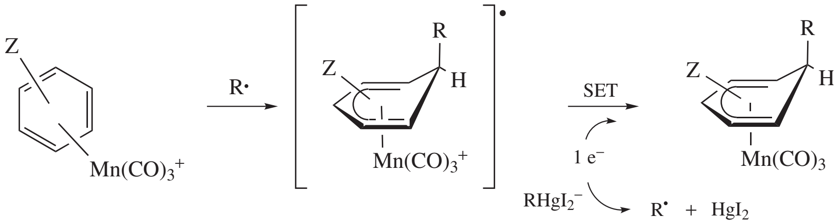
d. Radical additions. Reaction of alkylmercury chloride with η^6-arene-Mn complexes in the presence of NaI leads to the formation of the addition product through the corresponding 17 e^- intermediate, which is reduced by alkylmercury chloride via a single electron transfer process (Scheme 34)[109].

Alkyl radical addition can also be successfully carried out in H_2O/CH_3CN (1:2) medium with indium as the radical initiator. The reaction shows excellent tolerance with various functional groups such as ester, ketone, nitrile and alcohol[110].

e. Addition of heteroatom-containing nucleophiles. Addition of heteroatom nucleophiles such as N_3^-[118], OH^-[152], MeO^-, PhS[153, 154], PPh_2^-[118] give unstable η^5 complexes with low yields in most cases. In contrast, $[O{=}P(OR)_2]^-$ anions add to (η^6-benzene)$Mn(CO)_3^+$ complex to liberate stable η^5 complexes (R = Me, Et, Ph). By treating the addition products with BuLi, the formation of two compounds due to the isomerization and substitution of the phosphonate substituent by a butyl group is observed (Scheme 35)[155–157]. Chung and coworkers suggested that deprotonation of the sp^3 carbon bearing the phosphonate

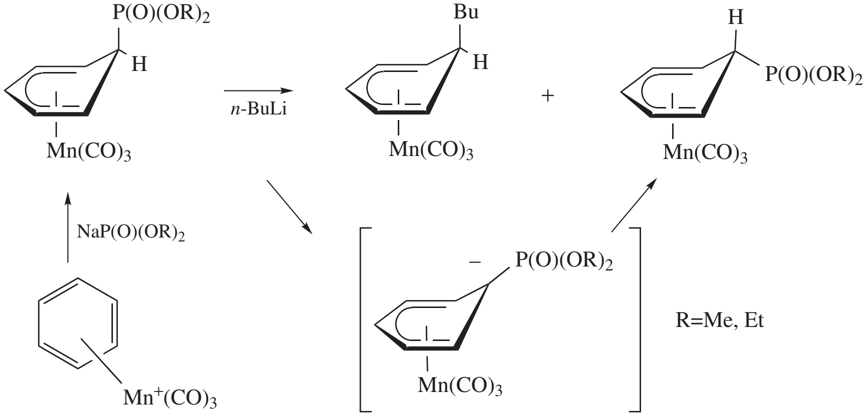


SCHEME 33



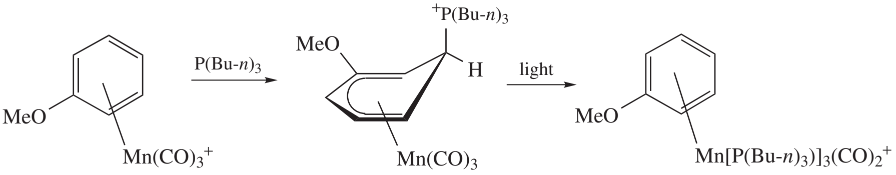
SCHEME 34

by BuLi followed by protonation with water generates the *endo* isomer in 65% yield (Scheme 35).



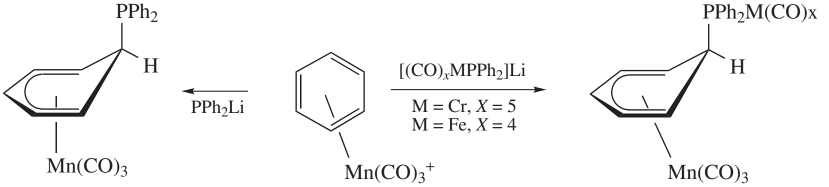
SCHEME 35

(η^6-Arene)Mn complexes (arene = C_6H_5Cl, $C_6H_5CH_3$, C_6H_5OMe) add $P(Bu\text{-}n)_3$ to give the η^5-cyclohexadienyl Mn complexes. Thermodynamic studies indicate that adduct formation is favored for arenes having electron-withdrawing groups, and disfavored with an increasing number of methyl groups[119]. When exposed to light in the absence of oxygen, the phosphonium ring adduct, which is formed reversibly, yields areneMn$(CO)_2PBu_3^+$, except for the chlorobenzene adduct (Scheme 36)[158, 159].



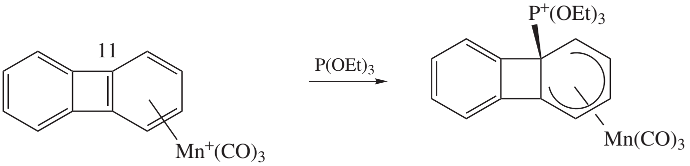
SCHEME 36

Reaction of phosphide Ph_2P^- or metallophosphide $[Ph_2PCr(CO)_5]^-$ and $[Ph_2PFe(CO)_4]^-$ anions with (arene)manganese complexes gives the addition compounds substituted at the sp^3 carbon atom by the P-containing anion (Scheme 37)[60].



SCHEME 37

Sweigart and coworkers showed that one of the most electrophilic η^6-arene Mn complexes, the η^6-biphenyleneMn$(CO)_3{}^+$ complex, reacts with a phosphite $P(OR)_3$ to give the neutral η^5-Mn complex (R = Et) with an unexpected regioselectivity. Indeed, the addition does not occur at an unsubstituted aromatic carbon atom (see the following subsection) but rather at the bridgehead carbon C11, probably because of the weak bond between the Mn and the carbon of the cycle junction as well as the relief of the steric constraints of the cyclobutadiene (Scheme 38)[43].



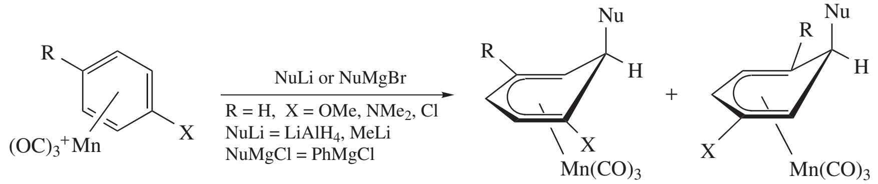
SCHEME 38

2. Regioselectivity of the nucleophile addition

The regioselectivity of the addition of a nucleophile to η^6-arenemetal complexes has been interpreted in the chromium series mainly in terms of charge distribution in the arene ligand[46], frontier orbital interactions[160], conformational preferences of the $M(CO)_3$ tripod[50, 63, 65, 161–168] and other factors such as the experimental conditions (solvent, temperature, etc.). For Mn complexes, similar factors can influence the regioselectivity of the nucleophile addition and they are described below.

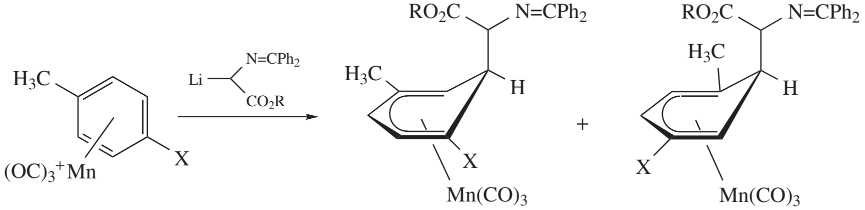
a. Electronic and steric effects of the arene substituents. Pauson and coworkers first described the electronic effects of the substituents on the regioselectivity of the nucleophile addition[17, 18]. They showed that for anisole–$[Mn(CO)_3]^+$ complex, the major addition of a nucleophile occurs at the electrophilic *meta*-carbon atoms, eclipsed by a Mn–CO vector. The same regioselectivity is observed with the analogous Cr complex where it was shown that nucleophiles prefer to react on an arenic carbon which is eclipsed by a Cr–CO bond[46–48].

For Mn complexes substituted by an electron-donating group, Grignard reagents, stabilized carbanions[16, 44, 69] and hydrides[69] in the majority of cases add to the *meta*-carbon atoms. Thus, in the case of (η^6-dimethylaniline)$Mn(CO)_3{}^+$ complex, Pauson and coworkers described the formation of the *meta*-disubstituted η^5 complex in 97% yield. However, for the (η^6-chlorobenzene)$Mn(CO)_3{}^+$ complex, the inductive effect of the Cl atom competes with its mesomeric effect, diminishing greatly the regioselectivity[16, 18], and η^5-disubstituted Mn complexes are formed where the addition of the hydride or the Grignard reagent occurs *ortho* and *para* to the chlorine atom. No *ipso* S_NAr nucleophilic aromatic substitution is observed (Scheme 39).



SCHEME 39

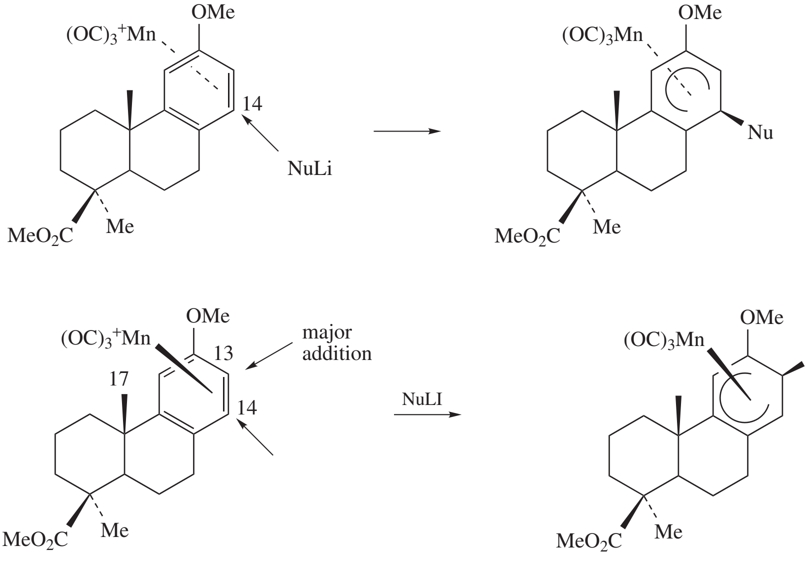
For toluene–Mn complex, α-iminoester carbanions give two η^5-regioisomers *ortho* : *meta* = 30: 70 (Scheme 40) and no *para*-addition is detected[70, 123].



SCHEME 40

In the particular case of dimethylpodocarpic acid coordinated to the α-face by the $Mn(CO)_3$ tripod, addition of a nucleophile takes place to the C14 carbon, *meta* to the methoxy group, whereas addition occurs to the C13 and C14 carbons when the tricycle is coordinated to the β-face, the C13 addition being the major one (Scheme 41)[369,170].

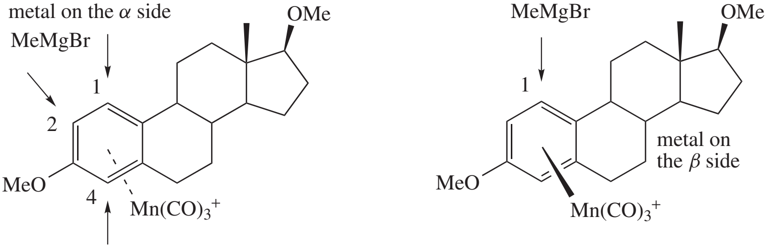
The difference of regioselectivity can be explained by the presence of two conformations of the $Mn(CO)_3$ tripod which should take place in solution at low temperature. Indeed, for the α-face Mn complex, the major conformation of the tripod in solution should be eclipsed with respect to the OMe group, thus inducing the nucleophile to add



SCHEME 41

to the electrophilic C14 carbon eclipsed by a Mn−CO bond. As for the β-face Mn complex, the main conformation in solution at low temperature is difficult to predict because of the opposite effects of the electron-donating OMe group and of the sterically demanding angular C17 methyl group on the same face as the $Mn(CO)_3$ tripod and addition of a nucleophile is no longer regioselective.

The two faces of 3,17-dimethoxyestradiol are coordinated by the $[Mn(CO)_3]^+$ entity with nearly equal facility affording α (down) and β (up) diastereoisomers. The β-isomer is attacked regioselectively at the C1 carbon by $NaBH_4$ or $LiCH_2C(O)CMe_3$, *meta* with respect to the MeO group in agreement with a conformation of the tripod eclipsing the methoxy group. In contrast, with the α-isomer, the regioselectivity of the addition of a carbanion is highly nucleophile-dependent. For example, $NaBH_4$ gives only the C1 isomer but MeMgBr leads to the C1, C2 and C4 regioisomers (Scheme 42)[44]. Thus, electronic and steric factors play a role and the conformation of the tripod $Mn(CO)_3$ of the α-isomer does not seem to govern the regioselectivity of the nucleophile addition.



SCHEME 42

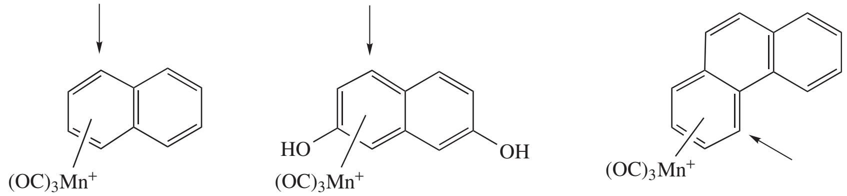
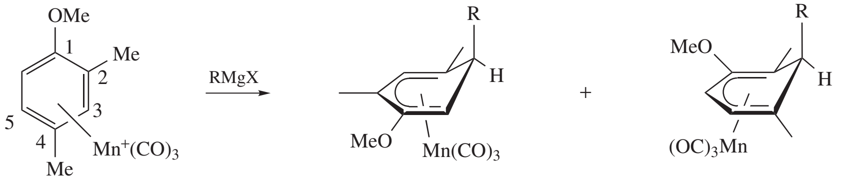


FIGURE 9

With fused ring hydrocarbon Mn complexes, carbanion addition occurs predominantly at the carbon *ortho* to the bridgehead carbon as indicated in Figure 9[171, 172].

Similar observations were made in the Cr complex series showing the difficulty in predicting the regioselectivity of the addition of a nucleophile. The following two examples are representative of the problem. Addition of stabilized carbanions $LiCMe_2CN$ to indoletricarbonylchromium occurs preferentially at the C4 position, whereas by using a more reactive anion such as a dithiane carbanion, the major addition takes place at the C7 carbon[173, 174]. The second example concerns the addition of 2-lithio-1,3-dithian in THF and HMPA and isobutyronitrile carbanion $LiCMe_2CN$, which gives exclusive attack at the C7 carbon of *N*-methylindoletricarbonylchromium[175]. The role of the conformation of the tripod in explaining the regioselectivity of the carbanion is still controversial[50, 51,160–163,168, 175–179]. An interesting discussion of this problem has been recently suggested[180].

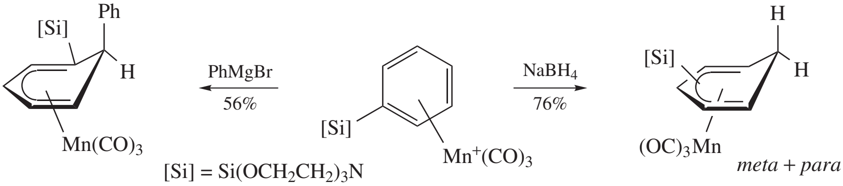
b. Effects of the nature of the nucleophiles and of the solvent. Addition of MeMgX and PhMgX to $tolueneMn(CO)_3{}^+$ complex occurs *ortho* and *meta* to the methyl group in 1:2 and 1:4 ratios, respectively[16]. Stephenson and coworkers reported an interesting regioselectivity by adding a Grignard reagent to the (η^6-2,4-dimethylanisole)$Mn(CO)_3{}^+$ complex. The two positions C3 and C5 *meta* to the OMe group are attacked in good agreement with a major conformation of the tripod in solution, eclipsing the methoxy group and the C3 and C5 carbons[148, 149]. The ratio between these two positions can change depending on the bulkiness of the Grignard reagent. With MeMgX, the major addition takes place on the C3 carbon, whereas with $CH_2{=}CHMgX$ and $MeCH{=}CHMgX$ the major addition occurs on the C5 carbon atom (Scheme 43).



R = CH=CH$_2$	4	1
R = CH=CHCMe$_3$	9	1
R = CH$_3$	1	4

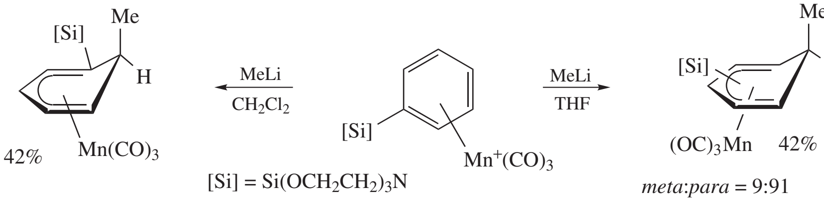
SCHEME 43

Chung and coworkers reported the regioselectivity of the addition of a nucleophile to a silatrane derivative which depends on the nature of the nucleophile. PhMgBr gives an *ortho* addition whereas $NaBH_4$ affords a mixture of *meta* and *para* adducts (Scheme 44)[181].



SCHEME 44

They showed that the nature of the solvent is also crucial. In the case of (η^6-phenylsilatrane)$Mn(CO)_3{}^+$ complex, reaction of Grignard reagents is solvent-dependent. Indeed, in CH_2Cl_2, RMgX adds only *ortho* to the Si atom whereas in THF, *meta* addition is the major one[126, 131, 182]. The regioselectivity of the addition can be reversed by using MeLi in THF or in CH_2Cl_2. In CH_2Cl_2, only the *ortho* adduct is recovered in 42% yield whereas a mixture of the *meta* and *para* adducts is obtained in THF in 42% yield in the ratio 9:91[181]. The authors conclude that a charge-controlled reaction would be predominant in the non-polar solvents and an orbital-controlled reaction would become significant in THF (Scheme 45)[126].

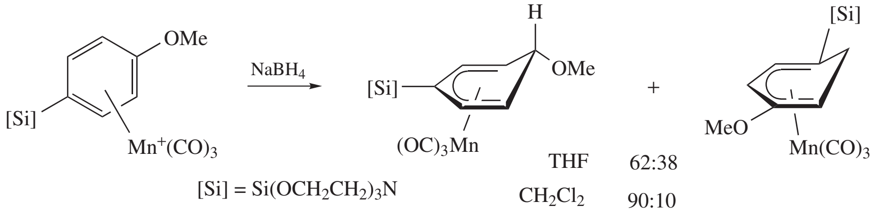


SCHEME 45

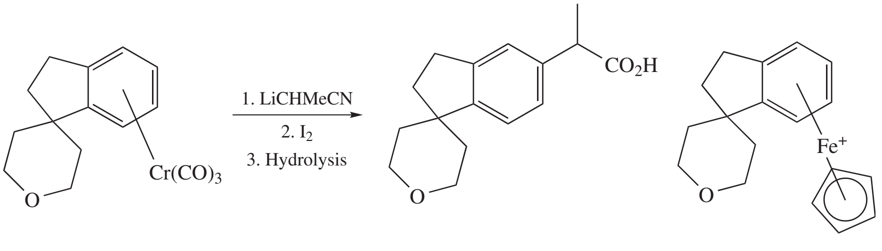
In the course of the same study, an unexpected complex is observed during the addition of $NaBH_4$ to the *para*-methoxy silatrane (Scheme 46). Indeed, besides the adduct *ortho* to the silicon substituent, the authors noted the formation of an η^5-Mn complex corresponding to the hydride addition to the carbon bearing the methoxy group[182].

c. Nature of the ligand of the Mn. The synthesis of 2-arylpropionic acids, whose anti-inflammatory properties are well precedented, can be realized using η^6-arenetricarbonylchromium complexes. Thus, addition of propionitrile carbanion to the spiroindane Cr complex occurs in 80% yield at the C5 carbon (Scheme 47). After removal of the Cr and hydrolysis of the nitrile, the acid is recovered[161]. No regioselectivity is observed with the corresponding cationic η^6-spiroindane–FeCp complex[183].

The addition of the same carbanion to the (η^6-spiroindane)$Mn(CO)_3{}^+$ complex leads to the formation of four regioisomers at the C4, C5, C6 and C7 positions almost equally[121, 184]. However, a slightly better regioselectivity is observed with isobutyronitrile carbanion which affords the four regioisomers C4, C5, C6 and C7 in the ratio 27:50:13

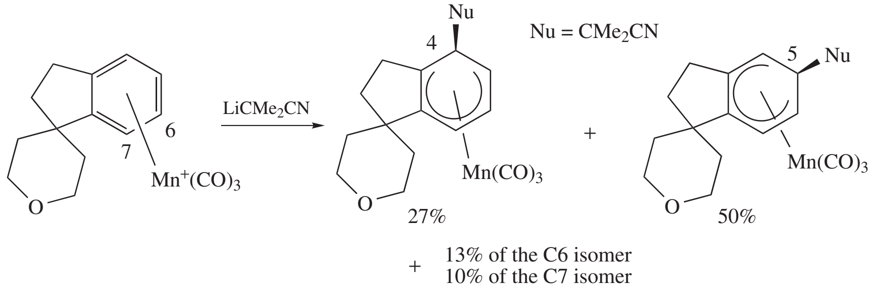


SCHEME 46



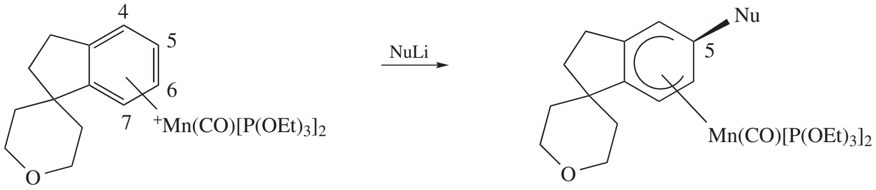
SCHEME 47

and 10, respectively (Scheme 48), the major one being the C5 regioisomer. They could not be separated, but crystals of two of them were fortunately obtained by recrystallization of the mixture of the four regioisomers. Their structures correspond to the C4 and C5 addition products with a classical η^5-cyclohexadienyl skeleton, where one Mn$-$CO bond eclipses the sp^3 carbon[71].



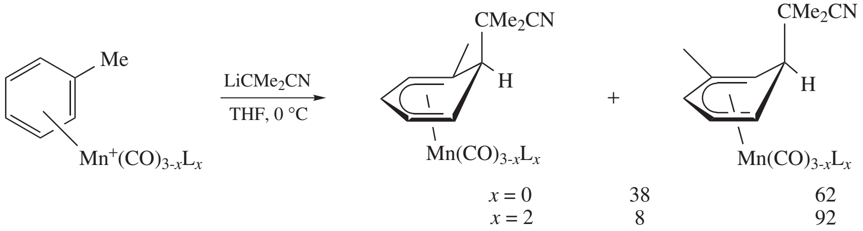
SCHEME 48

The η^6-spiroindane Mn complex has been crystallized, and the X-ray structure clearly shows that the conformation of the tripod $Mn(CO)_3$ is the same as that obtained with the Cr analog with the C5 carbon eclipsed by a metal$-$CO bond. The lack of regioselectivity may be attributed to a very high reactivity of the Mn complex. Indeed, if the electrophilicity of the complex is decreased thanks to the replacement of two CO ligands by two $[P(OEt)_3]$ ligands, a regioselectivity reaching 81% of the regioisomer at the C5 carbon is obtained with propionitrile carbanion (Scheme 49)[184]. Another way to change the regioselectivity of the addition of the nucleophile is to use another carbanion. Indeed, almost only the C5 isomer is observed on adding the methylmalonate carbanion to the $(\eta^6\text{-spiroindane})\mathrm{Mn(CO)_3}^+$ complex.



SCHEME 49

A change of regioselectivity due to a modification of the metal ligands has also been observed during the addition of isobutyronitrile carbanion to toluene$\mathrm{Mn(CO)_3}^+$ and toluene$\mathrm{Mn(CO)[P(OEt)_3]_2}^+$ complexes. Replacement of two CO ligands by two $\mathrm{P(OEt)_3}$ ligands improved the regioselectivity from *o* : *m* of 38:62 to 8:92 (Scheme 50)[70].



SCHEME 50

B. Physical Properties of (η^5-Cyclohexadienyl)tricarbonylmanganese Complexes

1. *In solution by IR and ^{1}H NMR spectroscopies*

^{1}H NMR spectra of $(\eta^5\text{-cyclohexadienyl})\mathrm{Mn(CO)_3}$ complexes present a characteristic fingerprint, showing in general well-defined signals in a large spectral window from 3 to 6 ppm. The H3 proton is the most deshielded proton. However, ^{13}C NMR of these complexes shows an inversion of this order for the C3 and C4 carbons. Thus the following order, $\delta(\mathrm{C2}) > \delta(\mathrm{C3}) > \delta(\mathrm{C1})$, is in good agreement with the corresponding partial charges on these carbons: C2: 0.070, C3: -0.094 and C1: -0.216. The C2 carbon is the carbon bearing the largest positive charge (Figure 10)[49].

The IR spectra of these compounds present two resonances around 1900 and 2050 $\mathrm{cm^{-1}}$.

2. *In the solid state by X-ray crystallography*

The first structures of η^5-cyclohexadienyl–$\mathrm{Mn(CO)_3}$ complexes were reported in the 1970s and showed the *exo*-addition of the nucleophile $\mathrm{Nu^-} = \mathrm{H^-}$[128], $^-\mathrm{CH(CO_2Et)_2}$[129] to the arene ring of the cationic η^6-Mn complex. The $\mathrm{Mn(CO)_3}$ tripod adopts an eclipsed conformation of the sp^3 carbon by a Mn=C=O bond. The cyclohexadienyl fragment is usually coplanar, and the interplanar angle between the cyclohexadienyl and the C1C6C5

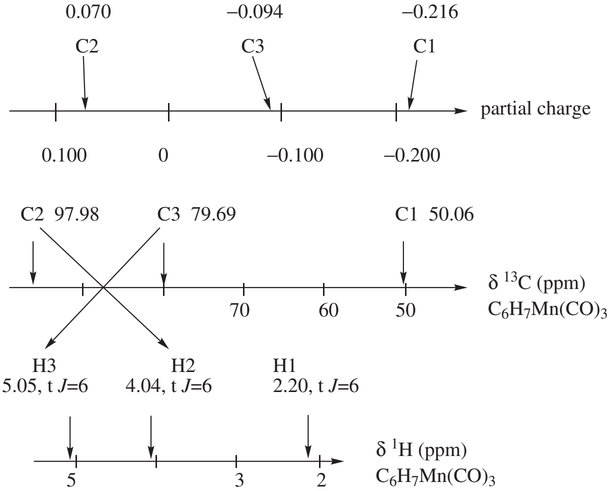


FIGURE 10

planes is around 40°. Figure 11 presents some examples studied by Rose-Munch, Rose and coworkers.

In e, the η^5 moiety does not exhibit the classical five-coplanar-carbon geometry (C1–C5) with one carbon, C6, lying out of this plane. Rather, two carbons, C6 and C2, are located out of the plane formed by the other C1, C3, C4 and C5 sp^2 carbons and away from the metal center. This could be better described as a π-allyl C3, C4, C5 σ-allyl C1 derivative which might be represented by a 'high-heeled-shoe' conformation. In m, the dihedral angle η^5/sp^3carbon = 34°.

C. Chemical Reactivity of (η^5-Cyclohexadienyl)tricarbonylmanganese Complexes

1. Photochemical reactions

Sheridan and coworkers described the reaction of η^5-cyclohexadienylMn(CO)$_3$ complexes with alkynes $R^1 \equiv R^2$ (R^1, R^2 = Me, Et, Ph) under UV irradiation and observed [5+2] cycloaddition products through the formation of a coordinatively unsaturated metal center by displacement of a CO molecule. A [3+2] cycloaddition is observed with a second equivalent of alkyne and decoordination of the Mn(CO)$_3$ tripod occurs either with CPh_3^+ by heating the reaction mixture in CH_3CN or with HBF_4 (Scheme 51).

Kreiter and coworkers also studied the reaction of (η^5-cyclohexadienyl)Mn(CO)$_3$ complex with alkynes $R^1 \equiv R^2$. Successive [5+2, 3+2] cycloadditions are observed and a possible mechanism is discussed to explain the formation of tricarbonyl-$\eta^{2:2:1}$-1,2,3,10-tetramethyltricyclo[5.2.1.0.4.9]deca-2,5,dien-10-yl-manganese (Scheme 52)[196].

Similarly, upon UV irradiation in THF, the (η^5-cyclohexadienyl)Mn(CO)$_3$ complex reacts with 1,1′-disubstituted cumulenes to deliver four kinds of cycloadducts[197].

More recently, a photochemical reaction has been described to obtain the free arenes: upon exposure to ultraviolet light in CH_2Cl_2 or in cyclohexane, η^5-C_6H_6RMn(CO)$_3$ was converted to the corresponding substituted free arenes R = H, Me, Ph, *t*-Bu, thienyl, $CH_2C(O)Bu$-*t* in high yields. In contrast, photoirradiation in CH_3CN or DMF leads to the formation of a mixture of cyclohexadienes and arenes. Finally, irradiation in CH_2Cl_2

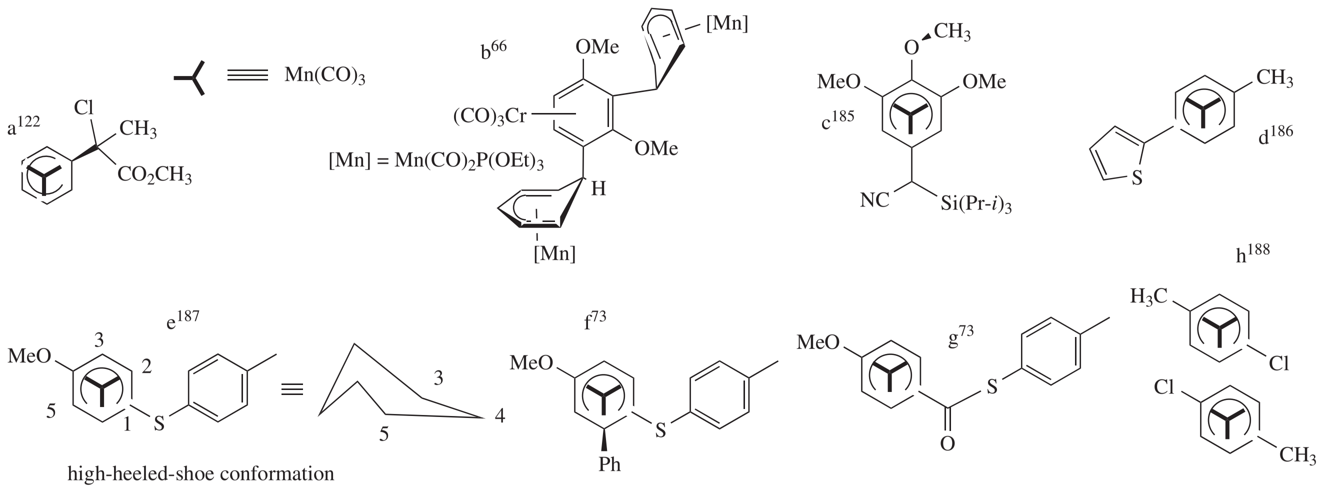

Mn(CO)3
a122
Cl
CH3
CO2CH3
b66
OMe
[Mn]
(CO)3Cr
OMe
[Mn] = Mn(CO)2P(OEt)3
H
[Mn]
c185
O
CH3
MeO
OMe
NC
Si(Pr-i)3
d186
CH3
S
h188
H3C
Cl
Cl
CH3
e187
MeO
3
2
5
1
S
3
4
5
high-heeled-shoe conformation
f73
MeO
S
Ph
g73
MeO
S
O

FIGURE 11.

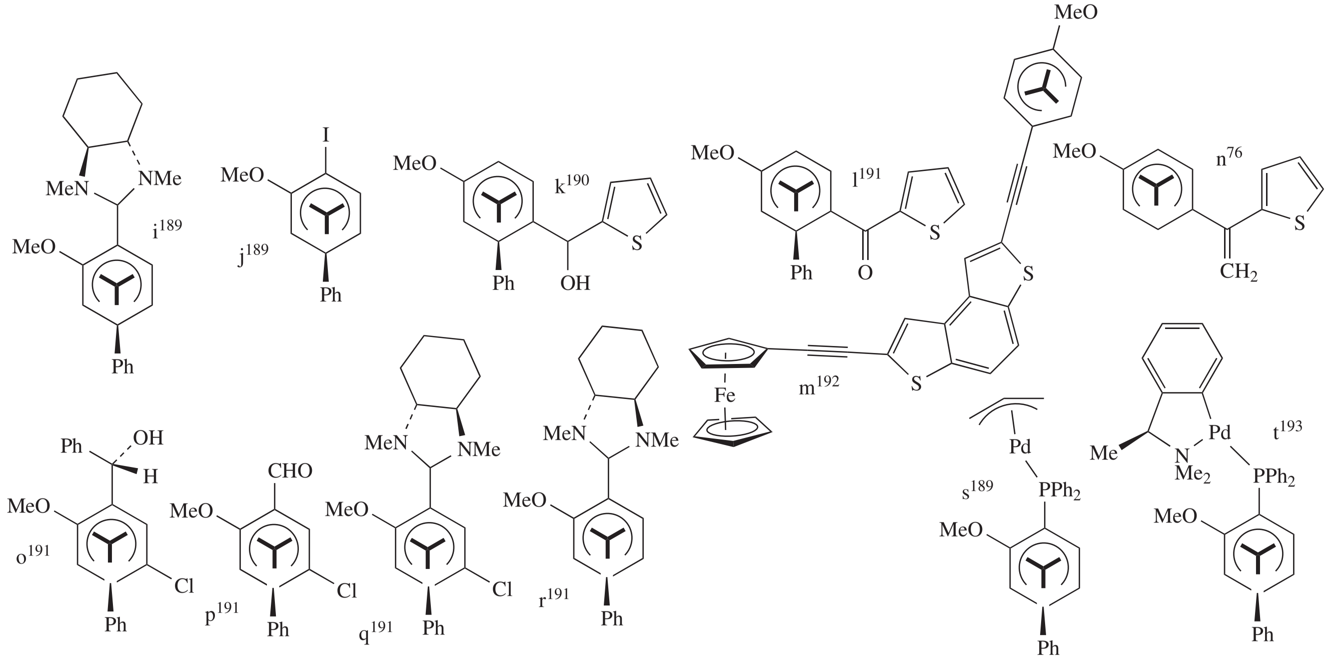
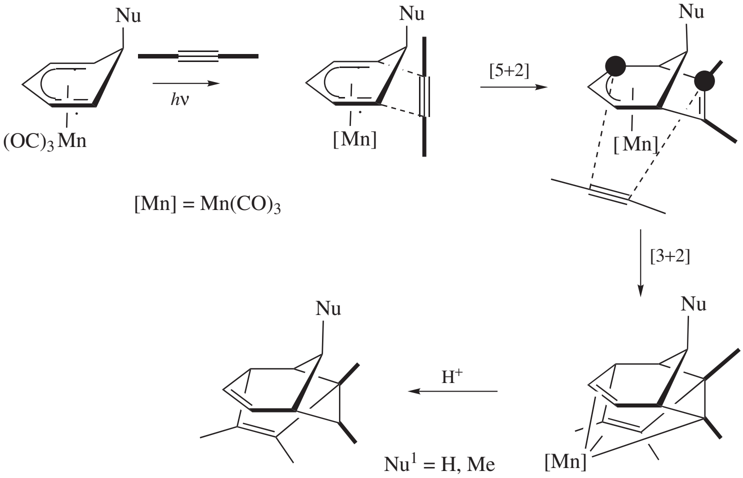
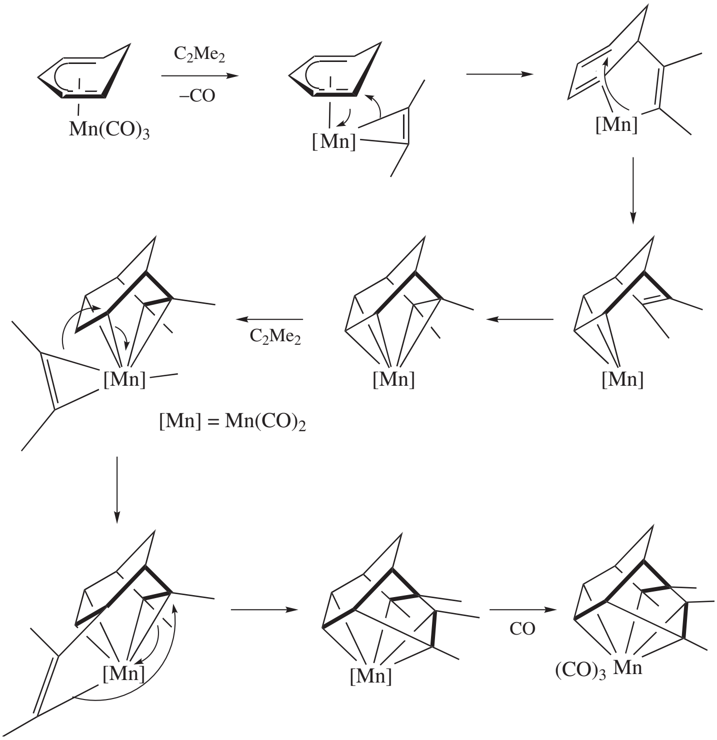


FIGURE 11 (*continued*)

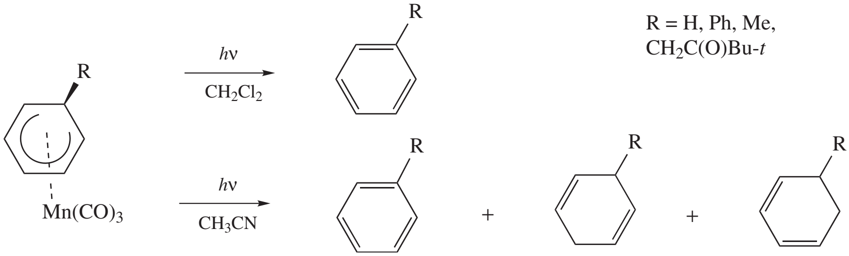


SCHEME 51



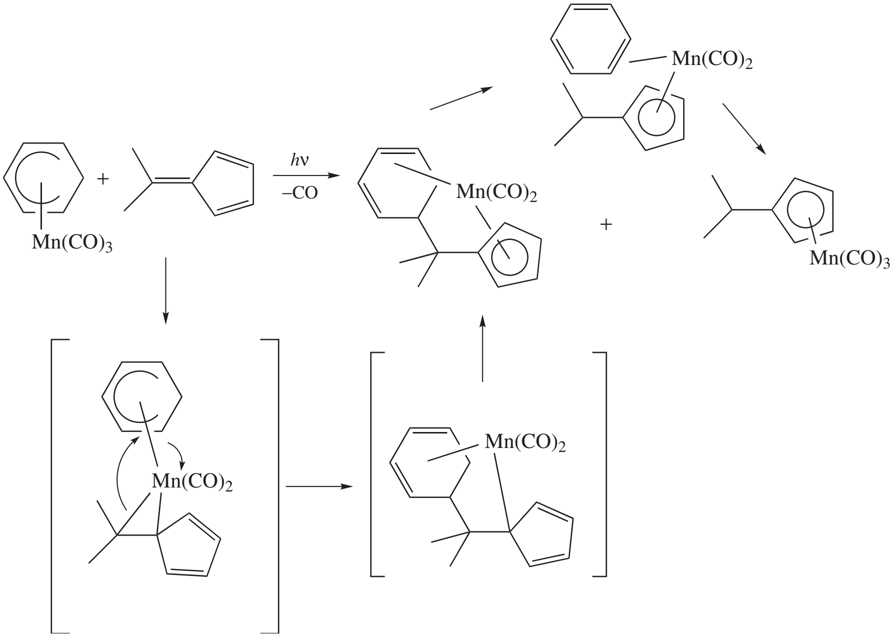
SCHEME 52

and/or CH_3CN and a stoichiometric amount of AcOH results in the formation of only the cyclohexadienes (Scheme 53). The authors suggest a cyclohexadienyl anion intermediate to interpret the fact that cyclohexadienes are deuteriated at the allylic positions using CH_3CO_2D[198].



SCHEME 53

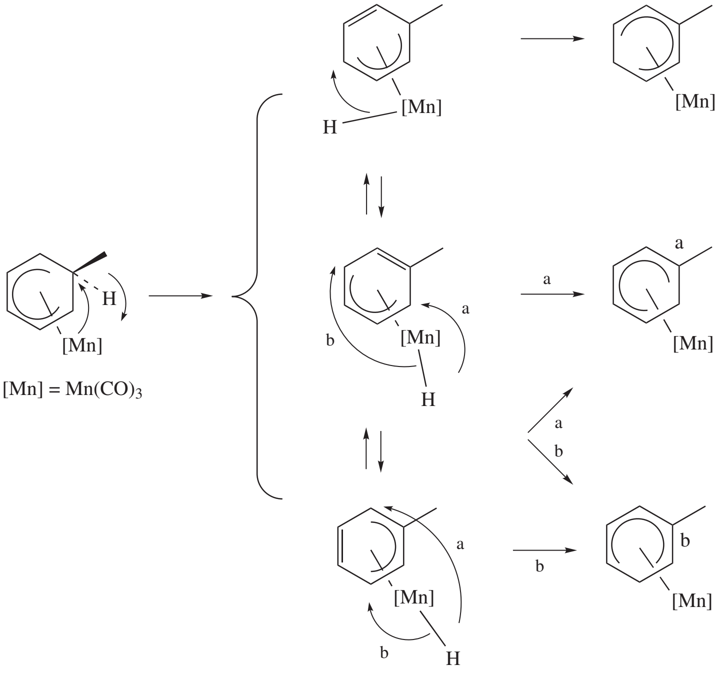
(η^5-Cyclohexadienyl)manganese complex reacts with 6,6-dimethylfulvene upon irradiation with UV light. By loss of CO and carbon–carbon bond formation between the C-6 fulvene carbon and a terminal sp^2 carbon atom of the η^5 ligand, the dicarbonyl Mn chelate is formed. However, the main product is the isopropylcyclopentadienyl Mn complex, which is formed by hydride transfer (Scheme 54)[199].



SCHEME 54

2. Thermal hydrogen migration

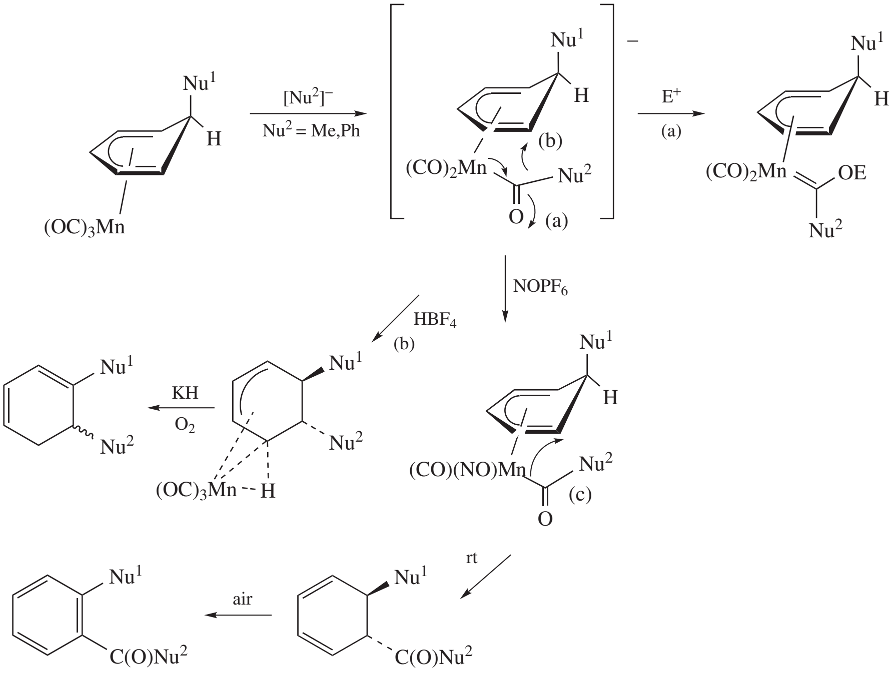
As much as it is easy to remove the *exo* hydrogen at the sp^3 carbon atom of an η^5-cyclohexadienyl Mn complex, it is also difficult to remove the *endo* hydrogen. But this difficulty can be circumvented by an interesting thermal rearrangement which allows the isomerization of η^5 complexes. Indeed, heating the η^5-(6-methylcyclohexadienyl)$Mn(CO)_3$ complex at 130 °C in a sealed tube in cyclohexane creates isomeric postulated η^4-cyclohexadienes manganese hydride intermediates which, after hydrogen migration, afford η^5-Mn complexes. The mechanism of this reaction has been probed by kinetic studies for the isomerization of *exo*-H-(η^5-$C_6D_6H)Mn(CO)_3$[23, 200, 201]. The reaction is first order in the complex, and scrambling of the hydrogen to all possible positions is observed in octane-d_{18}. The activation energy of this process is estimated to be around 17 kcal mol^{-1} (Scheme 55).



SCHEME 55

3. Reaction on the $Mn(CO)_3$ tripod: nucleophilic addition to the CO ligand

Sheridan and coworkers described how organolithium reagents react with neutral η^5-Mn complexes to give the acylmanganese complexes in good yields. If the acyl manganese complex is treated with an electrophile E^+, the Fischer-type carbene is recovered (Scheme 56, path a). Quenching the acylmanganese complexes with HBF_4 allows the manganese-assisted loss of the $[Nu^2]^-$ group which migrates to the *endo* face of the complex. The resulting complex adopts the preferred η^3-agostic structure instead of the η^4-cyclohexadiene manganese hydride (Scheme 56, path b)[202].



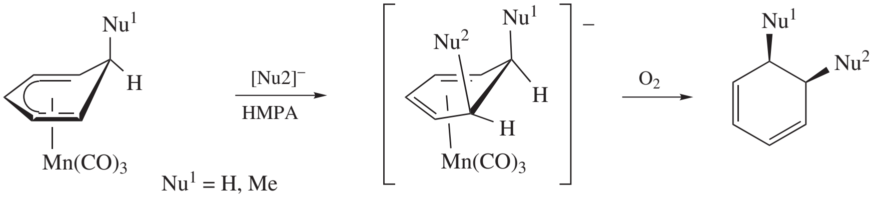
SCHEME 56

The agostic η^3 complex reacts with KH and O_2 or with bis(diphenylphosphino)ethane DPPE and liberates the free cyclohexadiene as a mixture of different isomers. Finally, if the anionic acylmanganese complex is treated with NO^+, substitution of a CO ligand occurs and the neutral η^5-acyl Mn−NO complex is recovered. The acylmanganese complexes release the free *trans*-disubstituted cyclohexadienes by warming the complex to 25°C via an *endo* migration of the acyl group CONu^2 *trans* to the first nucleophile Nu^1 (Scheme 56, path c). The cyclohexadiene (Nu^1 = Me, Nu^2 = Ph) undergoes slow transformation to an isomer via a 1,3 hydrogen shift as well as aromatization in air to 2-methylbenzophenone[202].

4. Nucleophilic additions to (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes

a. Formation of cyclohexadienes. McDaniel and coworkers have shown that carbon nucleophiles Nu^- such as Nu = $CHPh_2$, CPh_3, CMe_2CO_2Et, CMe_2CN in the presence of HMPA add to η^5-cyclohexadienyl−Mn(CO)$_3$ complex at one end of the π-system, stereospecifically *anti* with respect to the metal entity. Oxidative demetallation with O_2 affords the *cis*-disubstituted 1,3-cyclohexadienes in good yields (Scheme 57)[203].

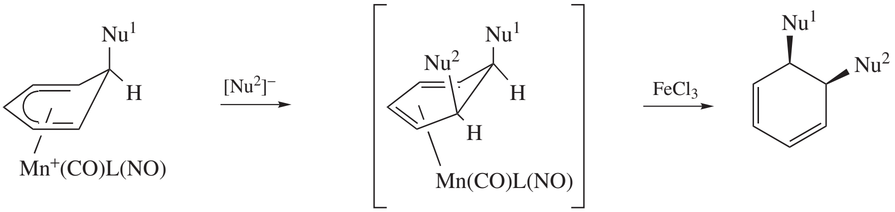
Sweigart and coworkers adopt a more general strategy by increasing the reactivity of the neutral η^5-Mn complexes via substitution of one CO ligand with NO^+. This gives a more electrophilic cationic η^5-Mn complex which permits the addition of less reactive anions. Thus *exo* addition of soft carbanions $[Nu^2]^-$ is possible and produces stable neutral *ortho*-disubstituted η^4-cyclohexadiene−Mn complexes which are converted to *cis*-disubstituted cyclohexadienes upon $FeCl_3$ oxidative demetallation. Increased yields have been obtained



Nu^1 = H, Me
Nu^2 = $CHPh_2$, CPh_3, CMe_2CN, CMe_2CO_2Et

SCHEME 57

by replacement of one CO by a phosphine or phosphite in order to diminish single electron transfer steps which usually lead to decomposition. It allows the addition of useful carbon nucleophiles to the η^5-Mn complexes which release the free cyclohexadienes by gentle oxidation (Scheme 58)[204−206].



L = CO, phosphine, phosphite, Nu^1 = Me, Ph,
Nu^2 = $CH(CN)_2$, $CH(CO_2Et)Z$, Z = CN, COMe, SO_2Ph

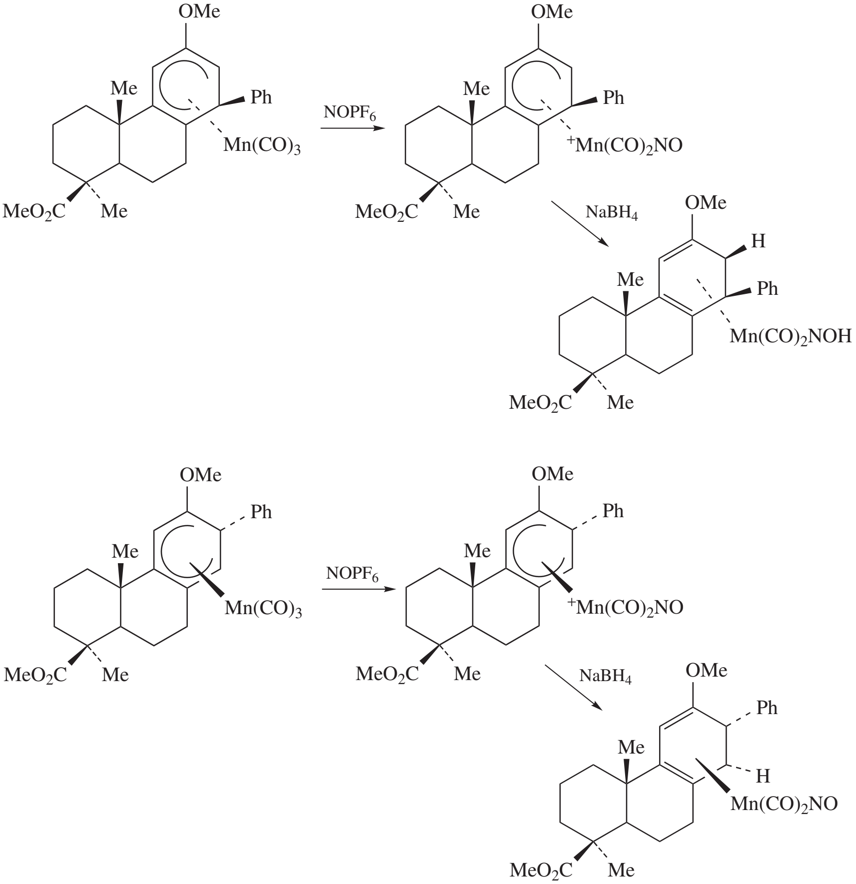
SCHEME 58

Neutral cyclohexadienyl complexes obtained by nucleophilic addition of PhMgBr to methylated podocarpic acid derivatives are converted into the corresponding electrophilic η^5-$Mn(CO)_2NO^+$ cations by treatment with $NOPF_6$[169, 170]. Another nucleophile such as $NaBH_4$ adds hydride to the cationic compounds to give stable cyclohexadienes (Scheme 59).

Addition of $NaBD_4$ to the cationic η^5-$Mn(CO)_2NO^+$ gives the *trans*-η^4-cyclohexadiene–Mn complex by a suggested mechanism involving D^- addition to the carbon of the $Mn^+{=}C{=}O$ entity followed by *endo* hydrogen migration of the Mn-formyl intermediate[204, 207]. Asymmetric induction is observed with chiral η^5-cyclohexadienyl–Mn complexes whose metal atom is substituted by three different ligands (Scheme 60)[208].

Miles and Brinkman described the synthesis of homochiral (+) juvabione based on manganese activation using the sequence involving cationic η^6/neutral η^5/cationic η^5/neutral η^4 Mn complexes (Figure 12)[209].

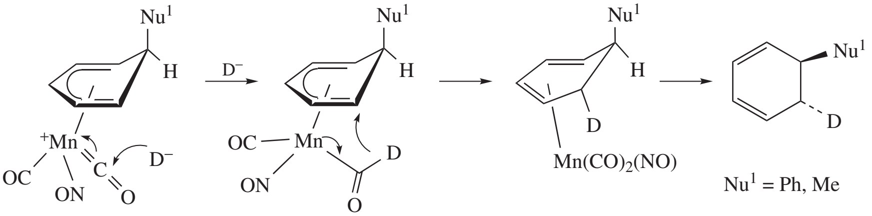
b. Application: synthesis of cyclohexenones. Pearson and Vickerman described an application of this methodology to prepare 5-substituted cyclohexenones. Indeed, nucleophilic addition of PhMgBr to an η^6-Mn complex substituted by a morpholine group at the nitrogen atom gives a neutral η^5-Mn, which is then activated by $NOPF_6$ to give a cationic η^5-Mn derivative. Reduction by $NaBH_4$ affords a neutral (η^4-cyclohexadiene)Mn complex



SCHEME 59

which yields the racemic cyclohexenone after HCl treatment in MeCN in 65% overall yield (Scheme 61)[210].

c. Mn complexes with agostic bonds. Brookhart and coworkers described in the 1980s the addition of hydride, KEt_3BH or $K(i\text{-PrO})_3BH$, to η^5-Mn complexes. In the case of 2-methoxycyclohexadienyltricarbonylmanganese, the anionic [η^4 (1-methoxy- and 2-methoxycyclohexadiene)$Mn(CO)_3]^-$ complexes which are formed by addition of a hydride H^{*-} can be trapped by an acid $H^{\circ+}$ or by an electrophile such as MeI or CF_3SO_3H. Thus protonation of the anionic complexes afford the neutral metal–hydride complex Mn–H° which could transfer the hydrogen H° on the *endo* face with respect to the Mn tripod. The resulting neutral complex does not correspond to an η^4-cyclohexadiene–Mn–hydride but instead possesses an original η^3-structure with a Mn–H°–C agostic bond characteristic of a two-electron, three-center Mn··· H°··· C bond with a low NMR frequency around -6 ppm for the H° proton (Scheme 62)[113, 114, 211].



SCHEME 60

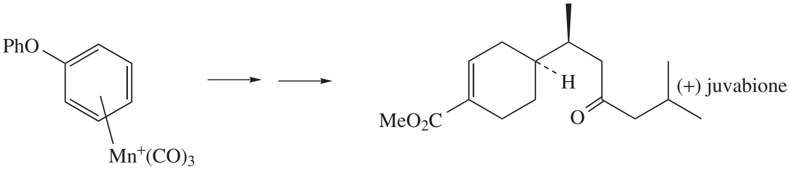
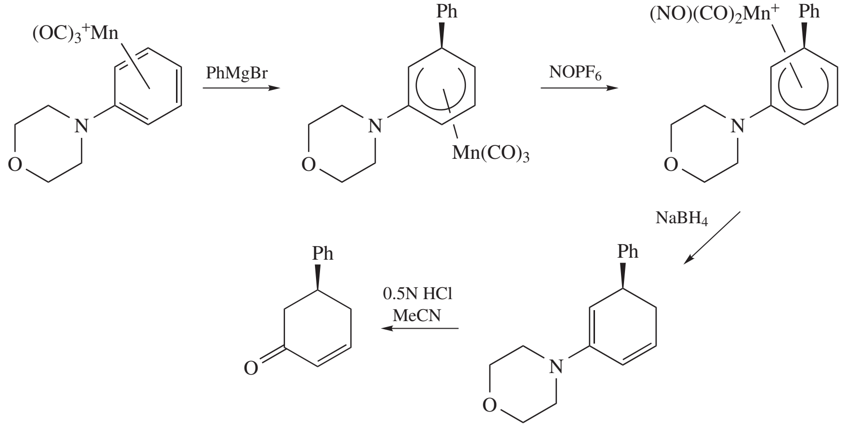


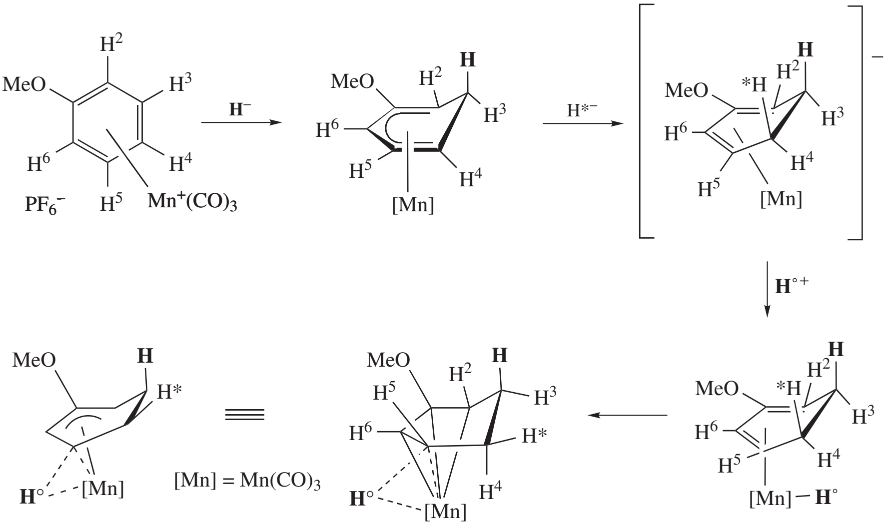
FIGURE 12



SCHEME 61

d. Cine and tele substitutions. Reactivity of agostic complexes substituted by O-, N- or S-containing groups or by Cl has been studied in a neutral medium as well as in an acidic medium, and C−O, C−N, C−S and C−Cl bond cleavages has been observed.

Cleavage of a C−O bond: When a methoxy complex with an agostic bond is heated in an NMR tube in THF-d_8, an equilibrium of η^3-complexes is established and an isomerization is observed at 70 °C. After 30 min a 80:20 ratio is observed which remains unchanged even after 3 h, the major isomer being the symmetrical η^3-2-methoxy π-allyl complex and the minor one the symmetrical η^3-5-methoxy π-allyl complex (Figure 13). This is in good agreement with a convincing demonstration of Brookhart and coworkers, who showed the facile isomerization of cyclohexenyl isomers[211].



SCHEME 62

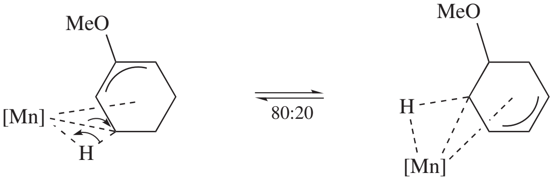


FIGURE 13

These data showed clearly that all the isomers are in equilibrium and that no MeOH elimination is observed in the absence of acid or base. Thus agostic η^3-Mn complexes are in equilibrium with η^4-cyclohexadiene Mn−H intermediates via 1,4-hydrogen shifts of the H°, H4 and H3 protons (Figure 14)[211].

However, in the presence of a proton source such as MeOH or CF_3CO_2H, elimination of MeOH occurs after 3 h in refluxing THF, resulting in the formation of an η^5-Mn complex via the departure of an agostic hydrogen and the methoxy group (1,2 or 1,5 elimination of H and OMe). The mechanism of this reaction has been proved by using deuterium labeling: H^-/H^+, H^-/D^+, D^-/H^+ and D^-/D^+. Addition of the first equivalent of L-selectride to the anisole Mn complex affords the η^5-2-methoxy Mn complex, which reacts with another equivalent of $LiEt_3BH$ and then with CF_3CO_2H in refluxing THF for 3 h to give the η^5-Mn complex in 65% yield. With $LiEt_3BD$ and CF_3CO_2H, the 2-methoxy η^5 complex affords the η^5 complex labeled at the C2 position. With L-selectride and CF_3CO_2D, a 1:1 mixture of the non-deuteriated complex and of the η^5-Mn complex labelled at the C6 *endo* position of the sp^3 carbon is recovered (Scheme 63)[212].

Finally, with $LiEt_3BD$ and CF_3CO_2D, a 1:1 mixture of the monodeuteriated complex at the C2 carbon and of the dideuteriated complex at the $C6_{endo}$ and C2 carbons is obtained by elimination of the methoxy group and of the agostic H3 and D atoms (Scheme 64)[212].

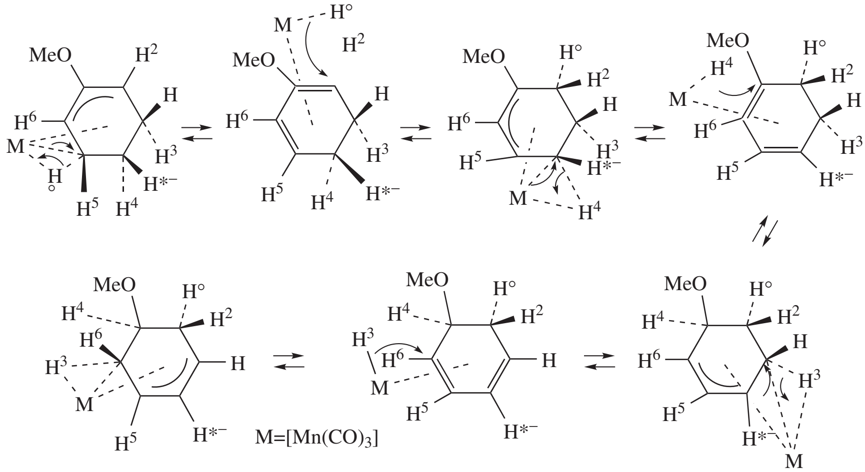
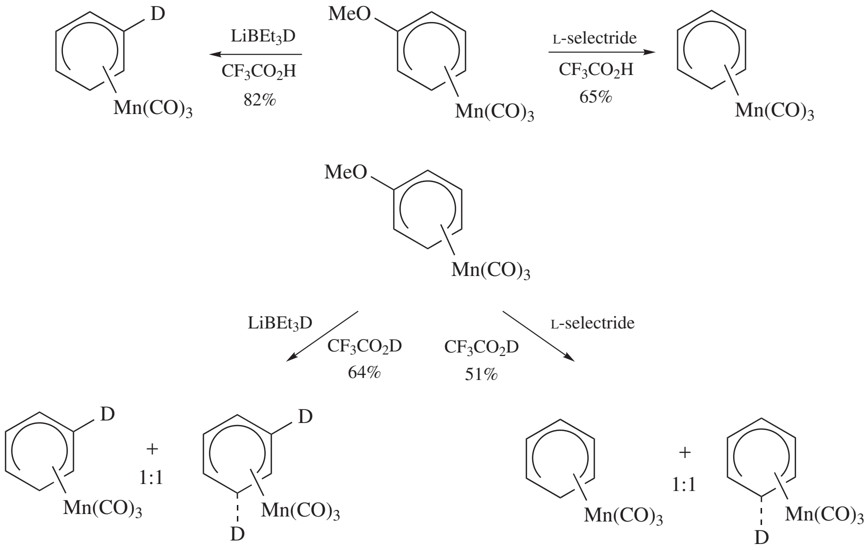
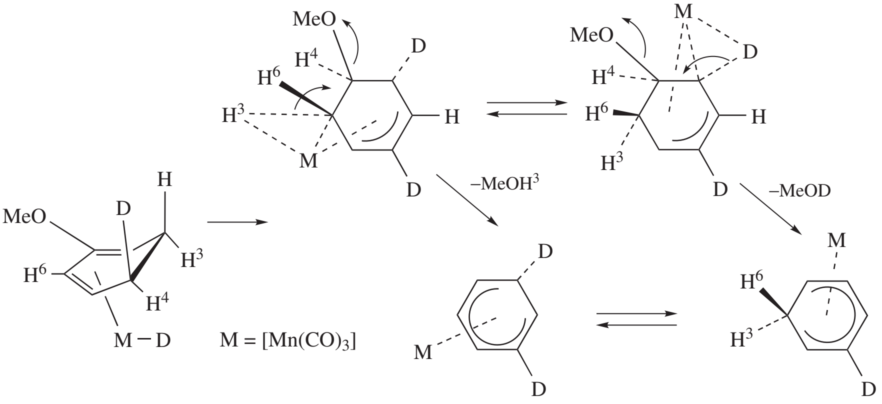


FIGURE 14

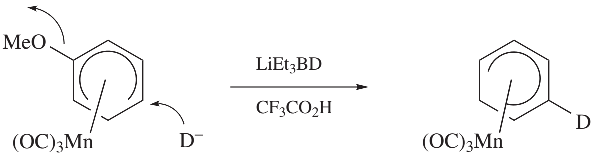


SCHEME 63

Taken together, the reactions reported in Scheme 63 represent a *para-tele* nucleophilic substitution which corresponds to the addition of the hydride (or deuteride) at a *para* position with respect to the methoxy leaving group, by analogy with the *cine*[164], *tele-meta*[165] and *tele-para*[166] reactions that the Rose group discovered in arenetricarbonylchromium complex series: *cine* S_NAr[64, 213–215], *tele-meta* S_NAr[53, 216, 217] and *tele-para* S_NAr[167, 184, 218] (Scheme 65).

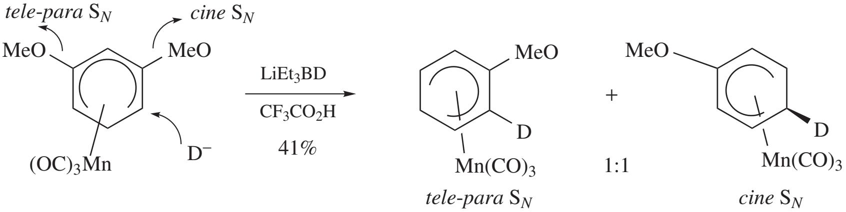


SCHEME 64



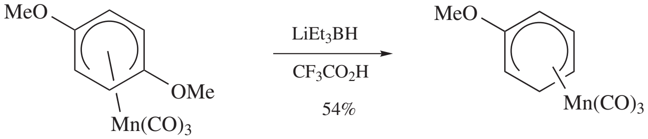
SCHEME 65

Similarly, the η^5-2,4-dimethoxycyclohexadienyl)Mn(CO)$_3$ complex reacts with deuteride and then with an acid to afford two monomethoxy η^5 deuteriated complexes via *cine* and *para-tele* nucleophilic substitutions S_N[212] (Scheme 66). Unexpectedly, 1,2- and 2,3-dideuteriated (η^5-$C_6H_5D_2$)Mn(CO)$_3$ complexes are obtained as minor compounds whose formation could be explained by a mechanism involving an *ipso* hydride addition to a carbon bearing the methoxy group.



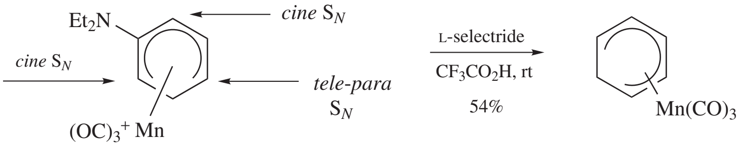
SCHEME 66

Addition of L-selectride to η^5-(1,4-dimethoxycyclohexadienyl)Mn(CO)$_3$ complex followed by protonation with MeOH and heating of the solution for 4 h resulted in the formation of a single monomethoxy isomer in 54% yield via a *cine* or a *tele-meta* nucleophilic substitution S_N (Scheme 67).



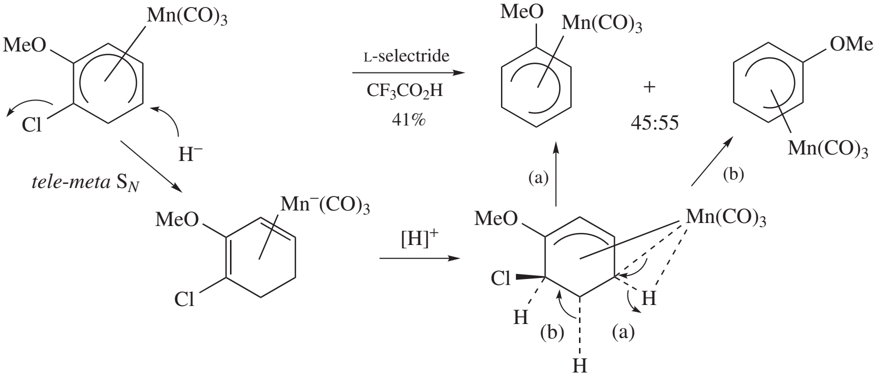
SCHEME 67

Cleavage of a C−N bond: With η^5-(2-diethylaminocyclohexadienyl)Mn(CO)$_3$ complex, addition of LiAlH$_4$ followed by protonation with CF$_3$CO$_2$H leads to the unsubstituted (η^5-cyclohexadienyl)Mn(CO)$_3$ complex in 54% yield, *via a cine or a tele-para* nucleophilic substitution (Scheme 68).



SCHEME 68

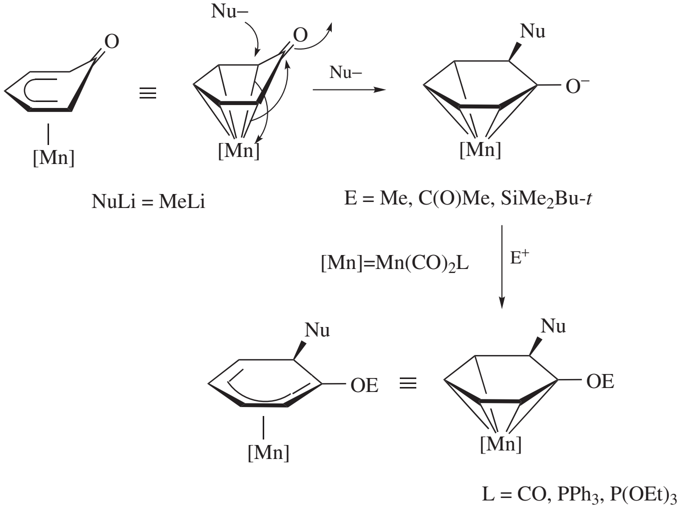
Cleavage of a C−Cl bond: Cleavage of the C−Cl bond occurs very quickly, even at low temperature, by adding H$^-$ and a proton source to η^5-(1-chloro-2-methoxycyclohexadienyl)Mn(CO)$_3$ complex; 2- and 3-methoxycyclohexadienylMn(CO)$_3$ are recovered in 54% yield without cleavage of a C−O bond. Addition of the hydride takes place *meta* to the chlorine atom; these reactions are *tele-meta* nucleophilic substitutions (Scheme 69)[212].



SCHEME 69

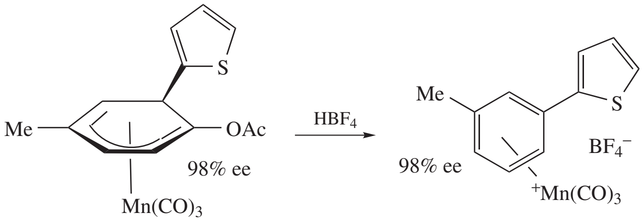
e. The case of oxocyclohexadienylMn(CO)$_3$ complexes. Chung and coworkers described the reactivity of a particular η^5-Mn complex, the (η^5-oxocyclohexadienyl)Mn(CO)$_3$ complex (η^5-(C$_6$H$_5$O)Mn(CO)$_2$L, L = CO, PPh$_3$, P(OEt)$_3$), which is easily obtained by deprotonation of the acidic proton of phenol-Mn(CO)$_3{}^+$. The neutral η^5-

oxocyclohexadienyl–Mn complex is a mesomeric form of the zwitterionic η^6-phenate Mn complex. It reacts with a nucleophile Nu^- to give an anion which can be trapped by an electrophile E^+. Thus a neutral η^5-cyclohexadienyl–Mn complex is obtained with a new sp^3 carbon located *ortho* to the starting oxocyclohexadienyl complex E = Me, C(O)Me, $SiMe_2$(Bu-*t*). Alternatively, the phenate can be demetallated to give the *ortho*-disubstituted phenol Nu = Me, Ph, *n*-Bu (Scheme 70)[31, 219, 220].



SCHEME 70

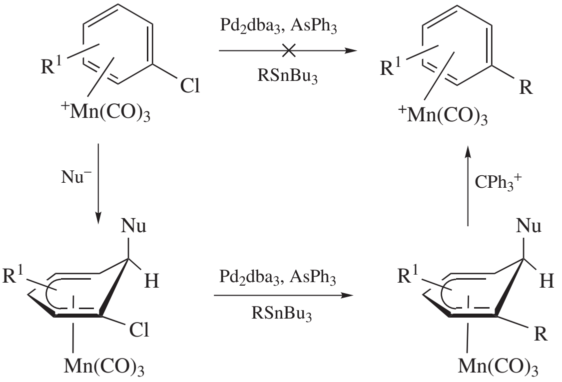
An enantioselective version of this unusual reaction has been described with Grignard reagents (Nu = Ph, thienyl, *n*-Bu) in the presence of (*S*)-binaphthol, an enantiopure ligand and a prochiral (η^5-oxocyclohexadienyl)Mn complex to give, for example, enantioenriched η^5-5-acetoxy-6-thienylcyclohexadienyl–Mn complex. After rearomatization with HBF_4, an enantioenriched η^6 complex is recovered, the driving force being the elimination of AcOH (Scheme 71)[220].



SCHEME 71

5. Pd-catalyzed reactions on (η^5-chlorocyclohexadienyl)Mn(CO)$_3$ complexes

Pallado-catalyzed coupling reactions in the manganese series have been studied as a versatile route for the functionalization of (η^6-arene)$Mn(CO)_3{}^+$ complexes. In the course of this study, it has been shown that (η^6-chlorobenzene)$Mn(CO)_3{}^+$ readily undergoes oxidative addition of $Pd(PPh_3)_4$ into the C−Cl bond[221] to afford a very stable bimetallic product (η^6-$C_6H_5PdCl(PPh_3)_2$)$Mn(CO)_3^+$. This bimetallic Pd/Mn complex presents a *cis* structure, which is very rare: usually the first−formed product is the *cis* complex which epimerizes into the more stable *trans* isomer[222]. In the case of the *cis* bimetallic Pd/Mn complex, even under very high CO pressure (50 atm), no carbonylation reaction occurs, in contrast to the (η^6-C_6H_5Cl)$Cr(CO)_3$ complex[223, 224]. On the contrary, the (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes undergo very easily Pd-catalyzed coupling reactions with a large variety of carbon nucleophiles, allowing the synthesis of complexes containing substituents that cannot be introduced in any other manner. Hydride may be abstracted from these η^5-Mn complexes with trityl cation $CPh_3{}^+$ generating new functionalized (η^6-arene)$Mn(CO)_3{}^+$ complexes, Nu = H (Scheme 72).

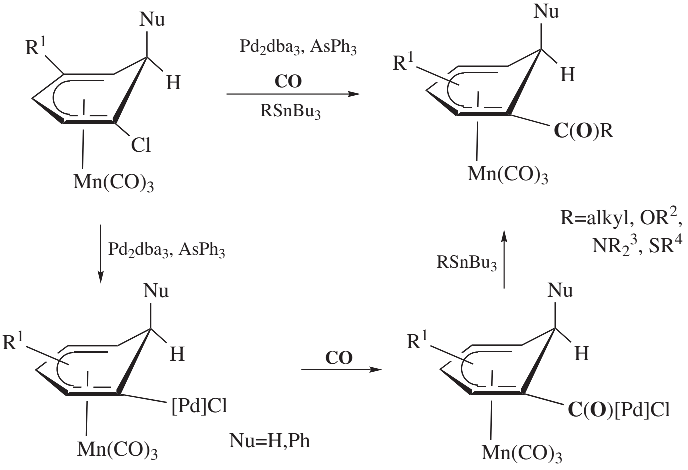


SCHEME 72

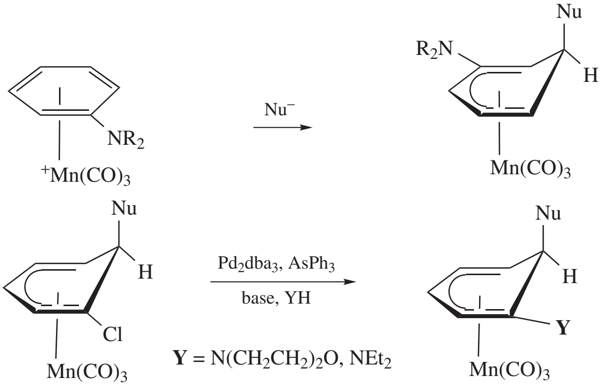
Thus, 1-Cl and 2-Cl η^5-Mn complexes are easily substituted by carbon derivatives: alkyl, thienyl, phenyl, double and triple bonds (Stille, Negishi, Heck and Sonogashira reactions). This methodology, extended to Buchwald−Hartwig reactions, permits the introduction of O, N, S and P substituents to the η^5-Mn complexes in 31 to 93% yield[73, 186, 187]. The most efficient and selective catalyst for these reactions was shown to be the association of Pd_2dba_3 and $AsPh_3$[72, 73].

Under carbonylative experimental conditions, these reactions can afford ketones, esters, thioesters and amides η^5-Mn derivatives. This general method of functionalization preserving the methylene *exo* fragment allows the rearomatization of the η^5-Mn complex by hydride abstraction, leading to new cationic η^6-Mn complexes. Such compounds are difficult or impossible to prepare selectively by direct complexation: for example, the synthesis of cationic Mn complexes, substituted by resonance withdrawing groups, is unknown by direct complexation of the arene to the $Mn(CO)_3$ entity because of the low electronic density of the aromatic cycle (Scheme 73)[73].

These synthetic methodologies also constitute a new route to substituted cyclohexadienyl manganese complexes possessing a regiochemistry not available via conventional nucleophilic addition to η^6-arene−$Mn(CO)_3{}^+$ complexes. For example, nucleophilic addition to an arene complex substituted by an electron-donating group (η^6-C_6H_5X)$Mn(CO)_3{}^+$ gives the η^5-Mn complex with the nucleophile on the *meta* carbon. However, starting with the 1-chloro η^5-Mn complex (X = Cl), which is the classical product of the nucleophilic



SCHEME 73

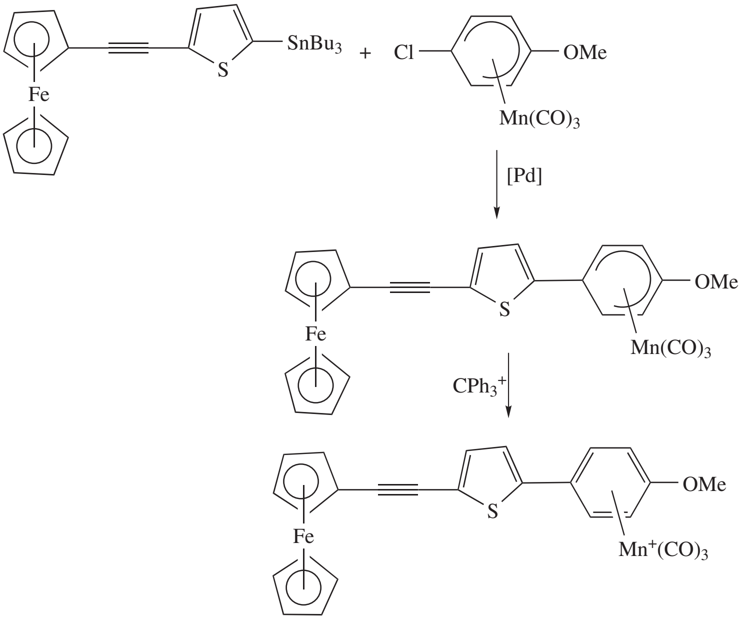


SCHEME 74

addition of Nu^- to the chlorobenzene complex, a Pd-catalyzed substitution generates the 1-substituted η^5-Mn complex which is impossible to prepare otherwise (Scheme 74)[187].

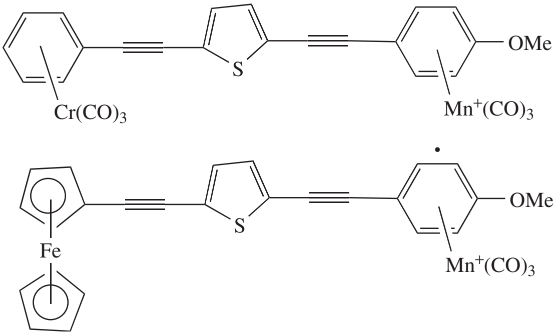
The Pd-catalyzed coupling methodogy has been used to prepare dimetallic conjugated complexes[7, 74]. They have been studied in solution in order to explore the extent of electron transfer from one metal to the other for interesting properties such as optoelectronic and electric applications and for non-linear optical materials. Thus Sonogashira reaction between an ethynylferrocene derivative and the η^5-1-chloro-4-methoxycyclohexadienyl Mn complex gives the dinuclear Fe/η^5 Mn 'push–pull' molecule, which can yield quantitatively the corresponding Fe/η^6-Mn derivative by treatment with CPh_3BF_4 (Scheme 75).

The dinuclear Fe/η^6-Mn complex with a spacer comprising two alkynes and one thiophene unit can also be prepared efficiently. The hyperpolarizabilities of these two ferrocene/η^6-Mn complexes shown below are, respectively, $\beta = 140 \bullet 10^{-30}$ esu ($\beta^\circ =$



SCHEME 75

$61 \bullet 10^{-30}$ esu) and $130 \bullet 10^{-30}$ esu ($\beta^{\circ} = 65 \bullet 10^{-30}$ esu). Alkyne links allow electronic communication but retain ground-state charge separation for these push–pull molecules. Cationic (η^6-arene)tricarbonylmanganese linked to neutral (η^6-arene)tricarbonylchromium complexes with different spacers are prepared similarly using the same methodology (Scheme 76)[67].



SCHEME 76

Pd-catalyzed coupling reaction of ethynylferrocene with 2-iodobenzodithiophene leads to the formation of the corresponding mononuclear Fe complex. Condensation of the corresponding iodo derivative with [η^5(1,5)-1-ethynyl-4-methoxycyclohexa-2,4-dienyl]tricarbonyl manganese affords the bimetallic Fe/η^5-Mn complex. Upon hydride abstraction, the Fe/η^5-Mn complex push–pull molecule is obtained (Scheme 77)[192].

Sonogashira Pd-catalyzed reaction has been applied to obtain the first η^5- and η^6-Mn complexes linked to a nucleoside spaced by an alkyne. Indeed, 2′-deoxyuridines substituted at the C5 position by an iodo atom can react with (η^5-ethynylcyclohexadienyl)Mn(CO)$_3$ complex to give the corresponding η^5-complex[224]. Reaction with CPh$_3$BF$_4$ gives rise to the rearomatization of the η^5 derivative into the corresponding cationic η^6 complex (Scheme 78)[225].

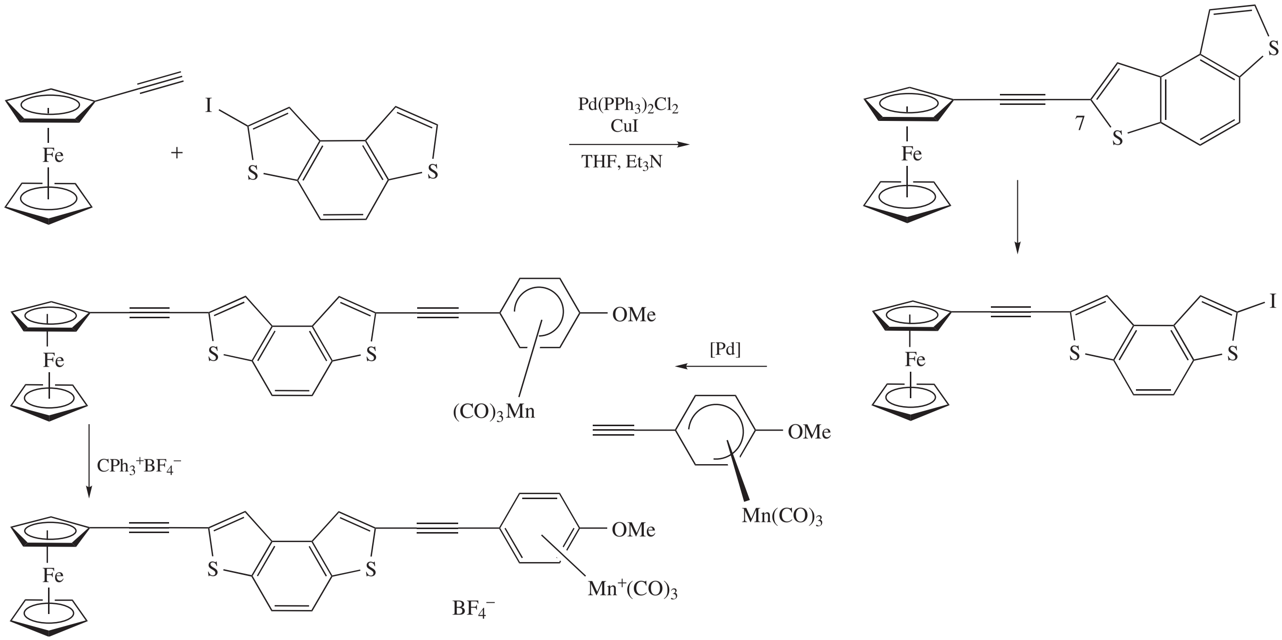
Although the compounds did not have antiviral activity in cell-based assays, the possibility to introduce at the strategic 5-position such highly electrophilic organometallic complexes opens wide perspectives in the chemical synthesis of new nucleoside analogues.

6. Lithiation and electrophilic quench

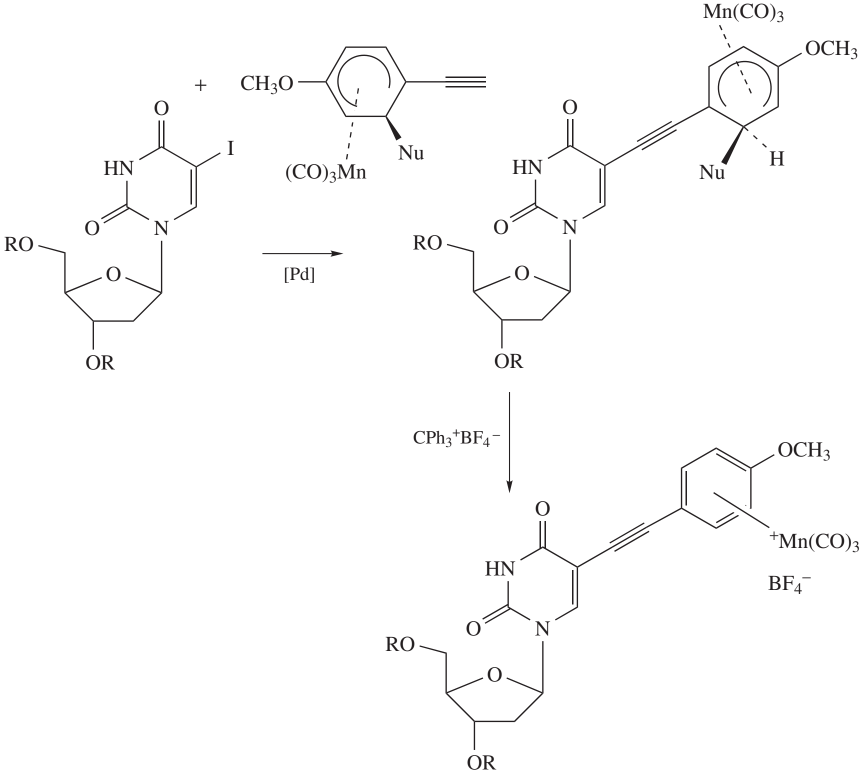
a. Lithiation/electrophilic quench sequence. Direct lithiation of (η^6-arene)Mn(CO)$_3^+$ could be a very versatile way for the synthesis of functionalized η^6 complexes. Unfortunately, despite time and trials, formation of lithiated η^6-Mn complexes has remained unsuccessful up to now. In contrast, the first lithiation of the isoelectronic neutral (η^6-arene)tricarbonylchomium complexes was reported in 1968 by Nesmeyanov and coworkers[225] and since then this reaction has seen extensive development[62, 63, 226–235]. The discovery of Pd cross-coupling reactions in η^5-Mn series[61] established that the presence of the Mn(CO)$_3$ tripod dramatically activates the carbon–halogen bonds in η^5-Mn complexes in the same way the Cr(CO)$_3$ entity does in η^6-Cr complexes for which Pd-catalyzed reactions have been well documented for many years. The similarities in reactivity properties between the two series of complexes raised the possibility that it could be also extended to the lithiation field, and lithiation of variously substituted η^5-Mn complexes has been successfully achieved.

Chloro- and methoxy-substituted η^5-Mn complexes were used for their good *ortho*-directing properties in the lithiation step. Addition of *n*-BuLi at −78 °C followed by an electrophilic quench gives the η^5-substituted Mn complexes with no competing halogen–lithium exchange and with a high degree of regiocontrol (Scheme 79)[236, 237].

For (η^5-2-methoxycyclohexadienyl)Mn and (η^5-2-chlorocyclohexadienyl)Mn complexes, where both the C1 and C3 positions are available, no lithiation was observed at one of the terminals C1 or C5 of the π-system. Theoretical investigations performed on η^5 complexes without any substituent on the π-system showed that the regioselectivity is fully controlled by selective lithiation at the C2 position eclipsed by a Mn−CO bond and is mainly governed by the stability of the deprotonated species on the C2 carbon. This reaction is efficient for the introduction of alkyl, ester groups, as well as tin derivatives, iodide, formyl, phosphines, amines, phenyl sulfide and amides: $E = Me$, CO$_2$Et, *n*-Bu$_3$Sn, I, PPh$_2$, CH$_2$NR$_2$, SPh, C(O)NMe$_2$[189, 191, 193, 238]. By using benzophenone or benzaldehyde as electrophiles, access to η^5-Mn complexes substituted by an alcohol function is possible. This procedure does not affect the substituent of the η^5-starting material, and when a chloride is present it remains available for subsequent Pd-catalyzed coupling reaction[73]. Particularly interesting are the (η^5-formylcyclohexadienyl)Mn(CO)$_3$ complexes obtained by a lithiation/DMF quench sequence of the (η^5-chloro- and/or methoxy-cyclohexadienyl)Mn complexes (Scheme 80), with yields ranging from 66 to 90%. For the anisole derivatives, $R = OMe, Nu = H$, Ph, formylation proceeds with complete regiocontrol at the C3 position, whereas with *para*-chloroanisole ($R^1 = Cl, R^2 = OMe$) two regioisomers in a C2:C3 ratio of 60:40, which are easily separated by silica gel chromatography, are obtained.


Fe
+
I
S
S
Pd(PPh$_3$)$_2$Cl$_2$
CuI
THF, Et$_3$N
Fe
7
S
S
Fe
S
S
I
[Pd]
OMe
Mn(CO)$_3$
Fe
S
S
OMe
(CO)$_3$Mn
CPh$_3$$^+BF_4$$^-$
Fe
S
S
OMe
Mn$^+$(CO)$_3$
BF$_4$$^-$

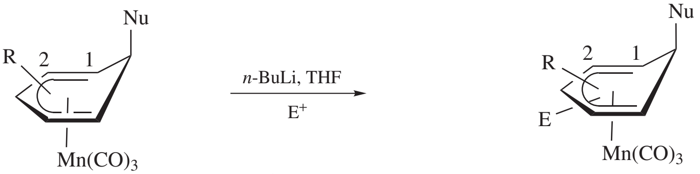
SCHEME 77



SCHEME 78

IR spectroscopic data show noticeable differences according to the position of the formyl group on the conjugated π-system. Thus, computational studies were undertaken on the three η^5-formyl regioisomeric complexes $[\eta^5\text{-}C_6H_6CHO]Mn(CO)_3$ without any substituent on the π-system and with two hydrogen atoms at the C6 sp^3 carbon, in order to obtain a better understanding of the electronic properties of the different regioisomers with the formyl group at the C1, C2 and C3 carbons, and compared with experimental results (Figure 15). The frequency of the formyl group of the C2 regioisomer has the largest value (1710 cm^{-1}). This is in good agreement with a better electronic delocalization when the aldehydic group is linked to the C1 and C3 carbons than when it is linked to the C2 carbon. Furthermore, the C1 regioisomer is the most stable by comparing the relative energies of the three regioisomers (Figure 15)[77].

b. Lithiation, organomanganese transmetallation. The η^5 complexes substituted by synthetically useful keto groups appear to be of crucial importance in the development of applications of such complexes. They can be prepared starting with η^5-Mn derivatives using Stille Pd coupling under carbonylative conditions or by lithiation/electrophilic quench. The first procedure is limited to η^5-chlorocyclohexadienyl—Mn complexes, and a CO atmosphere is required to tranform the Pd−Cl intermediate into the acyl−palladium

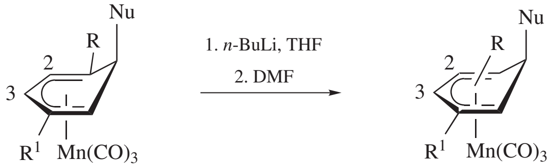


E = Me, CPh_2OH, CO_2Et, $n\text{-}Bu_3Sn$, I, PPh_2, CH_2NR_2, SPh, $C(O)NMe_2$

R = 2-OMe[a] 3-E 86%
R = 1-Cl 2-E 62%
R = 2-Cl E = $SiMe_3$ 3-E 61%

[a]Addition of TMEDA

SCHEME 79



	Product
R^1 = H, R = OMe, Nu = Ph	3-CHO 68%
R^1 = H, R = OMe, Nu = H	3-CHO 67%
R^1 = Cl, R = OMe, Nu = Ph	2-CHO:3-CHO 60:40 90%
R^1 = H, R = H, Nu = Ph	2-CHO:3-CHO 80:20 66%

SCHEME 80

complex. The use of a stannous derivative also narrows the convenience of the method. The second procedure is applied only to sterically demanding electrophiles such as 2,2-dimethylpropionic acid[237]. An efficient synthesis of keto-substituted η^5-Mn complexes was achieved by organomanganese transmetallation catalyzed by $Fe(acac)_3$[237]. Lithiation of a 2-methoxycyclohexadienyl η^5-Mn complex with BuLi in the presence of TMEDA gives only one lithiated complex, which, treated with $MnCl_4Li_2$, and PhCOCl in the presence of a catalytic amount of $Fe(acac)_3$ affords the corresponding ketone in 87% yield. Without the iron catalyst the yield decreases dramatically, proving definitively that the Fe intermediate presents an increased reactivity with respect to the manganese intermediate. This new methodology is valuable especially if the starting η^5 is substituted by a chlorine atom because the final keto-chloro-substituted product cannot be obtained via Stille reaction. Indeed, no synthesis of the starting dichloro(η^5-cyclohexadienyl)$Mn(CO)_3$ complex has been reported up to now. Furthermore, the chlorine atom remains available for subsequent functionalization. So, two efficient methods are now available (Pd catalysis and transmetallation) to introduce a keto function at any of the carbons of the η^5 complex (Scheme 81).

7. Lithium bromide exchange and electrophilic quench

In the case of bromo-substituted η^5 complexes, reaction with n-BuLi allows the quantitative formation of the lithiated complexes after lithium–bromide exchange. No competition between the Br/Li exchange and a lithiation *ortho* to the Br atom can be detected.

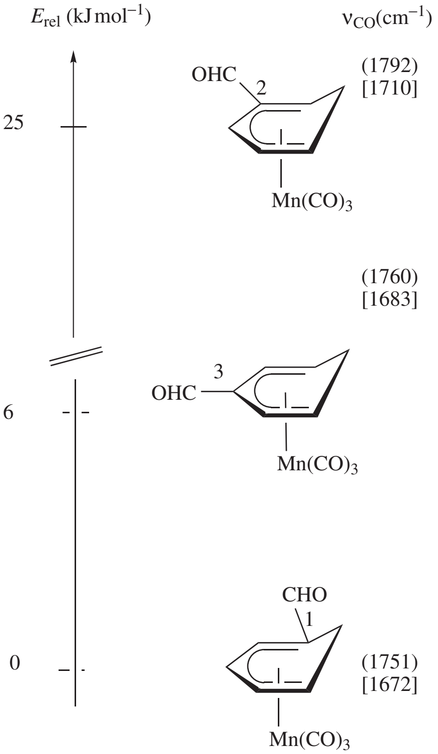


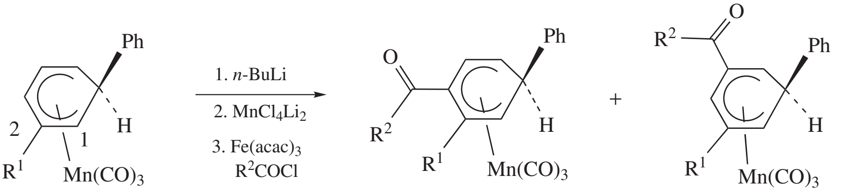
FIGURE 15. Energies relative to the most stable regioisomer and ν_{CO} computed vibrational frequencies (in parentheses, reported unscaled) and experimental vibrational frequencies (in brackets in cm^{-1}).

After an electrophilic quench, new functionalized η^5 complexes can be obtained in good to excellent yields (Scheme 82)[77].

This reaction, highly regioselective when the bromine atom is not adjacent to the *ortho*-directing group, offers a complementary functionalization method to palladium-catalyzed cross-couplings and to the lithiation/electrophilic quench reactions. Indeed, introduction of substituents at the C1 or C5 termini of the cyclohexadienyl ligand, or *meta* (or *para*) with respect to an *ortho*-directing group, is now possible. In particular, this methodology permits the introduction of a formyl group at the C1 carbon (Scheme 83).

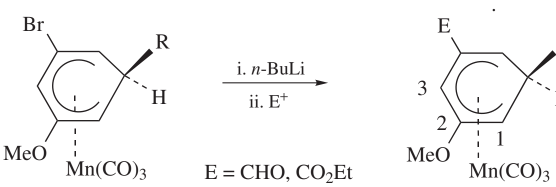
8. Rearomatization

As previously mentioned, the *exo* hydrogen is easily removed with $CPh_3{}^+BF_4{}^-$ giving the cationic η^6-Mn complex[17]. Two recent examples show the efficiency of this reaction, the η^5-2-methoxy-3-iodo, and the η^5-2-methoxy, 3-silyl η^5-Mn complexes give, in 76 and 78% yield, respectively, the corresponding η^6-iodo and silyl arene Mn complexes[236] (Scheme 84). Until recently, this represented the first synthesis of an η^6 iodoarene Mn complex. However, a method of direct complexation of the $Mn(CO)_3$ tripod to an iodoarene



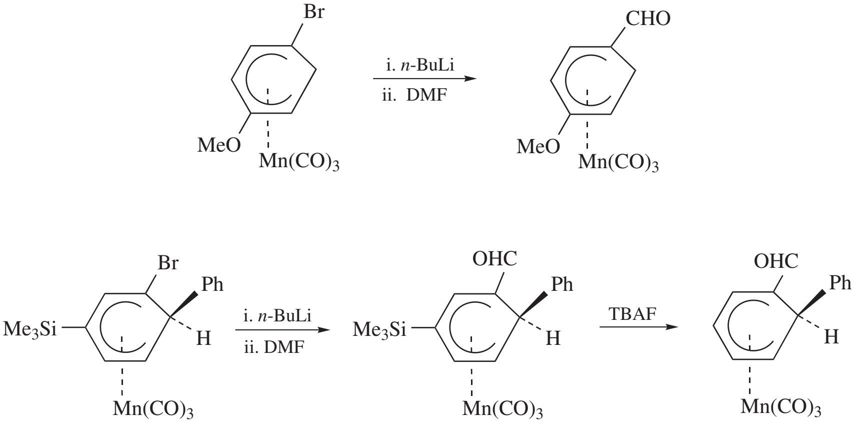
R^1 = OMe, H, Cl; R^2 = Ph, 2-thienyl

SCHEME 81



E = CHO, CO_2Et

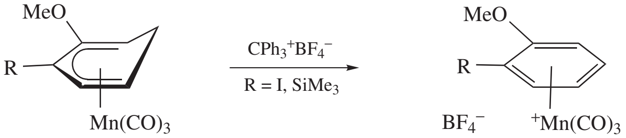
SCHEME 82



SCHEME 83

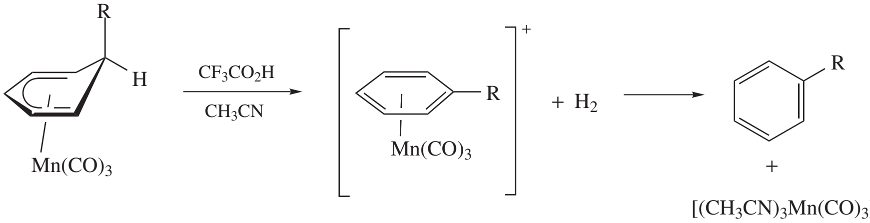
substituted by a methoxy or a silylated group has been developed in 2009 and allows a more straightforward synthesis of such iodoarene complexes[77].

Sweigart and coworkers showed that the rearomatization of the η^5 complex is possible in CH_3CN with CF_3CO_2H: the free arene and $[Mn(CO)_3(CH_3CN)_3]^+$ are recovered[16]. This finding would be of interest if the Mn(I) complex could be recycled for the preparation of η^6-Mn complexes, thus reducing the costs involved in the arene functionalization reactions[27]. This procedure involves an interesting *endo* hydride abstraction with acid in the presence of CH_3CN, a two-electron ligand known to compete with arenes for the



SCHEME 84

coordination sites on $Mn(CO)_3^+$ (Scheme 85). The driving force of the reaction is claimed to be the ready arene displacement by CH_3CN. In contrast, refluxing the η^5-Mn complex in aqueous 2M HCl gives no reaction. The possibility of protonation of the η^5-Mn complex and formation of a cationic η^4-cyclohexadiene Mn intermediate would be possible, but it is not easy to understand the oxidation of the cyclohexadiene into the corresponding arene.



SCHEME 85

Rearomatization of the η^5-Mn complexes with loss of the $Mn(CO)_3$ entity occurs by oxidation with Ce^{IV}[30], I_2[156], NBS[36, 131, 238, 239], Jones reagent[16] or DDQ[127] giving the free arenes.

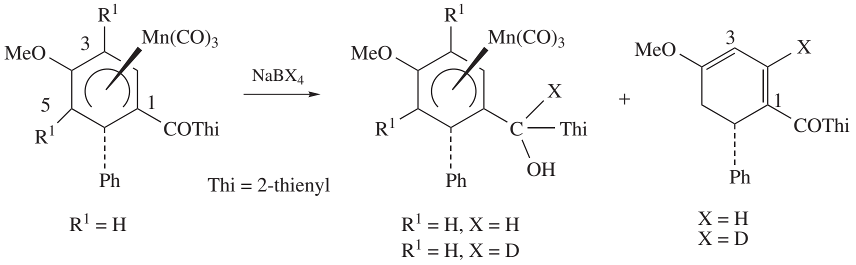
A photochemical reaction has been described to obtain the free arenes. Upon exposure to ultraviolet light in CH_2Cl_2 or in cyclohexane, η^5-$C_6H_6RMn(CO)_3$, R = H, Me, Ph, *t*-Bu, thienyl, $CH_2C(O)Bu$-*t*, were converted to the corresponding substituted free arenes in high yields, whereas photoirradiation in CH_3CN or DMF leads to the formation of a mixture of cyclohexadienes and arenes (*vide infra*, Scheme 53)[198].

9. Reactivity of keto- and formyl-(η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes

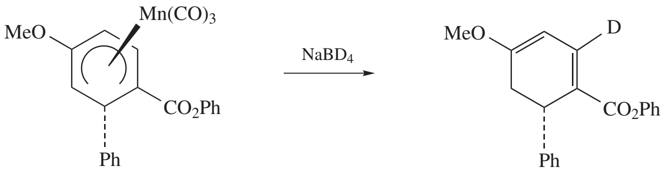
a. Addition of hydrides to a keto group. Reaction of hydrides with the carbonyl group of (η^5-ketocyclohexadienyl)$Mn(CO)_3$ complexes leads to the formation of alcohols with a new stereogenic center. The corresponding diastereoisomeric alcohols are obtained in 82% yield as major products (ratio 58/42) together with a cyclohexadiene in 13% yield due to the unexpected but interesting addition of hydride to the C2 carbon of the C1−C5 π-system. Indeed, nucleophilic additions to the cyclohexadienyl ring usually takes place at C1 and C5 carbon atoms (Scheme 86)[190].

The same reaction has been achieved with the (η^5-1-phenoxycarbonyl-4-methoxy-6-phenylcyclohexadienyl)$Mn(CO)_3$ complex with $NaBD_4$ as nucleophile to avoid the addition to the carbonyl group. Effectively, the deuteriated cyclohexadiene is obtained as the sole product in 36% yield besides unreacted starting material (40%) (Scheme 87).

The mechanism of the reaction suggests an *exo* 1,4 deuteride addition to the C2 carbon of the conjugated ester group giving the anionic $\eta^3 : \eta^1$ complex. β-Elimination or

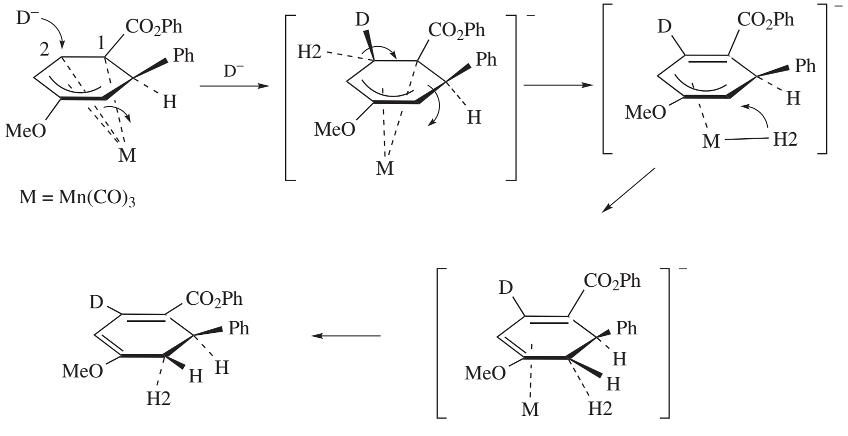


SCHEME 86



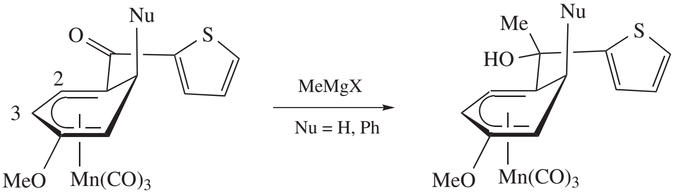
SCHEME 87

insertion of the Mn atom into the C−H2 *endo* hydrogen bond and decoordination of the C1=C2 double bond could afford the 18-electron η^3-anionic manganese hydride Mn−H2. Reductive elimination could afford the unstable η^4-anionic complex which could liberate the deuteriated cyclohexadiene (Scheme 88).



SCHEME 88

b. Addition of Grignard reagents to a keto group. Addition of Grignard reagents such as CH_3MgX to (η^5-keto-substituted cyclohexadienyl)Mn complexes leads to the corresponding alcohols in good yields (Scheme 89)[76].



SCHEME 89

For each alcohol, two diastereoisomers are formed. No diastereoselectivity is observed for the alcohol with the CH_2 sp^3 carbon (Nu = H). However, 40% de is observed for the CHPh sp^3 carbon (Nu = Ph). No 1,4-addition takes place in the π-system unlike the hydride (deuteride), *vide infra*. The diastereoselectivity observed when the sp^3 carbon is substituted by an *exo*-phenyl group stresses the importance of the steric hindrance of this carbon atom. Indeed, it hinders one face of the cyclohexadienyl ring opposite to the metal entity and favors a *syn* addition with respect to the $Mn(CO)_3$ tripod (Figure 16).

c. Addition of hydride and Grignard reagents to a formyl group. Addition of $NaBH_4$ to (η^5-2-methoxy-3-formylcyclohexadienyl)$Mn(CO)_3$ complex affords the corresponding alcohol in 87% yield. By adding PhMgCl to the same starting complex, only one diastereoisomer is identified by ^1H NMR spectra and the X-ray diffraction analysis allows the assessment of the relative configuration (R) for the newly created sp^3 carbon associated with the ($2pS$) configuration for the metal-coordinated cyclohexadienyl residue (Scheme 90)[191]. This very high diastereoselectivity is due, first, to the *anti* conformation of the formyl group with respect to the OMe group, which is adopted for steric reasons, and second, to the presence of the $Mn(CO)_3$ tripod which blocks exposure of one face of the cyclohexadienyl unit, enforcing an *exo* addition of the nucleophile opposite to the metal.

d. Reactivity of hydroxyalkyl-substituted η^5-Mn complexes. In the presence of an acid, the alcohols produce the corresponding 'styrene'-like complexes together with dienones[76]. The formation of the olefins conjugated to the $\pi\eta^5$-system can be explained by the protonation of the alcohol and formation of a 'benzylic' carbocation which eliminates a hydrogen of the methyl group. Decoordination of the $Mn(CO)_3$ tripod and acidic hydrolysis of the trienol ether give the dienones. Classical rearomatization of the η^5-cyclohexadienyl–Mn

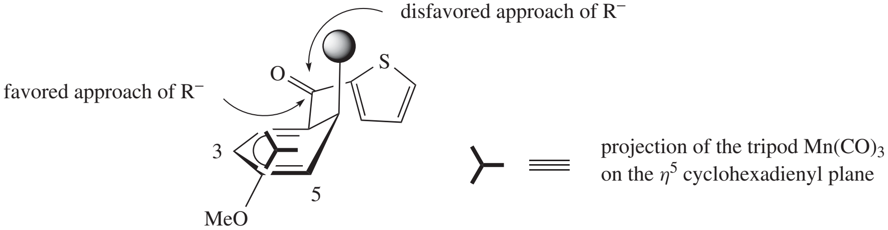
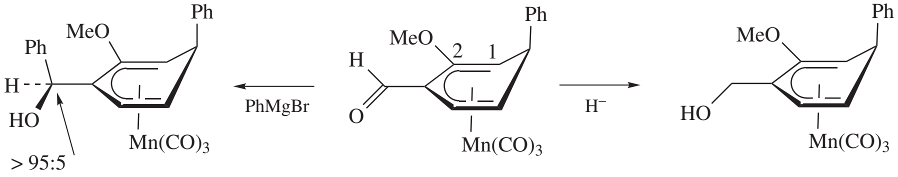
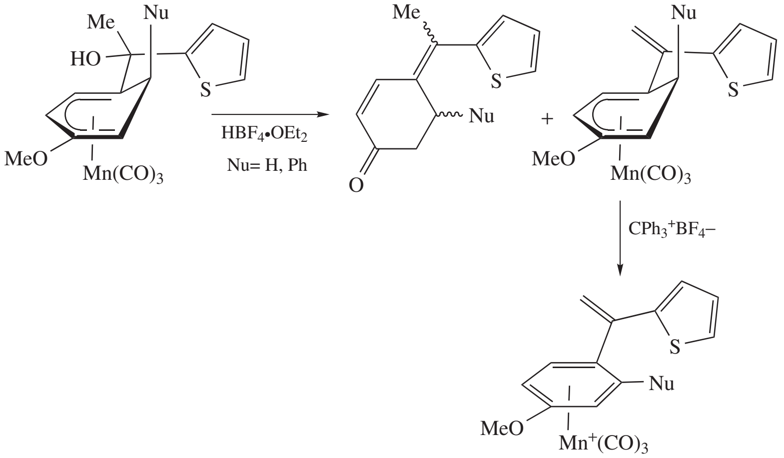


FIGURE 16



SCHEME 90

complex with an unsubstituted sp^3 carbon using $CPh_3^+BF_4^-$ affords the corresponding η^6-arene complexes (Scheme 91); the X-ray structure of one of them shows a staggered conformation of the $Mn(CO)_3$ tripod with respect to the carbon atoms of the arene ring. The double bond, oriented toward the metal, makes a dihedral angle of 40° with the arene ring.

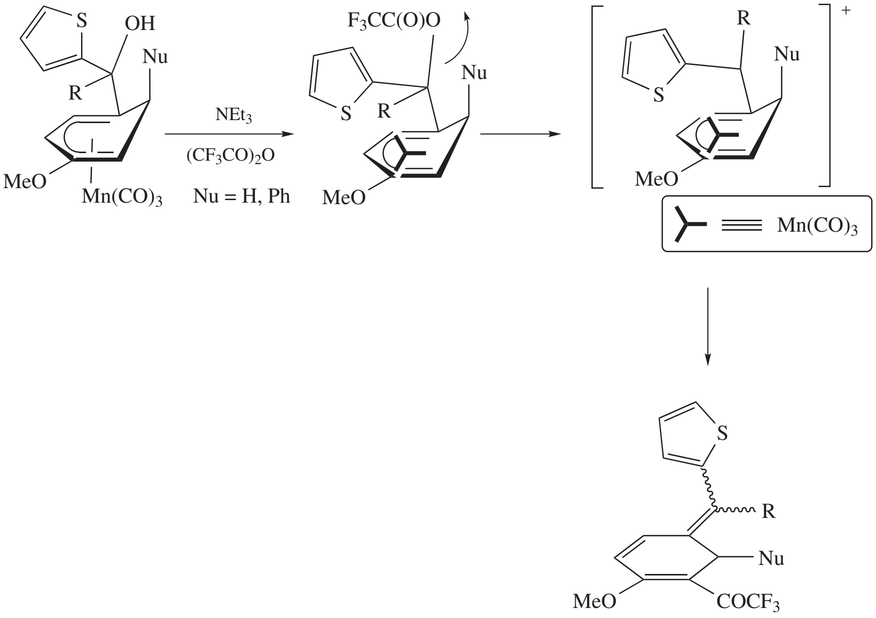


SCHEME 91

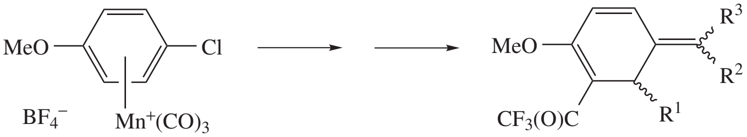
In the presence of NEt_3 and $(CF_3CO)_2O$, the benzylic alcohols do not give the expected trifluoroacetates but instead give dark red compounds which appeared to be trienones in 34% yield for Nu = H, R = Ph, in 80% yield for Nu = Thi, R = H and in 76% yield for Nu = Ph, R = H[240]. The suggested mechanism involves the formation of the unstable trifluoroacetate intermediate η^5-Mn complex, anti-eclipsed by a Mn−CO bond which would lead to the cationic complex after Mn-assisted elimination of the CF_3COO^- group. After decoordination of the tripod $Mn(CO)_3$, trifluoroacetylation would afford the corresponding trienones (Scheme 92).

The overall process starting from the cationic η^6-*p*-chloroanisole Mn complex (parent complex of the hydroxyalkyl complexes) represents a new Mn dearomatization reaction (Scheme 93). Up to now, Mn-mediated reactions required double addition of two nucleophiles to cationic η^6 complexes[96, 203, 205].

Different reactivities are observed with 2-hydroxyalkyl and 3-hydroxyalkyl (η^5-cyclohexadienyl)tricarbonylmanganese complexes toward trifluoroacetylation of the

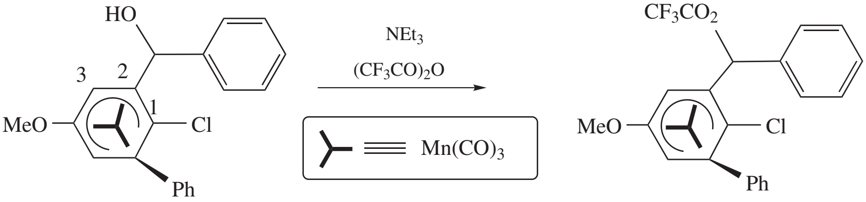


SCHEME 92



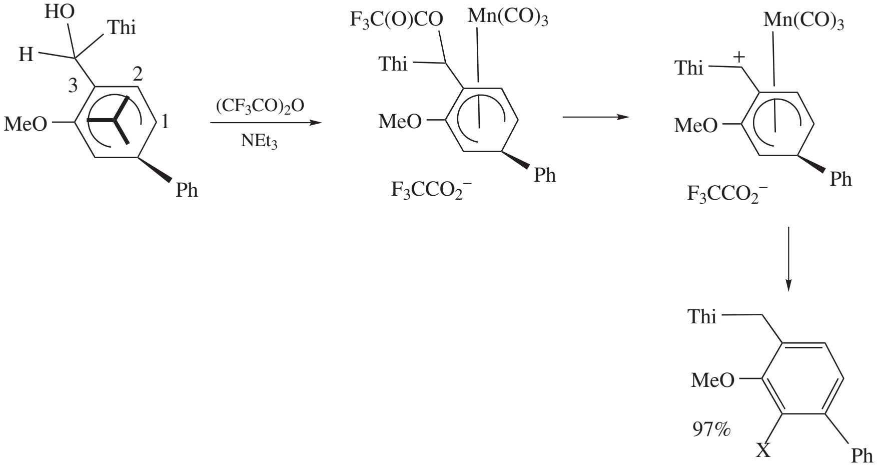
SCHEME 93

hydroxy group when submitted to the action of NEt_3 and $(CF_3CO)_2O$. Indeed, only the hydroxyalkyl complex, whose cyclohexadienyl unit is substituted at the C2 position (eclipsed by a Mn−CO bond) by the alcohol function, gives the expected stable trifluoroacetate (Scheme 94).



SCHEME 94

For the anti-eclipsed C3-hydroxyalkyl-substituted complex, elimination of the trifluoroacetate takes place followed by decoordination of the $Mn(CO)_3$ entity and 1,5-hydrogen shift to yield a free arene (Scheme 95)[240].



SCHEME 95

IV. CONCLUSION

The main reactivities described for η^5-Mn complexes correspond to nucleophilic addition, lithiation/electrophilic quench, lithium/halogen exchange and Pd-catalyzed reactions. These types of reactions can be efficiently compared with those well studied in η^6-arenetricarbonylchromium complexes.

In the case of nucleophilic additions, it is interesting to stress the relative stability of the resulting compounds in both series: the anionic (η^5-cyclohexadienyl)$Cr(CO)_3$ and the neutral (η^5-cyclohexadienyl)$Mn(CO)_3$, The addition of stabilized carbanions to an (η^6-arene)$Cr(CO)_3$ gives an unstable reversible anionic η^5-cyclohexadienyl$Cr(CO)_3$ complex whose features are reported in Figure 17[241], whereas the addition of the same carbanion to η^6-Mn compounds is in most cases irreversible and affords stable neutral (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes, which can be purified by silica gel chromatography. This is well demonstrated by the addition of the anionic $[(\eta^5\text{-cyclohexadienyl})Cr(CO)_3]^-$ complex to the cationic $[(\eta^6\text{-benzene}Mn(CO)_3]^+$ complex which affords the neutral (η^6-benzene)$Cr(CO)_3$ and (η^5-cyclohexadienyl$Mn(CO)_3$ derivatives (Figure 17, path b)[115].

The anionic $[(\eta^5\text{-Nu-cyclohexadienyl})Cr(CO)_3]^-$ derivatives (Nu^- = stabilized carbanion) give the starting (η^6-arene)$Cr(CO)_3$ complexes by adding water (Figure 17, path c), whereas treatment with strong acid such as CF_3CO_2H followed by an oxidation leads to cyclohexadienes (Figure 17, path d). The mechanism probably involves (η^4-cyclohexadiene)chromiumtricarbonyl hydride intermediates [Cr−H] (Figure 17, path e). The anionic Cr intermediate (Nu = H) can be trapped by reaction with a strong electrophile such as $ClSnPh_3$ to give the stable bimetallic Cr−Sn complex[115] similarly to the pioneering result found by Semmelhack and coworkers when Nu = dithiane[241] (Figure 17, path f). Finally, if the anionic η^5-Cr complex substituted by an X group (X = Cl, OR, NR_2) is treated with hydride and then with acid, S_NAr nucleophilic aromatic substitutions

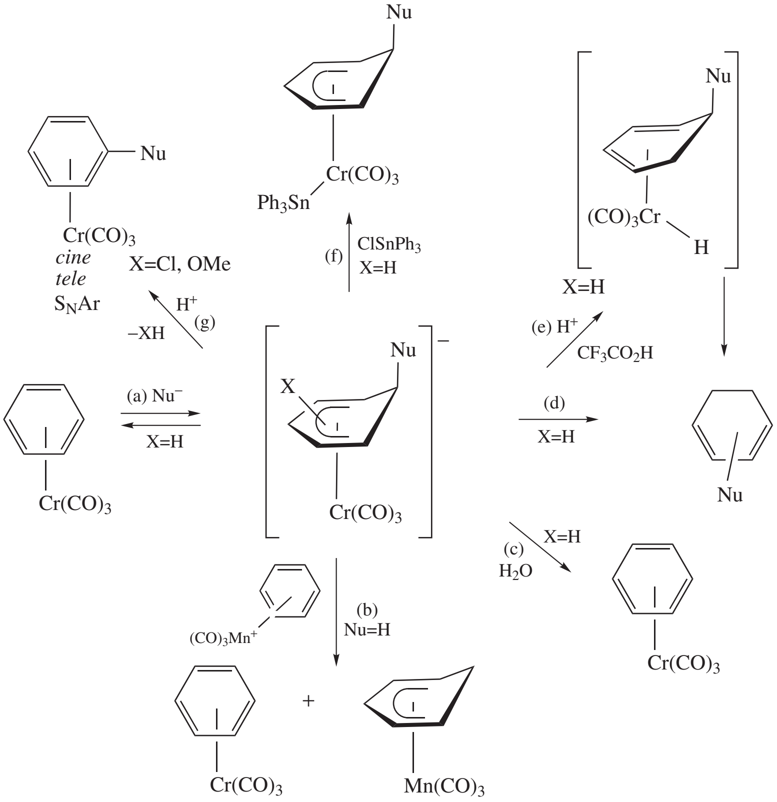


FIGURE 17

readily occur and the η^6-areneCr(CO)$_3$ complexes are recovered via reactions called by the Rose group: *cine, tele-meta* and *tele-para* S_NAr[164–166]. Indeed, the hydride reacts *ortho, meta* and *para* to the X leaving group, the driving force being the elimination of HX and rearomatization of the η^4-cyclohexadieneCr(CO)$_3$ complex into η^6-areneCr(CO)$_3$ (Figure 17, path g).

In contrast, neutral (η^5-cyclohexadienyl)Mn complexes are stable in water, but in the presence of an acid such as CF_3CO_2H, Sweigart and coworkers described how they probably revert to the cationic (η^6-arene)Mn complexes and H_2, via an *endo* hydride abstraction (Figure 18, path a) and then to the free biphenyl and $[(CH_3CN)_3Mn(CO)_3]^+$ (Figure 18, path b)[16]. The driving force is the ready arene displacement by three acetonitrile ligands. The authors noted that the η^5-Mn complex (Nu = Ph) is inert in boiling aqueous 2M HCl solution (Figure 18, path c). The η^5-Mn complex, treated with a strong oxidant, liberates the free substituted arene (Figure 18, path d). However, a reverse reaction can occur under different conditions. Indeed, Mawby and coworkers described the reaction of benzeneMn(CO)$_3{}^+$ with malonate carbanion $(EtO_2C)_2CH^-$ which yields the neutral cyclohexadienyl $[C_6H_6CH(CO_2Et)_2]Mn(CO)_3$ complex (Figure 18, path e). The reaction is reversed by adding Ph_3CBF_4. Thus the starting cationic benzene–Mn complex is recovered (Figure 18, path f)[129]. The authors suggest that the ease with which the substituent is

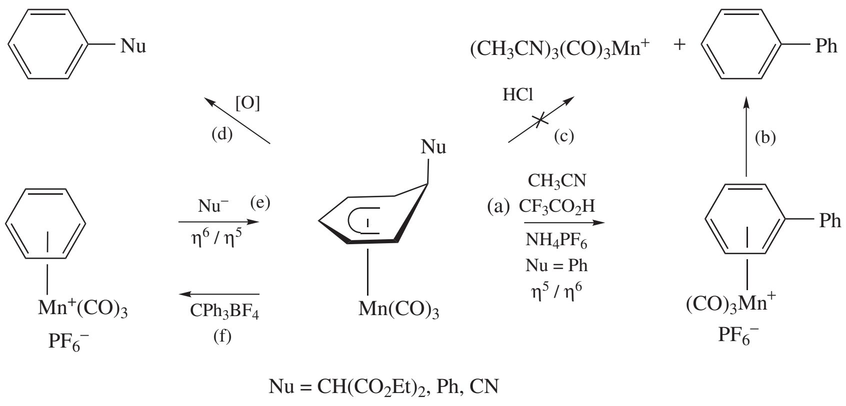


FIGURE 18

removed is presumably associated with the relief of the strain indicated by the bond lengths and angles in the C1−C6−C5 section of the ring, the C6 carbon being the sp^3 carbon substituted by the malonate residue. They described also this reverse reaction with η^5-(6-cyano-1,5-cyclohexadienyl)Mn(CO)$_3$ complex using CPh$_3$BF$_4$ or Et$_3$OBF$_4$ in CH$_2$Cl$_2$ or HBF$_4$, which affords the cationic [(benzene)Mn(CO)$_3$]$^+$ complex[118, 120]. Thus, the reagent removes the *exo*-cyano group rather than the *endo*-hydrogen atom (Figure 18, path f).

Lithiation and Pd-cross-coupling reactions have been compared in both series η^6-Cr (Figure 19) and η^5-Mn complexes (Figure 20), which showed similarities in reactivity properties[189].

Thus, it was possible to regioselectively functionalize chloro and bromo η^5-Mn derivatives using lithiation and Pd-catalysis methodologies. Lithiation *ortho* to the chlorine atom gives the corresponding compounds via a lithiation/electrophilic quench sequence (Figure 20, path a)[189]. In contrast, for the bromo derivatives bromine/lithium exchange yields new η^5-Mn complexes which corresponds to an *ipso* functionalization (Figure 20, path b)[77]. After treatment with a nucleophile and then with an acid, hydrodechlorination, hydrodealkoxylation, hydrodesulfurization and hydrodeamination take place via elimination of an agostic hydrogen and the chloro, alkoxy, thio and amino groups. These new reactions have been called *cine, tele-meta* and *tele-para* S$_N$ nucleophilic substitutions depending on the *ortho, meta* or *para* position of the addition of the hydride to the leaving group X = Cl, OR, SR and NR$_2$ by analogy with Cr complexes (Figure 20, path c)[212]. Finally, for chloro complexes, Pd-catalyzed reactions permit the synthesis of substituted η^5-Mn complexes (Figure 20, path d). This reaction performed under a CO atmosphere affords the first η^5-Mn complexes substituted by electron-withdrawing groups such as ketones, esters and amides (Figure 20, path e).

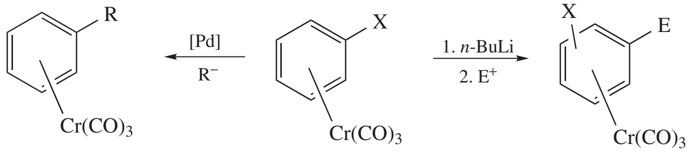


FIGURE 19

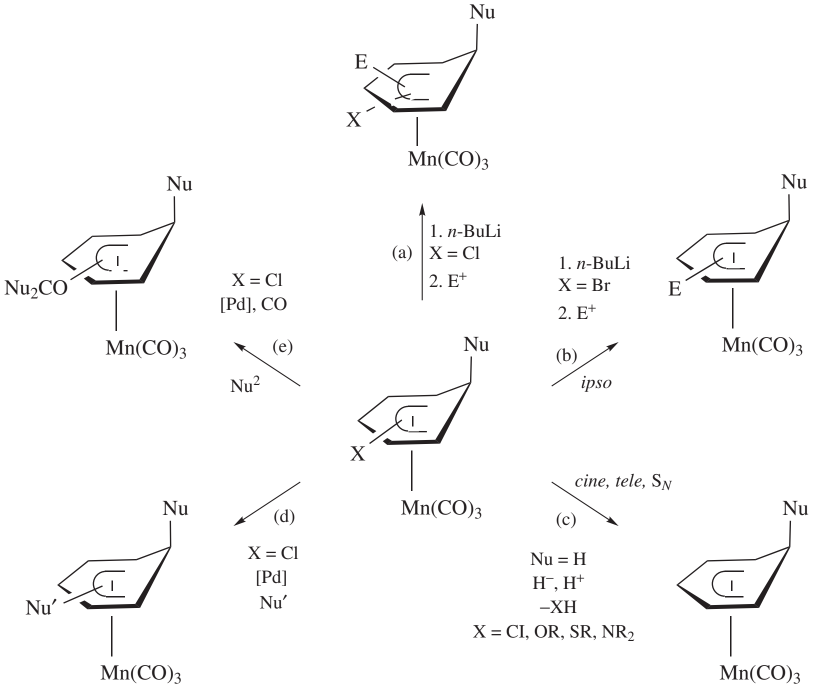


FIGURE 20

All these recent developments in the functionalization of η^5- and η^6-Mn complexes described in this chapter clearly open a revival period for this type of complexes which are starting to emerge as a valuable and versatile class of compounds more environmentally friendly than their Cr analogs. Another aspect of Mn complexes not discussed here involves their chirality, and in particular the preparation of enantiopure complexes to obtain new planar chiral Mn-based ligands for applications in asymmetric catalysis, as well as new planar chiral complexes for original building blocks in fine chemistry[71, 78]. This research is currently in progress in our group and will be published elsewhere.

V. ACKNOWLEDGMENTS

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Preparation and reactivity of organomanganese compounds

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I. INTRODUCTION

The first organomanganese compounds were prepared by Gilman and Bailie in 1937. However, the use of these reagents in organic synthesis was only developed from 1970 on. Until now, the chemistry of organomanganese reagents has clearly been less developed than that of other transition metals such as copper, palladium or nickel. It should be noted that, in light of current preoccupations related to sustainable development, manganese is very interesting for large-scale applications since it is cheap and toxicologically benign. It is, in abundance, the twelfth element of the Earth's crust[1] and, among all transition metals, only iron is more abundant and less expensive. In the light of these considerations, the results recently reported in homogeneous catalysis are very promising.

II. PREPARATION OF ORGANOMANGANESE REAGENTS

A. Introduction

Only a few organomanganese reagents were prepared before 1970. The interest in preparing these reagents increased when the first synthetic applications were described and most of the organomanganese halides known today were prepared after 1970. Until now, these reagents were mainly obtained by transmetallation from the corresponding organolithium or organomagnesium compounds (see Section II.C). The lithium–or magnesium–manganese exchange reaction generally takes place almost instantaneously. A few examples of halogen–manganese exchange were also reported but, until now, the scope of the reaction is very limited (see Section II.D). Another promising way is the direct manganation by using 2,2,6,6-tetramethylpiperidinylmanganese, in the presence of LiCl, as a metallating agent. Unfortunately, this *ortho*-metallation reaction is limited to a specific range of aromatic substrates (see Section II.E). It should be noted that manganese amides Ar(R)NMnX or $[Ar(R)N]_2Mn$ were also used to prepare manganese enolates by deprotonation of ketones. This reaction is discussed in another chapter of the book. Many efforts were made to prepare directly organomanganese reagents from organic halides and manganese metal (see Section II.F). Unfortunately, the preparative interest of such a path is currently limited to very reactive organic halides (see Section II.F.1). Thus, interesting results were obtained with allylic halides under Barbier conditions or α-halogenoesters (Reformatsky-like reaction).

B. Influence of Various Factors on the Stability of Organomanganese Reagents

The low thermal stability of many organometallics derived from a transition metal is a major drawback that precludes their use as stoichiometric reagents in organic synthesis (e.g. R_2Pd, R_2Ni, R_2Fe)[2, 3a, b, c], or obliges one to work at low temperature (e.g. RCu)[3d, e, f]. In the case of organomanganese compounds the situation is more favorable, since they are quite stable. Their stability is predominantly influenced by two factors:

The type of organomanganese compounds (decreasing stability is observed according to):

$$R_4MnLi_2 \text{ (or } (MgX)_2) \approx R_3MnLi \text{ (or MgX)} > RMnX \gg R_2Mn$$

The nature of the R groups bonded to the manganese atom.

In the early 1970s, Kochi and Tamura studied the decomposition of dialkylmanganeses, the most unstable organomanganese reagents (see above)[4]. They decompose via a β-hydrogen elimination process, like many alkyl transition metal derivatives, to give a mixture of alkane and alkene (Scheme 1).

$$(CH_3CH_2)_2Mn \xrightarrow[\text{r.t.}]{\text{THF}} H_2C{=}CH_2 + H_3C{-}CH_3 + Mn^0$$

SCHEME 1

This mechanism explains that the number of available β-hydrogen atoms is probably the most important factor with regard to the stability of organomanganese reagents. There is a clear correlation for organomanganese iodides prepared in ether (Table 1). Thus, *t*-butylmanganese iodide has to be prepared and used below −35 °C whereas the *n*-butyl analogue is stable up to room temperature. Moreover, organomanganese iodides having no β-hydrogen atom (aryl, alkenyl, methyl etc.) can be heated in ether until reflux.

Organomanganese halides are more stable in THF than in ether, owing to the strong complexation of manganese to this solvent which impedes the β-hydrogen elimination[5]. Indeed, in THF all organomanganese chlorides are stable in a 0–25 °C range and can often be heated until reflux (Table 1). It is interesting to note that the addition of 5 equivalents of THF to an organomanganese iodide prepared in ether has a significant stabilizing effect (Table 2)[6]. The influence of DMF as a ligand is even more dramatic since, in the presence of 5 equivalents of DMF, isopropylmanganese iodide is stable until 35 °C.

As explained above, the use of secondary or tertiary alkylmanganese iodides prepared in ether is sometimes tedious because of their low stability. Fortunately, organomanganese halides prepared in ether from Grignard reagents and the soluble ate-complex $MnBr_2{\bullet}2LiBr$ are more stable[7d]. A similar stabilizing effect is observed by using the ate-complex $MnI_2{\bullet}2LiBr$, instead of manganese iodide (Table 3)[7e]. It should be noted that this stabilization is due to the presence of both lithium and magnesium salts.

TABLE 1. Stability of RMnX prepared in ether or in THF

	Limit of stability, *T* (°C)	
R in RMnX	RMnI prepared in ether	RMnCl prepared in THF
t-Bu	−35	0
i-Pr	−30	10
n-Bu	20	25
Me, Ph, $Me_2C{=}CH$	reflux	reflux

TABLE 2. Stability of *i*-PrMnI prepared in ether

Ligand (5 equiv)	Limit of stability, *T* (°C)
no ligand	−35
THF	−5
DMF	35

TABLE 3. Stability of *i*-PrMnX prepared in ether from RMgX and $MnX_2 \bullet 2LiBr$

i-PrMnX	Limit of stability, T (°C)
i-PrMnI	−30
i-PrMnBr•2LiBr	−10
i-PrMnI•2LiBr	−10

C. Preparation by Magnesium–or Lithium–Manganese Exchange (Transmetallation)

1. Introduction

According to the ratio RLi/MnX_2 or $RMgX^1/MnX_2$, several types of organomanganese compounds can be prepared by transmetallation (Schemes 2, 3 and 4):

Organomanganese halides

$$\underset{(M = Li,\ MgX^1)}{RM + MnX_2} \longrightarrow RMnX\ (+\ LiX \text{ or } MgXX^1)$$

SCHEME 2

Diorganomanganeses

$$\underset{(M = Li,\ MgX^1)}{2\,RM + MnX_2} \longrightarrow R_2Mn\ (+\ 2\,LiX \text{ or } 2\,MgXX^1)$$

SCHEME 3

Organomanganates

$$\underset{(M = Li,\ MgX^1)}{3\,RM + MnX_2} \longrightarrow R_3MnM\ (+\ 2\,LiX \text{ or } 2\,MgXX^1)$$

$$\underset{(M = Li,\ MgX^1)}{4\,RM + MnX_2} \longrightarrow R_4MnM_2\ (+\ 2\,LiX \text{ or } 2\,MgXX^1)$$

SCHEME 4

Manganese iodide, bromide and chloride can be used to achieve the transmetallation reaction in ether or in THF. The starting manganese halide is generally chosen according to its solubility in the selected solvent, in order to have a rapid and efficient lithium–or magnesium–manganese exchange. As shown hereafter, organomanganese halides are highly chemoselective. As an example, various cosolvents too reactive to be used with the starting organolithium or Grignard reagent (AcOEt, MeCN, CH_2Cl_2 etc.) can be added to the reaction mixture when the transmetallation step is complete.

Commercial manganese chloride or bromide must be dried under vacuo (200 °C, 10^{-2} torr, 3 h) before using. A high-grade manganese bromide can also be readily prepared by adding bromine to a suspension of manganese powder in anhydrous ethyl acetate at room temperature (the temperature should not exceed 40 °C)[8]. Commercial manganese iodide is often too impure to be used as a starting material. Fortunately, manganese iodide is easily obtained by adding iodine to a suspension of manganese powder in anhydrous ether at room temperature. It is isolated in nearly quantitative yield by filtration and it can be employed without further treatment[7b,c]. This method of preparation was disclosed by Ducelliez in 1913[9]. Manganese iodide has to be stored in the absence of moisture in darkness.

For synthetic purposes it is important to note that a very large array of alkyl, alkenyl, alkynyl, allyl, benzyl and aryl or heteroaryl manganese compounds can be prepared by transmetallation. In fact, the only limitation is the preparation of the starting organolithium or organomagnesium reagent. Organomanganese compounds are generally prepared *in situ* for subsequent synthetic applications. It should be noted that a solution of methylmanganese chloride in THF can be stored for several months at room temperature without any decomposition[10].

2. Magnesium–or lithium–manganese exchange in ether

a. From manganese iodide. Manganese iodide, which is slightly soluble in ether, reacts rapidly with organolithium or organomagnesium reagents to give the corresponding organomanganese compounds quantitatively[7a,b,c]. A very convenient way to obtain organomanganese iodides is to prepare manganese iodide by treating manganese with iodine in ether, then to perform the transmetallation according to a one-pot procedure (Scheme 5). It is thus possible to avoid the handling of manganese iodide, which is hygroscopic and light-sensitive.

$$\mathrm{Mn} \xrightarrow[\text{2. RLi or RMgX, } T]{\text{1. } \mathrm{I_2}\text{, ether, r.t.}} \underset{ca\ 100\%}{\mathrm{RMnI}\ (+\ \mathrm{LiI\ or\ MgXI})}$$

R = *s*-, *t*-alkyl $T = -30$ °C
R = *n*-alkyl, allyl, benzyl, aryl, alkenyl, alkynyl... $T = -10$ °C to r.t.

SCHEME 5

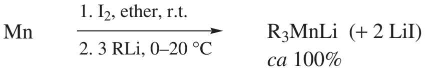
The thermal stability of organomanganese iodides depends on the nature of the R group bonded to the manganese atom. For example, secondary and tertiary alkylmanganese iodides have to be prepared and used below −30 °C to avoid their decomposition (β-hydrogen elimination). In the case of the more stable primary alkylmanganese iodides it is possible to operate between −10 °C and room temperature. Finally, with aryl-, alkenyl- and alkynylmanganese iodides, the transmetallation can be performed at room temperature.

Dialkylmanganeses are less stable than other alkylmanganese compounds. Thus, the transmetallation from organolithium or organomagnesium reagents has to be performed below −30 °C (Scheme 6).

$$\mathrm{Mn} \xrightarrow[\text{2. 2 RLi or 2 RMgX, }-30\ ^\circ\mathrm{C}]{\text{1. } \mathrm{I_2}\text{, ether, r.t.}} \underset{ca\ 100\%}{\mathrm{R_2Mn}\ (+\ 2\ \mathrm{LiI\ or\ 2\ MgXI})}$$

SCHEME 6

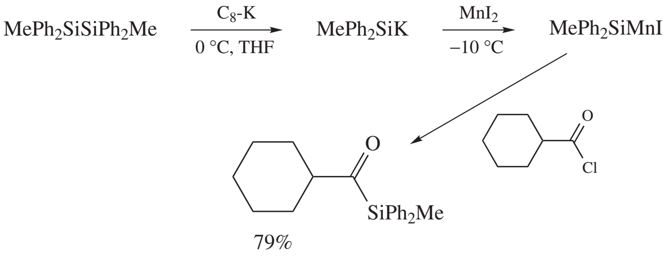
Lithium organomanganates are the most stable organomanganese compounds. As shown in Scheme 7, they can be quantitatively prepared from organolithium reagents between 0 °C and room temperature (the addition of RLi has to be performed at −40 °C when R = *s*- or *t*-alkyl). It should be noted that all attempts to prepare organomanganates R_3MnMgX from Grignard reagents in ether resulted in failure. However, this point is still under debate since the characterization of such species is not obvious and no detailed study was done[11].



$$\mathrm{Mn} \xrightarrow[\text{2. 3 RLi, 0–20 °C}]{\text{1. } I_2\text{, ether, r.t.}} \underset{\textit{ca}\ 100\%}{R_3MnLi}\ (+\ 2\ LiI)$$

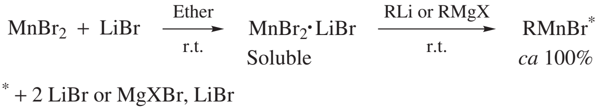
SCHEME 7

One example of potassium−manganese exchange was reported by Fürstner and Weidmann (Scheme 8)[12].



SCHEME 8

b. From manganese bromide. From an industrial point of view the use of manganese bromide[7d, e] instead of manganese iodide is very interesting since it is considerably less expensive, and not light-sensitive. Nevertheless, manganese bromide is not soluble in ether and cannot be used conveniently in this solvent to prepare organomanganese reagents. Fortunately, in the presence of one or two equivalents of anhydrous lithium bromide, a soluble ate-complex $MnBr_2$•LiBr or $MnBr_2$•2LiBr is formed at room temperature. Organomagnesium or organolithium reagents readily react, under mild conditions, with this ate-complex to give quantitatively the corresponding organomanganese bromides (Scheme 9). Currently, organomanganese bromides are the most suitable organomanganese halides to perform a reaction in ether.



$$MnBr_2 + LiBr \xrightarrow[\text{r.t.}]{\text{Ether}} \underset{\text{Soluble}}{MnBr_2{\cdot}LiBr} \xrightarrow[\text{r.t.}]{\text{RLi or RMgX}} \underset{\textit{ca}\ 100\%}{RMnBr^{*}}$$

* + 2 LiBr or MgXBr, LiBr

SCHEME 9

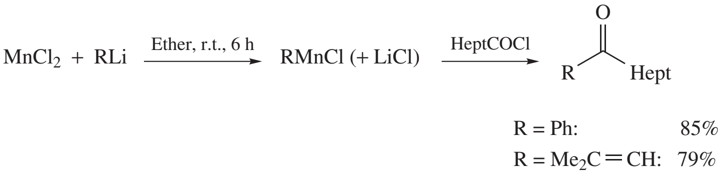
It is important to underline that alkylmanganese bromides prepared from the ate-complex $MnBr_2$•LiBr and a Grignard reagent are more stable than the corresponding alkylmanganese iodides prepared from manganese iodide (see Section II.B)[7d]. Symmetric organomanganeses and organomanganates can be conveniently prepared from the complex $MnBr_2{\bullet}LiBr$.

It is also possible to form an ate-complex by treating manganese bromide with anhydrous tetrabutylammonium bromide in ether for 4 hours[7e]. Further addition of a Grignard reagent thus affords the corresponding organomanganese reagent (Scheme 10).

$$MnBr_2 + Bu_4NBr \xrightarrow[\text{r.t.}]{\text{Ether}} MnBr_2{\cdot}Bu_4NBr \xrightarrow[-10\ ^\circ C]{\text{BuMgCl}} BuMnBr{\cdot}Bu_4NBr$$

SCHEME 10

c. From manganese chloride. Manganese chloride is insoluble in ether, even in the presence of lithium halide[13]. Consequently, the transmetallation takes place very slowly with Grignard reagents and gives poor results. With organolithium compounds, which are more reactive, the lithium–manganese exchange reaction occurs sluggishly at room temperature (6 h) and only aryl and alkenylmanganese chlorides are stable enough to be prepared successfully from manganese chloride in ether (Scheme 11).



R = Ph: 85%

R = $Me_2C{=}CH$: 79%

SCHEME 11

3. Magnesium–or lithium–manganese exchange in THF

Organomanganese compounds are more stable in THF than in ether (see Section II.B). Thus, numerous organomanganese reagents can be conveniently obtained and used in THF at room temperature[7c, e]. They are quantitatively prepared by transmetallation from manganese chloride or bromide. These salts are only slightly soluble in THF but it is possible to dissolve them by adding lithium chloride or bromide to form a soluble ate-complex $MnX_2{\bullet}2LiX$ ($X = Br$ or Cl). Manganese chloride is generally employed since it is the cheapest manganese halide (Scheme 12). Manganese iodide is not frequently used because it is much more expensive and requires a longer reaction time.

$$MnCl_2 + 2\,LiCl \xrightarrow[\text{r.t.}]{\text{THF}} MnCl_2{\bullet}2LiCl$$

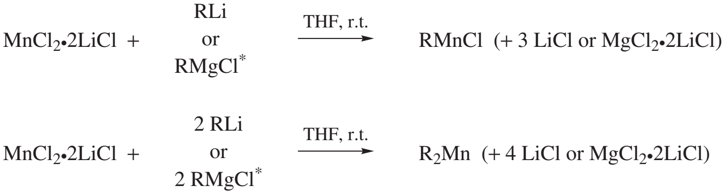
SCHEME 12

A soluble ate-complex can also be obtained by mixing manganese chloride with benzyltrimethylammonium chloride in THF at room temperature (Scheme 13). Various tetraalkylammonium chlorides can be employed[7e].

$$MnCl_2 + (PhCH_2)Bu_3NCl \xrightarrow[\text{r.t.}]{\text{THF}} MnCl_2{\bullet}(PhCH_2)Bu_3NCl$$

SCHEME 13

Organomanganese chlorides as well as symmetrical organomanganeses can be easily obtained from the complex $MnCl_2{\bullet}2LiCl$ and the corresponding organolithium or organomagnesium reagents (Scheme 14).



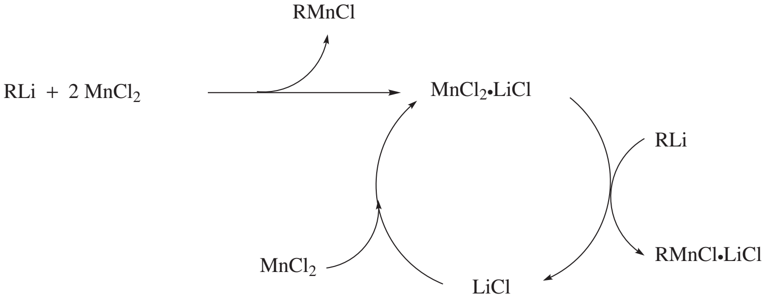
$$MnCl_2{\bullet}2LiCl + \begin{matrix}RLi\\ \text{or}\\ RMgCl^*\end{matrix} \xrightarrow{\text{THF, r.t.}} RMnCl\ (+\ 3\ LiCl\ \text{or}\ MgCl_2{\bullet}2LiCl)$$

$$MnCl_2{\bullet}2LiCl + \begin{matrix}2\ RLi\\ \text{or}\\ 2\ RMgCl^*\end{matrix} \xrightarrow{\text{THF, r.t.}} R_2Mn\ (+\ 4\ LiCl\ \text{or}\ MgCl_2{\bullet}2LiCl)$$

* Or RMgBr

SCHEME 14

In THF, organolithium reagents can react directly with manganese chloride. Indeed, the lithium chloride produced from the beginning of the lithium–manganese exchange progressively dissolves the unsoluble manganese species (RMnCl and/or $MnCl_2$) present in the reaction mixture (Scheme 15).



SCHEME 15

Organomanganate species are soluble in THF, thus it is possible to use indifferently manganese chloride or the ate-complex $MnCl_2{\bullet}2LiCl$ for their preparation. Organolithium or organomagnesium reagents give quantitatively the corresponding organomanganates R_3MnLi or R_3MnMgX at room temperature (Scheme 16).

$$MnCl_2 + 3\ RLi \xrightarrow{\text{THF, r.t.}} R_3MnLi\ (+\ 2\ LiCl)$$

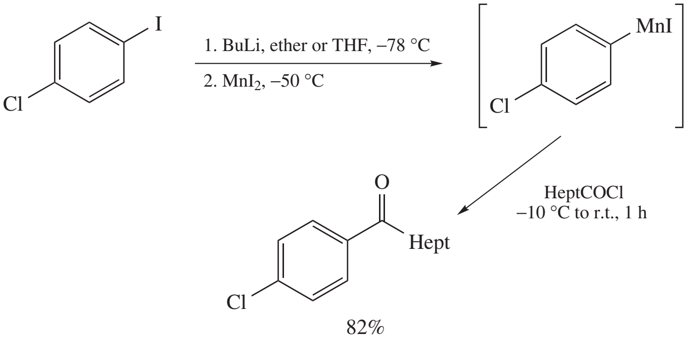
$$MnCl_2 + 3\ RMgX \xrightarrow{\text{THF, r.t.}} R_3MnMgX\ (+\ 2\ MgXCl)$$

SCHEME 16

It is important to note that magnesium organomanganates which cannot be obtained in ether are easily prepared in THF.

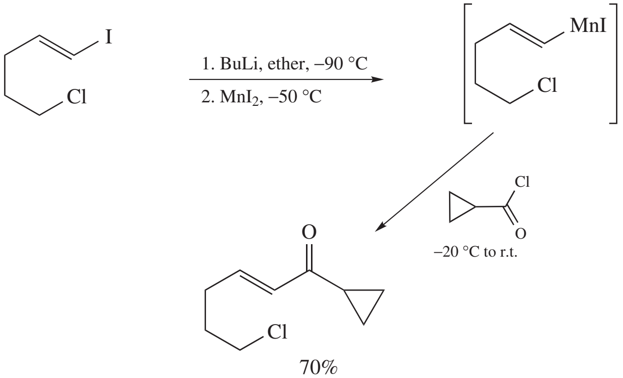
4. Preparation of functionalized organomanganese compounds by magnesium–or lithium–manganese exchange

Organomanganese halides are very interesting for preparative organic chemistry since they tolerate the presence of many functional groups (esters, nitriles, amides etc.). Numerous reports showed that functionalized aryl or alkenyllithium reagents can be readily prepared by halogen–lithium exchange at low temperature[14]. In 1997, Cahiez, Knochel and coworkers developed a one-pot procedure to prepare functionalized organomanganese halides via the corresponding organolithium compounds[15]. Thus, 4-chlorophenylmanganese iodide can be prepared in high yield via the 4-chlorophenyllithium obtained by iodine–lithium exchange at −78 °C (Scheme 17).



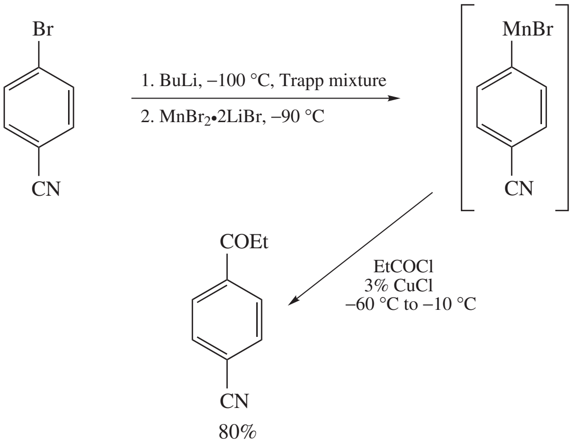
SCHEME 17

In the same way, it is also possible to prepare stereoselectively 5-chloropentenylmanganese iodide in ether (Scheme 18).

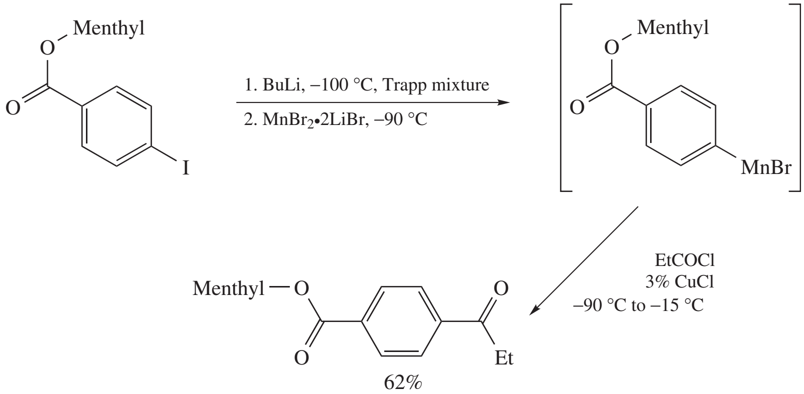


SCHEME 18

With aryl halides bearing a more reactive functional group such as CN, CO_2R, the lithium–halogen exchange has to be performed between −90 °C and −100 °C. However, manganese halides or their ate-complexes $MnX_2{\bullet}2LiX$ are completely insoluble in ether at this temperature and the transmetallation cannot take place. This drawback can be overcome by working with the Trapp mixture (THF−ether−pentane, 4:4:1). Indeed, the complex $MnBr_2 \bullet 2LiBr$ is then soluble enough in the reaction mixture at −90 °C to react efficiently[15]. This procedure was applied to the preparation of functionalized arylmanganese bromides from 4-bromobenzonitrile or menthyl 4-iodobenzoate (Schemes 19 and 20). It is important to employ a hindered ester like menthyl or pivalate ester, since, with a less hindered ester, the lithium−halogen exchange and the 1,2 addition compete.

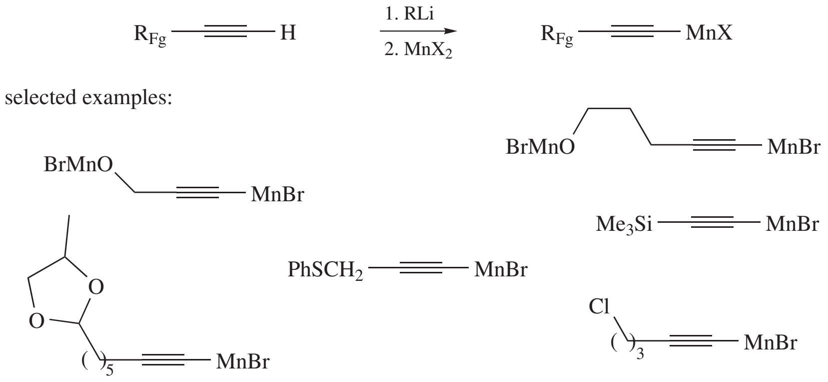


SCHEME 19



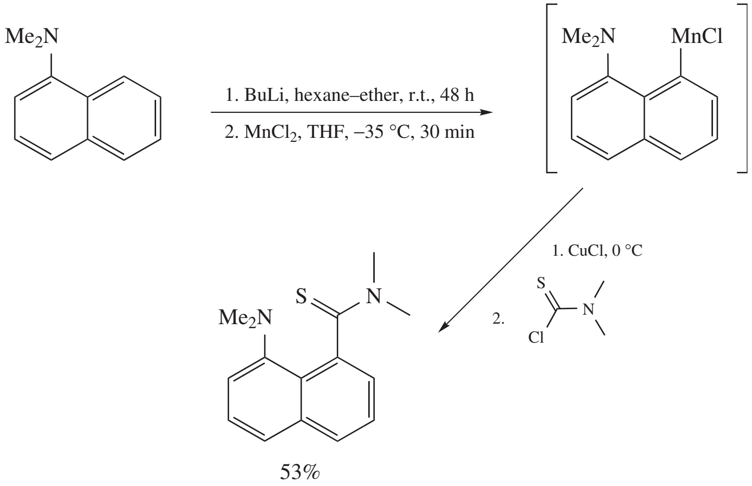
SCHEME 20

Likewise, various functionalized alkynylmanganese halides were prepared from the corresponding alkynyllithium compounds obtained by metallation of functionalized terminal alkynes (Scheme 21)[16c, f].



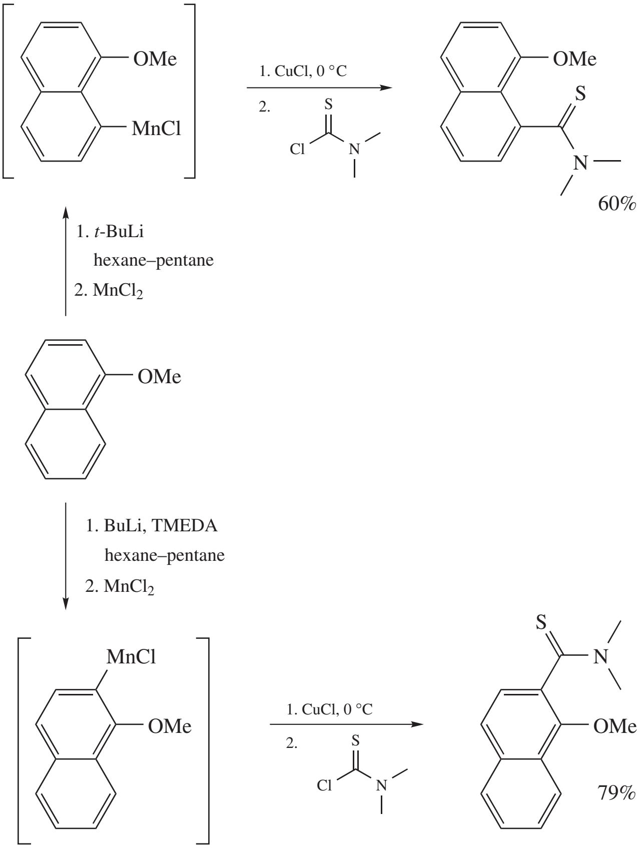
SCHEME 21

In 1995, Kiefl and Mannschreck described the preparation of 1,8-(dimethylamino)-naphthylmanganese chloride according to a one-pot procedure[17]. 1-(Dimethylamino)-naphthalene is first metallated with butyllithium, then the lithium–manganese exchange is achieved by adding manganese chloride (Scheme 22).



SCHEME 22

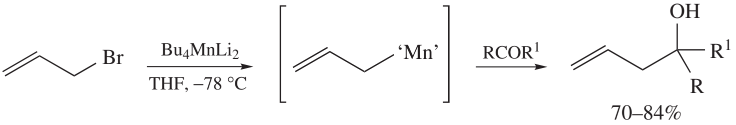
From 1-methoxynaphthalene, two regioisomers of the methoxynaphthylmanganese chloride can be obtained by changing the nature of the alkyllithium used for the metallation step (Scheme 23). Nevertheless, it is important to note that this reaction is not completely regioselective.



SCHEME 23

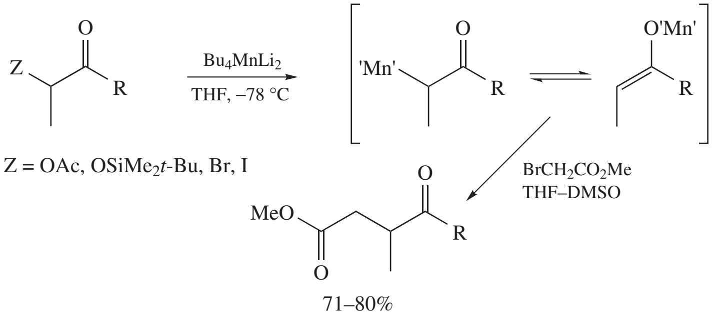
D. Preparation by Halogen–Manganese Exchange

Only few examples of preparation of organomanganese reagents by halogen–manganese exchange were reported. In 1997, Hosomi and coworkers introduced a new method to prepare allyl or propargyl manganese species by treating the corresponding allyl or propargyl bromides with the manganate Bu_4MnLi_2, in THF at −78 °C (Scheme 24)[18].



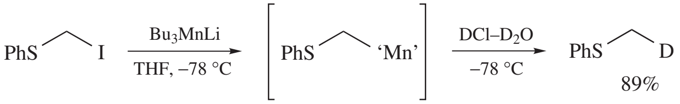
SCHEME 24

Under similar conditions, α-acetoxy-, α-silyloxy- or α-halogenoketones can be converted into the corresponding manganese enolates (Scheme 25)[19]. Although this reaction seems quite similar to the classical halogen–metal exchange, its mechanism is undoubtedly more complex and has not been clearly established.



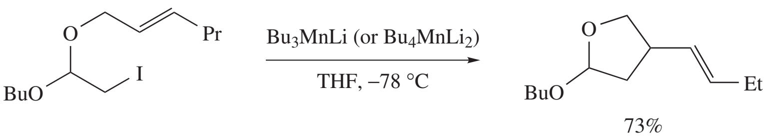
SCHEME 25

Iodomethyl sulfides react similarly with lithium tributylmanganate (Scheme 26)[20].



SCHEME 26

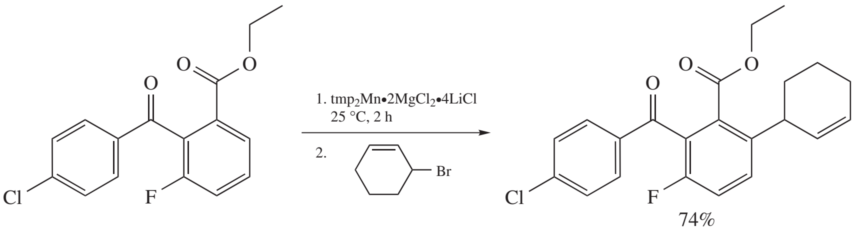
Oshima and coworkers studied the reaction of organomanganates Bu_3MnLi or Bu_4MnLi_2 with various ε-unsaturated organic iodides (Scheme 27)[16h, 21]. These reactions are presented above (see Section VIII.C).



SCHEME 27

E. Preparation by Manganation (Direct Metallation)

The *ortho*-directed manganation of various aromatic or heteroaromatic compounds with 2,2,6,6-tetramethylpiperidylmanganese (tmp_2Mn) was described. The presence of LiCl is essential to perform successfully the metallation (Scheme 28)[22].



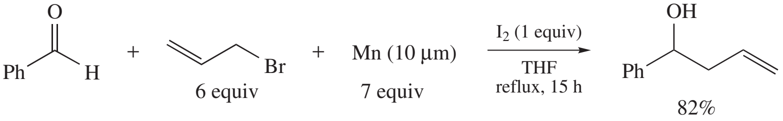
SCHEME 28

F. Preparation by Oxidative Addition to Manganese Metal

1. From commercial manganese

Organomanganese compounds are very useful in preparative organic chemistry, especially for their high chemoselectivity. Nevertheless, preparation of functionalized organomanganese reagents by transmetallation from manganese halides and functionalized organolithium or magnesium reagents is difficult since the latter are too reactive to tolerate many functional groups. Thus, the preparation of organomanganese compounds by oxidative addition of organic halides to commercial manganese (massive metal) is potentially very attractive.

In 1983, Hiyama and coworkers described the first Barbier reaction using micronized commercial manganese powder[23]. When the reaction is performed with allyl bromide in the presence of an aldehyde, various alcohols are obtained in good yields (Scheme 29).

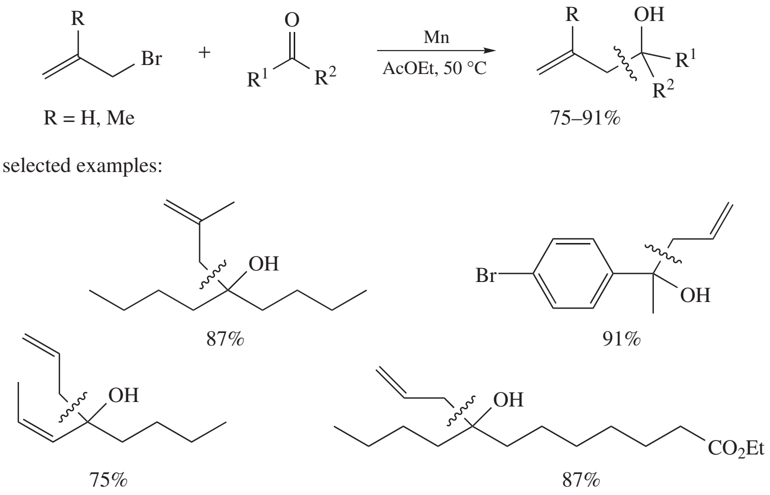


SCHEME 29

This procedure presents some significant limitations. First, it is necessary to activate the metallic manganese with iodide and to heat the reaction mixture to reflux for 15 hours. In addition, a large excess of reagents is required (7 equivalents of Mn and 6 equivalents of allyl bromide). Moreover, substituted allyl halides such as $RCH{=}CHCH_2X$ or $R_2C{=}CHCH_2X$ ($R = $ alkyl) lead to poor yields.

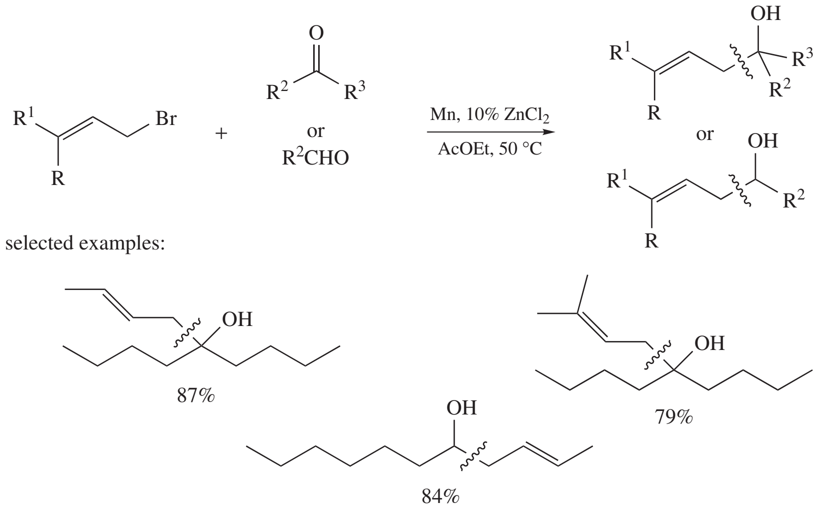
In 1989, we disclosed that commercial massive coarse-ground manganese, a cheap and easily available material, can be efficiently used to prepare organomanganese compounds from reactive organic halides such as allylic halides or α-halogenoesters[24]. The choice of the solvent is decisive, thus in the case of allyl or methallyl bromides we found that only ethyl acetate leads to satisfactory results (Scheme 30). All the experiments were performed in the presence of a ketone to trap the organomanganese reagent as soon as it formed (Barbier conditions).

Unfortunately, this method cannot be extended to γ-substituted allylic halides such as crotyl bromide. Moreover, the use of aldehydes and methyl ketones leads to poor yields. Fortunately, we found that the reaction takes place smoothly when manganese is treated with 10% zinc chloride before use. A manganese/zinc couple is probably the reactive species. It should be noted that various metallic salts like cadmium, mercury or



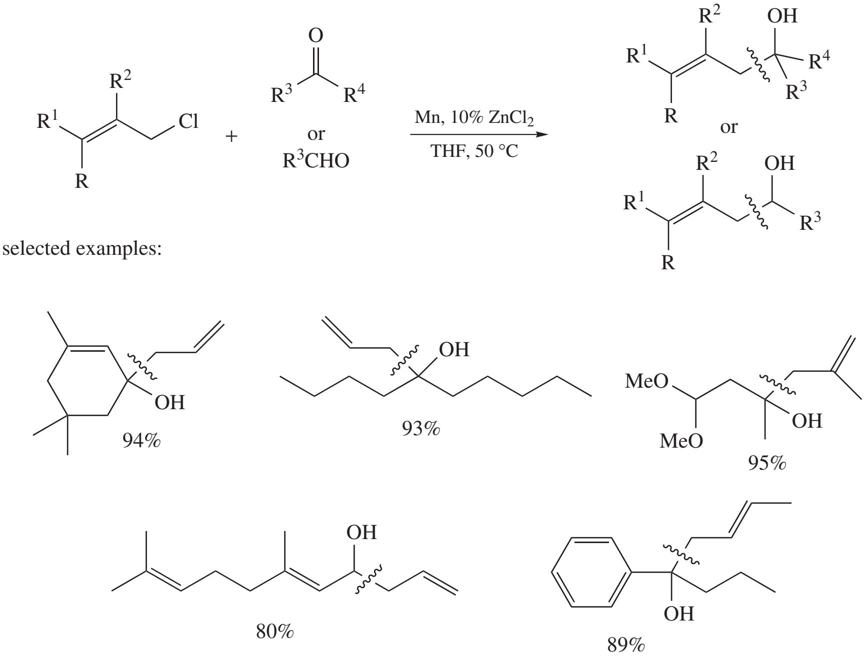
SCHEME 30

copper(II) chlorides can be successfully used in place of zinc chloride[24]. Owing to this procedure, the reaction was extended to crotyl and prenyl bromides as well as ketones and aldehydes (Scheme 31).



SCHEME 31

By using manganese activated by addition of 10% zinc chloride, the reaction could be performed in THF. Furthermore, it should be noted that allyl chlorides can also be used successfully under these conditions (Scheme 32).



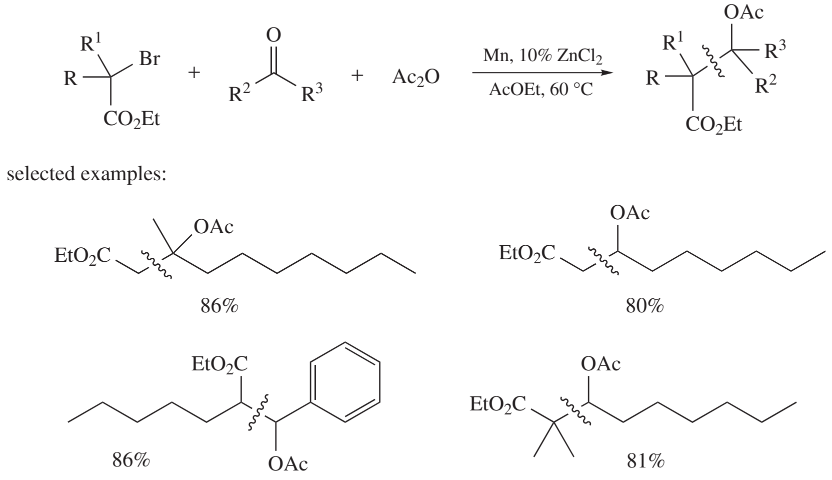
SCHEME 32

Finally, we showed that such a zinc/manganese couple allows various manganese-mediated Reformatsky-type reactions[24a]. In the presence of a stoichiometric amount of acetic anhydride, in order to trap the resulting alcoholate, good yields of β-acetoxyesters are obtained from methyl ketones or aldehydes (Scheme 33).

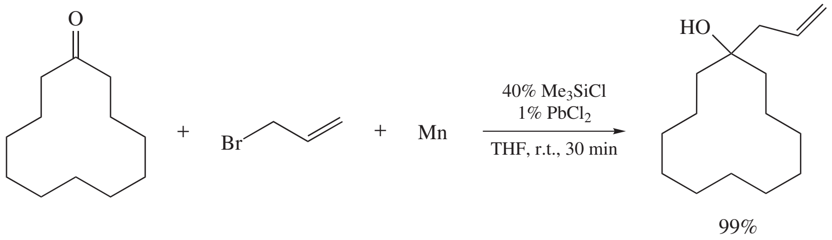
In 1996, Takai and coworkers found that manganese can also be activated by adding catalytic amounts of both $PbCl_2$ and Me_3SiCl (Scheme 34)[25]. The latter probably strips the surface of the metal by removing the manganese oxide coating. On the other hand, the role of lead chloride in this reaction has not been clearly explained; a manganese/lead couple could be involved.

2. From activated manganese

As shown above (see Section II.C), massive commercial coarse-ground manganese only reacts with very reactive organic halides such as allylic halides or α-halogenoesters. However, the reactivity of a metal considerably increases when it is used as a very fine powder (dispersed metal, particles size < 1 mm). On the other hand, it is also established that a metal can be activated by using mechanical (e.g. with Mg, the dry-stirring procedure) or chemical methods (e.g. with Mg, the activation by I_2 or a 1,2-dihaloethane), mainly to remove metal oxide coating[26]. On the basis of these considerations, Rieke showed that it is possible to obtain very reactive metal powders by reducing a metal salt with potassium in THF[27]. In this solvent, sodium or lithium naphthalenide also led to excellent results. The resulting activated metal, so-called Rieke metal, is highly reactive. Indeed, the size of the metallic particles is very small and the dispersed metal is used *in situ* to avoid passivation processes.



SCHEME 33

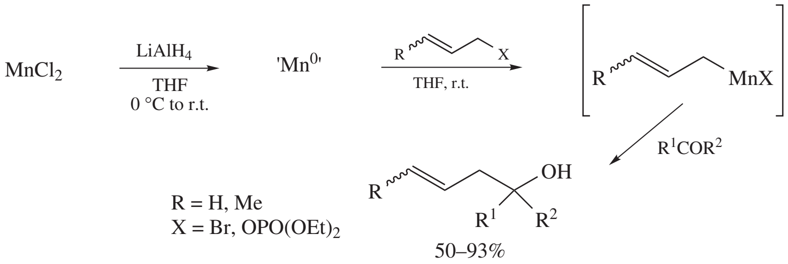


SCHEME 34

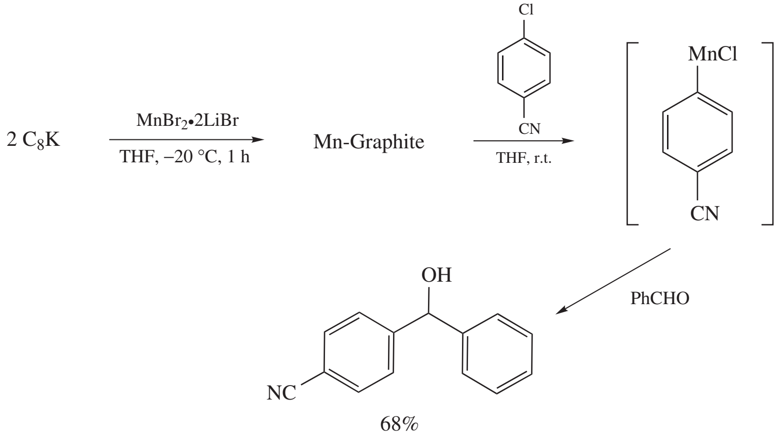
To increase the reactivity of manganese towards organic halides, several procedures involving an activated manganese were reported. In 1982, Hiyama and coworkers described the first procedure[28]. He showed that manganese chloride can be readily reduced by lithium aluminum hydride (molar ratio = 1 : 1) in THF at 0 °C. Allyl and crotyl bromides react with this activated manganese to give the corresponding allylmanganese reagents in good yields. However, unsatisfactory results were obtained with prenyl bromide or allyl chloride (Scheme 35). This procedure is not very attractive from a practical point of view, since the manganese powder thus obtained is not more reactive than the commercial massive coarse-ground metal.

In 1996, Fürstner and Brunner proposed a new interesting procedure through the reduction of the soluble ate-complex $MnBr_2{\bullet}2LiBr$ by potassium-graphite C_8K[29]. The manganese-graphite thus obtained smoothly reacts with allyl, alkenyl, aryl and heteroaryl halides (Scheme 36). Moreover, it should be noted that manganese-graphite can be used to prepare various functionalized organomanganese halides (nitrile, sulfonamide).

At the same time, Rieke and coworkers showed that manganese halides can be efficiently reduced with two equivalents of lithium in the presence of a catalytic amount of naphthalene as electron carrier[30]. This highly reactive manganese powder easily reacts with simple primary, secondary or tertiary alkyl bromides, as well as with 3-bromothiophene

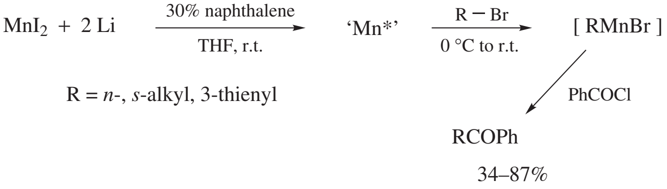


SCHEME 35



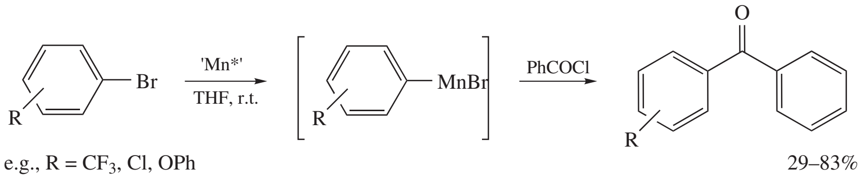
SCHEME 36

under mild conditions (Scheme 37). The nature of the counter ion is critical, thus the oxidative addition rate is clearly faster when the activated manganese is prepared from manganese iodide (3 equivalents) or bromide (4 equivalents) rather than from manganese chloride[31]. It is important to note that, before using the organomanganese reagent for synthetic applications, the excess of activated manganese must be destroyed, for instance by adding 1,2-dibromoethane. Indeed, the presence of Rieke manganese can lead to various side reactions when functionalized compounds are employed. As a rule, 3-bromothiophene gives better yields than primary alkylmanganese halides whereas secondary and tertiary derivatives give poor yields.



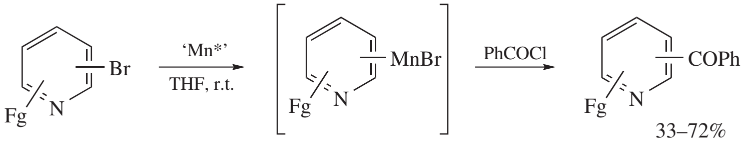
SCHEME 37

The procedure was applied to the preparation of arylmanganese halides (Scheme 38)[31].

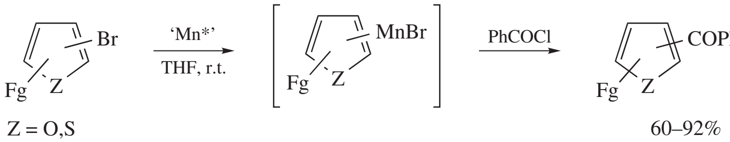


SCHEME 38

Interestingly, Rieke manganese can be used to prepare heteroaryl manganese halides[32]. The oxidative addition occurs chemoselectively with functionalized heteroaryl bromides bearing an ether, an ester, as well as a chlorine or a fluorine atom (Schemes 39 and 40). However, only heteroaryl bromides bearing an electron-withdrawing group lead to satisfactory results.

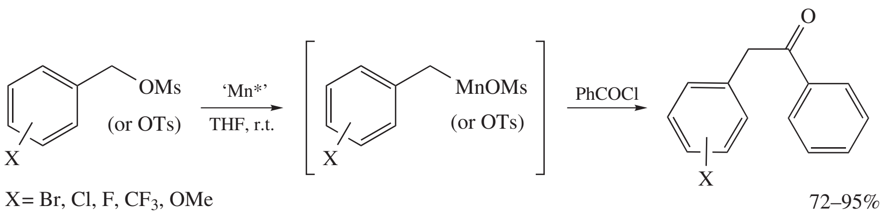


SCHEME 39



SCHEME 40

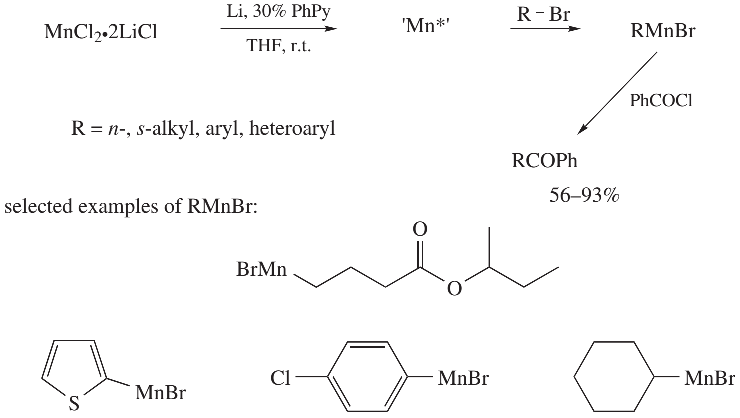
In 1999, Kim and Rieke showed that the procedure can be extended to benzyl sulfonates (Scheme 41)[33].



SCHEME 41

As mentioned above, the Rieke procedure uses naphthalene as electron carrier. Therefore, the latter has always to be separated from the final product and the purification procedure is sometimes tricky. To avoid this drawback, Cahiez and coworkers replaced naphthalene by 2-phenylpyridine (PhPy), as a new electron carrier[34].

In THF, activated manganese is readily obtained by treating a solution of the ate-complex $MnCl_2{\bullet}2LiCl$ with two equivalents of lithium in the presence of 2-phenylpyridine (0.3 equivalent). Further oxidative addition of primary or secondary alkyl, as well as aryl or heteroaryl bromides, leads to excellent yields of the expected organomanganese bromides. For large-scale preparative chemistry, this procedure offers several advantages. Indeed, phenylpyridine is easily eliminated and recycled during the final work-up by simple acidic treatment. In addition, it should be noted that with this procedure the nature of the counter ion has no influence. Therefore, the activated manganese can be efficiently prepared from the very cheap manganese chloride whereas expensive manganese iodide is generally used in the Rieke method. The greater synthetic potential of the lithium-phenylpyridine procedure is exemplified by the preparation of a primary alkylmanganese bromide bearing an ester group (Scheme 42).



SCHEME 42

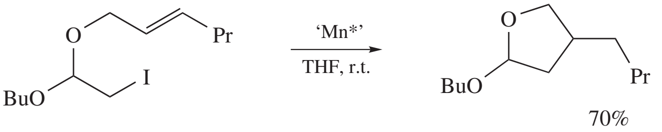
In 1999, Oshima and coworkers reported that magnesium can also reduce the ate-complex $MnCl_2{\bullet}2LiCl$ in THF (Scheme 43)[35].

$$\text{Mg} \xrightarrow[\text{THF, r.t.}]{13\%\ \text{BrCH}_2\text{CH}_2\text{Br}} \text{‘Mg*’} \xrightarrow[\text{r.t., 24 h}]{\text{MnCl}_2{\bullet}2\text{LiCl}} \text{‘Mn*’}$$

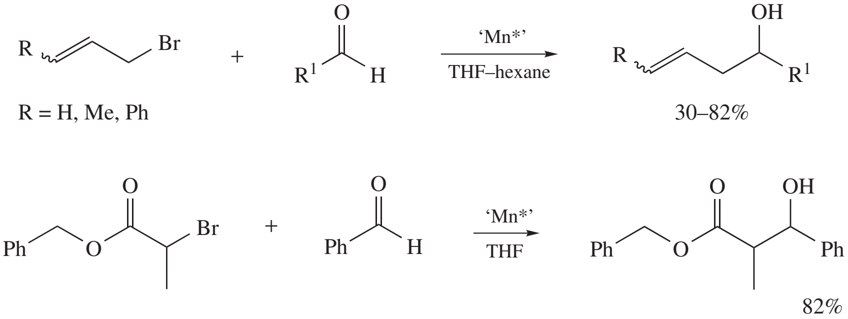
SCHEME 43

The activated manganese thus prepared was used in some cyclization reactions (see Section VIII.C) (Scheme 44).

Barbier and Reformatsky reactions can also be achieved by using this activated manganese (Scheme 45)[36].



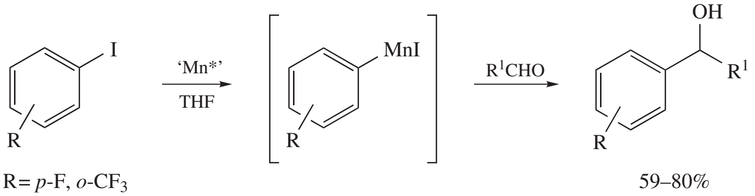
SCHEME 44



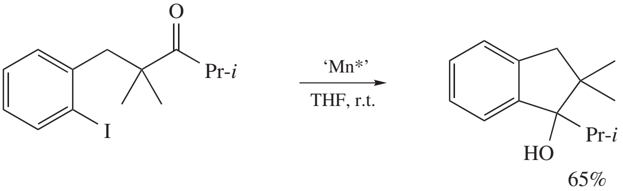
SCHEME 45

Oshima and coworkers showed that activated manganese, prepared by the reduction of the ate-complex $MnCl_2$•2LiCl with magnesium, reacts with aryl iodides[36]. However, only aryl iodides bearing an electron-withdrawing group lead to satisfactory results (Scheme 46).

A cyclization via an intramolecular Barbier reaction was also described (Scheme 47).



SCHEME 46

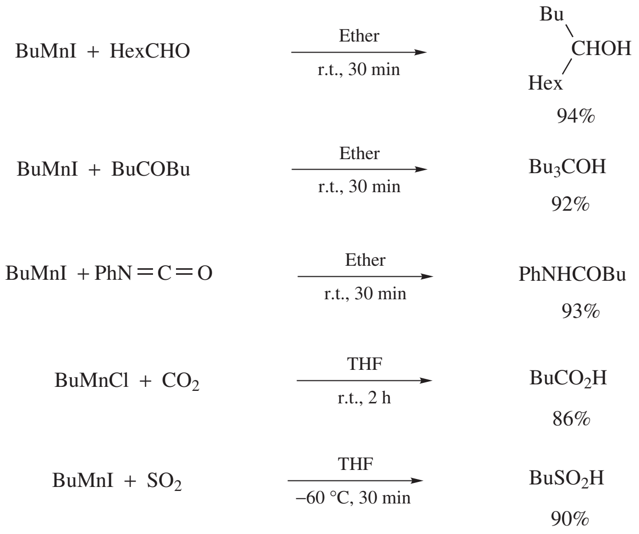


SCHEME 47

III. REACTION WITH KETO COMPOUNDS AND RELATED DERIVATIVES

A. Reaction of Organomanganese Reagents with Keto Compounds and Related Derivatives

Organomanganese halides add to aldehydes, ketones, carbon dioxide, sulfur dioxide and isocyanates (Scheme 48)[37]. As a rule, the reactions take place under milder conditions than with the corresponding Grignard reagents.



SCHEME 48

On the other hand, there is no reaction with esters, nitriles or amides (Scheme 49).

$$\mathrm{BuMnI + BuCO_2Et\ (or\ BuCN,\ BuCONMe_2)} \xrightarrow[\text{r.t.}]{\text{Ether}} \text{No reaction}$$

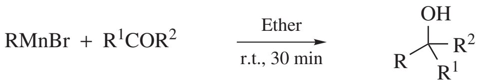
SCHEME 49

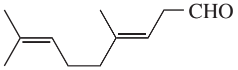
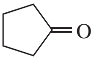
Nevertheless, alkyl formates, which are more reactive than the other carboxylic esters, react smoothly (Scheme 50)[37b].

$$\mathrm{2\ BuMnI\ +\ HCO_2Me} \xrightarrow[\text{r.t., 30 min}]{\text{Ether}} \underset{98\%}{\mathrm{Bu_2CHOH}}$$

SCHEME 50

TABLE 4. 1,2-Addition of RMnBr to aldehydes and ketones

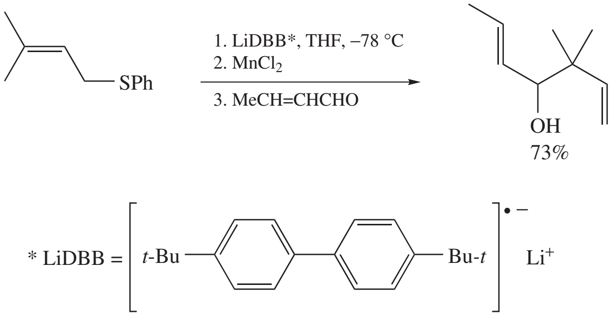


R	R^1COR^2	Yield (%)
Bu	HexCHO	93
Ph	HexCHO	94
$Me_2CH{=}CH$	HexCHO	98
Bu	Et_2CHCHO	95
Hept	t-BuCHO	87
Me	PhCHO	93
Me		91
Bu	PrCOPr	98
$BuC{\equiv}C$	PrCOPr	95
Bu	PhCOPr	89
Bu	$Me_2C{=}CHCOMe$	91
Bu		86

B. 1,2-Addition to Aldehydes and Ketones

In ether, organomanganese compounds react easily under mild conditions with ketones and aldehydes to give the corresponding alcohols in excellent yields (Table 4). Alkyl, alkenyl, alkynyl and arylmanganese halides were successfully used[38].

Allylic organomanganese chlorides react by their more substituted side. They can be prepared by transmetallation from the corresponding organolithium or organomagnesium reagents (Scheme 51)[39].



SCHEME 51

In ether, the 1,2-addition reaction to aldehydes is usually complete in less than 20 minutes at 0 °C by using organomanganese reagents prepared indifferently from organolithium or organomagnesium compounds. The yield of alcohol is often slightly higher when the organomanganese halide is prepared from a Grignard reagent (Scheme 52)[40].

$$\text{BuMnBr·2LiBr}^{a} \xrightarrow[\text{Ether, 0 °C, 20 min}]{\text{HexCHO}} \text{HexCHOHBu}$$

80%

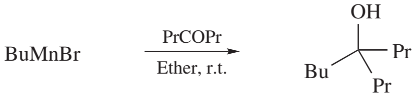
$$\text{BuMnBr·LiBr; MgBr}_2{}^{b} \xrightarrow[\text{Ether, 0 °C, 20 min}]{\text{HexCHO}} \text{HexCHOHBu}$$

93%

[a] From BuLi + $MnBr_2$·LiBr. [b] From BuMgBr + $MnBr_2$·LiBr.

SCHEME 52

This difference is probably due to an electrophilic activation of the carbonyl group by the magnesium salts. Indeed, in the case of ketones, which are less reactive, the reaction is more rapid when it is achieved in the presence of magnesium salts and the final yields are clearly higher (Scheme 53).

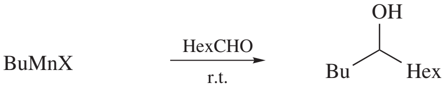


	10 min	30 min	2.5 h	6 h
BuMnBr•2LiBr[a]	34%	53%	63%	80%
BuMnBr•LiBr; $MgBr_2$[b]	80%	90%	93%	93%

[a] From BuLi + $MnBr_2$•LiBr. [b] From BuMgBr + $MnBr_2$•LiBr.

SCHEME 53

It should be emphasized that the reaction is much slower in THF. Thus, at room temperature, the 1,2-addition occurs almost instantaneously with an aldehyde in ether whereas in THF the reaction lasts about one hour (Scheme 54).

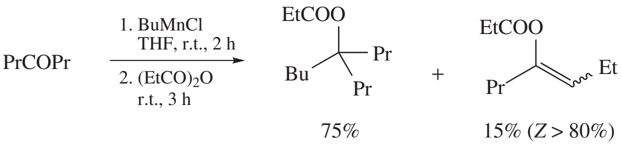


	5 min	1 h
BuMnBr, ether[a]	97%	-
BuMnBr, THF[b]	54%	92%

[a] From BuMgBr + $MnBr_2$•LiBr. [b] From BuMgCl + $MnCl_2$•2LiCl.

SCHEME 54

The 1,2-addition to ketones is also much slower in THF (1.5 to 2 h at r.t.) and, as a consequence, the deprotonation of the ketone is frequently observed as a side reaction (5 to 25%, Scheme 55).



SCHEME 55

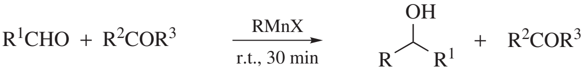
Interestingly, organomanganese halides selectively add to an aldehyde in the presence of a ketone at room temperature. As shown by the results presented in Table 5, the addition can be performed in ether or in THF, and the selectivity is higher than 99% in all cases.

Organomanganese halides are probably one of the most efficient organometallics to prepare ketols from ketoaldehydes. Thus, 11-oxotridecanal reacts with butylmanganese halide to give exclusively the expected ketol (Scheme 56)[40].

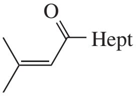
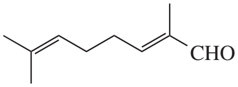
Of course, the high chemoselectivity of organomanganese halides allows one to convert ketones or aldehydes into the corresponding alcohols in high yields in the presence of less reactive functional groups such as an ester, a nitrile, or an alkyl halide (Scheme 57)[16f, 38].

A chemoselective 1,2-addition of vinylmanganese iodide to a functionalized aldehyde was used by Ireland and Thompson for the synthesis of chlorothricolide (Scheme 58)[41].

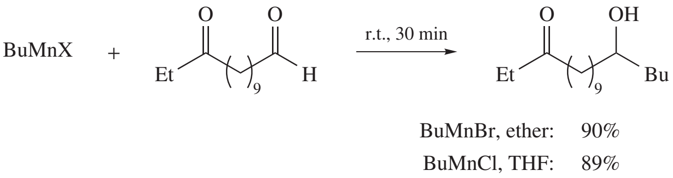
TABLE 5. Chemoselective addition of RMnX to aldehydes in the presence of a ketone



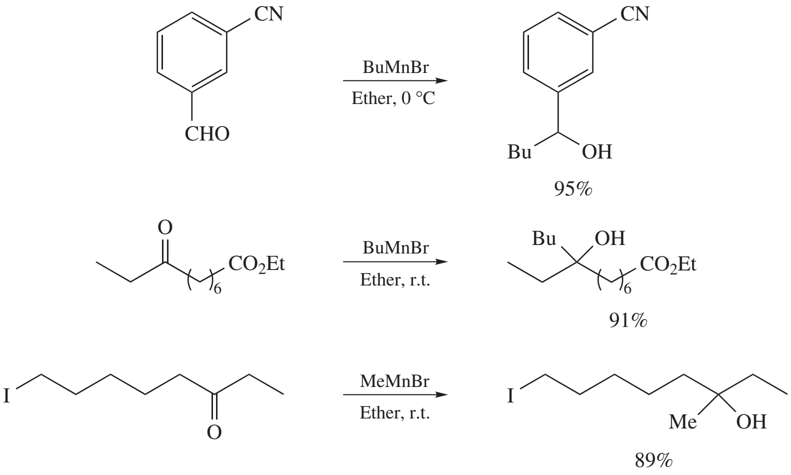
selectivity > 99%

R^{1}CHO	R^{2}COR^3	R	Yield (%)[a] of alcohol	
			RMnBr[b]	RMnCl[c]
HexCHO	PrCOPr	Bu	93	90
HexCHO	PenCOMe	Bu	96	95
HexCHO	PhCOPr	Bu	95	90
HexCHO		Bu	90	95
HexCHO	PrCOPr	Me	95	88
HexCHO	PrCOPr	Ph	94	88
HexCHO	PrCOPr	Me$_2$C=CH	98	88
HexCHO	PrCOPr	BuC≡C	80	72
	PrCOPr	Me	90	91
PhCHO	PrCOPr	Me	90	93
HexCHO	PrCOPr	Hept	87	86

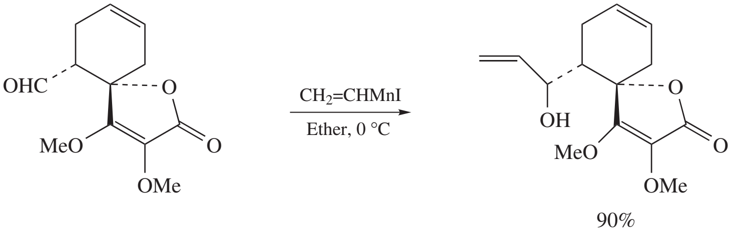
[a] Recovered yield of ketone ≥ 99%.
[b] RMnBr prepared in diethyl ether from RLi.
[c] RMnCl prepared in THF from RLi or RMgBr.



SCHEME 56



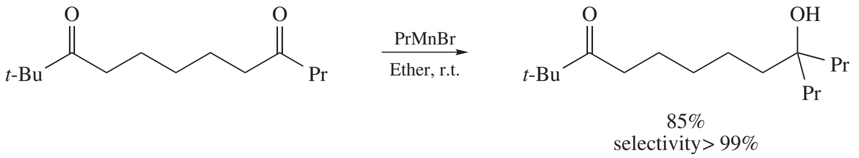
SCHEME 57



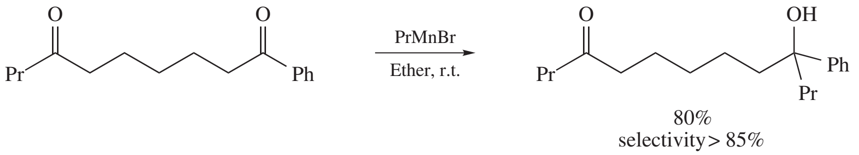
SCHEME 58

It is interesting to note that it is also possible to perform a chemoselective 1,2-addition to unsymmetrical diketones (Scheme 59). The discrimination results from a difference between the steric environment of the two carbonyl groups[16c, f].

The reactivity of organomanganese halides with ketones is more dependent on steric than on electronic effects. Thus, in the following example (Scheme 60), the conjugated carbonyl group which is deactivated, but more accessible, preferentially undergoes the 1,2-addition[16c, f].

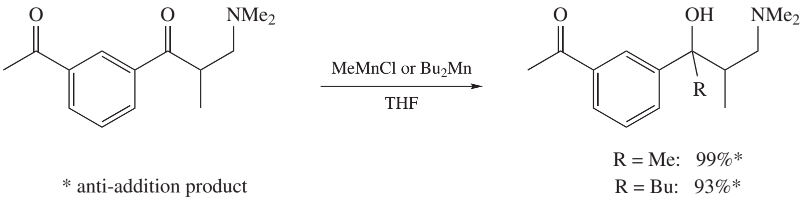


SCHEME 59



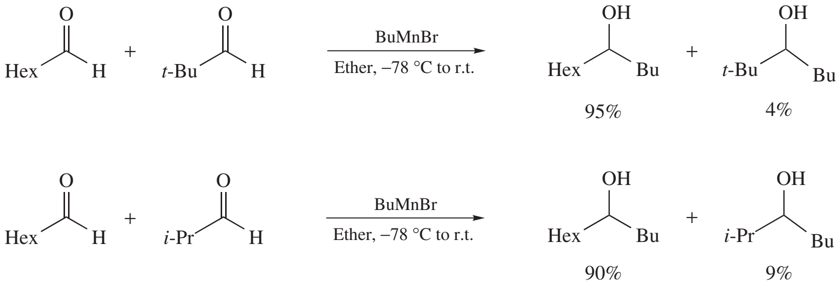
SCHEME 60

The discrimination can also result from the formation of a chelate with one of the two carbonyl groups and a neighboring complexing group such as Me_2N (Scheme 61)[42].



SCHEME 61

Surprisingly, organomanganese reagents were also used successfully to perform aldehyde–aldehyde competition experiments (Scheme 62). Once more, the less hindered



SCHEME 62

carbonyl group reacts preferentially in spite of the very high reactivity of the two aldehydes. The selectivity is not as good as in the case of ketones, but it is exceptional for such difficult competitions[16c, f].

C. Diastereoselective 1,2-Addition to Ketones and Aldehydes

The first diastereoselective addition of organomanganese compounds was reported by Oshima and coworkers in 1992 (Table 6)[43].

Thus, 3-alkyl (or 3-aryl)-3-hydroxy-2-methyl amides **A** and **B** are obtained in good yields in ether or in THF at 0 °C from the corresponding β-ketoamides. It should be noted that alkylmanganese halides give one diastereomer whereas phenylmanganese halides mainly give the other one. In all cases the reaction is highly stereoselective.

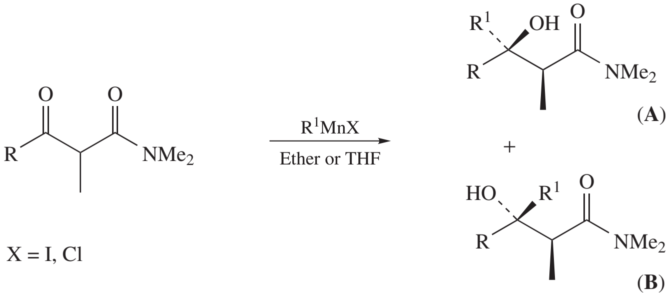
In the same year, Reetz and coworkers reported the diastereoselective addition of acyloxyalkylmanganese to 4-*t*-butylcyclohexanone[44]. It should be noted that only alkyl groups can be transfered with good diastereoselectivities. Later on, we showed that the reagents used by Reetz are not the organomanganese reagents $t\text{-BuCO}_2\text{MnR}$ but probably the heteroorganomanganates $(t\text{-BuCO}_2)_2\text{RMnLi}$ (Scheme 63)[45].

As a rule, such heteroorganomanganates lead to better diastereoselectivities than the corresponding organomanganese halides (Scheme 64)[45].

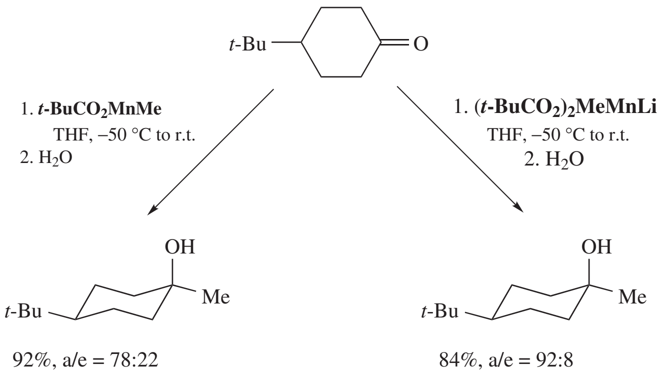
Later on, Reetz and coworkers described the chelation control addition of organomanganese halides to *N*-protected α-aminoaldehydes (Table 7). Alkylmanganese reagents generally give good diastereoselectivities whereas aryl and vinyl give poor ones. It is interesting to note that the corresponding organolithium or organomagnesium reagents generally lead to lower selectivities[46].

Cahiez, Knochel, Ricci and coworkers reported the diastereoselective addition of alkyl- and allylmanganese halides to 2-phenylpropanal and to the corresponding α-chiral acylsilane. The expected alcohols are obtained in good yields and the diastereoselectivity is excellent (Table 8)[47].

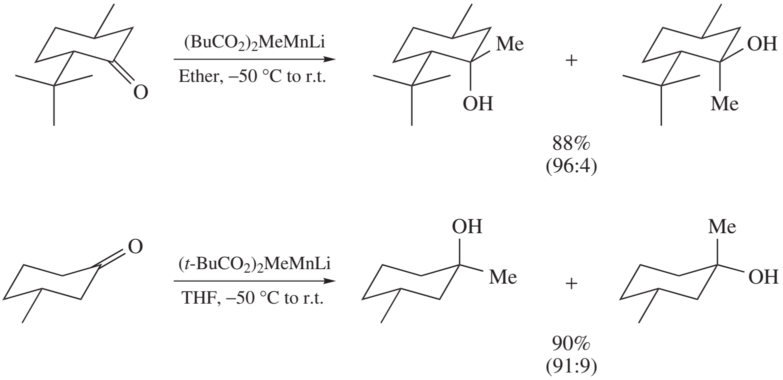
TABLE 6. Diastereoselective addition of RMnX to β-ketoamides



R	R^1	Yield (%)	**A/B**
Ph	Me	93	>99:1
Ph	Bu	98	>99:1
Ph	Vinyl	83	>99:1
Me	Ph	83	1:99
Et	Ph	52	7:93

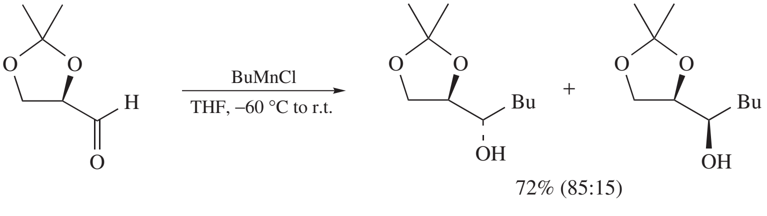


SCHEME 63



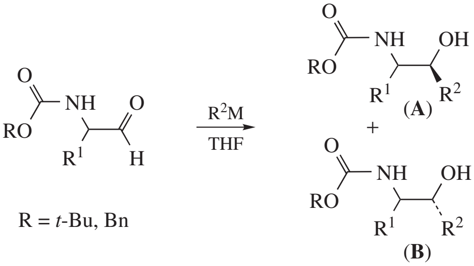
SCHEME 64

2,3-*o*-Isopropylideneglyceraldehyde, a useful chiral starting material in asymmetric synthesis, readily reacts with organomanganese chlorides to give mainly the *anti*-alcohols (Scheme 65). The diastereoselectivity is better than that reported in the literature for other organometallic reagents[47].



SCHEME 65

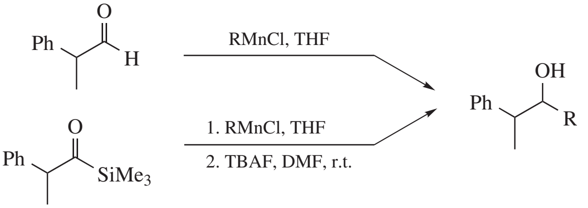
TABLE 7. Reaction of RMnX with *N*-BOC or *N*-CBZ protected *α*-aminoaldehydes

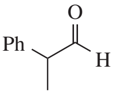
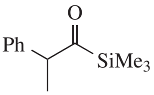


R	R^1	R^2M	Conversion (%)[a]	**A/B**
t-Bu	Me	MeMnBr	90	95:5
$PhCH_2$	Me	BuMnBr	82	93:7
t-Bu	Me	BuMnBr	82	86:14
t-Bu	$PhCH_2$	MeMnBr	85	89:11
t-Bu	$PhCH_2$	MeMgI	66	54:46
t-Bu	*i*-Bu	MeMnBr	97	96:4
t-Bu	*i*-Bu	MeLi	85	39:61

[a] The yield is not reported.

TABLE 8. Diastereoselective addition of RMnX to aldehydes and acylsilanes



Substrate	R	Yield (%)	*syn*/*anti*
	Me	95	96:4
	Bu	75	≥99:1
	Allyl	85	93:7
	Me	75	96:4
	Bu	70	97:3
	Allyl	83	76:24

D. Carbonation of Organomanganese Reagents

In 1979, Cahiez and coworkers reported the first carbonation of organomanganese reagents[37b]. Organomanganese halides, symmetrical organomanganeses and organomanganates were used successfully (Scheme 66). It should be noted that all R groups bonded to the manganese atom participate in the reaction.

$$\text{HeptMnCl} \xrightarrow[\text{2. } H_2O]{\text{1. } CO_2\text{, ether, r.t.}} \text{HeptCO}_2\text{H}$$

88%

$$\text{Hept}_2\text{Mn} \xrightarrow[\text{2. } H_2O]{\text{1. } CO_2\text{, ether, r.t.}} 2\ \text{HeptCO}_2\text{H}$$

86%

$$\text{Hept}_3\text{MnM} \xrightarrow[\text{2. } H_2O]{\text{1. } CO_2\text{, THF, r.t.}} 3\ \text{HeptCO}_2\text{H}$$

M = Mg, Li

83%

SCHEME 66

The carbonation can be performed at room temperature since the resulting manganese carboxylate does not react with the starting organomanganese compound. It is a clear advantage compared to the organolithium or organomagnesium reagents which must be carbonated at low temperature to prevent the formation of side products and to control the important exothermic effect.

The scope of the reaction is very large; numerous carboxylic acids can be prepared in good yields under mild conditions (Table 9).

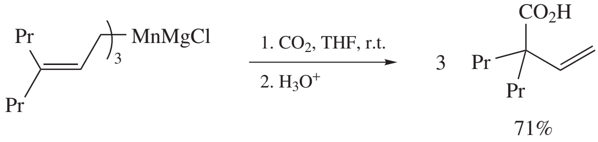
Allylic organomanganese compounds selectively react at their more substituted side (Scheme 67).

Alkenylmanganese halides lead stereospecifically to the corresponding α,β-ethylenic carboxylic acids in good yields (Scheme 68).

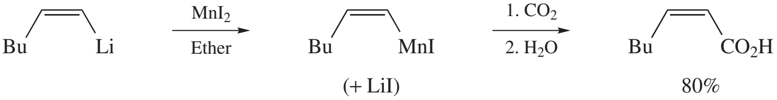
TABLE 9. Carbonation of organomanganates

$$R_3MnM \xrightarrow[\text{2. } H_2O]{\text{1. } CO_2\text{, THF, r.t.}} 3\ RCO_2H$$

R_3MnM	Yield (%)
$Bu_3MnMgCl$	86
Ph_3MnLi	89
Mesityl_3MnLi	73
$(Me_2C{=}CH)_3MnLi$	96
$(BuC{\equiv}C)_3MnLi$	83



SCHEME 67



SCHEME 68

IV. REACTION OF ORGANOMANGANESE COMPOUNDS WITH ACYL CHLORIDES AND RELATED COMPOUNDS

Organomanganese compounds readily react with a vast array of acyl chlorides or related acylating reagents to give the corresponding ketones in excellent yields. The acylation generally takes place under mild conditions and the reaction is highly chemoselective. An impressive number of functionalized ketones were prepared in this way. This reaction is the first preparative procedure developed with organomanganese reagents. Thus, it was first performed with organomanganese iodides, the only organomanganese halides easily accessible at the time, then with their less expensive bromide or chloride counterparts which are more suitable for large-scale preparations. Finally, after about ten years, a catalytic procedure was disclosed: the acylation of Grignard reagents by acyl chlorides in the presence of manganese chloride. This manganese-catalyzed procedure is very efficient for large-scale applications.

A. Acylation of Organomanganese Halides by Acyl Chlorides in Ether

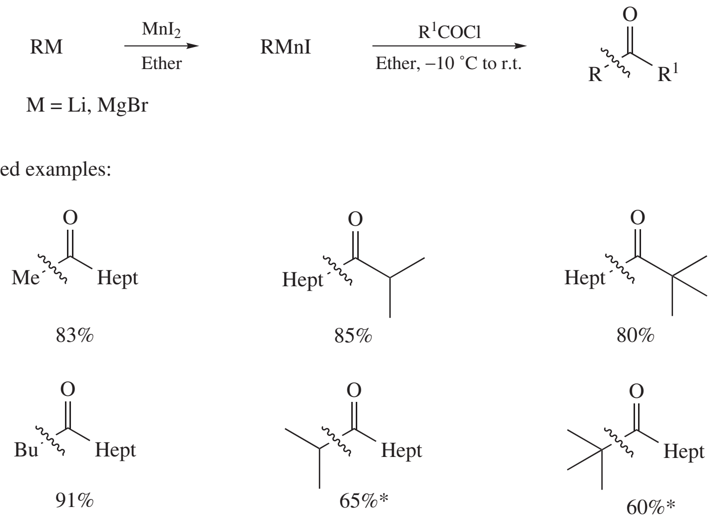
1. Preparation of ketones from organomanganese reagents derived from manganese iodide

The first results concerning the acylation of organomanganese compounds were published in 1976[48]. This report shows that organomanganese iodides readily react with a stoichiometric amount of acyl chlorides in diethyl ether to give the corresponding ketones in good yields (Scheme 69).

As shown in Scheme 69, aliphatic ketones are easily obtained from aliphatic acyl chlorides. The reaction is generally performed between −10 °C and room temperature but it is possible to operate as low as −50 °C. Primary alkylmanganese compounds always lead to good to excellent yields. On the other hand, secondary and tertiary alkylmanganese iodides, that are clearly less stable (see Section II.B), give lower yields. It should be pointed out that the formation of the 1,2-addition product is never observed.

In the case of the unstable secondary and tertiary alkylmanganese iodides, yields could be improved by using an excess of organometallic reagent (1.5 equivalents) or by adding THF as a ligand (5 equivalents, Scheme 70)[6].

However, it is more convenient to prepare secondary or tertiary alkylmanganese iodides from the complex MnI_2•2LiBr instead of MnI_2. The presence of LiBr has a stabilizing



* 1.5 equivalents of RMnI were used

SCHEME 69

$$i\text{-PrMnI} + \text{HeptCOCl} \xrightarrow{\text{Ether}} i\text{-PrCOHept}$$

1.1 *i*-PrMnI, −30 °C: 40–48%
1.5 *i*-PrMnI, −30 °C: 60–65%
1.5 *i*-PrMnI, **5 THF**, −10 °C: 78%

SCHEME 70

effect on the alkylmanganese reagent and the acylation can be efficiently performed at $-10\,^{\circ}\text{C}$ (Scheme 71)[7e].

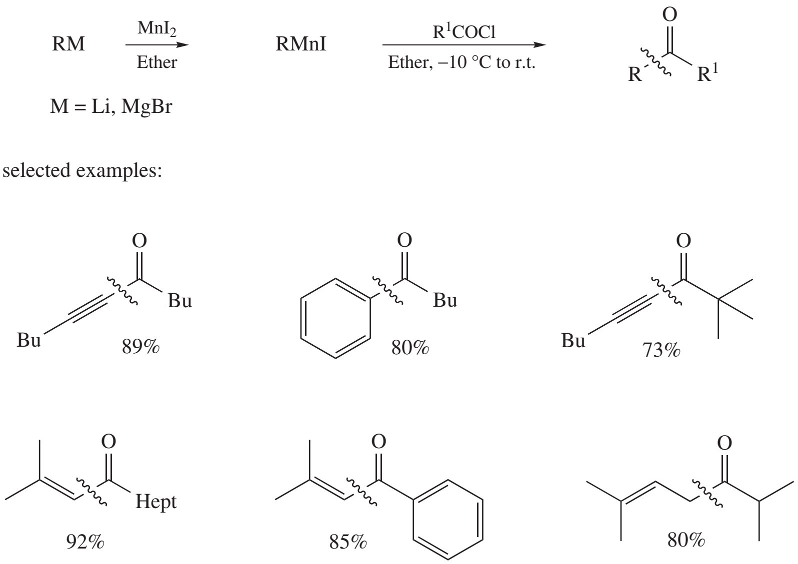
$$i\text{-PrMgBr} \xrightarrow[\text{Ether, }-10\,^{\circ}\text{C}]{\text{MnI}_2\bullet 2\text{LiBr}} i\text{-PrMnI}\bullet 2\text{LiBr} \xrightarrow[-10\,^{\circ}\text{C}]{\text{HeptCOCl}} \underset{92\%}{i\text{-PrCOHept}}$$

SCHEME 71

Allyl-, alkenyl-, alkynyl- and arylmanganese iodides were used successfully (Scheme 72). As a rule, the acylation takes place smoothly at 0 °C to afford good yields of unsaturated ketones[7a, b].

Symmetrical organomanganeses and organomanganates prepared from manganese iodide in ether also lead to ketones in good yields (Table 10). All the R groups bonded to the manganese atom react.

Interestingly, (*Z*)-alkenylmanganese iodides can be obtained stereoselectively from the corresponding lithium reagent prepared by lithium–iodine exchange from (*Z*)-alkenyl



SCHEME 72

TABLE 10. Acylation of organomanganese compounds prepared from MnI_2 in ether

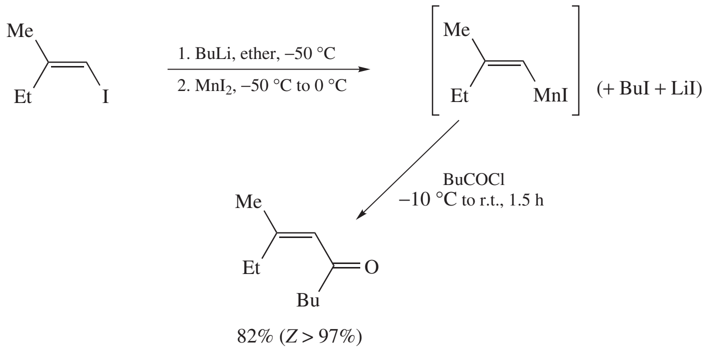
$$\mathrm{MnI_2} \xrightarrow[\text{Ether}]{\text{1 to 3 RLi (or RMgX)}} \text{‘RMn’} \xrightarrow[\text{Ether, −10 °C to r.t.}]{\mathrm{R^1COCl}} \mathrm{RCOR^1}$$

RMnI (**A**) R_2Mn (**B**) R_3MnLi (or MgX) (**C**)

‘RMn’ (‘RMn’/R^1COCl)	R	R^1	Yield (%)
A (1:1)	BuC≡C	Bu	89
B (1:2)	BuC≡C	Bu	80
C (1:3)	BuC≡C	Bu	70–75
A (1:1)	Bu	Hept	90
B (1:2)	Bu	Hept	85
C (1:3)	Bu	Hept	75–80

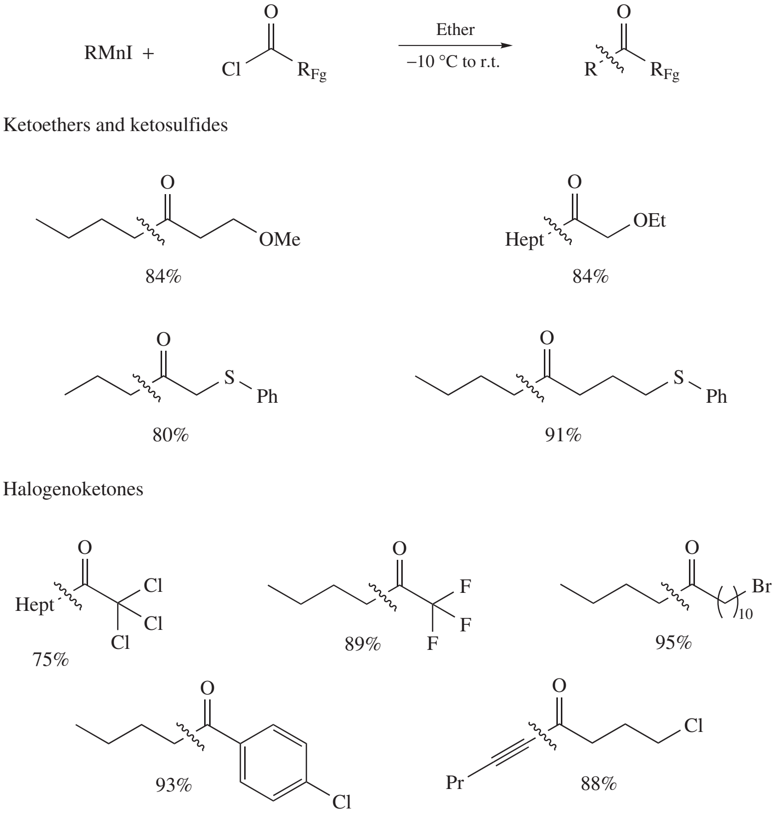
iodides (Scheme 73)[48]. These organomanganese reagents can be acylated to give the expected conjugated enones in good yields with an excellent stereochemical purity[16a].

It is interesting to note that the reaction takes place chemoselectively since the presence of the very reactive butyl iodide resulting from the lithium–iodine exchange is well tolerated.

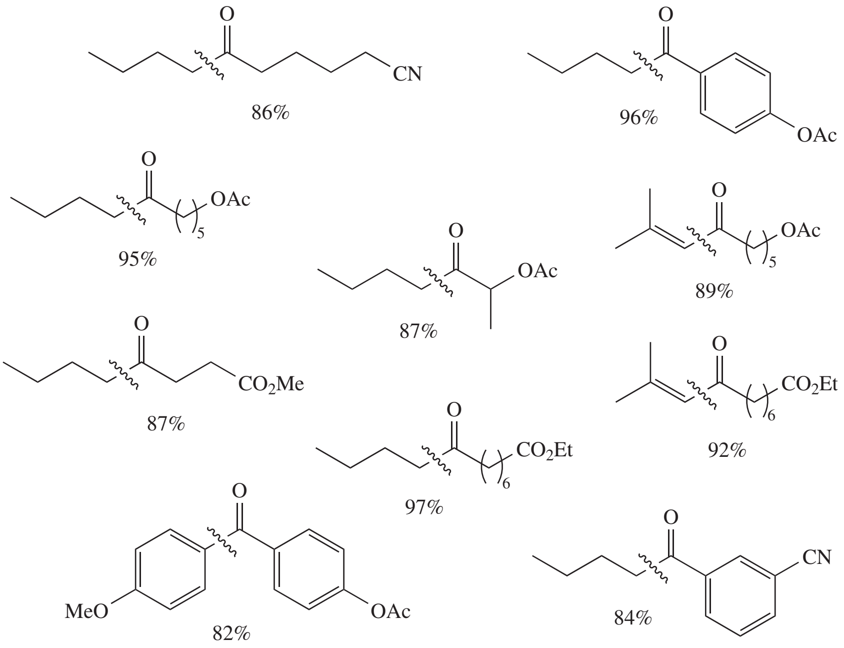


SCHEME 73

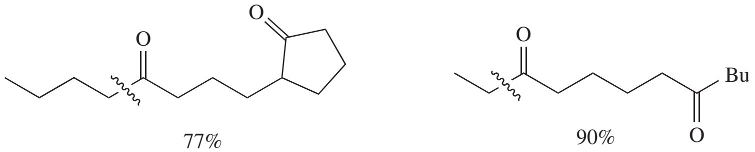
The chemoselectivity of organomanganese iodides is well demonstrated by the impressive number of functionalized ketones synthesized from functionalized acyl chlorides[7a, b, 49]. As shown in Scheme 74, numerous reactive functional groups are



Ketoesters and ketonitriles



Diketones



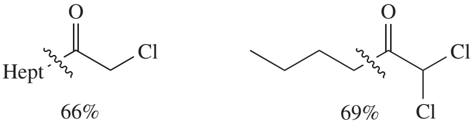
SCHEME 74

tolerated. Thus, it is easy to prepare various ketoethers, ketosulfides, halogenoketones as well as ketoesters, ketonitriles, or even unsymmetrical diketones. In all cases, no side reaction is observed and good to excellent yields are obtained.

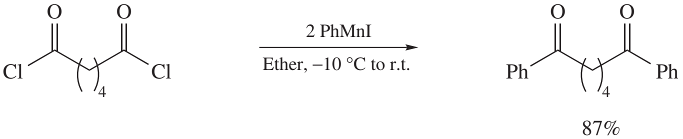
Mono- and dichloromethylketones are easily prepared from mono- or dichloroacetylchlorides. It is important to underline that the reaction must be performed in ether from an alkylmanganese choride prepared in the minimum of THF (Scheme 75)[7b]. The presence of metallic iodides in the reaction mixture must be avoided to prevent a chlorine/iodine exchange in the α-position of the ketones. Let us recall that these ketones are generally too reactive to be obtained efficiently by acylation of an organometallic compound.

Symmetrical diketones can be synthetized from dicarboxylic acid dichlorides and organomanganese iodides (Scheme 76)[49].

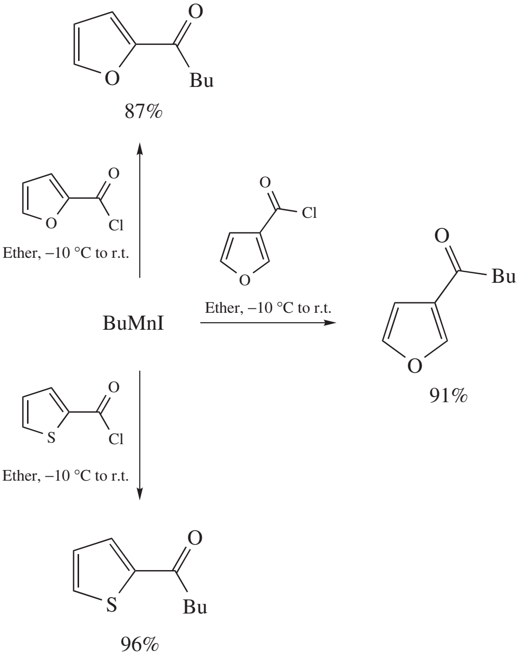
Heterocyclic acyl chlorides derived from furan or thiophene were also used successfully (Scheme 77).



SCHEME 75



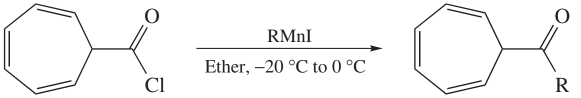
SCHEME 76



SCHEME 77

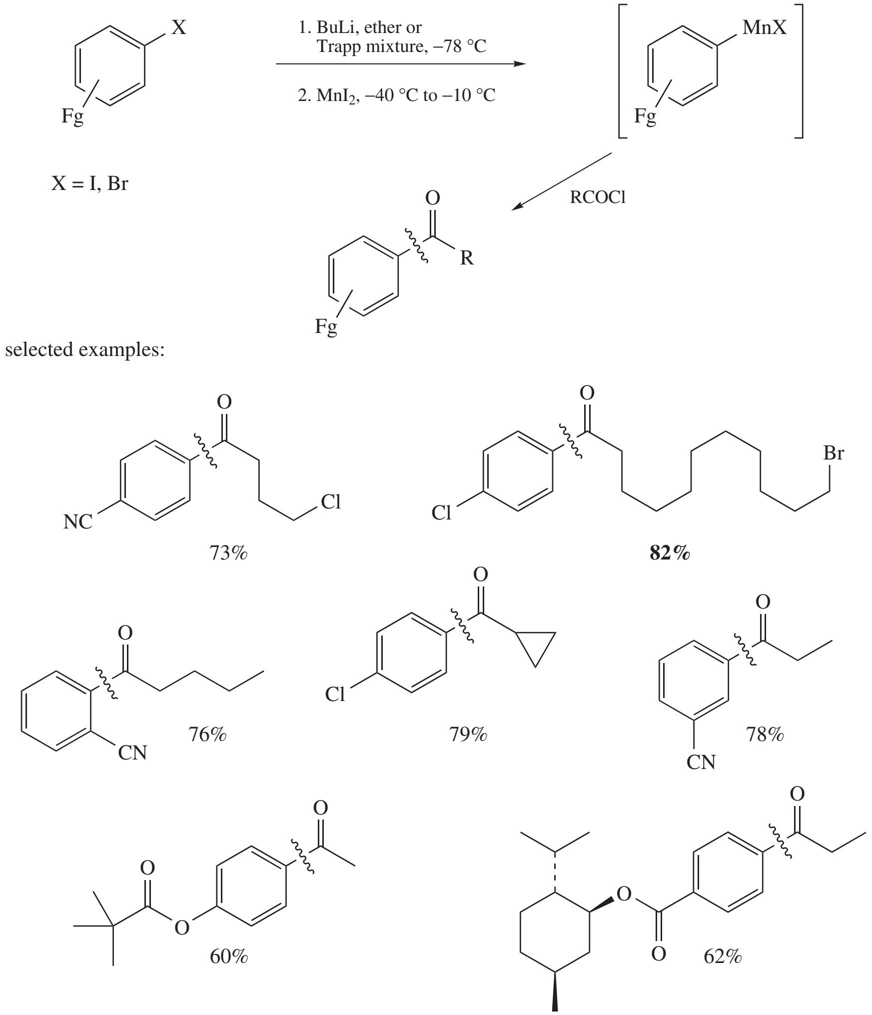
In 1985, Ritter and Hanack used organomanganese iodides to synthesize various cycloheptatrienyl ketones of synthetical interest in moderate to good yields (Scheme 78)[50].

In 1997, we described the acylation of functionalized aryl- and alkenylmanganese compounds. They are prepared from various aryl or alkenyl iodides or bromides via the corresponding organolithium reagents (lithium–halogen exchange)[15]. Highly polyfunctionalized ketones were thus obtained in good yields (Schemes 79 and 80).

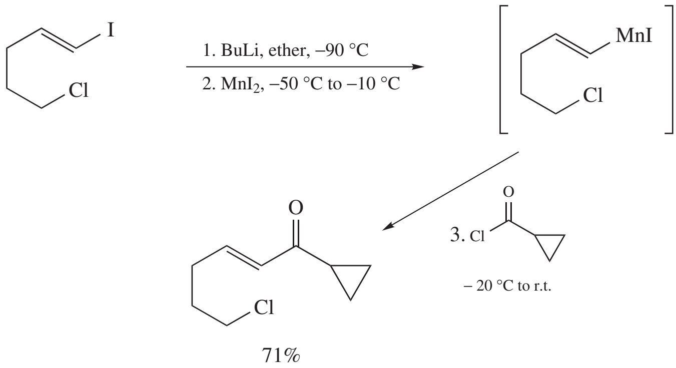


R = Ph: 75%; Me: 60%; *c*-Pr: 50%

SCHEME 78



SCHEME 79

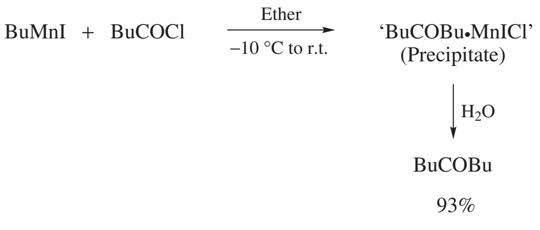


SCHEME 80

2. Mechanism of the reaction

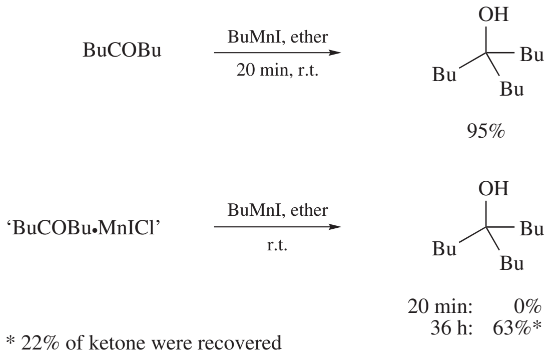
The acylation of organomanganese iodides by acyl chlorides is a very clean reaction. Thus, the formation of tertiary alcohol as a side product is never observed. This result is surprising since organomanganese iodides easily react with ketones in ether (see Section III). Moreover, the reaction rates of the acylation and the 1,2-addition reactions are not different enough to prevent the formation of carbinol. Further investigations showed that the ketone is formed as a complex with the manganese salts (MnICl) present in the reaction mixture[51]. This complex is only destroyed during the final aqueous work-up.

For instance, the reaction of butylmanganese iodide with pentanoyl chloride in ether leads to a sticky precipitate (Scheme 81). In fact, no trace of 5-nonanone was detected in the ethereal phase. On the other hand, the ketone is obtained in 93% yield after hydrolysis. Let us remark that the 5-nonanone can be quantitatively displaced from the complex BuCOBu•MnICl, under anhydrous conditions, by adding triethylamine (15 equivalents) or acetone (10 equivalents).



SCHEME 81

This complexation considerably slows down the addition rate of the organomanganese reagent to the carbonyl group. Thus, butylmanganese iodide adds to uncomplexed 5-nonanone in 15 to 20 minutes at room temperature to give 95% yield of tertiary alcohol, whereas the complexed ketone (BuCOBu•MnICl) only leads to 63% yield after 36 hours (Scheme 82).



* 22% of ketone were recovered

SCHEME 82

3. Preparation of ketones from organomanganese bromides

Organomanganese bromides are readily prepared in ether from the soluble ate complex $MnBr_2$•2LiBr (see Section II). As their iodide analogues, they readily react with acyl chlorides under mild conditions to afford the corresponding ketones in excellent yields (Table 11)[7d, e, 13]. This is very interesting for synthetic applications since they are cheaper and often more stable.

As an example, secondary and tertiary alkylmanganese bromides prepared from Grignard reagents are stable enough to be acylated efficiently at $-10\,^{\circ}C$ whereas, with the corresponding alkylmanganese iodides, it is necessary to operate at $-30\,^{\circ}C$ by using an excess of organometallic. Various branched ketones can thus be prepared in excellent yields (Scheme 83)[7e, 13].

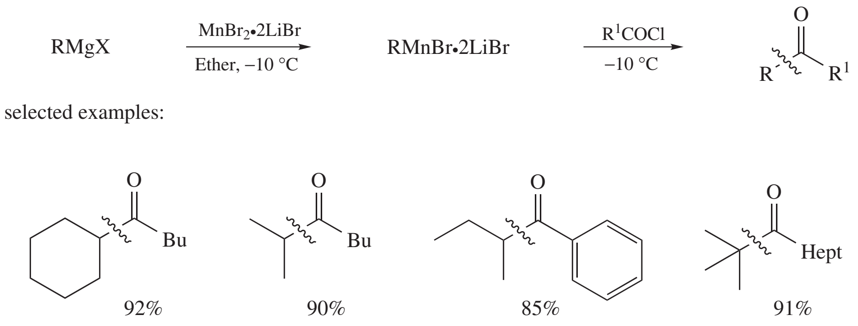
On the other hand, it is interesting to prepare organomanganese compounds from $MnBr_2$ instead of MnI_2 since the formation of iodine sometimes observed during the final work-up is avoided. This is very important for the preparation of iodine-sensitive products. Thus, all our attempts to prepare the polyunsaturated ketone described in Scheme 84 from 1-hexynylmanganese iodide resulted in failure, whereas good yields were obtained from 1-hexynylmanganese bromide[7d].

This procedure is especially convenient for the preparation of conjugated polyunsaturated ketones (Scheme 85)[13].

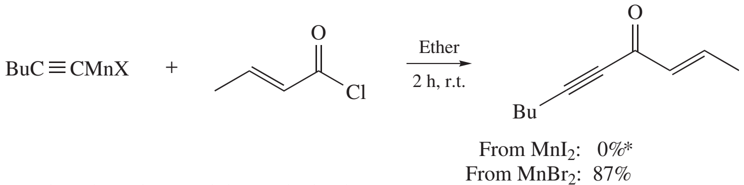
TABLE 11. Acylation of RMnBr in ether

$$\mathrm{RLi} \xrightarrow[\text{Ether, } -10\,^{\circ}\mathrm{C}]{\mathrm{MnBr_2\cdot 2LiBr}} \mathrm{RMnBr\cdot 2LiBr} \xrightarrow[-10\,^{\circ}\mathrm{C}]{\mathrm{R^1COCl}} \mathrm{RCOR^1}$$

R	R^1	Yield (%)
Bu	Hept	97
$Me_2C{=}CH$	Hept	87
Bu	$Me_2C{=}CH$	95
Ph	Bu	95
Bu	Ph	92
$BuC{\equiv}C$	Bu	95

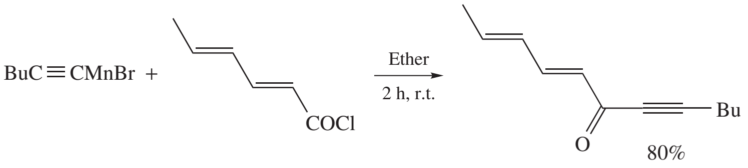


SCHEME 83



* Only polymeric material was obtained

SCHEME 84



SCHEME 85

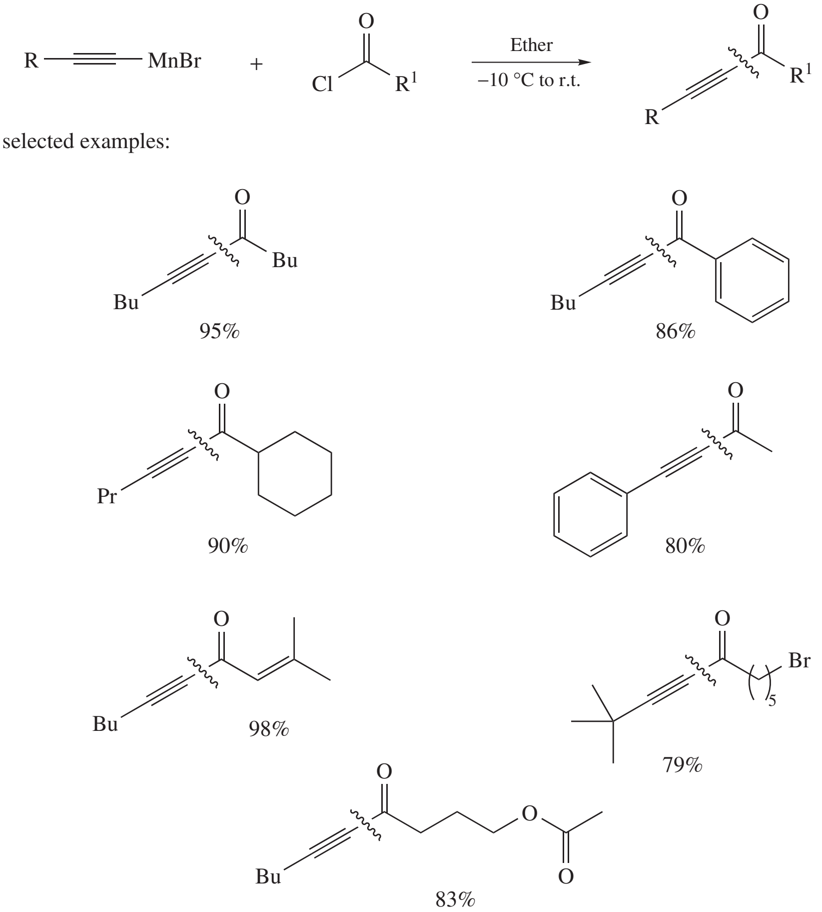
As a rule, alkynylmanganese bromides were used to synthezise a vast array of acetylenic ketones (Schemes 86 and 87)[16c, f].

It is interesting to note that functionalized alkynylmanganese bromides can also be employed successfully (Scheme 87).

Organomanganese alcoholate derived from propargylic alcohol undergoes a double acylation to give ketoesters in good yields (Scheme 88)[13].

B. Acylation of Organomanganese Halides with Acyl Chlorides in THF

In THF, organomanganese chlorides are easily prepared from the soluble ate-complex $MnCl_2$•2LiCl and react with acyl chlorides to give the desired ketones in good yields[5]. It is very interesting since organomanganese chlorides are cheaper than their bromide or iodide counterparts (Scheme 89).

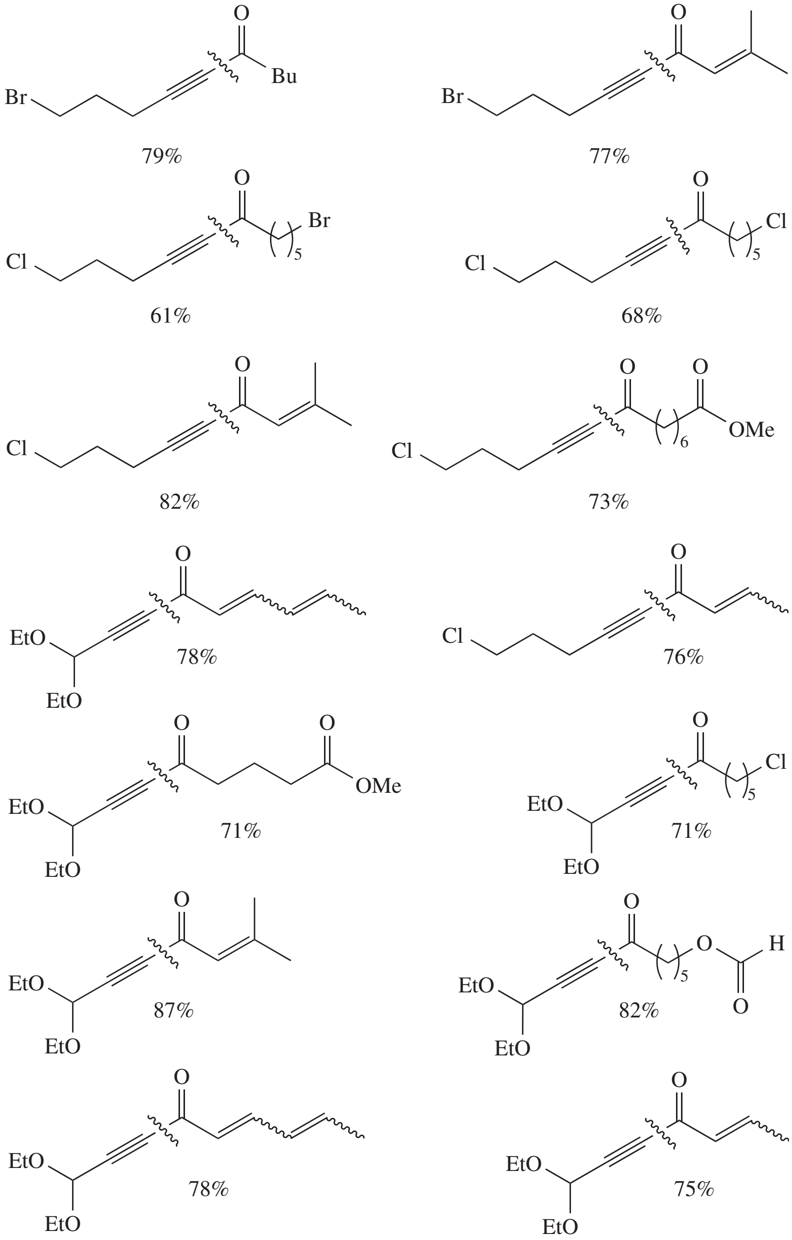


SCHEME 86

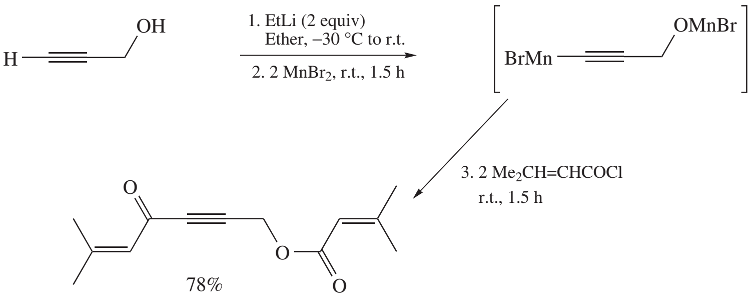
Alkyl-, alkenyl- and alkynylmanganese chlorides as well as allylic organomanganese reagents are easily acylated. On the other hand, linear and branched acyl chlorides as well as the less reactive conjugated aromatic and ethylenic acyl chlorides lead to the corresponding ketones in excellent yields.

Organomanganese chlorides can be used to prepare numerous functional ketones since the reaction is highly chemoselective (Scheme 90)[5].

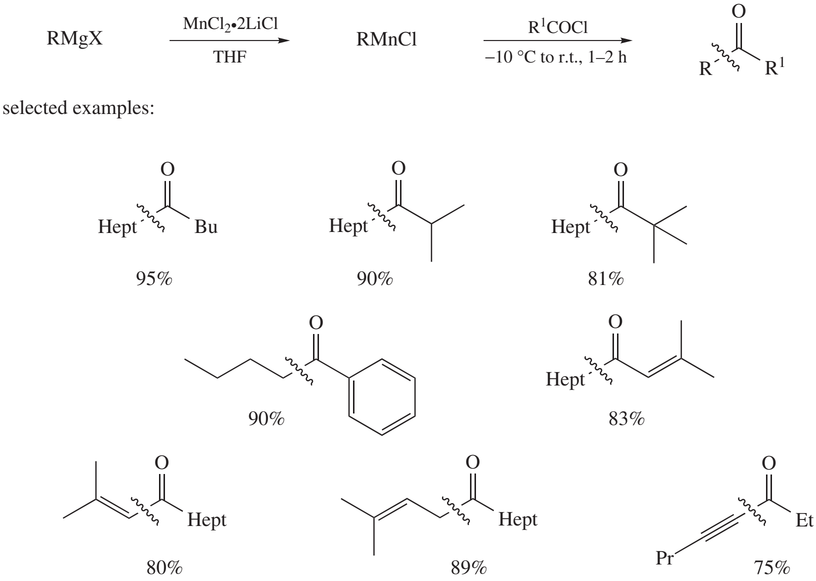
In THF, methyl-, aryl- as well as secondary alkylmanganese halides give lower yields than in ether. In addition, tertiary alkylmanganese halides do not lead to the expected ketones. Fortunately, these limitations were circumvented (Table 12) by the use of a catalytic amount of copper chloride (3%). A dramatic influence is observed in the case of the *tert*-butylmanganese chloride since the yield jumps from 0% to 92%[5].


O
Bu
Br
79%
O
Br
77%
O
Br
5
Cl
61%
O
Cl
5
Cl
68%
O
Cl
82%
O
O
6
OMe
Cl
73%
O
EtO
EtO
78%
O
Cl
76%
O
O
OMe
EtO
EtO
71%
O
Cl
5
EtO
EtO
71%
O
EtO
EtO
87%
O
5
O
H
O
EtO
EtO
82%
O
EtO
EtO
78%
O
EtO
EtO
75%

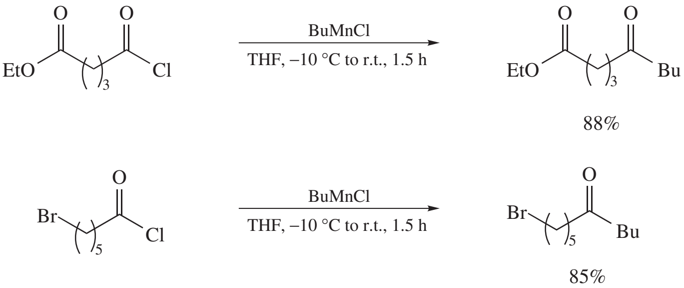
SCHEME 87



SCHEME 88

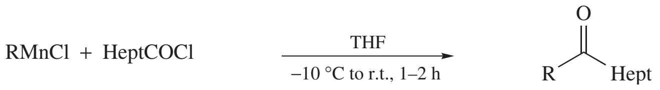


SCHEME 89



SCHEME 90

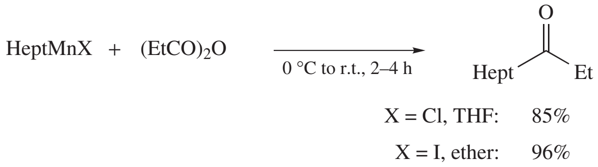
TABLE 12. Cu-catalyzed acylation of RMnCl in THF



R	Yield (%)	
	without CuCl	with CuCl (3%)
Me	40	91
i-Pr	69	93
t-Bu	0	92
Ph	75	92

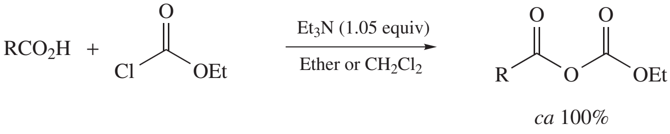
C. Acylation with Other Acylating Reagents Derived from Carboxylic Acids

Organomanganese halides react with carboxylic acid anhydrides under mild conditions, in ether or in THF, to afford ketones in good yields (Scheme 91)[6, 52].



SCHEME 91

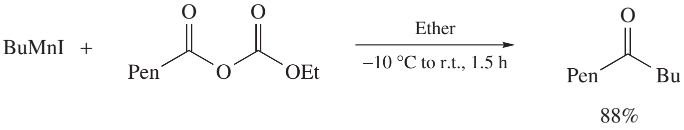
Mixed carbonic–carboxylic anhydrides RCOOCOOEt are easily obtained from the corresponding carboxylic acid and ethyl chloroformate in quantitative yields (Scheme 92). These acylating agents are prepared under milder conditions than the corresponding acyl chlorides. It is especially interesting in the case of acid-sensitive carboxylic acids. Thus, they were widely employed for the synthesis of peptides.



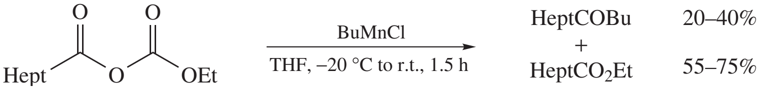
SCHEME 92

In ether, they replace efficiently the acyl chlorides and give similar results (Scheme 93)[6]. On the contrary, in THF, they lead to the ketones in only moderate and irreproducible yields (20 to 40%). Indeed, the formation of the ethyl ester RCOOEt, which is often the main product, competes seriously with the acylation reaction (Scheme 94)[6].

This drawback was circumvented by the preparation of the organomanganese chlorides from the complex $MnCl_2{\bullet}R_4NCl$ (see preparation in Scheme 13). The ketones are then

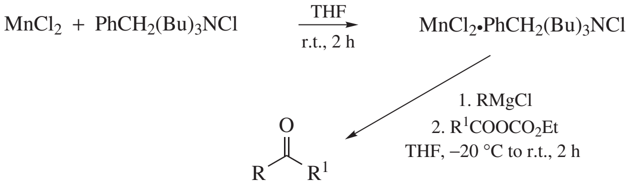


SCHEME 93



SCHEME 94

TABLE 13. Acylation of RMnCl by $RCOOCO_2Et$ in the presence of $PhCH_2(Bu)_3NCl$



R	R^1	Yield (%)
Bu	Hept	79
Ph	Hept	68
Hept	*i*-Pr	78
Bu	Ph	85
i-Pr	Ph	79
Hept	$Me_2C{=}CH$	83

obtained in good yields since the acylation occurs almost instantaneously in the presence of a tetraalkylammonium chloride (Table 13)[7e].

Similar or even higher yields can be obtained by using an organomanganese chloride in the presence of a catalytic amount of copper chloride (Table 14)[13]. From an economical point of view, this is the best alternative since copper chloride is a cheap material.

Finally, symmetric ketones were also synthesized from phosgene (Scheme 95)[53].

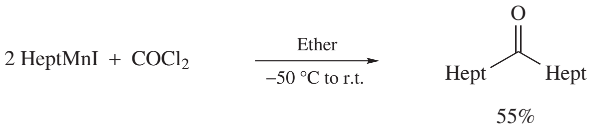
D. Catalytic Procedure: Reaction of Grignard Reagents with Acyl Chlorides in the Presence of Manganese Salts

Diorganomanganese compounds R_2Mn and organomanganates R_3MnLi or R_3MnMgX as well as R_4MnLi_2 or $R_4Mn(MgX)_2$ can be efficiently acylated (Table 10). It is important to note that, in all cases, all R groups bonded to the manganese atom react. With the

TABLE 14. Acylation of RMnCl by $RCOOCO_2Et$ in the presence of 3% CuCl

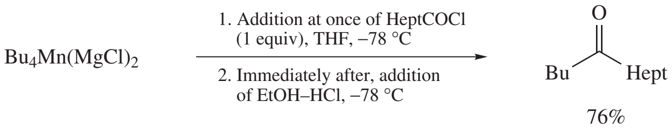
R^a	R^1	Yield (%)
Bu	Hept	81
Bu	$Me_2C{=}CH$	76
t-Bu	Hept	76
Ph	Hept	78

[a] RMnCl was indifferently prepared from RLi or RMgX and $MnCl_2{\bullet}2LiCl$.



SCHEME 95

tetraorganomanganates $R_4Mn(MgX)_2$, it was demonstrated that the acylation of the first R group bonded to the manganese atom takes place almost instantaneously, even at low temperature (Scheme 96)[54].



SCHEME 96

This preliminary experiment leads to the discovery of a very efficient method for the preparation of ketones by manganese-catalyzed acylation of Grignard reagents. Good yields were thus obtained under very mild conditions (Table 15)[54].

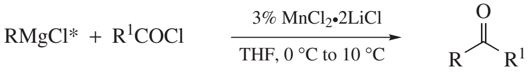
It is important to underline that the success of this reaction closely depends on the rate of the addition of the Grignard reagent. A catalytic cycle involving a manganate $R_4Mn(MgX)_2$ as the key intermediate was proposed (Figure 1).

Various functionalized ketones were prepared in good yields according to this catalytic procedure (Scheme 97).

The reaction is sensitive to steric hindrance. Thus, tertiary alkyl ketones are only obtained in moderate to poor yields. However, it is possible to circumvent this drawback by using a copper–manganese co-catalysis. This is efficient in the case of tertiary alkylmagnesium reagents (Scheme 98) but also in the case of tertiary alkyl acyl chlorides (Scheme 99)[7f].

The manganese-catalyzed procedure is especially convenient for large-scale preparative applications (Table 15, Schemes 97–99) since it is very simple to carry out. It should be noted that manganese chloride is a very cheap catalyst. From an economical point of

TABLE 15. Mn-catalyzed acylation of RMgX



* RMgCl is added dropwise for 30 to 45 min

R	R^1	Yield (%)
Bu	Hept	87
Hept	*i*-Pr	94
Hept	*t*-Bu	52
Hept	$Me_2C{=}CH$	79
Bu	Ph	85
i-Pr	Hept	74
$Me_2C{=}CH$	Hept	73
Ph	Bu	85
i-Pen	*i*-Bu	83

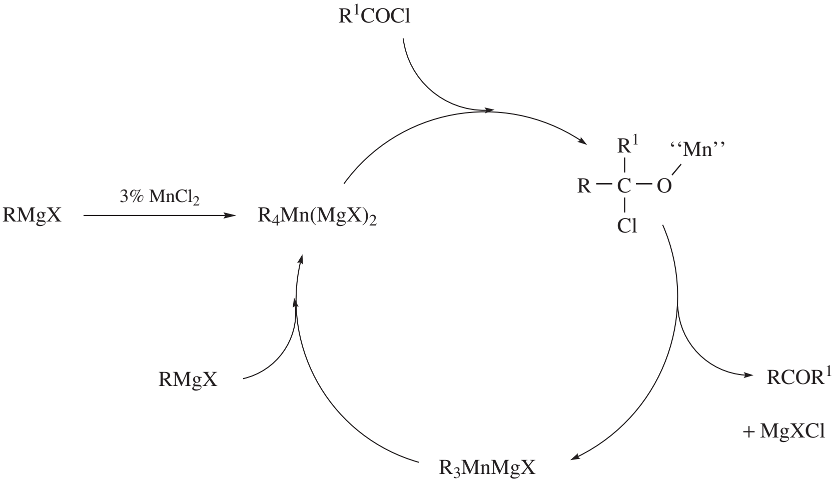
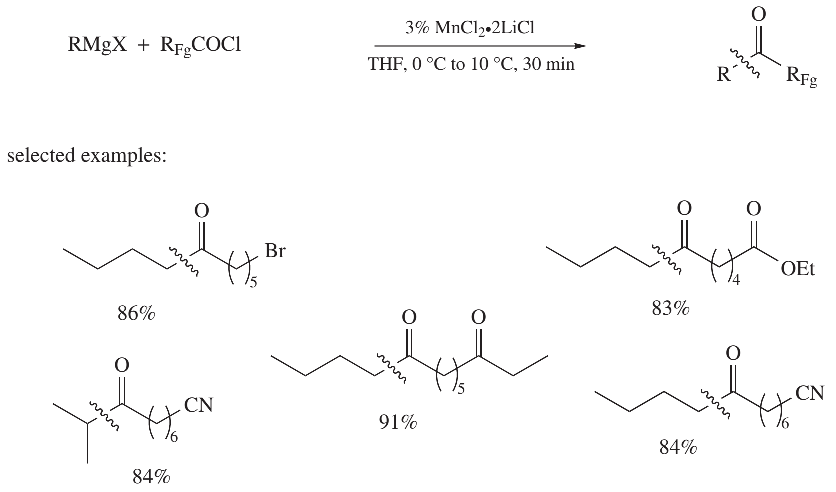


FIGURE 1

view, only the iron-catalyzed acylation of Grignard reagents can be compared. However, the manganese-catalyzed reaction is clearly less dependent on the concentration of the reaction mixture, a very important point for large-scale applications (Table 16)[55].

E. Acylation of Organomanganese Halides with Ethyl Chloroformate

Ethyl chloroformate reacts with organomanganese iodides in diethyl ether to give good yields of esters (Scheme 100)[53].



SCHEME 97

$$t\text{-BuMgCl}^{*} + \text{HeptCOCl} \xrightarrow[\text{THF, 0 °C to 10 °C}]{\substack{\text{3\% CuCl} \\ \text{3\% MnCl}_2\bullet\text{2LiCl}}} t\text{-BuCOHept}$$

* *t*-BuMgCl was added in 45 min

80%
(27% without CuCl)

SCHEME 98

$$\text{HeptMgCl}^{*} + t\text{-BuCOCl} \xrightarrow[\text{THF, 0 °C to 10 °C}]{\substack{\text{3\% CuCl} \\ \text{3\% MnCl}_2\bullet\text{2LiCl}}} \text{HeptCOBu-}t$$

* HeptMgCl was added in 30 min

97%
(52% without CuCl)

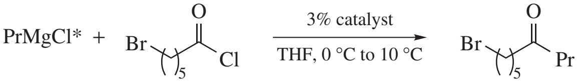
SCHEME 99

R= Hept:	83%[a]
R= Hept:	77%[b]
R= $Me_2C{=}CH$:	70%[b]
R= Ph:	77%[b]

[a] From RMgX. [b] From RLi.

SCHEME 100

TABLE 16. Comparison between the Mn- and Fe-catalyzed acylations of RMgX

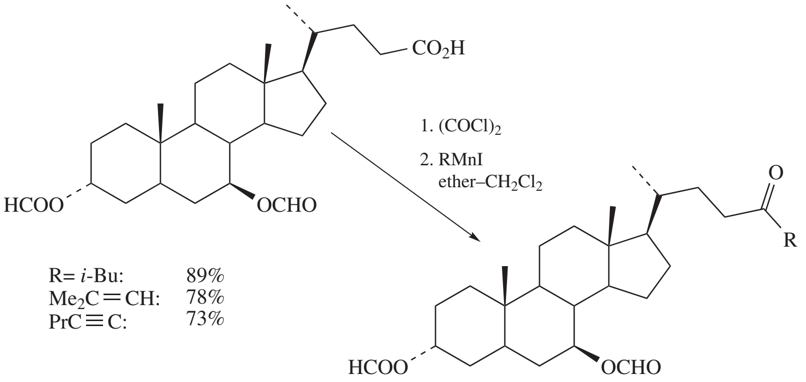


* PrMgCl was added in 30 min

Catalyst	Concentration of the reaction mixture	Yield (%)
$Fe(acac)_3$	0.4 M	91
$Fe(acac)_3$	1.2 M	38
$MnCl_2{\bullet}2LiCl$	1.2 M	86

F. Preparation of Ketones from Organomanganese Compounds: Applications in Organic Synthesis

Because of its chemoselectivity, the acylation of organomanganese compounds is a very useful reaction to synthesize various natural compounds such as fragrances or bioactive products. The first applications relate to the synthesis of ketosteroids (Scheme 101)[56].



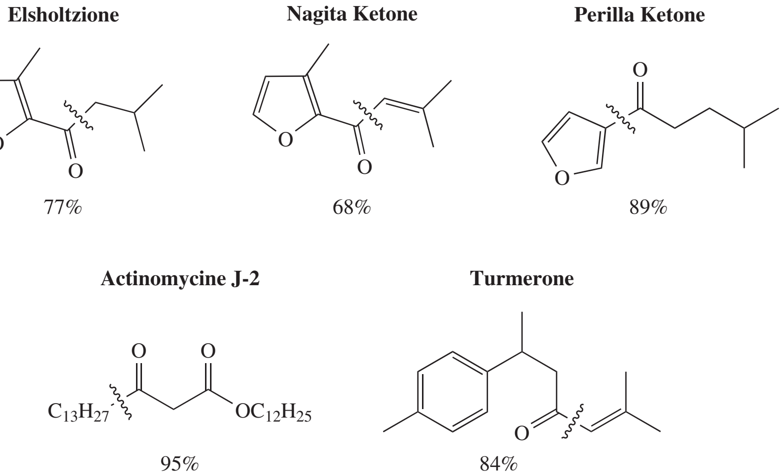
SCHEME 101

Excellent yields were obtained in spite of the presence of formyloxy groups. It should be noted that, owing to the high chemoselectivity of organomanganese reagents, an ether-dichloromethane mixture can be used as a solvent in order to solubilize the starting acyl chloride.

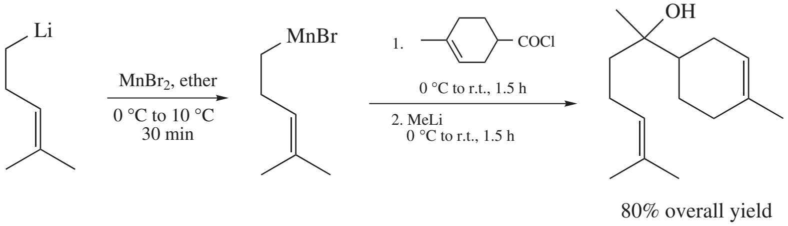
Various natural products were prepared in good yields by acylation of organomanganese iodides (Scheme 102)[8, 57].

(±) α-Bisabolol, a tertiary alcohol, was prepared according to a one-pot acylation/1,2-addition procedure via the 4-methyl-3-pentenylmanganese bromide (Scheme 103)[58].

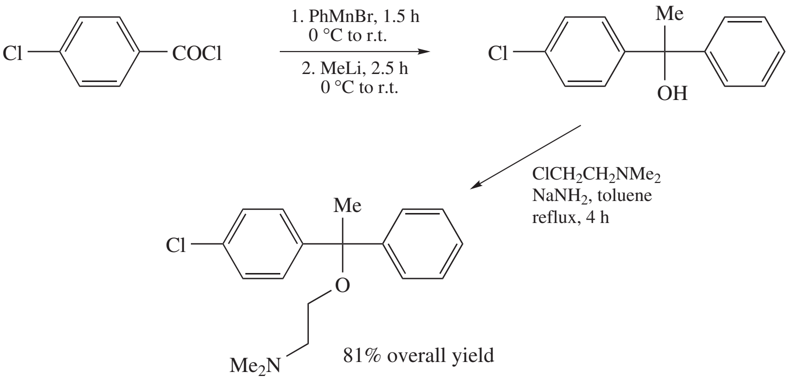
The same procedure was applied to the synthesis of chlorphenoxamine, an antihistamine (Scheme 104)[58].



SCHEME 102

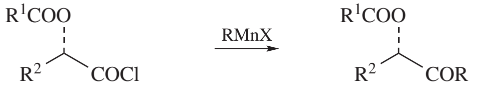


SCHEME 103



SCHEME 104

Various chiral α-acyloxyketones were easily prepared in high yields and with an excellent enantiomeric purity from enantiopure α-acyloxy acyl chlorides (Scheme 105)[59].

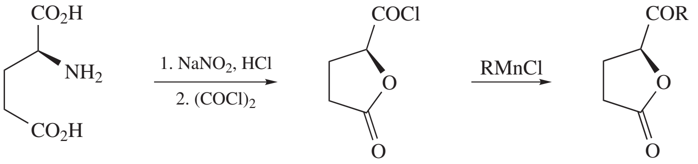


64–93%
ee: 91–99.5%

X = Cl, Br
R^1 = Me, *t*-Bu, Ph
R^2 = Me, *i*-Pr, Ph, $PhCH_2$
R = Me, Bu, Hex, *i*-Pr, *t*-Bu, Ph, $Me_2C{=}CH$, Pen‑C≡C

SCHEME 105

Similarly, optically active δ-ketobutanolides were synthesized in good yields with an excellent enantiomeric purity by acylation of organomanganese reagents with the butyrolactone acyl chloride prepared from natural (L)-glutamic acid (Scheme 106)[60].



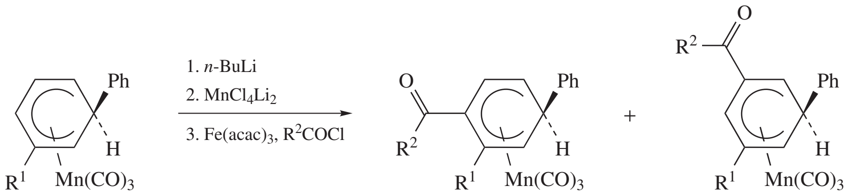
58–92%
ee: 96–98%

R = Me, Bu, Hex, $C_{12}H_{25}$, *i*-Pr, *t*-Bu, Ph, Pen‑C≡C

SCHEME 106

Organomanganese iodides were also used in solid-phase synthesis for the chemoselective conversion of acyl chlorides to tertiary alcohols (one-pot acylation/1,2-addition procedure)[61].

Finally, an iron-catalyzed acylation of organomanganese reagents derived from various (n^5-cyclohexadienyl)$Mn(CO)_3$ complexes (Scheme 107) were described very recently. This reaction gives efficient access to the corresponding ketones in good to excellent yields[62].



R^1 = H, OMe, Cl
R^2 = Thi*, Ph
* Thi = 2-thienyl

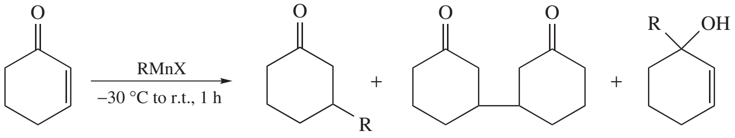
45–91%

SCHEME 107

V. 1,4-ADDITION OF ORGANOMANGANESE COMPOUNDS TO CONJUGATED ENONES AND RELATED DERIVATIVES

A. Reaction of Organomanganese Reagents with Conjugated Enones and Related Derivatives

Organomanganese reagents react with cyclohexenone to give variable amounts of the 1,2- and 1,4-addition products as well as the β-reductive dimerization product (Scheme 108)[63]. Several parameters can deeply influence the course of the reaction: the nature of the organomanganese reagent, the nature of the solvent, the presence of metallic salts (LiX or MgX_2) and the temperature.



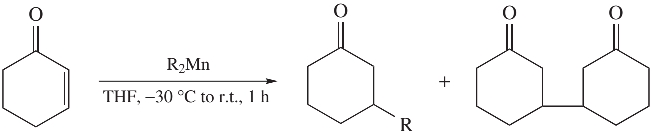
MeMnBr, ether:	7%	25%	34%
BuMnBr[a], ether:	18%	27%	20%
BuMnBr[b], ether:	26%	35%	3%
BuMnCl[a], THF:	10%	0%	10%
i-PrMnCl[c], THF:	23%	33%	4%

[a] Prepared from BuLi. [b] Prepared from BuMgCl. [c] Prepared from *i*-PrMgCl.

SCHEME 108

Organomanganese halides generally lead to a mixture of the three products depicted in Scheme 108 in moderate yields. Accordingly, the reaction cannot be used for preparative purposes.

With symmetrical organomanganese reagents, only the 1,4- and the β-reductive dimerization products are formed. Moreover, it is sometimes possible to obtain mainly one of the two products. However, the yields of 1,4-addition product are never excellent (Scheme 109).

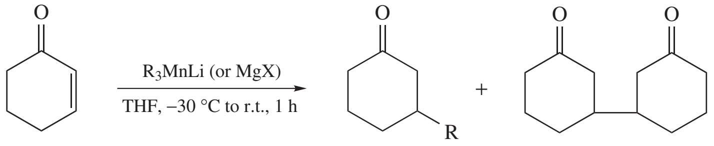


Me_2Mn[a]:	40%	0%
Me_2Mn[b]:	72%	5%
Bu_2Mn[a]:	30%	50%
Bu_2Mn[b]:	70%	25%
i-Pr_2Mn[b]:	4%	83%
Ph_2Mn[b]:	62%	21%

[a] Prepared from RLi. [b] Prepared from RMgX.

SCHEME 109

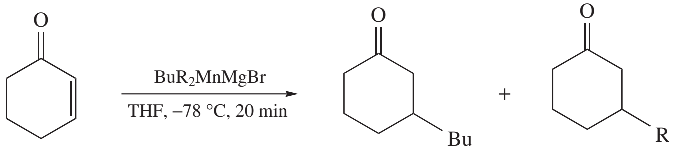
Lithium or magnesium organomanganates also give a mixture of 1,4-addition and β-reductive dimerization products. The issue of the reaction clearly depends on the stability of the organomanganate. Thus, trialkylmanganates having β-hydrogen atoms mainly lead to the β-reductive dimerization product. On the contrary, with the organomanganates which cannot decompose by β-elimination (more stable), the 1,4-addition product is generally predominantly obtained, albeit in moderate yields. In Scheme 110, yields are based on the transfer of only one of the three R groups of the organomanganate.



$Me_3MnMgCl$:	42%	21%
Bu_3MnLi:	18%	74%
$Bu_3MnMgCl$:	20%	74%
i-$Pr_3MnMgCl$:	13%	74%
$Ph_3MnMgCl$:	45%	16%

SCHEME 110

Heteroorganomanganates $BuR_2MnMgBr$ bearing two non-transferable R groups such as Me, Me_3SiCH_2 or RC≡C were used[64]. Only 3-butylcyclohexanone is obtained but yields are moderate and the scope of the reaction is very limited (Scheme 111).

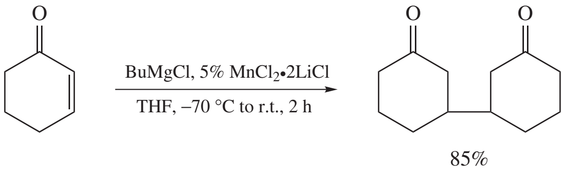


R = Me:	50%	< 1%
R = Me_3SiCH_2:	61%	< 1%
R = HexC≡C:	72%	< 1%

SCHEME 111

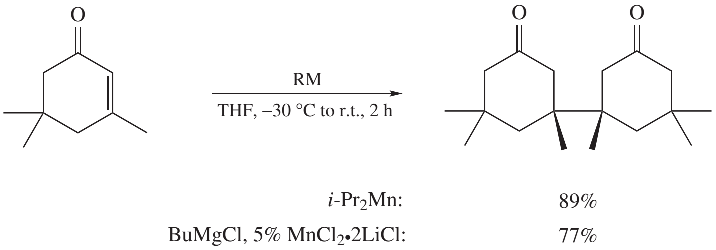
It is important to note that the report concerning the conjugate addition of organomanganese reagents to cyclohexenone published in 1984[65] should not be taken into account. Indeed, in the light of our results, the authors tried to repeat their experiments and they finally confirmed the results described in Schemes 108 to 110.

The reaction of Grignard reagents with cyclohexenone in the presence of a catalytic amount of manganese salt also affords a mixture of conjugate addition and β-reductive dimerization products. By using n-butylmagnesium chloride at $-70\,^{\circ}$C, a good yield of β-reductive dimerization product is obtained (Scheme 112)[63]. The manganese catalysis is very efficient since the 1,2-addition to cyclohexenone is not observed.



SCHEME 112

It should be noted that the results described above with cyclohexenone cannot be extended to other conjugated enones. Thus, good yields of β-reductive dimerization product were obtained from isophorone (Scheme 113) but 2- or 3-methylcyclohexenone, 1-acetylcyclohexene as well as various β-mono- or β,β-bisubstituted acyclic enones lead to the 1,4-addition product or to the β-reductive dimerization product in low yields (<30%).



SCHEME 113

All attempts to react conjugated enones with organomanganese reagents show that the conjugated addition product is frequently formed but generally in low yields. The 1,2-addition and the β-reductive dimerization reactions are often very competitive. However, the conjugate addition can be favored by using more powerful Michael acceptors such as alkylidene malonic esters[7c]. The scope of the reaction is then very large since alkyl-, aryl-, alkenyl-, allyl- and even the less reactive alkynylmanganese chlorides readily react in THF to give satisfactory yields of conjugate addition product (Table 17). With alkylmanganese halides having β-eliminable hydrogen atoms, the formation of the reduction product is partially (R = i-Pr) or mainly (R = t-Bu) observed.

Interestingly, functionalized organomanganese reagents can be used (Scheme 114)[15]. It should be noted that the reaction also takes place in ether.

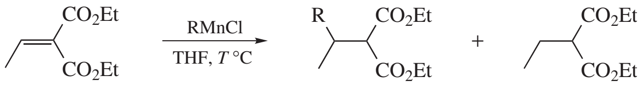
Let us recall that Grignard reagents can also react with alkylidene malonic esters to give mainly the 1,4-addition product (Table 18). However, the yields are often lower than with the corresponding organomanganese reagents and the scope of the reaction is more limited[7c].

Grignard reagents add to β-alkoxy alkylidene malonic esters to lead only to the double addition product (Scheme 115), even by using an excess of ester.

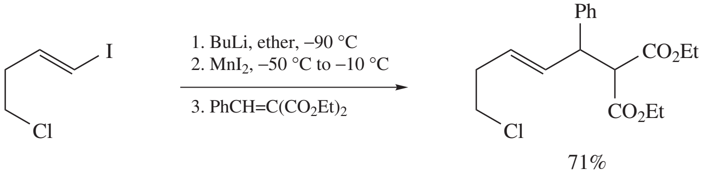
On the other hand, with organomanganese reagents it is possible to obtain selectively the monoaddition product (neutral hydrolysis) as well as the monoaddition-elimination product (acid hydrolysis) in good yields (Scheme 116).

As a rule, organomanganese compounds react more chemoselectively than the corresponding Grignard reagents (Scheme 117)[7c].

TABLE 17. Conjugate addition of RMnX to alkylidene malonic esters

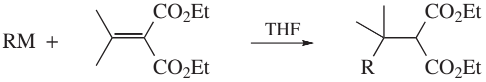


R	T (°C)	1,4-Addition (%)	Reduction (%)
Me, Bu, Ph	−30	85–89	-
$Me_2CH{=}CH$, BuC≡C, Allyl	20	72–91	-
i-Pr	−30	70	11
t-Bu	−30	10	40



SCHEME 114

TABLE 18. Comparison between the conjugate addition of RMgCl and RMnCl to alkylidene malonic esters

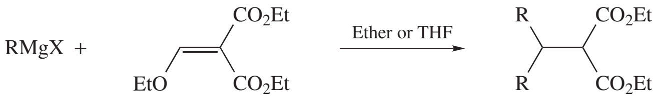


R	Yield (%) from	
	RMgCl	RMnCl
Bu	62	74
Me	5	82
Ph	5	87

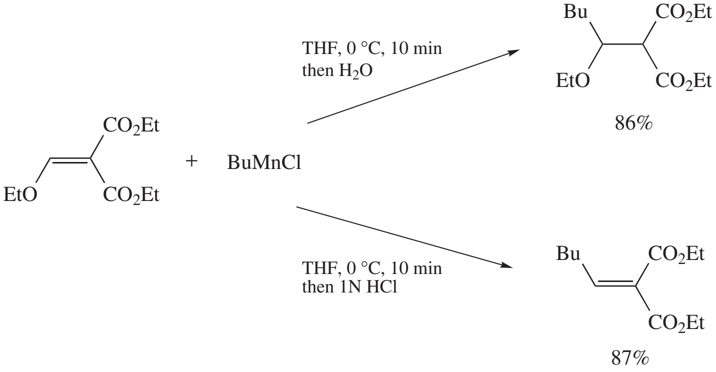
With β,β-disubstituted alkylidene malonic esters the conjugate addition is clearly more difficult than with the β-monosubstituted analogues. Thus, with alkenyllithium, magnesium and manganese compounds, which are not very reactive, it is necessary to add a catalytic amount of copper chloride to favor the conjugate addition reaction. However, even in this case, organomanganese chlorides are still more efficient (Scheme 118).

Various Michael acceptors related to alkylidene malonic esters were used successfully (Scheme 119)[7c].

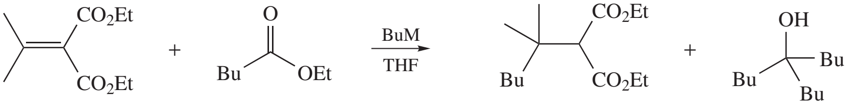
In spite of their very high reactivity as Michael acceptors, conjugated nitroolefins react with Grignard reagents to give poor yields of 1,4-addition product since the main reaction is the 1,2-addition to the nitro group. Namboothiri and Hassner reported that organomanganese reagents are more selective[66]. Thus, BuMnCl reacts with nitrostyrene



SCHEME 115

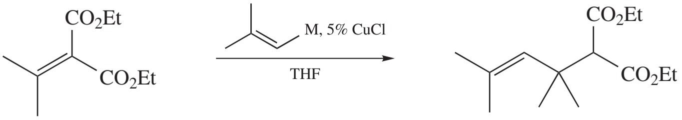


SCHEME 116



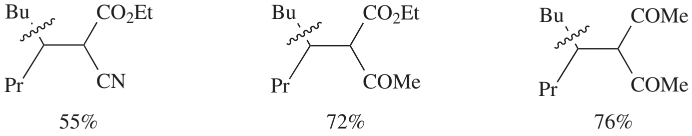
BuMgCl:	45%	15%
BuMnCl:	71%	0%

SCHEME 117



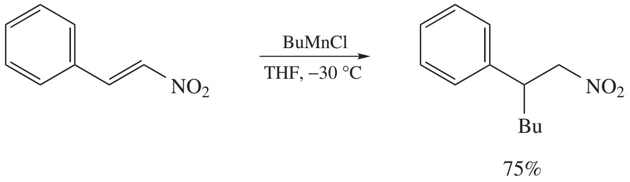
$Me_2C{=}CHLi$:	40%
$Me_2C{=}CHMgCl$:	45%
$Me_2C{=}CHMnCl$:	83%

SCHEME 118



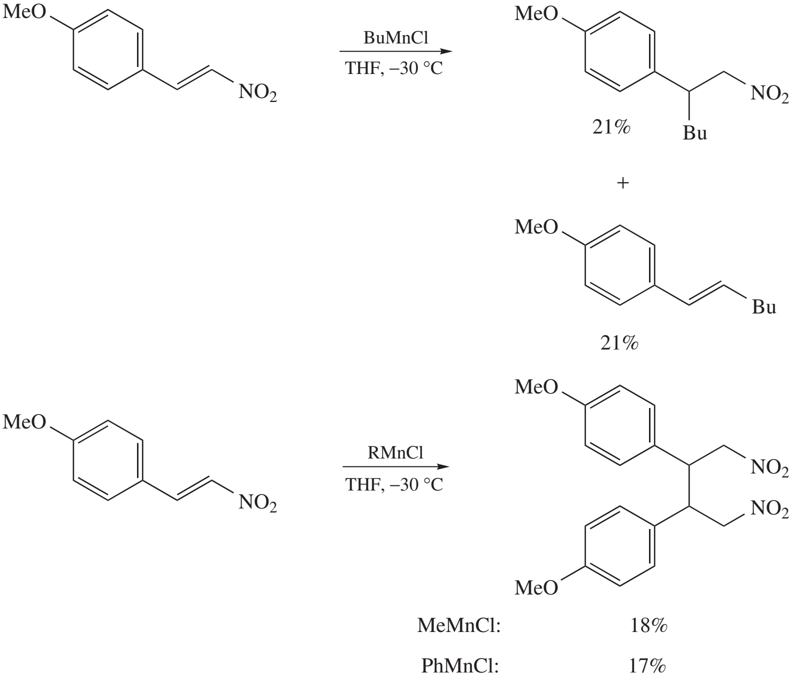
SCHEME 119

in THF at −30 °C, to give the 1,4-adduct in 75% yield (Scheme 120). Only 5% of 1,2-addition product is formed. The addition of copper salts or Me_3SiCl has no significant influence on the course of the reaction.



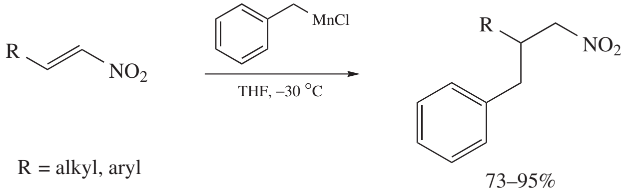
SCHEME 120

Unfortunately, this result cannot be extended to other conjugated nitroolefins. Thus, 4-methoxy-β-nitrostyrene reacts with butylmanganese chloride to give a mixture of 1,4- and 1,2-addition-elimination products and with methyl- and phenylmanganese chlorides to afford the β-reductive dimerization product (Scheme 121). In all cases poor yields are obtained.



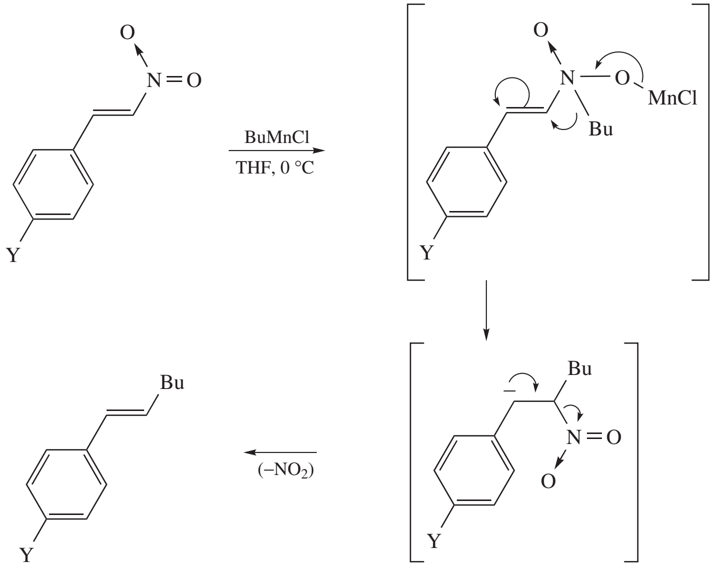
SCHEME 121

Unexpectedly, benzylmanganese chloride gives better results (Scheme 122).



SCHEME 122

In some cases, the reaction of butylmanganese chloride with various β-nitrostyrenes leads to the 1,2-addition-elimination product. Namboothiri and Hassner proposed the following mechanism to explain the formation of this product corresponding formally to the substitution of the nitro group (Scheme 123)[66].



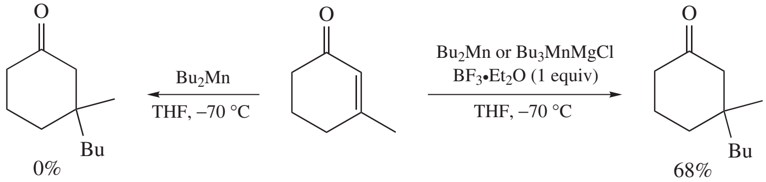
Y = H: 56%; OMe: 40%; Cl: 62%

SCHEME 123

B. Copper-catalyzed 1,4-Addition of Organomanganese Halides to α,β-Ethylenic Ketones

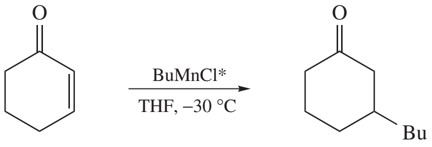
Various attempts to favor the 1,4-addition of organomanganese reagents to conjugated enones by adding a Lewis acid were reported[67]. The only interesting results were obtained with $BF_3 \bullet Et_2O$. Nevertheless, yields never exceeded 65 to 70% (Scheme 124).

On the other hand, a significant improvement was observed when the reaction is performed in the presence of some metal salts[67]. Thus, the conjugate addition of



SCHEME 124

butylmanganese chloride to 2-cyclohexenone, which does not occur in the absence of a catalyst at −30 °C, takes place in the presence of a catalytic amount of $NiCl_2$, $FeCl_3$ or CuCl, to provide satisfactory yields of 3-butylcyclohexanone (Scheme 125). It should be noted that the yield of the reaction is dramatically improved in the presence of copper salts. Moreover, only 0.1% CuCl is necessary to catalyze the reaction efficiently[68].



No catalyst:	0%
2% $NiCl_2$:	68%
5% $FeCl_3$:	79%
5% CuCl:	95%
0.1% CuCl:	93%

* Prepared from BuMgCl

SCHEME 125

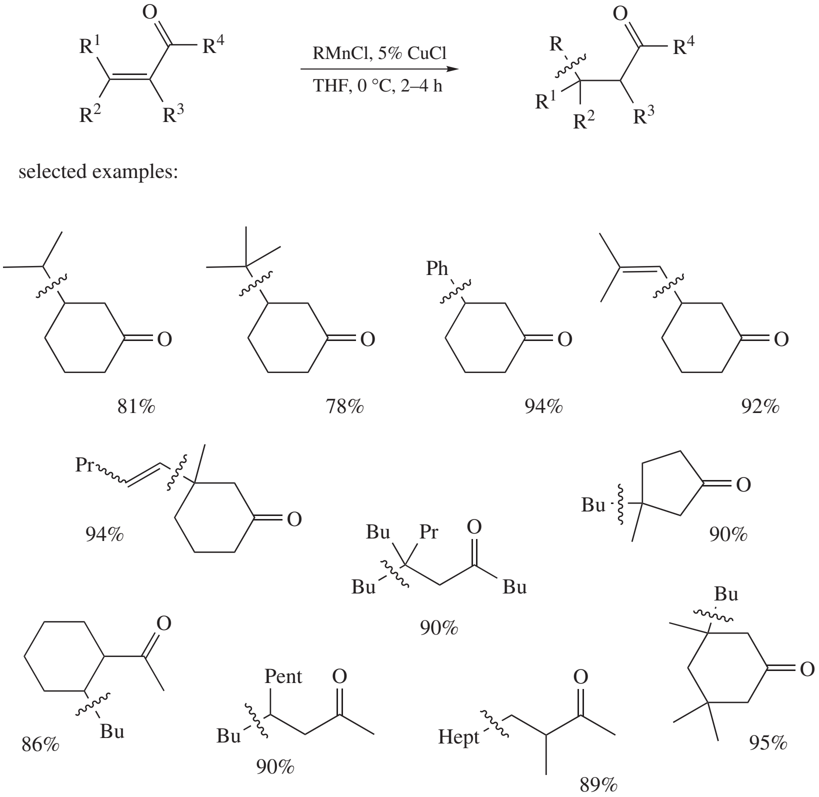
The Cu-mediated 1,4-addition of organometallic reagents to conjugated enones is well-known to be a very efficient procedure[3f, 69]. However, the study of the copper-catalyzed addition of organomanganese reagents to enones showed that the scope of the reaction could be different from the more classical copper-catalyzed procedures.

As a rule, the presence of CuCl (5%) has a dramatic beneficial influence and the reaction takes place under very mild conditions[7]. Excellent yields of 1,4-addition products were obtained from a vast array of cyclic or acyclic conjugated enones (Scheme 126). The scope of the reaction is very large, thus primary, secondary or tertiary alkyl- as well as alkenyl- or arylmanganese chlorides lead to high yields.

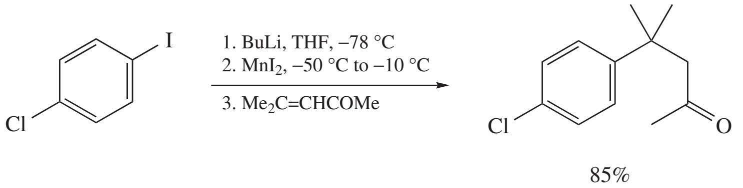
Functionalized organomanganese reagents also add to conjugated enones (Scheme 127)[15].

Interestingly, it was reported that Grignard reagents react efficiently with α-enones to give the conjugate addition product in almost quantitative yields under manganese–copper co-catalysis (Scheme 128)[68, 70]. As a rule, the use of 30% $MnCl_2$ and 1 to 3% CuCl leads to the best results.

This manganese–copper-catalyzed procedure is as efficient, and sometimes more efficient, than the copper-catalyzed conjugate addition of organomanganese compounds



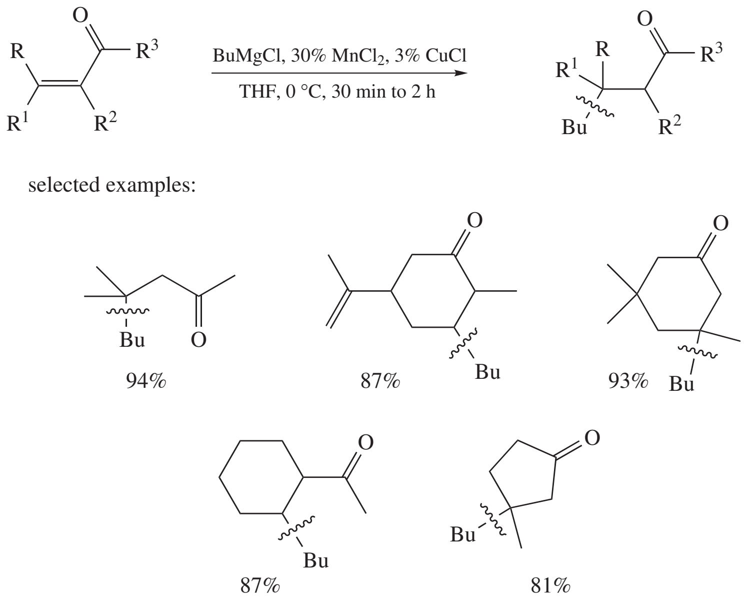
SCHEME 126



SCHEME 127

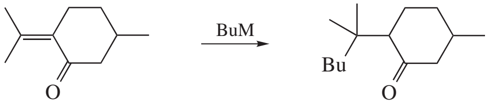
described above. The two manganese-mediated reactions take place under mild conditions.

The difference of efficiency between the manganese-mediated procedures and the classical copper-catalyzed Grignard reagent or cuprate procedures is even greater when the starting conjugated enone is not very reactive, for instance with a β,β-disubstituted enone such as pulegone (Table 19)[70].



SCHEME 128

TABLE 19. Conjugate addition to pulegone: Comparison between various conjugate addition procedures

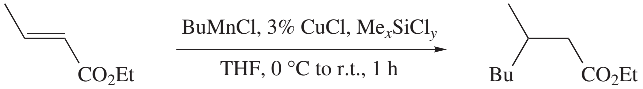


BuM	Reaction conditions	Yield (%)[a]
BuMgCl	30% $MnCl_2$, 3% CuCl, THF, 0 °C, 2 h	94
BuMnCl	3% CuCl, THF, 0 °C, 1 h	95
BuMgCl	5% CuCl, THF, 0 °C	51
BuCu	Ether–Me_2S, −50 °C to −10 °C	43[b]
BuCu	1.1 Me_3SiCl, ether, −10 °C	70[b]
BuCu(CN)Li	Ether, −50 °C to −10 °C	13
0.6 Bu_2CuLi	Ether, −78 °C to −30 °C	33
1.2 Bu_2CuLi	Ether, −50 °C to −10 °C	85[c]
1.2 $Bu_2CuMgCl$	THF, −50 °C to −10 °C	47[c]
2 $Bu_2Cu(CN)Li_2$	Ether, −78 °C, 5 h then 0 °C	69[c,d]

[a] Yield of isolated product. All reactions were performed on a 30 mmol scale.
[b] BuCu from CuBr•Me_2S.
[c] 1,2-Addition partially occurs.
[d] Yield based on the starting enone.

C. Copper-catalyzed 1,4-Addition of Organomanganese Halides to α,β-Ethylenic Esters

Organomanganese reagents easily react with α,β-ethylenic esters in the presence of both CuCl (3%) and Me_3SiCl (1.2 eq.), under mild conditions in THF (0 °C, 1 h), to afford the 1,4-addition product in good yields (Scheme 129)[71]. In the absence of Me_3SiCl, the enolate resulting from the conjugate addition reacts with the starting ester (Claisen condensation). Interestingly, Me_3SiCl can be advantageously replaced by $MeSiCl_3$ which is cheaper. Only 0.5 equivalent of $MeSiCl_3$ is enough to obtain satisfactory results (Scheme 129).

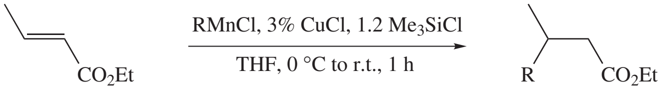


1.2 Me_3SiCl: 95%

0.5 $MeSiCl_3$: 93%

SCHEME 129

Primary, secondary and tertiary alkylmanganese chlorides react with β-monosubstituted conjugated esters to give excellent yields of 1,4-addition product. On the other hand, the less reactive methyl- and phenylmanganese chlorides only lead to moderate yields (Scheme 130).



R = *i*-Pr : 96%

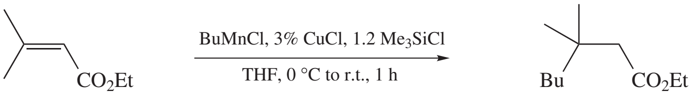
R = *t*-Bu : 75%

R = Ph : 55%

R = Me : 49%

SCHEME 130

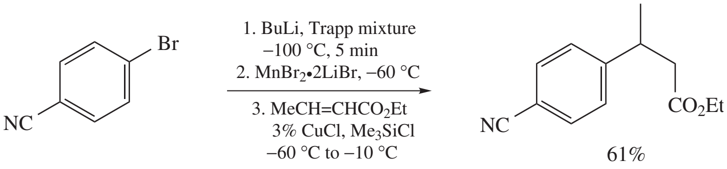
The reaction is very slow with the less reactive β,β-disubstituted esters and the starting ester is partially recovered at the end of the reaction (Scheme 131).



65%
(conversion rate = 66%)

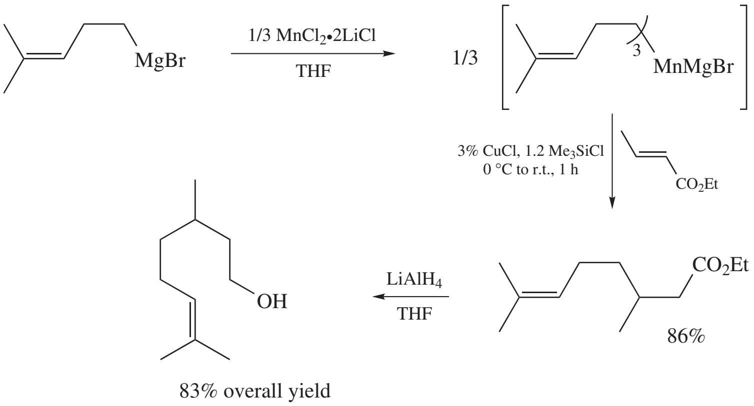
SCHEME 131

Functionalized organomanganese reagents can also be used (Scheme 132)[15].



SCHEME 132

The 1,4-addition of organomanganese reagents to α,β-ethylenic esters is the key step of a short synthesis of citronellol (Scheme 133)[71]. Interestingly, the conjugate addition was performed efficiently with an organomanganate and the three alkyl groups bonded to the manganese atom are transferred.



SCHEME 133

D. Copper-catalyzed 1,4-Addition of Organomanganese Halides to α,β-Ethylenic Aldehydes

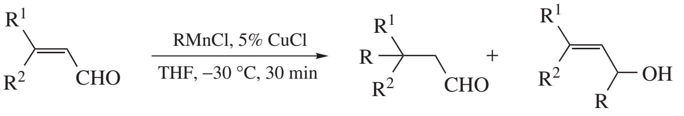
The conjugate addition of organometallic reagents to α,β-ethylenic aldehydes is not easy to perform since the competitive 1,2-addition to aldehyde is a very fast reaction. In the presence of CuCl, organomanganese reagents mainly react with α,β-ethylenic aldehydes to give the 1,4-addition product (Table 20)[72]. Thus, alkyl-, aryl- and alkenylmanganese chlorides add to β-mono- or β,β-disubstituted conjugated enals to give good yields of conjugate addition products.

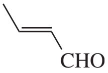
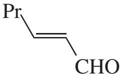
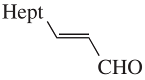
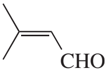
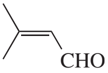
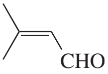
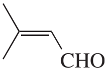
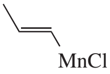
In some particular cases, the yield of 1,4-addition product was improved by performing the reaction in the presence of Me_3SiCl (Scheme 134).

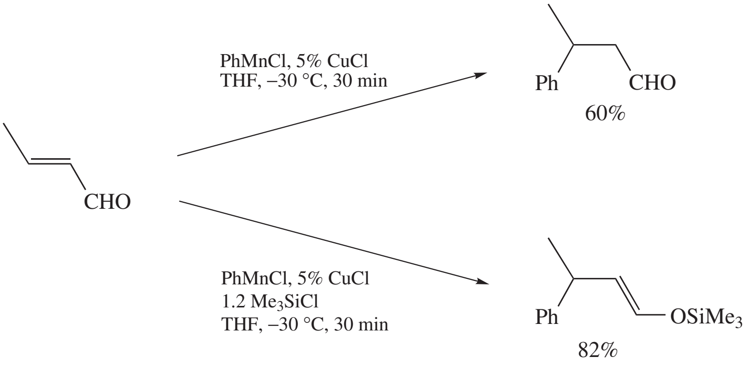
With α,β-disubstituted conjugated enals, the conjugate addition is slower and the 1,2-addition competes seriously (Scheme 135).

Recently, the copper-catalyzed 1,4-addition of BuMnCl to *trans*-cinnamaldehyde was studied by Deshmukh and coworkers[73]. They found that the best result was obtained by

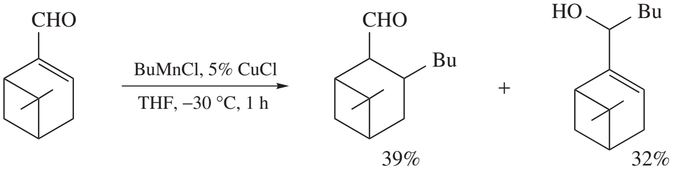
TABLE 20. Cu-catalyzed conjugate addition of organomanganese chloride to α,β-ethylenic aldehydes



α-Enal	RMnCl	1,4-Addition product (%)	1,2-Addition product (%)
	HeptMnCl	72	10
	BuMgCl	72	7
	MeMgCl	80	5
	HeptMnCl	80	7
	MeMnCl	83	3
	PhMnCl	76	6
		49	20

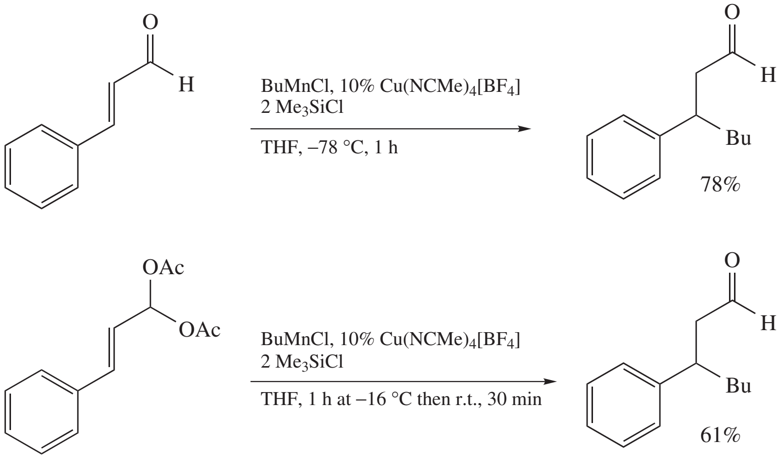


SCHEME 134



SCHEME 135

using the complex $Cu(NCMe)_4[BF_4]$ in the presence of two equivalents of Me_3SiCl. Unfortunately, this procedure always gives a mixture of 1,2- and 1,4-addition products. The acylal derived from cinnamaldehyde can also be employed (Scheme 136).



SCHEME 136

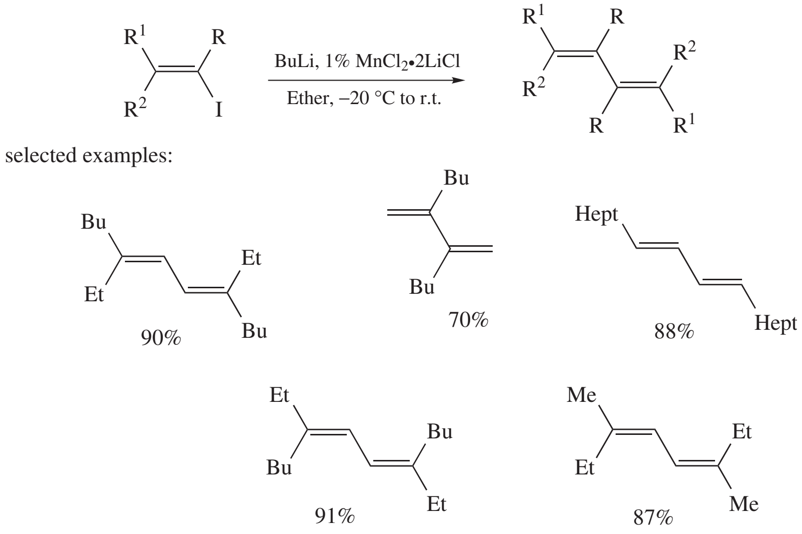
VI. HOMOCOUPLING AND HETEROCOUPLING REACTIONS

A. Manganese-catalyzed Homocoupling Reactions

The homocoupling of organometallic compounds is generally performed by using an oxidant in the presence of a catalyst[2,74].

With manganese, the first homocoupling reaction was published in 1976. This report shows that various conjugated dienes are stereospecifically obtained in excellent yields by treating alkenyl iodides with butyllithium in the presence of $MnCl_2$ in ether (Scheme 137)[11].

The mechanism of the reaction was studied (Figure 2). The reaction proceeds via an alkenyl lithium **1** formed by iodine–lithium exchange from the starting alkenyl iodide. The transmetallation of the alkenyllithium **1** with $MnCl_2$ gives the trialkenylmanganate **2**. Butyl iodide then reacts with **2** to lead to the unstable Mn^{IV} derivative **3**, which decomposes rapidly by β-hydrogen-elimination to afford a mixture of butane/butene and the putative intermediate **4**. The latter then undergoes a reductive elimination to afford



SCHEME 137

the diene **5** and the dialkenylmanganese **6**. The trialkenylmanganate **2** is then regenerated from **6**. It is important to note that almost all steps of this mechanism were reproduced by using stoichiometric amounts of organomanganese reagent[11].

The homocoupling of aryl, alkenyl and alkynyl Grignard reagents is very efficiently performed under manganese catalysis by using atmospheric oxygen as an oxidant under mild conditions. The reaction is highly chemo- and stereoselective (Table 21)[75] and various biaryls, 1,3-dienes and 1,3-diynes were obtained in good yields. In contrast, all attempts to couple alkylmagnesium halides meet with failure. It should be noted that the use of atmospheric oxygen is very interesting both from an economical and environmental point of view.

A catalytic cycle was proposed (Figure 3). At first, a stable symmetrical organomanganese(II) **7** is formed by transmetallation from the Grignard reagent. Oxidative addition of oxygen then leads to the manganese(IV) peroxo complex **8**. The latter undergoes a rapid reductive elimination that gives the homocoupling product **9**. On the other hand, the putative $\mathrm{Mn^{II}}$ peroxo complex **10** finally reacts with the Grignard reagent to regenerate the symmetrical organomanganese **7**.

N-Methylcrinasiadine, a natural product extracted from *Lapiedra martinezzi*, was successfully synthesized according to this procedure (Scheme 138)[75]. The 2,2′-diiodo-*N*-methyl-4,5-methylenedioxybenzanilide was treated with *i*-PrMgCl to prepare the corresponding di-Grignard reagent via an iodine–magnesium exchange. The cyclization was then achieved under the coupling conditions previously reported and the *N*-methylcrinasiadine was obtained in 46% global yield.

Aryl-, alkenyl- and alkynyltributylstannanes can also be homocoupled under manganese catalysis, in DMF or NMP at 100 °C, by using iodine as an oxidant[76]. The three butyl groups do not react and various biaryls, 1,3-dienes or 1,3-diynes were obtained in good to excellent yields (Scheme 139).

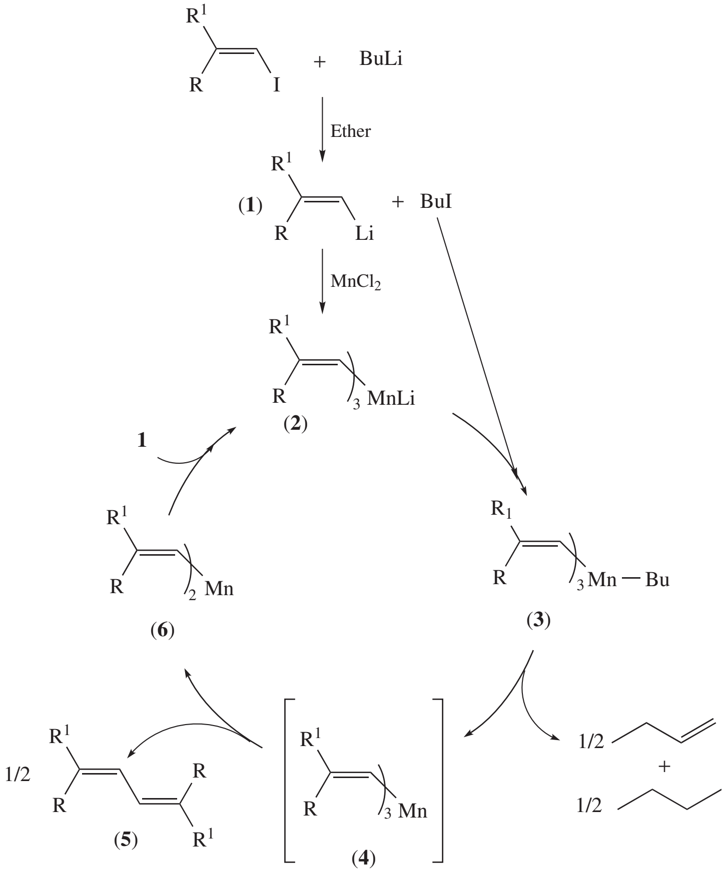


FIGURE 2

B. Manganese-catalyzed Cross-coupling Reactions

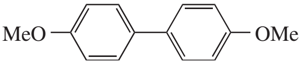
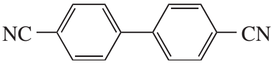
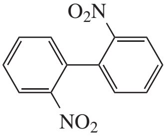
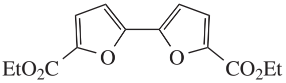
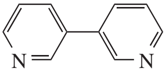
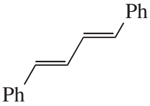
It is very interesting to use manganese salts as catalysts to replace palladium or nickel complexes since they are cheap and more eco-friendly[74]. In spite of these considerable advantages, the development of manganese-catalyzed cross-coupling reactions is still in its infancy.

A manganese-catalyzed coupling of aryl or styryl iodides with aryl-, alkenyl- or alkynylstannanes was described (Scheme 140)[77]. The reaction was performed in the presence of manganese bromide in NMP at 100 °C. It is essential to add one equivalent of sodium chloride to obtain the cross-coupling product in satisfying yields instead of the homocoupling product.

Activated aryl halides and aryl ethers couple under mild conditions with Grignard reagents in the presence of manganese chloride (Table 22)[78]. The reaction gives good yields with aryl halides (Z = Cl, Br or F) or aryl ethers (Z = OMe) bearing an electron-withdrawing group in the *ortho*- (nitrile, imine or oxazoline) or in the *para*-position (imine). It should be noted that the *meta*-substituted aromatic halides do not react.

TABLE 21. Mn-catalyzed homocoupling of RMgX by using atmospheric oxygen as an oxidant

$$2\ \mathrm{RMgX} \xrightarrow[\text{THF, r.t., 45 min}]{\text{Dry air, 5\% MnCl}_2\bullet\text{2LiCl}} \mathrm{R-R}$$

R– R	Yield (%)
	95
	78
	75
	88
	80
	90
	89
	85

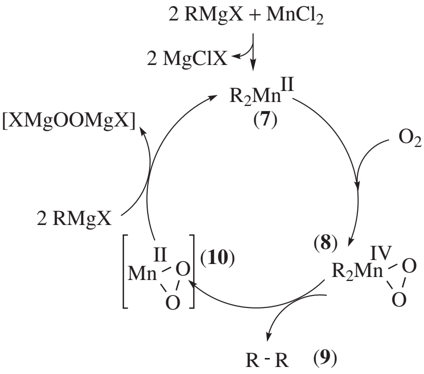
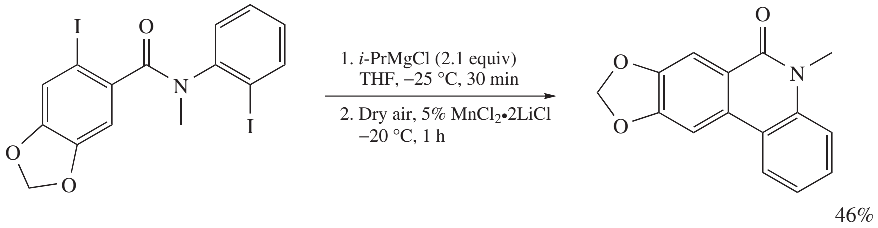


FIGURE 3



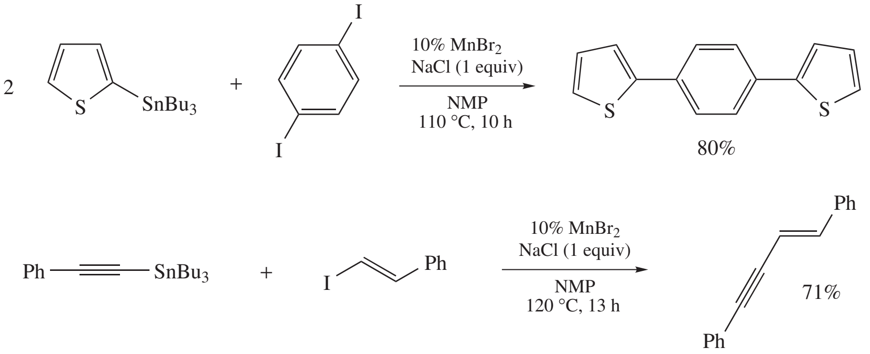
SCHEME 138

$$2\ RSnBu_3 \xrightarrow[\text{NMP, 100 °C}]{\text{10\% MnBr}_2\text{, I}_2\text{ (0.5 equiv)}} R-R$$

70–90%

R = aryl, heteroaryl, alkenyl, alkynyl

SCHEME 139



SCHEME 140

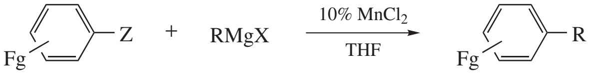
This procedure is more efficient than a nucleophilic aromatic substitution (Table 23). The manganese-catalyzed reaction is faster (Z = OMe, F), its scope is larger (X = Cl, Br), and it leads to higher yields whatever the nature of the leaving group.

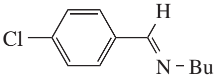
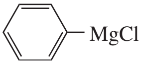
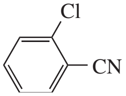
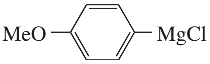
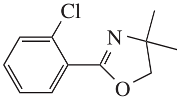
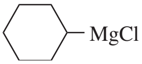
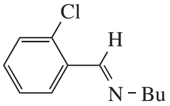
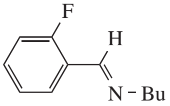
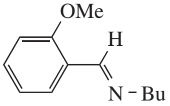
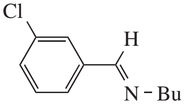
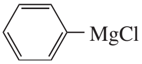
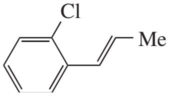
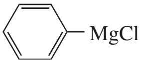
From the chloro fluoro imine depicted in Scheme 141, the manganese-catalyzed reaction mainly gives the disubstituted product. However, when a sequence nucleophilic aromatic substitution/manganese-catalyzed procedure is used, it is possible to introduce selectively two different organic groups (Scheme 141)[78].

2-Chloroaryl ketones readily couple with aryl Grignard reagents in the presence of manganese chloride to afford the corresponding *ortho*-substituted aryl ketones in good yields (Scheme 142)[79].

It is interesting to note that the 1,2-addition to the carbonyl group is never observed. However, with a more reactive Grignard reagent such as butylmagnesium chloride the 1,2-addition product is formed in large amounts (50–60%). Interestingly, it is possible

TABLE 22. Mn-catalyzed cross-coupling reaction of RMgX with activated aryl halides or ethers



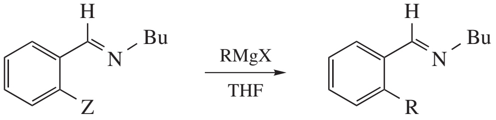
ArZ	RMgX	Reaction conditions	Yield (%)
		0 °C, 6 h	93
		0 °C, 2 h	85
		r.t., 2 h	64
	BuMgCl	0 °C, 30 min	93
	BuMgCl	0 °C, 2 h	90
	BuMgCl	r.t., 20 min	91
		r.t., 24 h	0
		r.t., 24 h	0

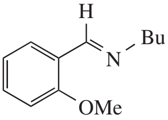
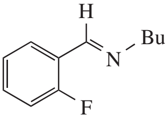
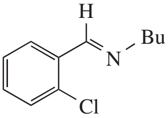
to perform a chemoselective coupling reaction by using an organomanganese compound (see Section VI.G, Table 29)[79].

This manganese-catalyzed coupling reaction is used, on a ton scale, for the industrial preparation of 2-cyano-4′-methylbiphenyl (Scheme 143), an important intermediate for the preparation of Irbesartan®[80].

This procedure was extended to 2- and 3-chloroquinolines and to related heterocyclic chlorides (Scheme 144)[81]. Coupling products were obtained in moderate to good yields (40–74%), under mild conditions, with primary and secondary alkyl or aryl Grignard reagents.

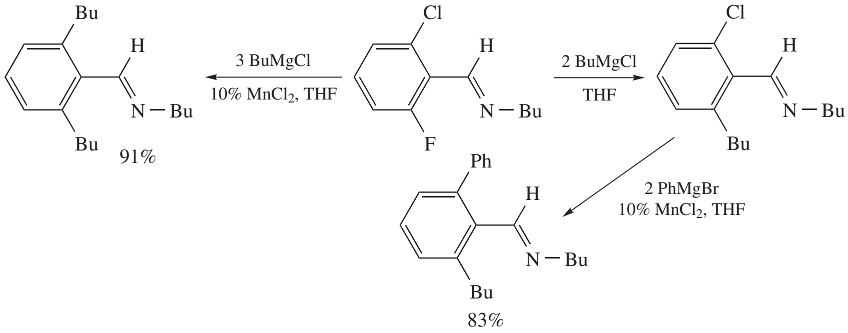
TABLE 23. S_NAr *versus* Mn-catalyzed substitution of 2-chloro-, 2-fluoro- and 2-methoxybenzaldimines by RMgX



ArZ	RMgX	Reaction conditions	Yield (%)[a]
	BuMgCl	10% $MnCl_2$ r.t., 20 min	91
	BuMgCl	r.t., 24 h	75
	BuMgCl	10% $MnCl_2$ 0 °C, 2 h	90
	BuMgCl	r.t., 24 h	40
	PhMgBr	10% $MnCl_2$ r.t., 2 h	88[b]
	PhMgBr	r.t., 24 h	0

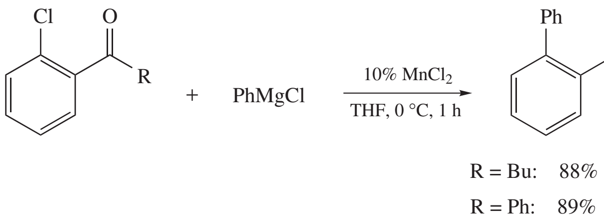
[a] Quantitative yields of crude imine were obtained. The yield of isolated product is based on the corresponding aldehyde obtained after chromatography on silica gel.

[b] 2-Bromo benzaldimine gives a similar yield.

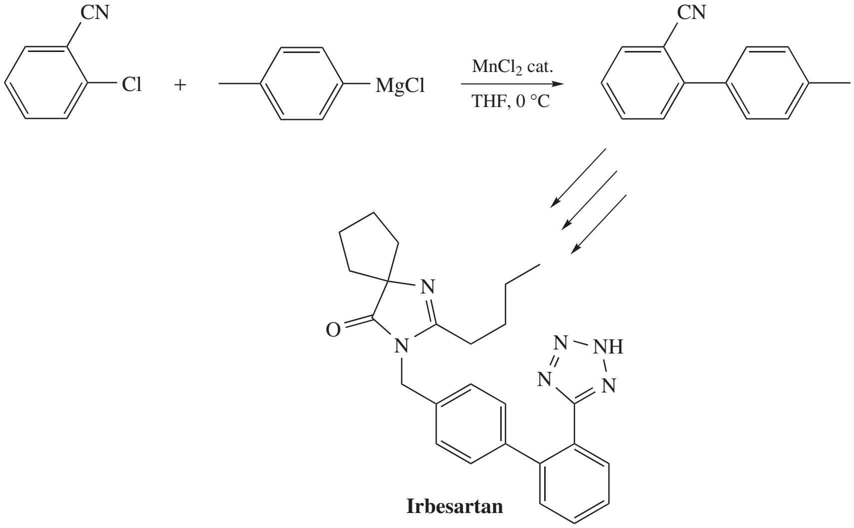


SCHEME 141

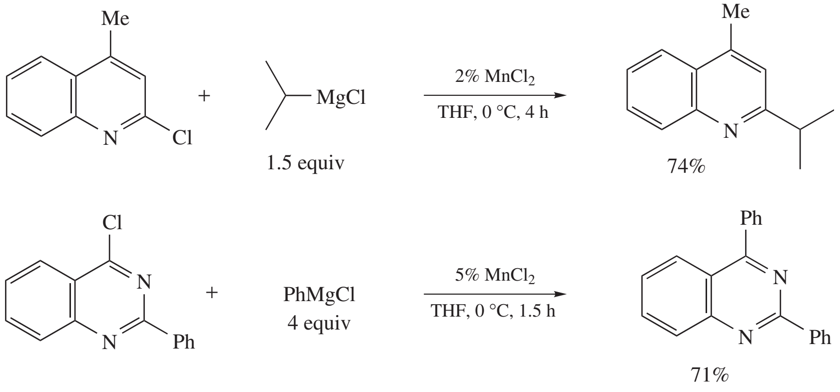
Recently, Yuan and coworkers described a $MnCl_2$-catalyzed tandem acylation/cross-coupling reaction from *o*-halobenzoyl chlorides and diorganomagnesium compounds. Primary and secondary alkyl or aryl Grignard reagents readily react to afford the coupling products in moderate to excellent yields (53–96%). However, this procedure is limited



SCHEME 142

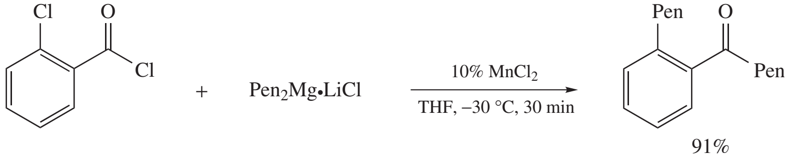


SCHEME 143



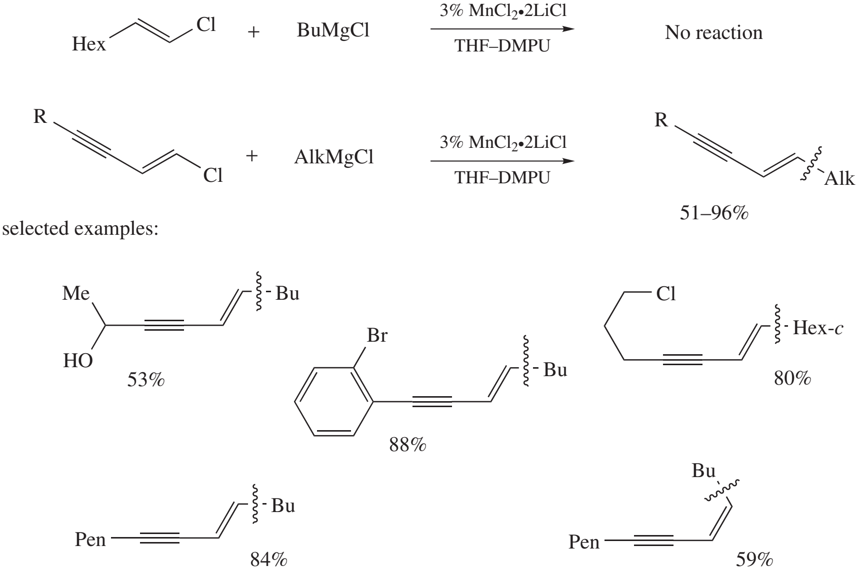
SCHEME 144

since it is only possible to transfer twice the same R group (Scheme 145)[82]. It should be noted that a more versatile procedure introducing two different R groups was described (see Scheme 188)[79].



SCHEME 145

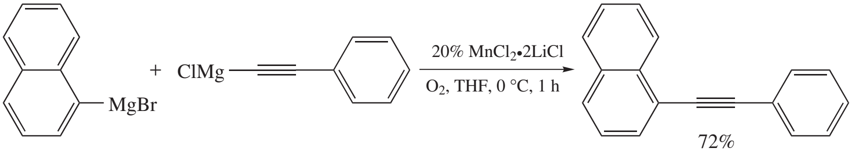
Chloroenynes and chlorodienes easily react with alkylmagnesium reagents under manganese catalysis in the presence of DMPU as a cosolvent (Scheme 146)[83]. The reaction is stereoselective.



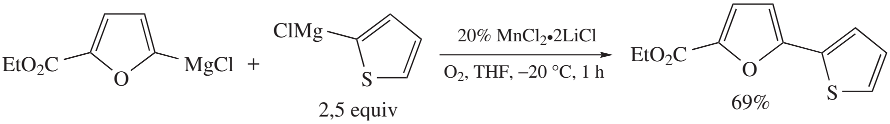
SCHEME 146

On the other hand, the manganese-catalyzed oxidative heterocoupling reaction between two different Grignard reagents was recently reported. When the two organic groups coming from the Grignard reagents are different enough (steric and electronic parameters), the heterocoupling product is obtained predominantly at the expense of the two homocoupling products. Various functionalized aryl acetylenes were prepared in good yields (Scheme 147)[84].

Nevertheless, in most cases, the use of an excess of one of the Grignard reagents is necessary to obtain satisfactory yields. The procedure was used to synthesize chemoselectively various biaryls in moderate to good yields (Scheme 148).

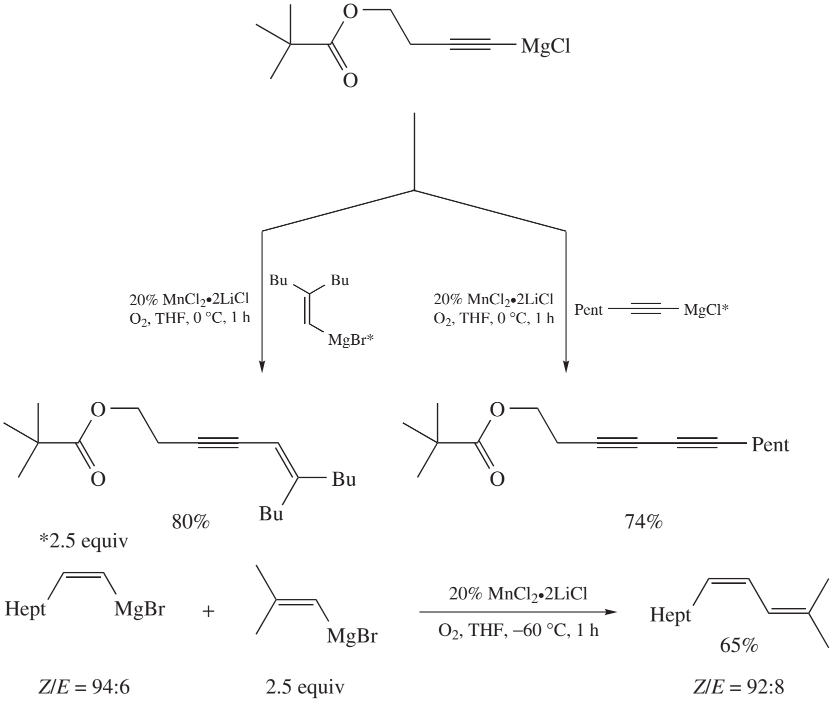


SCHEME 147



SCHEME 148

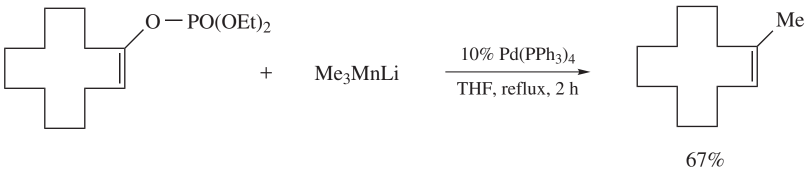
The reaction was extended to alkynyl–alkynyl, alkenyl–alkynyl and alkenyl–alkenyl coupling. Good yields were obtained and the reaction is highly stereoselective (Scheme 149).



SCHEME 149

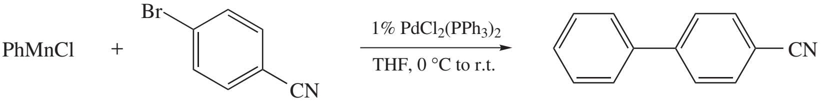
C. Palladium-catalyzed Coupling Reactions between Organomanganese Reagents and Organic Halides

Pd-catalyzed cross-coupling reactions were performed with a large variety of organometallic compounds (Mg, Sn, Zn, Cu, B, etc.)[74]. Organomanganese reagents can also be used. Thus, under palladium catalysis, enol phosphates react with alkyl- or arylmanganese halides, in THF under reflux, to provide the substitution product in moderate to excellent yields[85]. Nevertheless, two equivalents of organomanganate (6 equivalents of the starting RMgX or RLi) are used (Scheme 150).



SCHEME 150

The first palladium-catalyzed cross-coupling between aryl halides and organomanganese reagents was reported in 1997[86]. As an example, phenylmanganese chloride reacts with *p*-bromobenzonitrile under very mild conditions in the presence of only 1% $PdCl_2(PPh_3)_2$ to afford 4-phenylbenzonitrile in 79% yield. Interestingly, the use of DME as cosolvent allows a faster reaction in better yields (Scheme 151).



With DME (4 equiv), 15 min: 98%
Without DME, 2 h: 79%

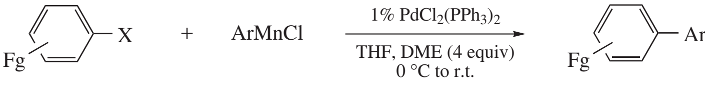
SCHEME 151

A vast array of functionalized unsymmetrical biaryls were prepared in excellent yields from aryl iodides as well as activated aryl bromides and triflates bearing an electron-withdrawing group (Table 24).

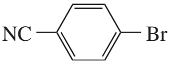
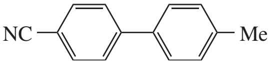
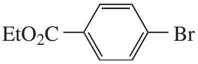
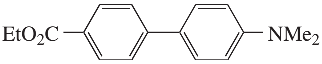
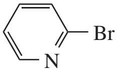
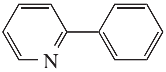
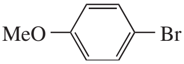
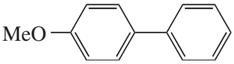
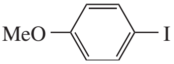
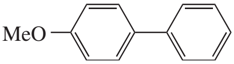
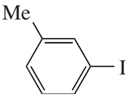
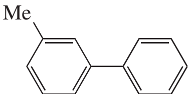
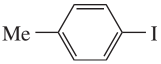
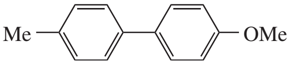
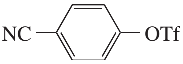
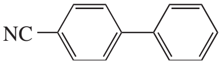
Unfortunately, with deactivated aryl bromides or triflates bearing an electron-donating group or with *ortho*-substituted aryl bromides, the procedure described above is less efficient. However, the use of $PdCl_2$(dppp) as a catalyst allows one to obtain satisfactory results (Scheme 152)[87]. Various functionalized biaryl compounds, including some challenging *o*,*o*′-disubstituted biaryls, were thus obtained in excellent yields.

Interestingly, this procedure was successfully extended to alkyl-, benzyl-, alkenyl- and alkynylmanganese chlorides. With alkylmanganese chlorides such as OctMnCl or *c*-HexMnCl, it is better to prevent the β-hydrogen elimination by using $PdCl_2$(dppf) instead of $PdCl_2$(dppp) as a catalyst (Table 25)[87].

TABLE 24. Pd-catalyzed cross-coupling reaction of aryl halides with ArMnCl



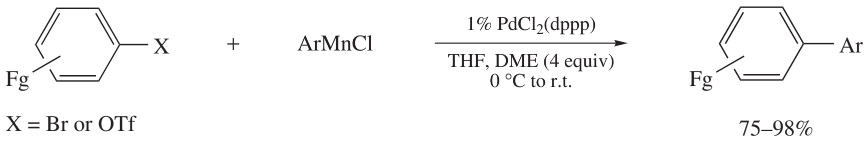
X = I, Br or OTf

Fg-ArX	Product	Yield (%)
		91
		91
		96
		42
		91
		93
		93
		98

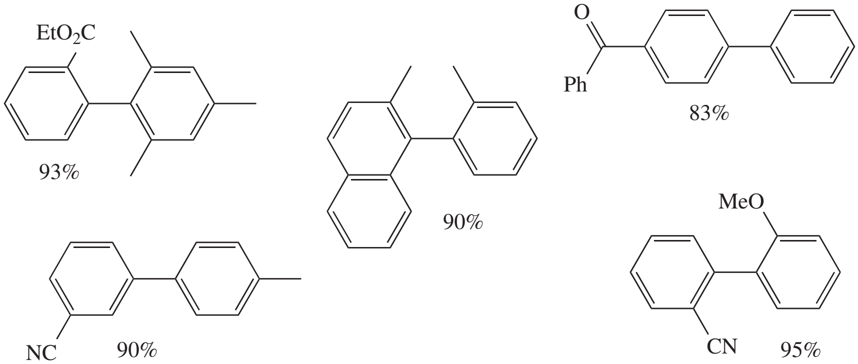
D. Nickel-catalyzed Coupling Reactions between Organomanganese Reagents and Organic Halides

Nickel complexes are well known to be powerful catalysts for the cross-coupling reactions between aryl halides and organometallic reagents[74]. Arylmanganese reagents couple with aromatic halides in the presence of nickel carbene complexes[88]. The best catalytic system was obtained by using 10% N,N'-bis(2,6-diisopropylphenyl)imidazolium chloride (**IPrHCl**) associated with 5% Ni(acac)$_2$. Simple and functionalized arylmanganese chlorides react under very mild conditions with aryl iodides, bromides and also triflates to afford the corresponding biaryls in high yields (Scheme 153).

Numerous functionalized electron-rich and electron-deficient aryl bromides were used successfully. However, electron-deficient arylmanganese chlorides lead to poor results (Scheme 154).

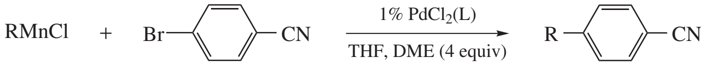


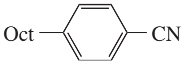
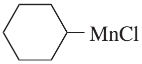
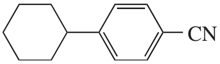
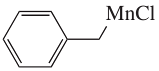
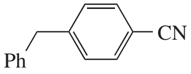
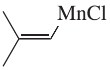
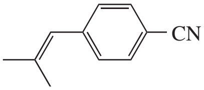
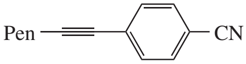
selected examples:



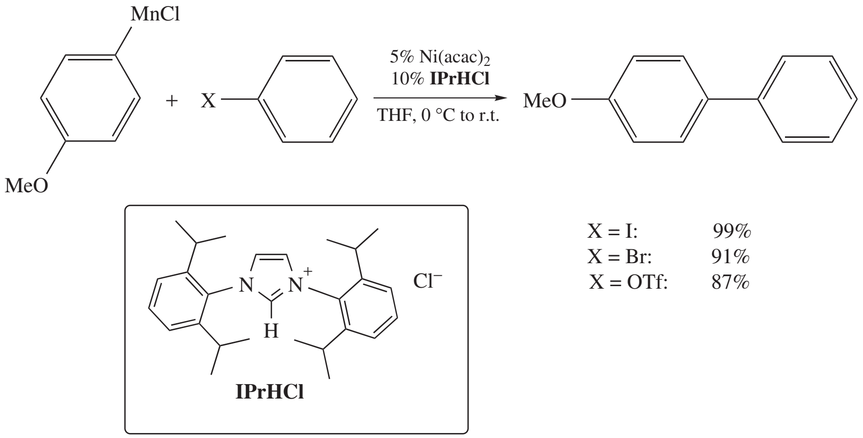
SCHEME 152

TABLE 25. Pd-catalyzed cross-coupling reaction from various RMnCl

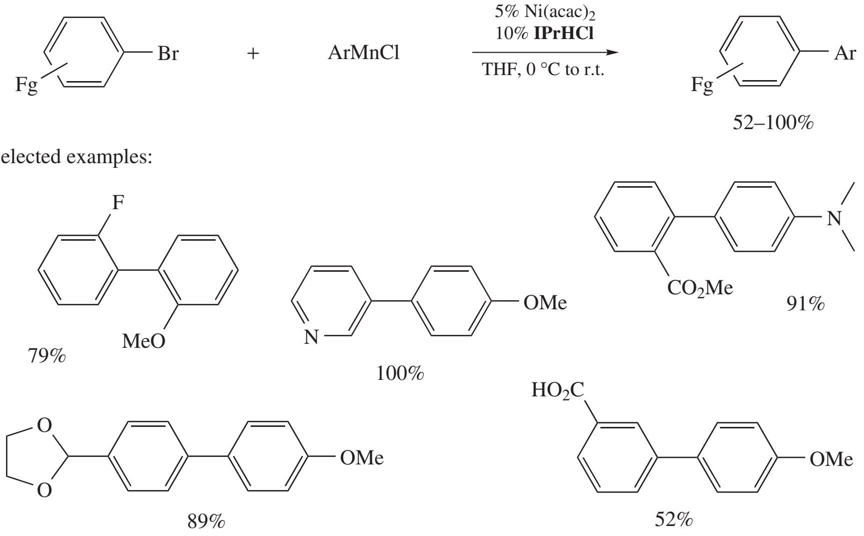


RMnCl	Product	Time (h)	Yield (%)
OctMnCl		0.3	91[a]
		0.5	93[a]
		1	91[b]
		0.6	92[b]
Pen—≡—MnCl		24	91[b]

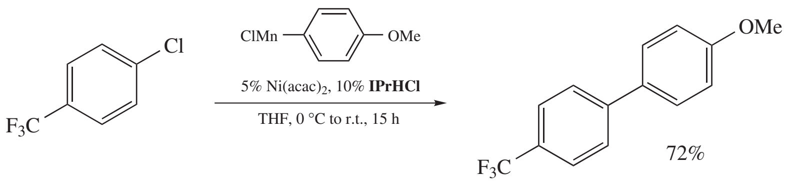
[a] $PdCl_2$(dppf).
[b] $PdCl_2$(dppp).



SCHEME 153



SCHEME 154

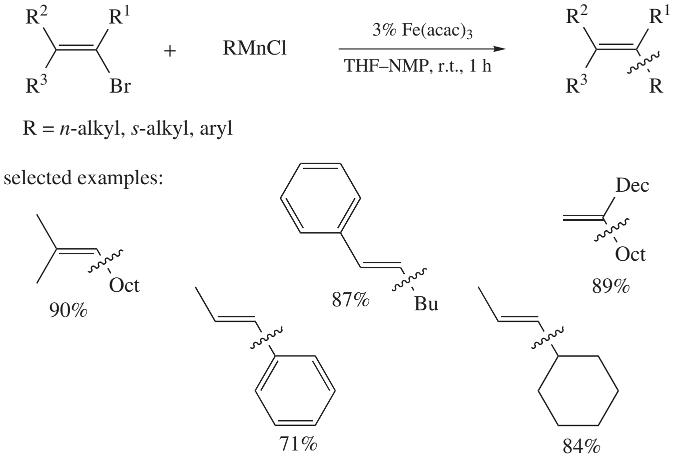


SCHEME 155

Finally, it is even possible to couple various electron-deficient aryl chlorides in spite of their low reactivity. On the other hand, electron-rich aryl chlorides cannot be employed satisfactorily (Scheme 155).

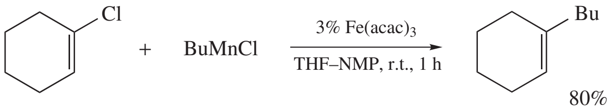
E. Iron-catalyzed Coupling Reactions between Organomanganese Reagents and Organic Halides

The iron-catalyzed alkenylation of organomanganese reagents was reported in 1996. The reaction takes place under very mild conditions and leads to good to excellent yields (Scheme 156)[89, 90].



SCHEME 156

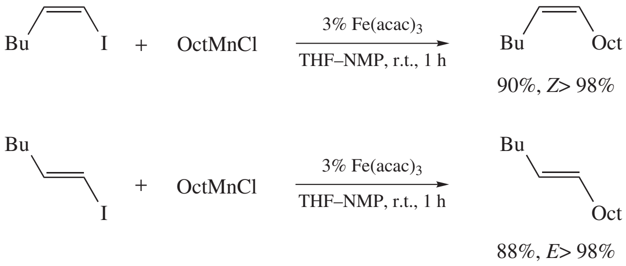
The best results are obtained by using 3% $Fe(acac)_3$ and NMP as a cosolvent. $Fe(acac)_3$ is a very convenient catalyst since it is cheap and non-hygroscopic. Good yields are obtained by coupling various aryl- and primary or secondary alkylmanganese chlorides with alkenyl iodides, bromides and even chlorides (Scheme 157). Let us recall that alkenyl chlorides are generally not reactive enough to be used in cross-coupling reactions.



SCHEME 157

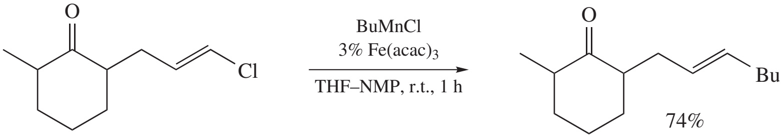
It should be noted that tertiary alkyl- as well as alkenylmanganese chlorides only lead to moderate yields.

The reaction is highly stereoselective ($\geq$ 98%, Scheme 158).



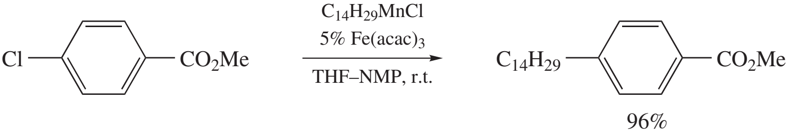
SCHEME 158

In addition, it is also very chemoselective. For instance, even a keto group is tolerated (Scheme 159)[89, 90].



SCHEME 159

The reaction conditions described above were applied a few years later to the coupling of alkylmanganese compounds with activated aryl chlorides[91]. Thus, methyl 4-chlorobenzoate couples with tetradecylmanganese chloride and with ditetradecylmanganese as well as the corresponding magnesium manganate, to give the substitution product in excellent yields (Scheme 160).



SCHEME 160

F. Copper-catalyzed Coupling Reactions between Organomanganese Reagents and Organic Halides

The copper-catalyzed coupling of organomanganese chlorides with alkyl bromides was reported in 1993. Excellent yields are obtained provided that the reaction is performed in the presence of a polar cosolvent such as DMF, DMSO or NMP (Scheme 161)[90, 92].

Alkyl iodides or sulfonates also lead to excellent yields (Scheme 162) whereas the less reactive alkyl chlorides afford poor yields.

The procedure was successfully extended to alkenyl- as well as primary, secondary and tertiary alkylmanganese chlorides (Scheme 163).

Surprisingly, the presence of NMP has a detrimental influence in the case of arylmanganese chlorides and better results were obtained by working in THF alone (Scheme 164).

$$C_4H_9MnCl + C_9H_{19}Br \longrightarrow C_{13}H_{28}$$

3% $CuCl_2$•2LiCl, THF, r.t., 1 h: 25%
3% $CuCl_2$•2LiCl, THF–NMP, r.t., 1 h: 93%

SCHEME 161

$$C_4H_9MnCl + C_{12}H_{25}X \xrightarrow[\text{THF–NMP, r.t.}]{3\%\ CuCl_2\bullet 2LiCl} C_{16}H_{34}$$

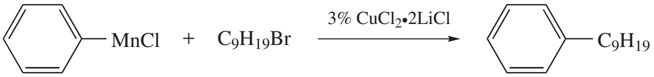
X = Br: 91%; I: 90%; OSO_2Ph: 76%; Cl: 7%

SCHEME 162

$$RMnCl + C_9H_{19}Br \xrightarrow[\text{THF–NMP, r.t., 1 h}]{3\%\ CuCl_2\bullet 2LiCl} R\text{-}C_9H_{19}$$

R= Bu: 93%; *i*-Pr: 79%; *t*-Bu: 86%; $Me_2C{=}CH$: 66%

SCHEME 163



THF–NMP, 40 °C: 40%
THF, r.t.: 86%

SCHEME 164

The reaction is highly chemoselective, thus alkyl bromides bearing an ester, a ketone or a sulfonate group react selectively (Scheme 165)[90, 92].

Bromoalkanols or bromoalkanoic acids were used. Of course, the hydroxy or the carboxylic acid groups are metalated by the organomanganese compound (two equivalents of RMnX are required) (Scheme 166).

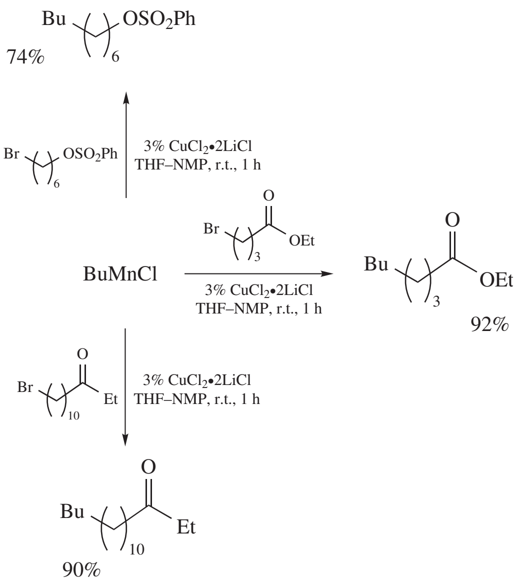
It is well known that, with alkyl bromides such as 1,2-dibromoalkanes or 1-bromo-2-acyloxyalkanes, the elimination of the leaving group in the β-position is very often observed as a competitive or even as the sole reaction. Interestingly, excellent yields of alkylated product were obtained from various β-acyloxy alkyl bromides by using an organomanganese chloride in the presence of copper chloride (Scheme 167)[90, 92].

1-Bromo-2-chloroethane leads to the substitution product in only 38% yield. However, it is important to note that only the elimination occurs when the other copper-mediated procedures are used (Scheme 168).

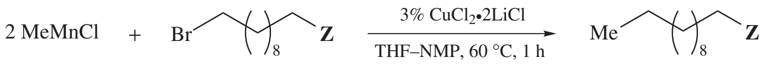
A mixture of manganese complex **A** (10%) and CuCl (5%) was used as a catalyst to couple Grignard reagents with alkyl bromides[93]. This manganese–copper-catalyzed procedure is very chemoselective and leads to excellent yields (Scheme 169).

Even secondary alkyl bromides lead to excellent results (Scheme 170)[93b].

Copper-catalyzed opening of epoxides by organomanganese reagents was also reported[92]. Secondary alcohols are obtained in good yields from monosubstituted epoxides. 1,2-Disubstituted epoxides also react but they only lead to moderate yields (Scheme 171).

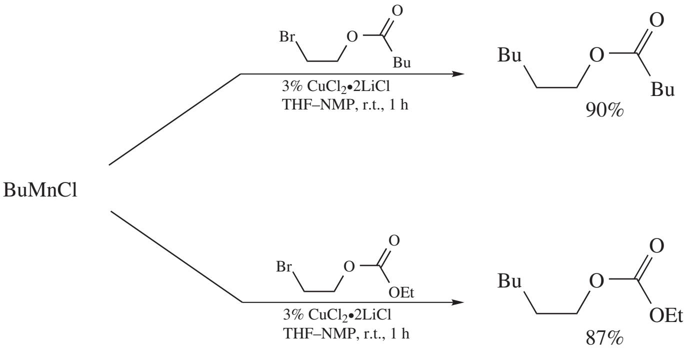


SCHEME 165

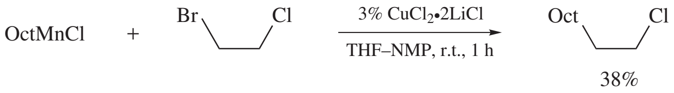


Z = OH: 94%; CO_2H: 99%

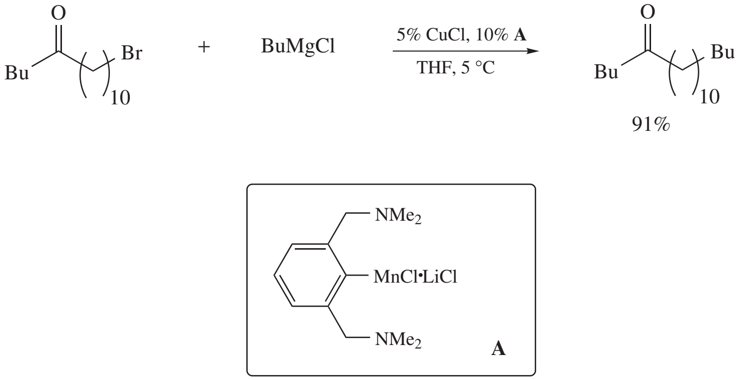
SCHEME 166



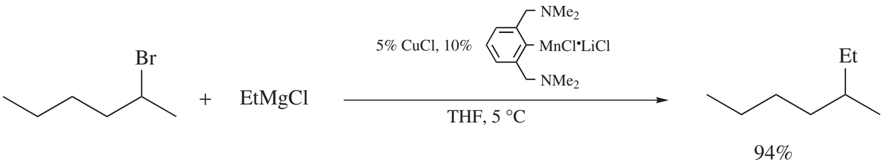
SCHEME 167



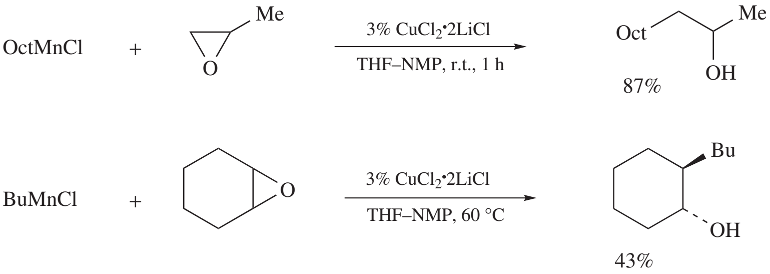
SCHEME 168



SCHEME 169



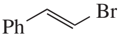
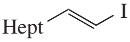
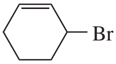
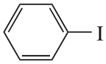
SCHEME 170



SCHEME 171

TABLE 26. Reaction of Me_3MnLi and Bu_3MnLi with various organic halides

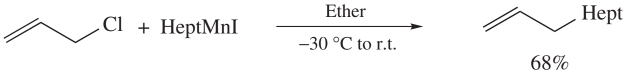
$$\underset{\text{5 equiv}}{R_3MnLi} + R^1X \xrightarrow[T\,^{\circ}C]{\text{Ether}} R{-}R^1$$

Halide	R_3MnLi	Reaction conditions	Yield (%)
	Me_3MnLi	0 °C, 46 h	82
	Bu_3MnLi	0 °C, 1 h	65
	Me_3MnLi	0 °C, 1 h	82
	Bu_3MnLi	−78 °C, 2 h	30
	Me_3MnLi	−20 °C, 1 h	75
	Bu_3MnLi	−20 °C, 1 h	10
	Me_3MnLi	0 °C, 48 h	50
	Bu_3MnLi	0 °C, 48 h	30
DecI	Me_3MnLi	0 °C, 21 h	55
	Bu_3MnLi	0 °C, 20 h	0

G. Reaction of Organomanganese Compounds with Organic Halides

The first reactions between lithium organomanganates and various organic halides were reported by Corey and Posner in 1970 (Table 26)[94c]. Good yields are obtained by coupling lithium trimethylmanganate with vinylic or allylic halides (X = Br, I). On the other hand, the reaction is clearly less efficient with aryl and primary alkyl iodides or when lithium tributylmanganate is employed in place of the trimethyl analogue. In all cases, a large excess of organometallic is required (15 equivalents of BuLi or MeLi).

Allylic halides also react with organomanganese halides to give satisfactory yields (Scheme 172)[90].



SCHEME 172

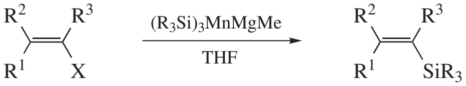
Trisilylmanganates $(R_3Si)_3MnMgMe$ react with alkenyl halides and sulfides at 0 °C to provide the corresponding vinylsilanes in good to excellent yields (Table 27)[16g, 95]. The reaction is stereoselective but it is sometimes necessary to operate at lower temperature to improve the stereoselectivity.

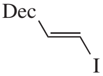
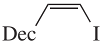
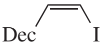
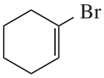
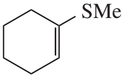
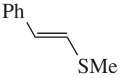
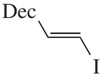
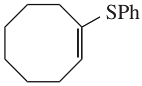
The procedure was extended to enol phosphates and triflates (Scheme 173)[16g].

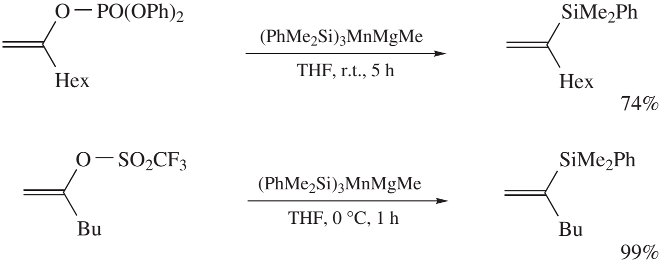
The reaction of enol triflates with magnesium triarylmanganates affords good yields of substituted styrenes (Scheme 174)[85]. Manganese-catalyzed cross-coupling with aryl, allyl or benzyl Grignard reagents was also described (Scheme 174).

Trisilylmanganates $(R_3Si)_3MnMgMe$ or silyl Grignard reagent $PhMe_2SiMgMe$ in the presence of manganese chloride react smoothly with allylic sulfides or ethers (Scheme 175)[16g, 95a]. The S_N2 product is formed selectively in good yields.

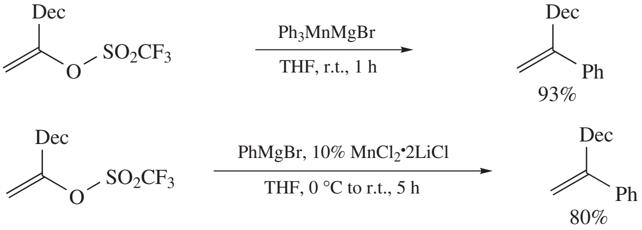
TABLE 27. Cross-coupling between $(R_3Si)_3MnMgMe$ and alkenyl halides or sulfides



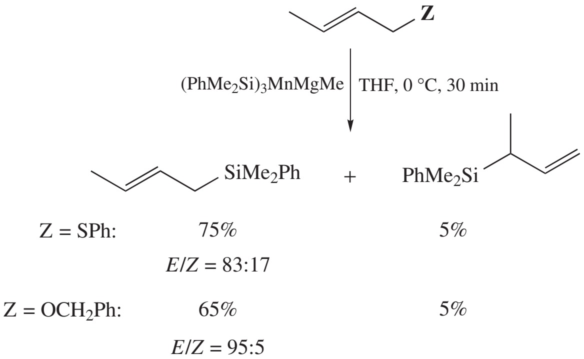
Alkenyl halide	R_3Si from $(R_3Si)_3MnMgMe$	Reaction conditions	Yield (%)	Ratio E/Z
	$PhMe_2Si$	0 °C, 30 min	72	100:0
	$PhMe_2Si$	0 °C, 30 min	73	20:80
	$PhMe_2Si$	−95 °C, 1.3 h	40	0:100
	$PhMe_2Si$	0 °C, 2 h	93	-
	$PhMe_2Si$	0 °C, 1 h	75	-
	$PhMe_2Si$	0 °C, 1 h	70	100:0
	Me_3Si	−95 °C, 2 h	100	30:70
	Me_3Si	0 °C, 3 h	89	-



SCHEME 173

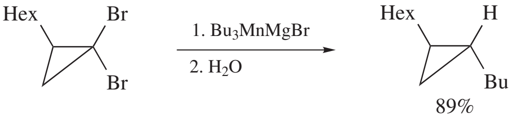


SCHEME 174



SCHEME 175

Oshima and coworkers reported that *gem*-dibromocyclopropanes react with organomanganates to afford, after hydrolysis, the debromomonoalkylated product (Scheme 176)[16h, 96].



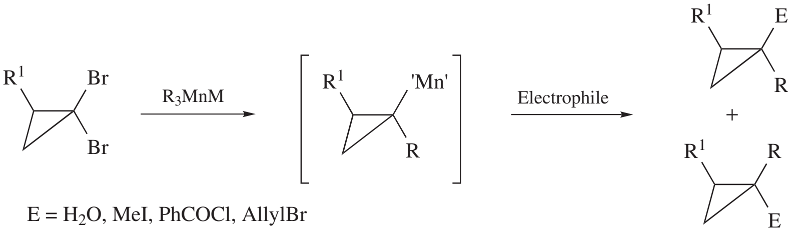
SCHEME 176

The intermediate organometallic species (Scheme 177) can be trapped with an electrophile to give a trisubstituted cyclopropane (diastereoisomeric mixture) in moderate to good yields (50–90%).

Only primary alkyl-, allyl- and (dimethylphenylsilyl)manganates R_3MnMgX (or Li) give satisfactory yields (Table 28). As a rule, magnesium organomanganates lead to better results than the lithium analogues.

A similar reaction was described with Grignard reagents in the presence of manganese chloride (Scheme 178)[16h, 96].

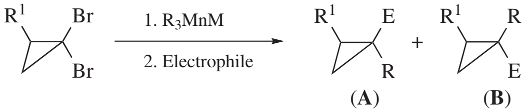
gem-Dibromoalkanes can also be used (Scheme 179). In this case, the organomanganese species formed as an intermediate undergoes a β-hydrogen elimination to give a mixture of alkenes[16h, 97].

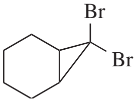
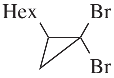
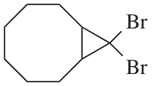
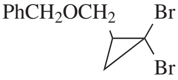
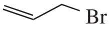


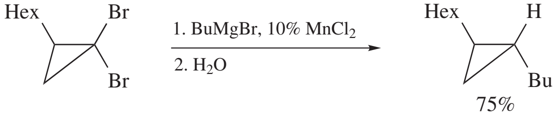
E = H_2O, MeI, PhCOCl, AllylBr

SCHEME 177

TABLE 28. Stereoselective disubstitution of *gem*-dibromocyclopropanes

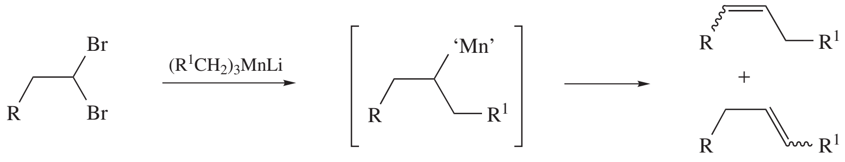


Substrate	R_3MnM	Electrophile	Yield (%)	**A/B**
	Bu_3MnLi	H_2O	56	87:13
	$Bu_3MnMgBr$	H_2O	82	97:3
	$Bu_3MnMgBr$	MeI	65	94:6
	$Bu_3MnMgBr$	PhCOCl	72	83:17
	$(PhMe_2Si)_3MnLi$	H_2O	84	58:42
	$Allyl_3MnMgBr$	H_2O	64	83:17
	$Bu_3MnMgBr$		66	88:12

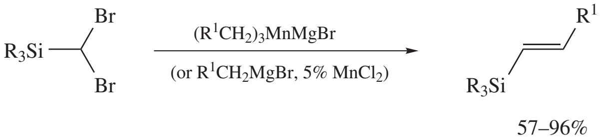


SCHEME 178

Interestingly, with dibromomethylsilanes (Scheme 180) a (E)-vinylsilane is formed since the β-hydrogen elimination can only occur on one side. The stereoselectivity is due to the presence of the bulky R_3Si group.



SCHEME 179

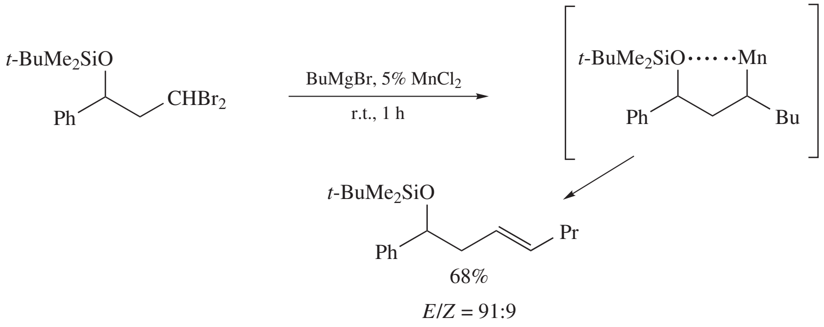


$R_3Si = Ph_2MeSi$, $t\text{-}BuMe_2Si$, $i\text{-}Pr_3Si$

$R^1 = H, Me, Pr, Me_3Si$

SCHEME 180

Another way to orientate the β-hydrogen elimination is to start from a substrate bearing a silyloxy group in the β-position of the $CHBr_2$ group to complex the manganese atom (Scheme 181)[16h, 97].

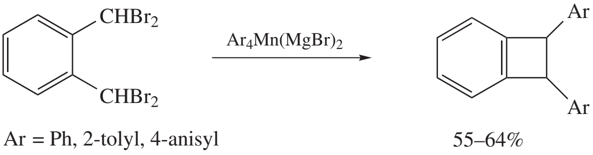


SCHEME 181

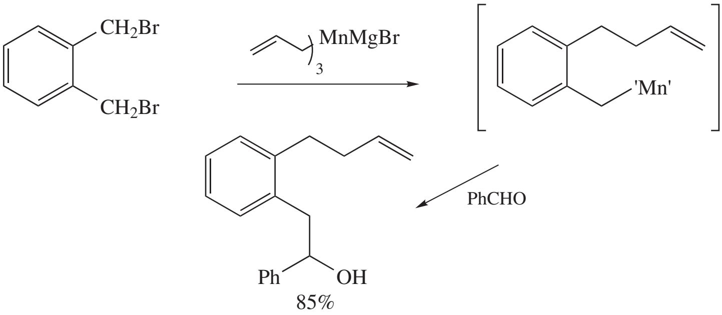
trans-Diaryl benzocyclobutanes are obtained in moderate yields by treating 1,2-bis(dibromomethyl)benzene with triaryl, or better with tetraarylmanganates (Scheme 182)[98].

By using a triallylmanganate, a benzylmanganese is formed. It can be trapped with an electrophile in good yields (Scheme 183).

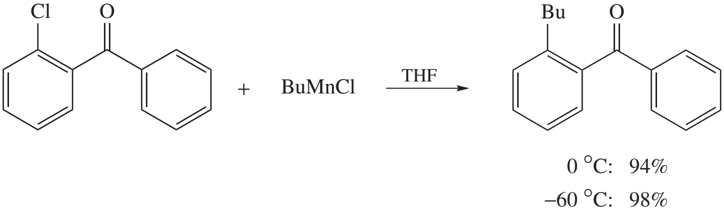
In 2004, a report showed that organomanganese chlorides react with various *ortho*-chloroaryl ketones to afford the corresponding *ortho*-substituted aryl ketones[79]. In some cases, the reaction can be performed at low temperature. Thus, the reaction of butylmanganese chloride with 2-chlorobenzophenone leads to similar results at 0 °C and at −60 °C (Scheme 184).



SCHEME 182



SCHEME 183



SCHEME 184

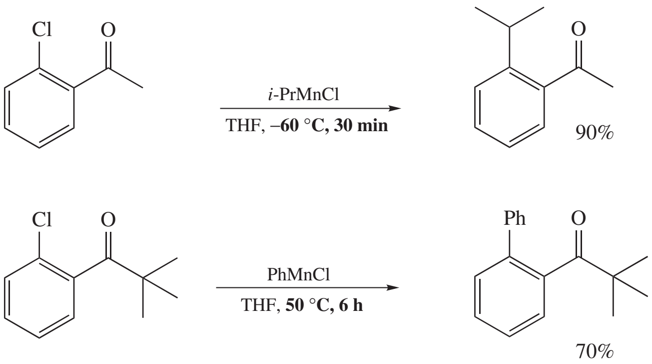
In fact, the reaction conditions closely depend on the nature of the reagents. Thus, isopropylmanganese chloride and 2-chloroacetophenone react in 30 minutes at −60 °C, whereas phenylmanganese chloride couples with *tert*-butyl-2-chlorophenyl ketone in 6 hours at 60 °C (Scheme 185).

Various aromatic and heteroaromatic functionalized ketones were prepared in excellent yields according to this procedure (Table 29).

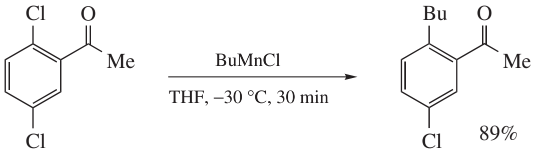
A 2,5-dichloroaryl ketone is selectively alkylated in the *ortho*-position (Scheme 186).

The reaction is highly chemoselective; the presence of an ester, a nitrile, a ketone or an alkyl iodide is tolerated (Scheme 187).

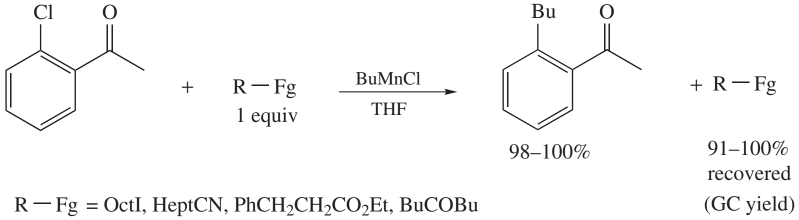
A one-pot acylation-substitution procedure was described from 2-chlorobenzoyl chloride (Scheme 188). At first, a copper-catalyzed acylation reaction is performed in THF with an organomanganese chloride. Then, a second organomanganese compound is added to alkylate the resulting 2-chloroaryl ketone[79].



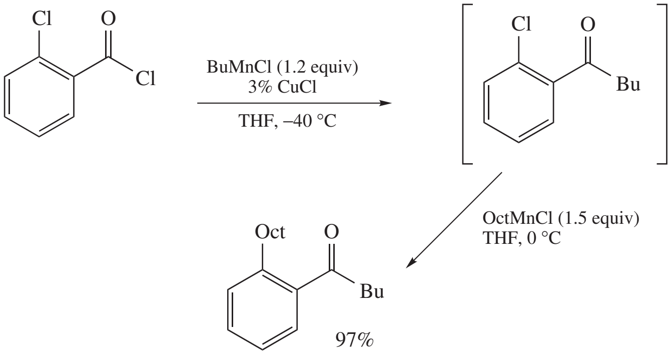
SCHEME 185



SCHEME 186

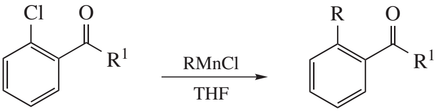


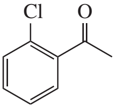
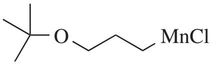
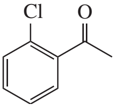
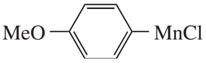
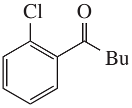
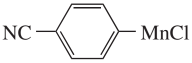
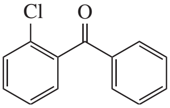
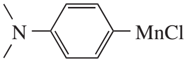
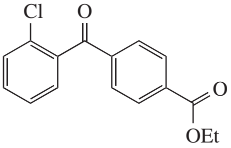
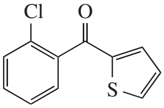
SCHEME 187



SCHEME 188

TABLE 29. Cross-coupling of various RMnX with 2-chloroaryl ketones



ArCl	RMnCl	Reaction conditions	Yield (%)
		0 °C, 30 min	73
		0 °C, 30 min	92
		−10 °C to r.t., 1 h	75
		0 °C, 30 min	81
	BuMnCl	−40 °C, 1 h	97
	BuMnCl	0 °C, 30 min	90

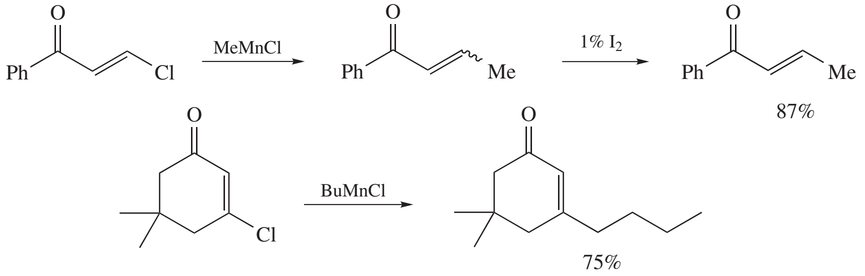
In 1991, Kasatkin and coworkers reported that β-substituted enones can be obtained by reacting β-chloroalkenyl ketones with alkylmanganese compounds in THF at −78 °C (Scheme 189)[99].

It should be noted that, in our hands, all attempts to reproduce these results led to very poor yields, except in the presence of iron salts.

VII. MANGANESE-CATALYZED CARBOMETALLATION REACTIONS

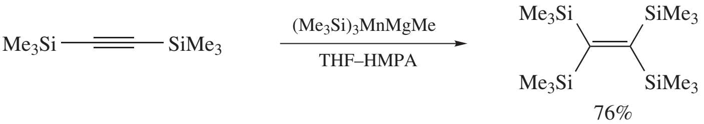
A. Carbometallation of Acetylenic Compounds

In 1985, Oshima and coworkers showed that disilylalkenes are formed by treating terminal alkynes with silylmanganates $(R_3Si)_3MnMgMe$ (Table 30)[16g,h,100]. Similarly, distannylalkenes are obtained by using the stannylmanganate $(Bu_3Sn)_3MnMgMe$.



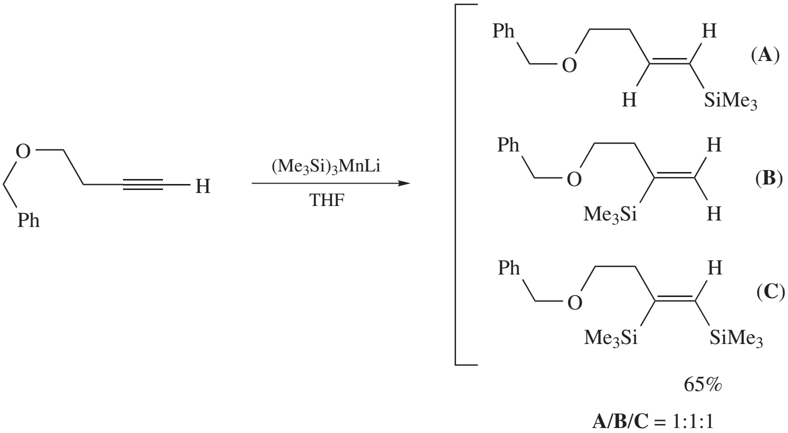
SCHEME 189

Tetrakis(trimethylsilyl)ethylene was efficiently prepared for the first time according to this procedure (Scheme 190).



SCHEME 190

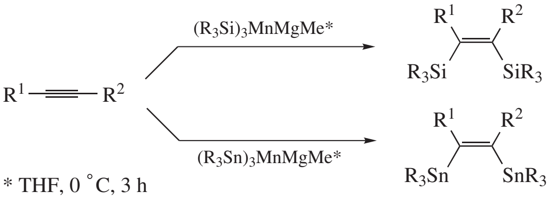
The use of the manganates $(R_3Si)_3MnLi$ in place of $(R_3Si)_3MnMgMe$ generally leads to a mixture of disubstituted and trisubstituted alkenes (Scheme 191)[16g, h, 100].

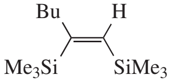
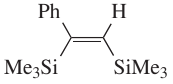
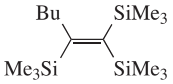
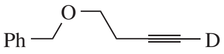
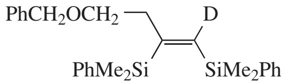
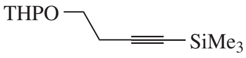
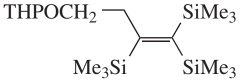
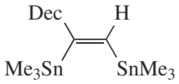
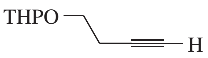
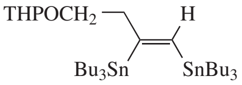


SCHEME 191

In the presence of manganese chloride, the silyl Grignard reagent $PhMe_2SiMgMe$ can add to alkynes (Scheme 192)[16h, 101]. Terminal or internal alkynes bearing an ether group

TABLE 30. Reaction of acetylenes with trisilyl- and tristannylmanganates

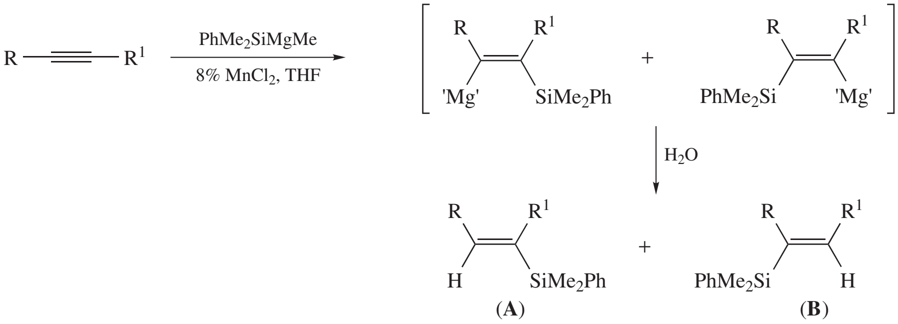


R^1—≡—R^2	Product	Yield (%)
Bu—≡—H		66
Ph—≡—H		65
Bu—≡—$SiMe_3$		80
		55
		83
Dec—≡—H		56
		48

in the β-position of the triple bond lead to the best yields of addition product (90–95% instead of 40–50%) and to the best regioselectivity.

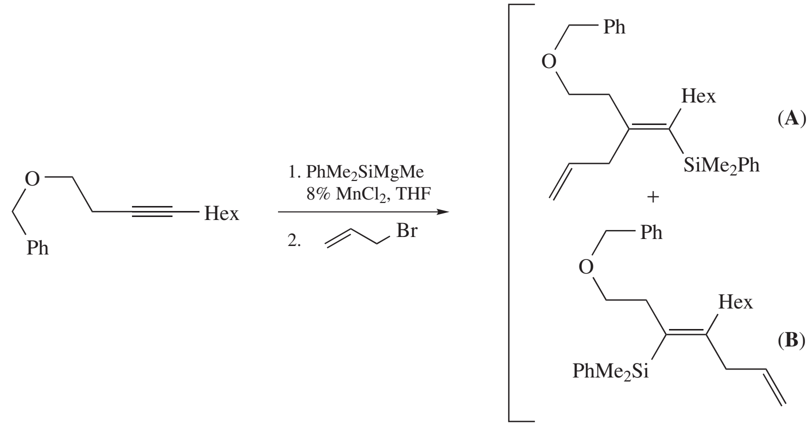
The alkenylmagnesium thus obtained can react with various electrophiles such as allyl bromide (Scheme 193) or benzaldehyde (Scheme 194).

The allylmetallation of the reactive β-methoxyalkynes was also described[16h, 102, 103]. Magnesium tetraallylmanganate, or allylmagnesium halides in the presence of manganese iodide, can be used in THF (Scheme 195). Subsequent allylation with allyl bromide affords a tetrasubstituted alkene in good yields.



R = Hex, R^1 = H: 40%, **A/B** = 80:20
R = $PhCH_2OCH_2CH_2$, R^1 = H: 90%, **A/B** = 95:5
R = $PhCH_2OCH_2CH_2$, R^1 = Hex: 95%, **A/B** = 73:27

SCHEME 192



68%, **A/B**= 80:20

SCHEME 193

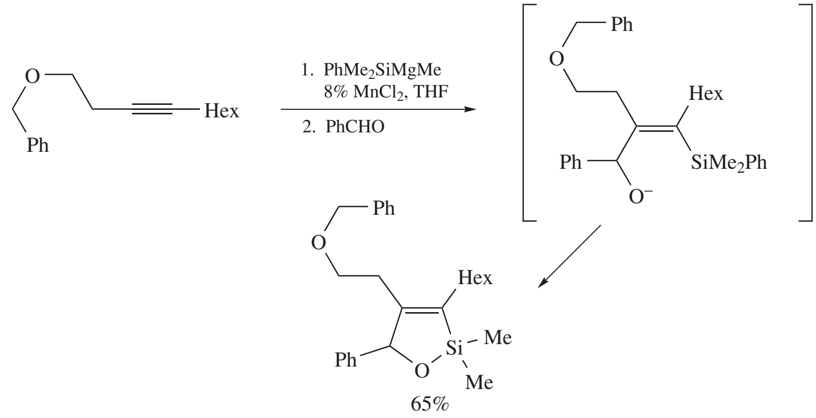
The complexation with the oxygen atom in the β-position is determinant. Thus, only moderate yields are obtained with bulkier alkoxy groups such as benzyl ethers (Scheme 196).

On the other hand, non-functionalized alkynes do not react, even after 10 hours under reflux (Scheme 197).

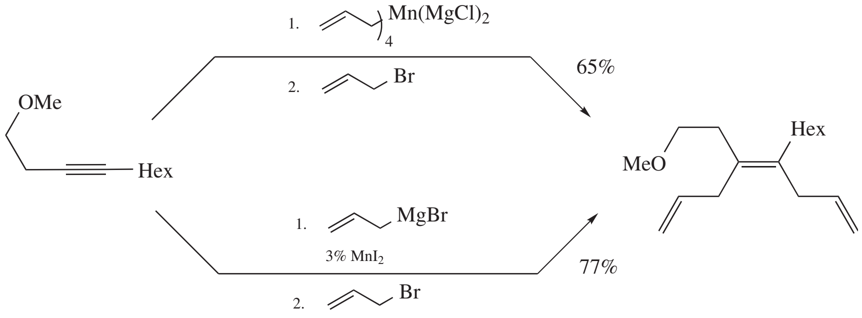
With propargylic ethers, the Mn-catalyzed allylmagnesiation leads to an allene via an unstable β-alkoxyvinylmagnesium derivative (Scheme 198)[16h, 102, 103].

Interestingly, when the allylmetallation is performed with a tetraallylmanganate in the presence of an oxidant (O_2, PhI) two allyl groups are transferred (Scheme 199)[16h, 103].

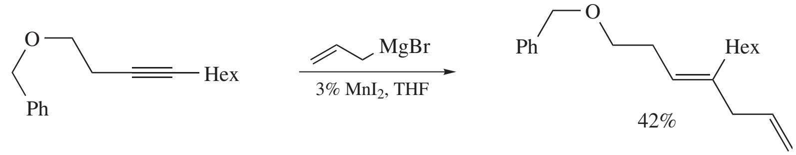
A similar product is obtained when the allylmetallation is performed via the manganese-catalyzed procedure (Scheme 200)[16h, 102, 103]. The reaction leads to better yields when $(MeC_5H_4)Mn(CO)_3$ is used as a catalyst instead of manganese iodide.



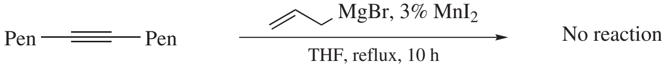
SCHEME 194



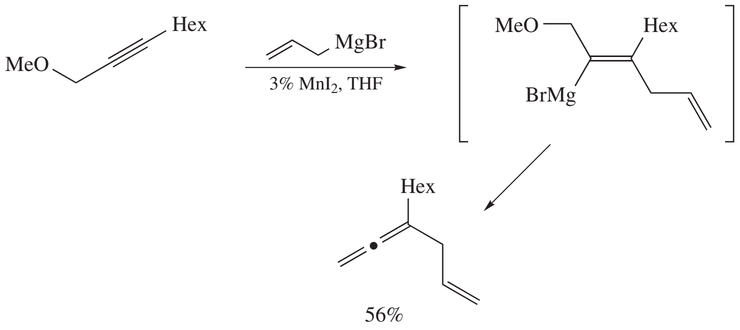
SCHEME 195



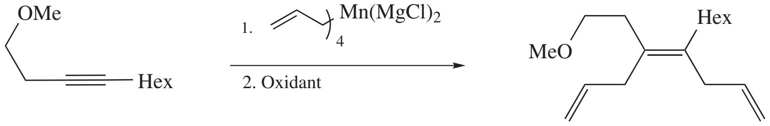
SCHEME 196



SCHEME 197



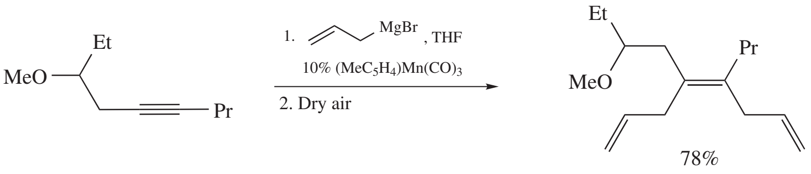
SCHEME 198



Oxidant = O_2: 73%

Oxidant = PhI: 80%

SCHEME 199



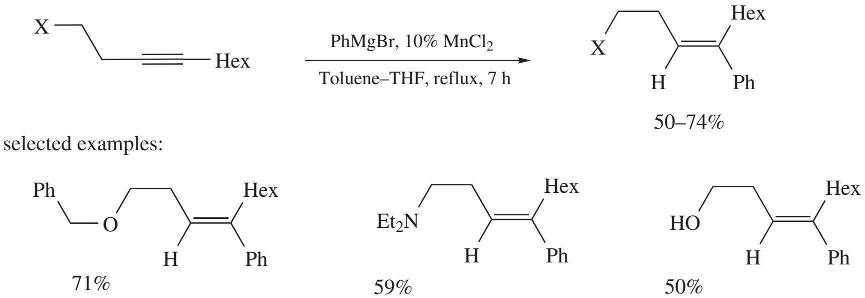
SCHEME 200

The phenylmagnesiation of homopropargylic alcohols, ethers and amines can be performed in a toluene–THF mixture under manganese catalysis (Scheme 201)[104a]. It should be noted that the examples of arylmetallation are very rare.

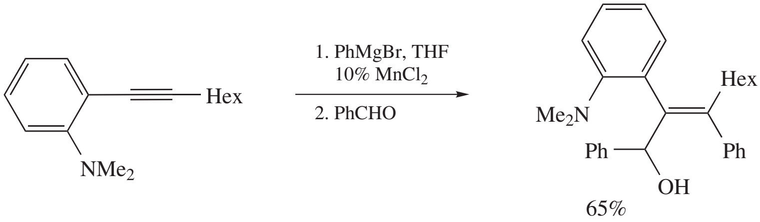
In the presence of manganese chloride, phenyl-[104a] or alkylmagnesium bromides[104b] add to phenylacetylenes bearing a hydroxy or an amino group in the *ortho*-position (Scheme 202).

B. Carbometallation of 1,3-Dienes

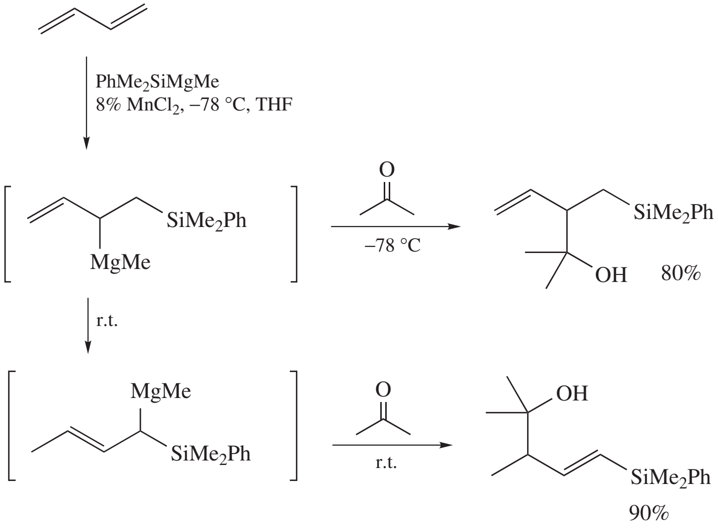
The manganese-catalyzed silylmagnesiation[101] and silylmanganation[16g, 105] of conjugated dienes were reported. As a rule, the silylmagnesiation leads to a β-silyl allylmagnesium compound at $-78\,^{\circ}$C whereas, at room temperature, an α-silyl allylmagnesium reagent is obtained (Scheme 203).



SCHEME 201

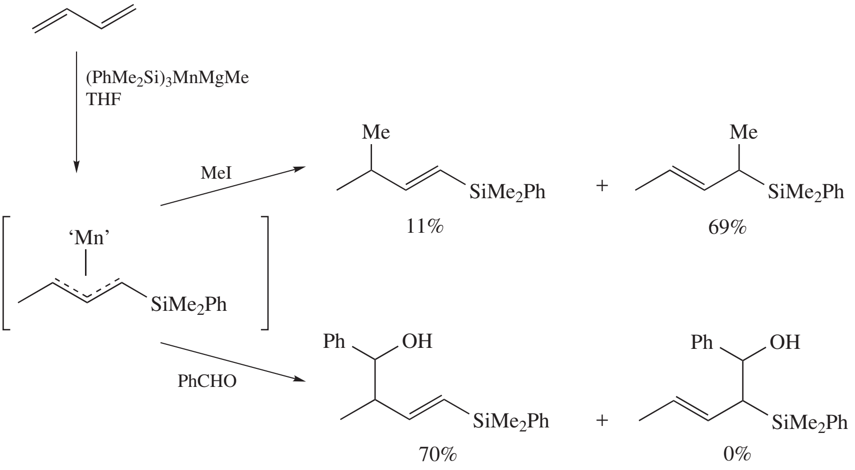


SCHEME 202



SCHEME 203

The isomerization is more rapid with the silylmanganate $(PhMe_2Si)_3MnMgMe$, and the reaction always leads to an α-silyl allylmanganate (Scheme 204)[16g, 105]. This one reacts with various electrophiles to give either a vinyl or an allylsilane.

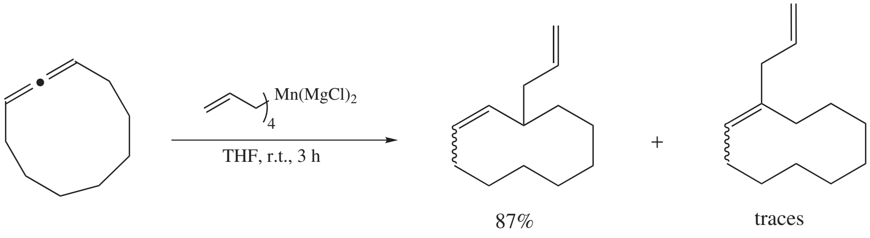


SCHEME 204

In the case of 2-substituted butadienes, the addition takes place on the less hindered side of the dienic system[16g, 101, 105].

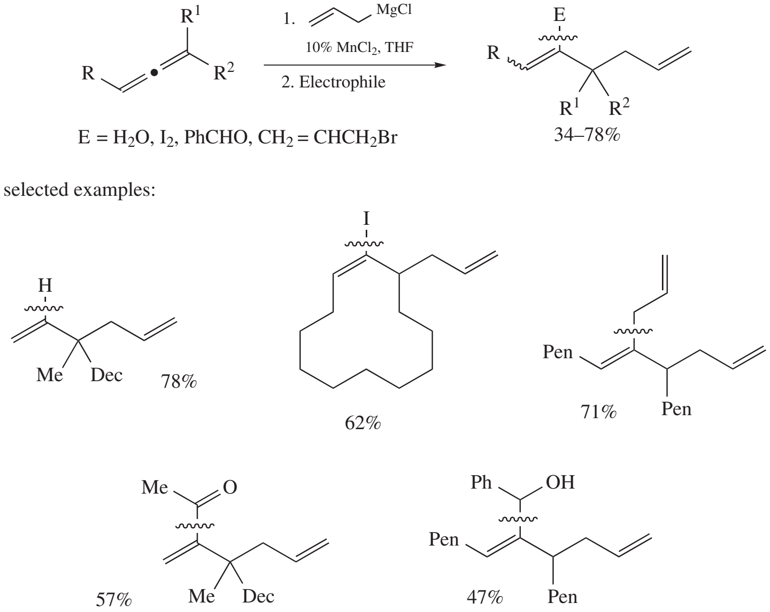
C. Carbometallation of Allenes

In THF, tetraallylmanganate adds to allenes at room temperature[106] (Scheme 205). The addition is highly regioselective, since the allyl group is mainly introduced on the terminal carbon atom of the allenic system.



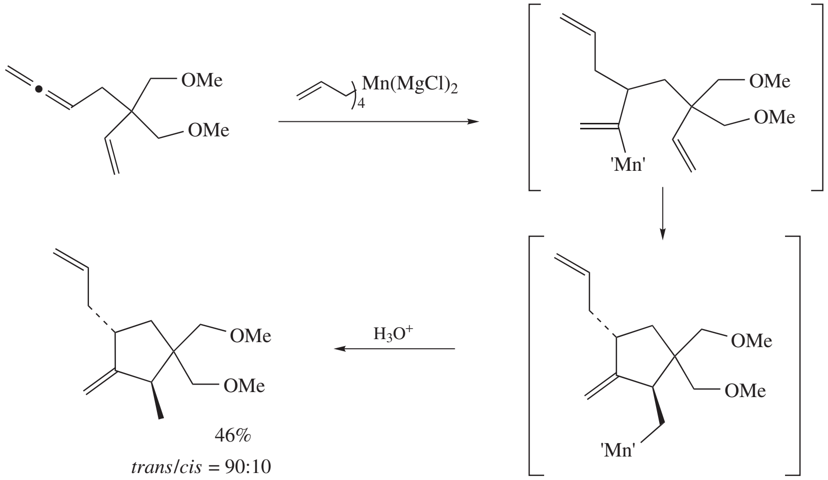
SCHEME 205

The manganese-catalyzed addition of allylmagnesium chloride was also reported (Scheme 206). Various 1,5-dienes were prepared in good to moderate yields by reacting the resulting alkenylmagnesium reagent with an electrophile.



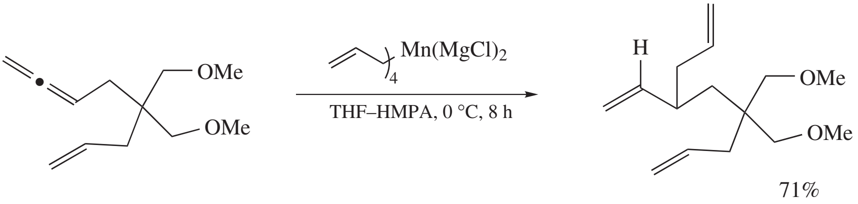
SCHEME 206

A stereoselective synthesis of a highly substituted cyclopentane from a 1,2,6-heptatriene was reported (Scheme 207). The allylmanganation is followed by a cyclization of the organometallic intermediate[106].



SCHEME 207

This procedure cannot be extended to the preparation of a cyclohexane from a 1,2,7-heptatriene since the cyclization step does not occur (Scheme 208).



SCHEME 208

VIII. MISCELLANEOUS MANGANESE-MEDIATED REACTIONS

A. Manganese-catalyzed Reduction of Aryl or Alkenyl Halides by Grignard Reagents

In THF, alkenyl bromides or iodides as well as aryl chlorides or bromides are efficiently reduced by isopropylmagnesium chloride in the presence of manganese chloride under mild conditions (Table 31)[107]. Excellent yields of dehalogenated product are generally obtained.

A tentative catalytic cycle was proposed (Figure 4). Isopropylmagnesium chloride reacts with manganese chloride to give the triisopropylmanganate **11** which is not stable at room temperature. It decomposes by β-elimination to give a hydridomanganate $H_3MnMgCl$ (**12**) which reacts with the aryl halide to afford the unstable Mn^{IV} intermediate H_3MnAr (**13**). A reductive elimination then leads to the reduction product. The manganese hydride **14** then reacts with the starting Grignard reagent to regenerate the manganate $H_3MnMgCl$ (**12**) via **15**. A similar catalytic cycle is proposed in the case of alkenyl halides.

A mixture of reduction and coupling products is obtained when the reaction is performed with butylmagnesium chloride instead of isopropylmagnesium chloride (Scheme 209).

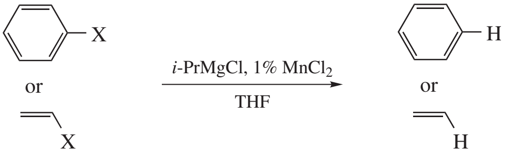
This result shows that the butyl group can be partially transferred contrary to the isopropyl group (Figure 5).

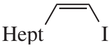
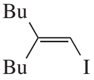
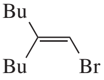
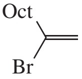
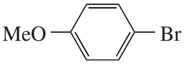
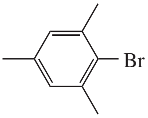
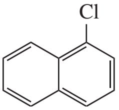
B. Preparation of Dialkylzincs via a Mn/Cu-catalyzed Halogen–Zinc Exchange

Organozinc compounds are very powerful reagents in organic synthesis, since they tolerate numerous functional groups[108]. In 1994, Cahiez, Knochel and coworkers showed that alkylzinc bromides are efficiently prepared from alkyl bromides and diethylzinc[109] via a Mn/Cu-catalyzed bromine–zinc exchange (Scheme 210). Let us recall that the direct preparation of alkylzinc bromides from primary alkyl bromides and zinc dust is not very efficient. Various functionalized alkylzincs were thus prepared in high yields under mild conditions.

A putative mechanism is described in Figure 6. At first, it is important to note that the bromine–zinc exchange cannot be performed in the presence of copper salts alone. Thus, the oxidative addition step **16** to **17** probably involves a Mn^0 rather than a Cu^0 species (**16**, M = Mn) since the oxidative addition is easier with manganese. Then, **17** reacts with diethylzinc to afford alkylzinc bromide. After that, the catalytic intermediate

TABLE 31. Mn-catalyzed reduction of aryl or alkenyl halides by *i*-PrMgCl



Organic halide	Equivalents of *i*-PrMgCl	Reaction conditions	Yield (%)
	1.5	3 h, r.t.	93
	1.5	3 h, r.t.	90
	2	4 h, r.t.	88
	2	4 h, r.t.	92
	2	4 h, 45 °C	84
	2	10 h, 45 °C	65
	2	4 h, 45 °C	94

18 decomposes by β-elimination to give a mixture of ethane/ethylene and the catalytic intermediate **16**. Copper is probably involved in the decomposition of **18** to **16** since ethylcopper is less stable than ethylmanganese derivatives. The nature of M in **17** or **18** is not clear and the reaction probably involves at least two transmetallation reactions.

Functionalized alkylzinc reagents prepared by this method were coupled with aryl iodides or bromides in the presence of 5% $PdCl_2$(dppf) to give polyfunctionalized aromatic compounds in good yields. They also react with allylic bromides. After transmetallation to copper, conjugate additions to reactive Michael acceptors can also be performed. Some examples are depicted in Scheme 211[109].

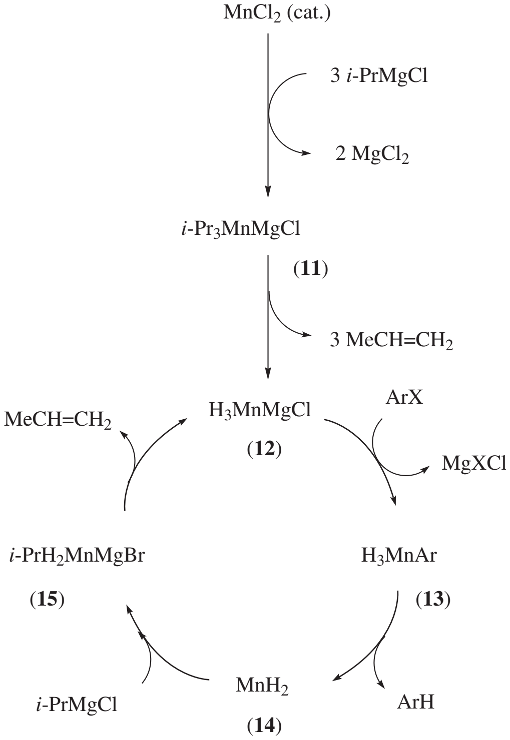
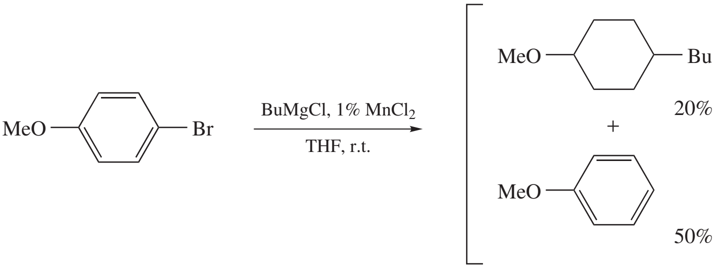


FIGURE 4



SCHEME 209

This Mn/Cu-catalyzed bromine–zinc exchange was used to perform radical cyclizations[110, 111]. Various substituted 5-membered ring compounds were stereospecifically prepared in good yields from δ-halogenoalkenes (Scheme 212)[110]. The organometallics formed by carbometallation can then be trapped with various electrophiles.

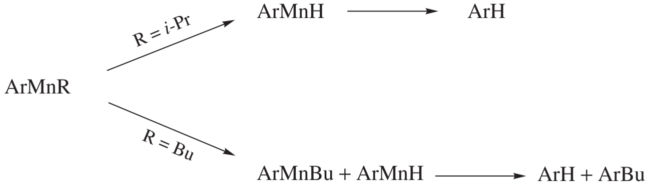


FIGURE 5

$$R_{Fg}CH_2Br \quad + \quad Et_2Zn \xrightarrow[\text{DMPU, r.t., 4–10 h}]{\text{5\% MnBr}_2\text{, 3\% CuCl}} \underset{80\text{–}90\%}{R_{Fg}CH_2ZnBr}$$

SCHEME 210

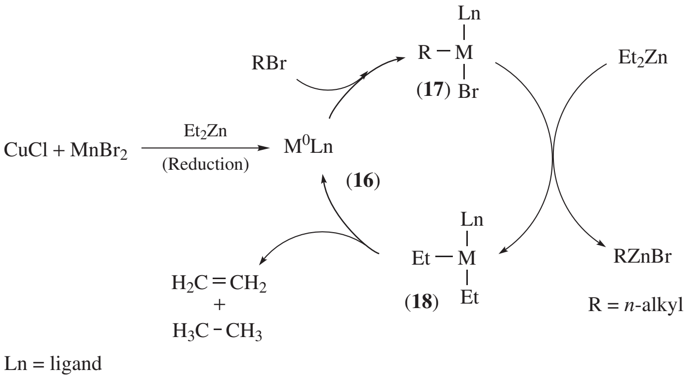


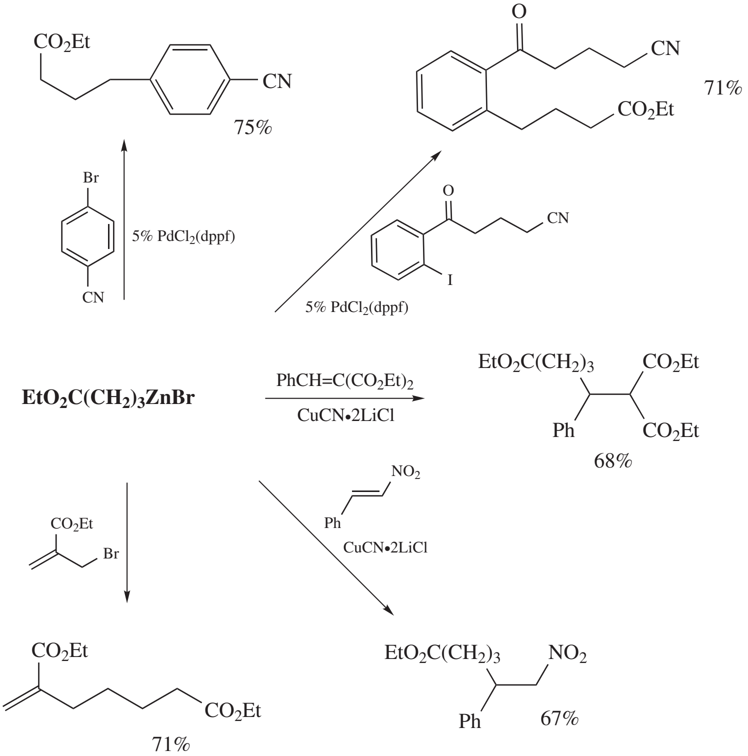
FIGURE 6

This halogen–zinc exchange reaction was used to prepare diastereoselectively various polysubstituted cyclopentenols from δ-bromo- or δ-iodoaldehydes and ketones. The cyclization occurs via an intramolecular 1,2-addition Barbier-type reaction (Scheme 213)[110, 111].

C. Radical Cyclizations Promoted by Trialkylmanganate Reagents

Indolyl- or benzofuranylmanganese compounds are prepared under mild conditions by reacting 2-iodophenyl allyl ethers or *N*,*N*-diallyl 2-iodoanilines with lithium or magnesium tributylmanganates (Schemes 214 and 215)[16h, 21]. The cyclization which occurs during the halogen–manganese exchange leads to an organomanganese reagent. In some cases, it is possible to trap the latter with a good electrophile such as benzoyl chloride; however, it generally decomposes to give the reduction or the β-elimination product.

Cyclization products can also be obtained from δ-halogenoalkenes. Thus, various α-alkoxyfurans were synthesized from the iodoacetals depicted in Schemes 216 and 217[16h, 21].



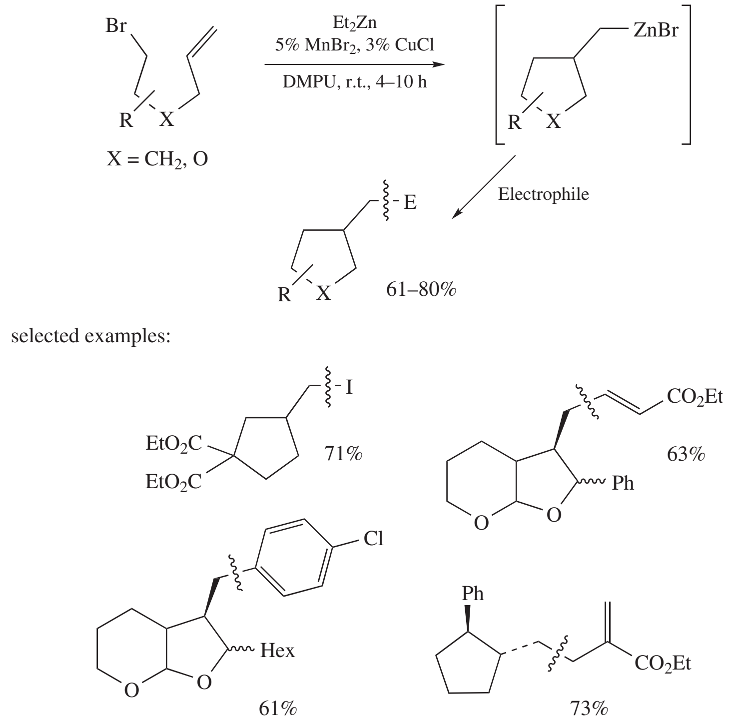
SCHEME 211

A similar reaction can be performed by using butylmagnesium bromide in the presence of a catalytic amount of manganese chloride in place of lithium or magnesium tributylmanganates. It is important to underline that the presence of oxygen is required to achieve the reaction when an aryl iodide is used as a starting material (Scheme 218).

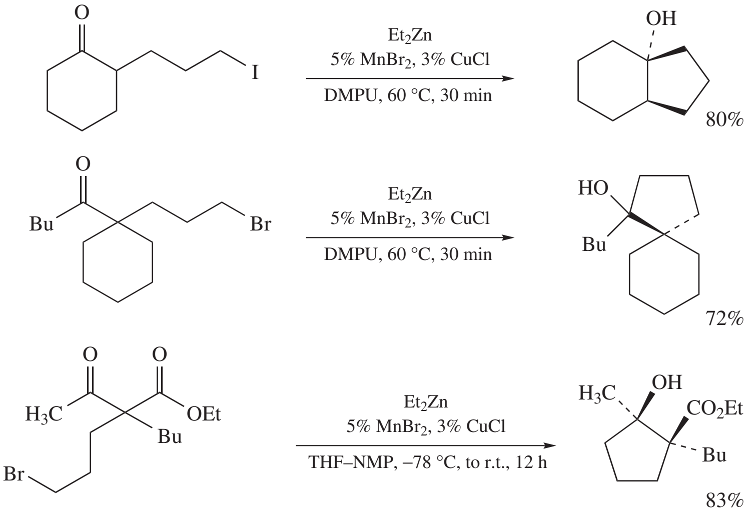
IX. CONCLUSION

In spite of the recent development of organomanganese(II) reagents in organic synthesis, numerous synthetic procedures competitive with those using traditional organometallic reagents have been developed (i.e. especially with respect to chemoselectivity). Organomanganese compounds can be used as soft Grignard reagents, for instance to perform chemoselective 1,2-addition, copper-catalyzed conjugated addition, acylation, and carbonation reactions. On the other hand, these reagents can also behave as transition metal derivatives. It is well exemplified by the mild and efficient manganese-catalyzed homo- and heterocoupling reactions described above (cf VI).

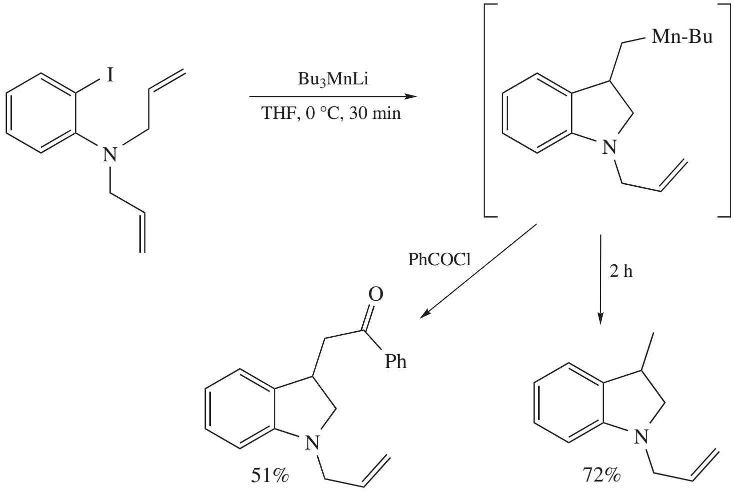
Owing to their chemoselectivity, affordability and reduced environmental impact, organomanganese compounds are amenable to large-scale applications. To date, only a few manganese-catalyzed cross-coupling reactions have been reported since organomanganese(II) species are generally stable and do not easily undergo a reductive



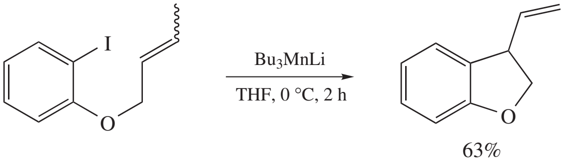
SCHEME 212



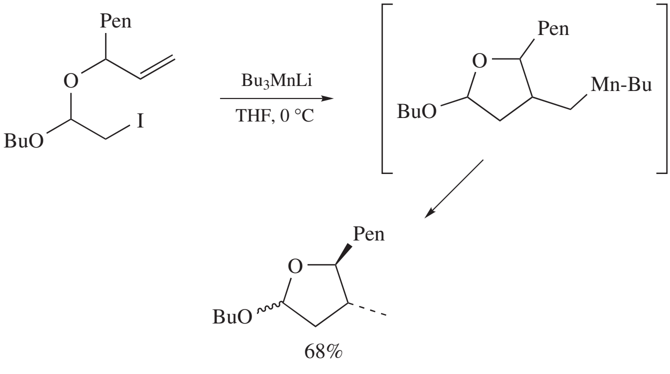
SCHEME 213



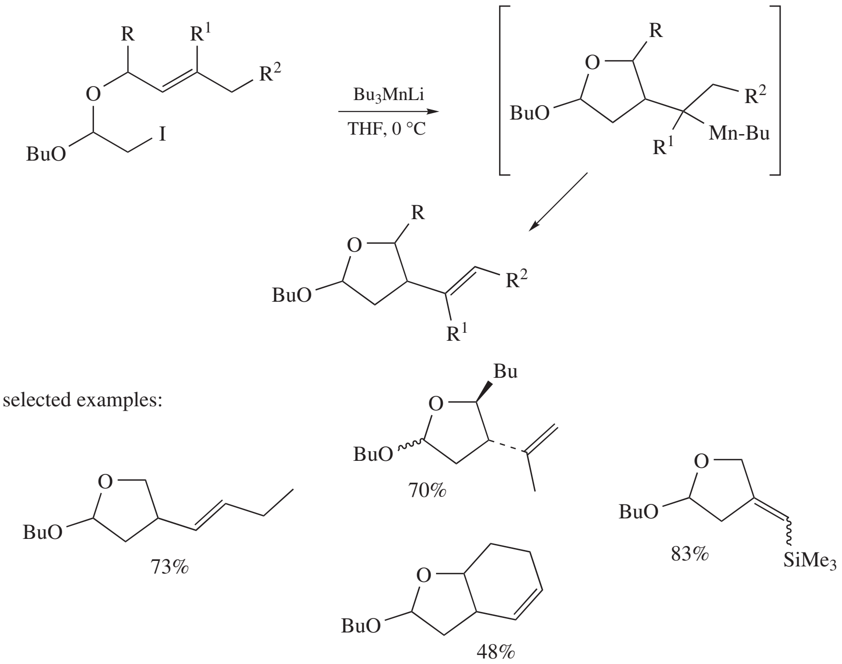
SCHEME 214



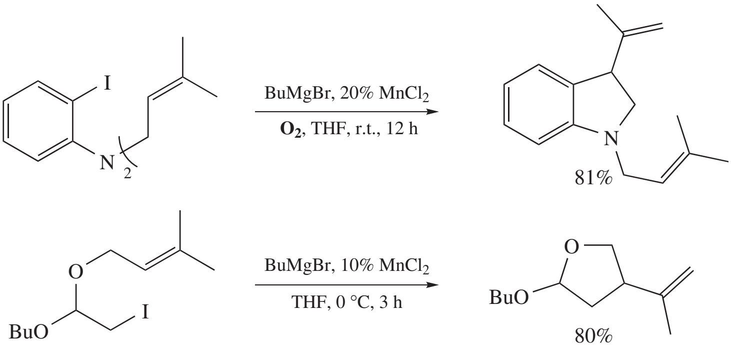
SCHEME 215



SCHEME 216



SCHEME 217



SCHEME 218

elimination process. Recently, however, a few manganese-catalyzed coupling reactions involving a reductive elimination step have been reported. It seems to be a promising field of investigation. Finally, efforts to prepare organomanganese halides directly from massive commercial manganese metal have only led to limited success until now. No convenient preparative method has been disclosed and it is a very interesting and challenging area for future investigations, especially regarding the preparation of functionalized organomanganese reagents.

X. ACKNOWLEDGMENTS

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Manganese in biological systems: Transport and function

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I. ABBREVIATIONS

EDTA	ethylene diamine tetraacetic acid.
OEE	oxygen evolution enhancer.
OM	outer membrane.
PM	plasma membrane.
POX	peroxide.
PSI	Photosystem I.
PSII	Photosystem II.
ROS	reactive oxygen species.
SOD	superoxide dismutase.
TM	thylakoid membrane.
tMI	transition metal ion.

II. INTRODUCTION

Manganese import, transport, accumulation, sensing and control pathways are important for all organisms, and are of unique importance for oxygenic photosynthetic organisms due to their role in the catalysis of water oxidation by photosystem II (PSII) complexes. In this review we will describe general aspects of Mn biochemistry, its known roles in cellular processes and its mode of function in PSII. We will describe in detail different chemical mechanisms that have evolved to obtain and control Mn ions, focusing on cyanobacterial systems as an example of organisms with absolute Mn requirements that exist in a wide variety of environments. We will describe the steps and mechanisms by which Mn transport is performed under Mn deficient or replete conditions. Under deficient conditions a high affinity Mn transporter is expressed and becomes functional in the cyanobacterial plasma membrane. This ATP dependent transporter must overcome a number of mechanistic problems to perform its function, which is to bind Mn ions with high affinity and specificity at very low Mn concentrations in the possible presence of higher concentrations of similar metal ions. The Mn cluster of PSII functions within the cyanobacterial cell, yet studies suggest that it is assembled in the plasma membrane facing the periplasmic space rather than in the thylakoid membrane. The topology of the two processes, Mn transport and Mn cluster assembly, should therefore be regulated in order to insure efficient biogenesis and repair of PSII complexes. Based on the available results, we attempt to map the constraints imposed by Mn transport on PSII biogenesis events in cyanobacteria.

III. TRANSITION METALS IN BIOLOGY

Biological viability is dependent on the availability of a large number of chemicals, many of which cannot be synthesized but must be obtained from outside the organism. Many of these essential chemicals, or nutrients, are needed at relatively minute concentrations and are thus collectively called ‘micro-nutrients’. Among the micro-nutrients, one of the most important classes are the transition metal ions (tMI). The most prevalent tMIs in most organisms are Fe, Zn, Cu and Mn[1]. tMIs are essential for the function of many proteins, by facilitating redox or chemical group transfer reactions or by stabilizing protein structure. To satisfy the requirements for these metals, cells have numerous mechanisms for the solubilization and uptake of metals from the extracellular environment. Cells must, however, simultaneously protect themselves from the hazards inherent to the chemical characteristics of these metals. If cytosolic metal concentrations are not carefully regulated, spurious redox reactions can produce toxic free radicals. Therefore, each organism contains active and passive transport systems that identify, bind and transfer tMIs from the outside into the necessary cellular compartments. Almost no free cytosolic tMIs exist, indicating that tMIs are sequestered into their final destination or stored by tMI storage proteins[2]. Excellent reviews have been published over the past 20 years that describe the biochemistry of tMI[2–7], specifically that of Mn[3, 4]. The biochemistry of tMIs cannot be easily described without including the proteins that bind and utilize them for their various activities.

A. Manganese Characterization in Biological Systems

Mn is recognized as an absolutely required micro-nutrient, as reflected by a number of well-known diseases, disorders or syndromes that occur in organisms suffering from Mn deficiency[8] or uncontrolled excess[9]. The major enzymatic functionalities imparted by Mn on proteins are the ability to reduce reactive oxygen species in Mn-superoxide dismutatse (MnSOD) and catalase, in electron transfer dependent catalysis (for instance in certain class I ribonucleotide reductases) and in the oxidation of water by Photosystem II (PSII). In the following section we will discuss issues pertaining to the sensing, transport and control of Mn as well as one of its most important roles in biology, in photosynthesis.

Mn is found in most terrestrial locations, comprising about 0.1% of the earth's crust, but found at concentrations of only about 1–10 nM in the earth's oceans[10]. The intracellular concentration is usually greater by one order of magnitude, but higher concentrations would induce potentially deleterious precipitation reactions with phosphate or carbonate anions. In its solvated form it is found as the stable Mn^{2+} ion, and this is the state that is typically recruited and transported into the cell. Once in the cell, and depending on its role, it can be oxidized to other redox stable states. Mn is a versatile tMI in that it has the largest potential range of redox states (-3 to $+7$), however the actual stable redox states found in biological molecules are typically Mn^{2+} and Mn^{3+} (and Mn^{4+} found in PSII). Both Mn^{2+} and Zn^{2+} are high spin (d^5 and d^{10}, respectively), and thus do not exhibit the characteristic energies due to ligand field stabilization. Indeed, Mn and Zn are chemically quite similar and the specificity of binding by different proteins must take this into account. The redox potentials of the different Mn redox states is highly variable, but it is important to recognize that the E^0 of the reduction of Mn^{3+} to Mn^{2+} (1.56 V) is more than twice that of the similar reduction of Fe^{3+} to Fe^{2+} (0.77 V)[11] and much higher than the reduction of Cu^{2+} to Cu^{1+}. Thus Mn has the chemical potential to serve in roles requiring the removal and transfer of highly energetic electrons. The actual redox state of a bound Mn ion will be quite different than in standard solutions and will be tuned by the protein environment, especially by the pKa's of nearby acids, by the presence or absence of bound oxygen species (including water) and by the presence of nearby hydrophobic residues.

Mn^{2+} is the hardest Lewis acid of the four major tMIs, and will prefer hard ligands in its coordination sphere, such as the negatively charged oxygen atoms of aspartate, glutamate, tyrosinate, the polar oxygen atoms of asparagine, glutamine or small solvated ions such as HO^- or $O_2{}^-$ (or H_2O which is an intermediate strength Lewis base). The imidazole nitrogen atoms of histidine are considered ligands of borderline hardness and are also found in many cases as appropriate ligands for Mn^{2+}[11]. The involvement of histidine residues indicates that binding of Mn^{2+} within a protein imparts significant changes in its chemical properties as compared to the ion in solution. Mn^{2+} coordination geometry is usually square pyramidal or trigonal bipyramidal for coordination number = 5; octahedral geometry is also observed with coordination number = 6 and occasionally 4-coordinated complexes with tetrahedral geometry exist. As we shall describe below, many of the characteristics of Mn binding, in functionally different protein families, are actually quite similar. Rather small variations in the first and second shells surrounding the Mn impart whether its role will be in electron transfer, in reduction of substrates or in transport.

B. Transition Metals in Photosynthesis

In the photosynthetic apparatus, tMIs are required as cofactors in electron transport processes[12]. Among these are Fe cofactors such as Fe-S clusters, cytochromes and non-heme Fe, Cu in plastocyanin and Mn in Photosystem II. As a result of the absolute importance of photosynthesis for cyanobacteria, algae and plants, the demand for these tMIs far exceeds that required by other non-photosynthetic organisms. The transition from non-oxygenic to oxygenic photosynthesis was an extremely successful step from an evolutionary standpoint[13], however it resulted in a *ca* 100 times higher internal Mn requirement[14]. Nevertheless, oxygenic photosynthesis is not without its risks. Transporting, accumulating and assembling tMIs into functional cofactors are particularly dangerous tasks when photosynthetic processes are concerned. The photosynthetic apparatus performs some of the most extreme enzymatic reactions, in energetic terms[15]. Consequently, reactive oxygen species can be formed in the course of normal photosynthetic activity. Hot spots for oxygen radical production include antenna complexes, PSII and photosystem I (PSI) (reviewed in Reference 16). In order to overcome inherent dangers from radical chain reactions between transition metals and intermediates in photosynthetic catalysis, the handling of these metals is tightly regulated[16, 17]. The evolutionary selection of manganese as a cofactor in PSII water oxidation processes is not a trivial one. Although Mn ions can donate up to 6 electrons, only a limited number of enzymes utilize Mn as a cofactor[17]. Current hypotheses on the origins of water oxidation revolve around the utilizations of bicarbonate-manganese adducts as templates for the evolution of the water splitting enzyme[18].

C. Redox Active Mn Enzymes

As described above, Mn serves as the active tMI center in many redox active centers. While each enzyme has its own unique structural characteristics that enable performance of all of its required functionalities, we can reduce our discussion here to the basic facets that are common to all: (i) the requirements for stable and specific binding of Mn; (ii) establishment of the conditions required for efficient electron transfer to and from the bound Mn; (iii) obtaining the correct redox potential for performance of the activity; and (iv) providing structural attributes that allow for useful substrate binding and product release. Of the enzymes that use Mn as its major cofactor, we will use the rather ubiquitous Mn superoxide dismutase (MnSOD) as a general example.

Superoxide dismutases are enzymes that function to catalyze the conversion of a superoxide radical to oxygen and hydrogen peroxide, thus protecting the cell against toxic products of cellular respiration. These enzymes carry out catalysis at near diffusion controlled rate constants via a general mechanism that involves the sequential reduction and oxidation of the metal center, with the concomitant oxidation and reduction of superoxide radicals. The enzymes are classified according to their metal ion in the active site. The catalytically active metal can be copper, iron, manganese or nickel. Structures of the different SOD families have recently been reviewed in depth elsewhere[19], and we will thus limit our discussion here to questions relevant to Mn chemistry.

The actual binding site of the metals is quite similar, with four ligating residues (His and/or Asp residues) and a bound solvent molecule (water or hydroxide ion) forming a trigonal bipyramidal coordination (Figure 1)[19]. However, despite this similarity, SOD activity requires exquisite matching between the protein environment, which is maintained mostly by second and third shell residues, and the bound tMI. Although the folding and the active site of MnSOD and FeSOD are nearly identical, the replacement of the Mn in *E. coli* MnSOD by Fe inactivates the enzyme. This is most likely due to protein induced changes in the reduction potential (E°), which is appropriate for Mn catalysis but not

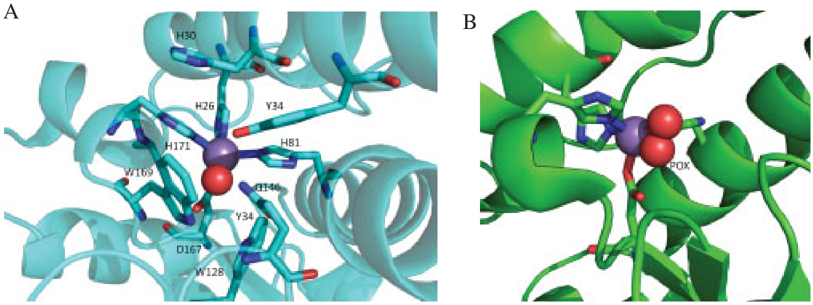

FIGURE 1. The active site of *E. coli* MnSOD (PDB code 2VEW). (A) Bound Mn (pink sphere) with water (red sphere) at ligating position 5. The ligating residues and the second shell of residues that are important for activation and ligand binding are depicted in sticks. (B) MnSOD (PDB code 3K9S) with a bound peroxide molecule (POX, red spheres) replacing the fifth Mn (pink sphere) coordinating ligand

for Fe. Apparently residues in the second coordination sphere strongly affect E°, thus insuring the effectiveness of the enzyme activity and its specificity[20].

Crystallography is the major source of high resolution information on MnSOD, although other methods have been utilized[21, 22]. Crystallography cannot always provide a definitive visualization of the wild-type active site with bound substrate(s) in pre-reaction binding modes, due to fast reaction rates (nearly diffusion-rate limiting in SOD), crystal lattice effects and the presence of crystal stabilization solutions that are far from the physiological surroundings of the enzyme. Recently, the structure of the MnSOD from *E. coli* was determined with bound peroxide molecule (POX)[23]. This structure actually shows four different views of the same enzyme, since each monomer in the asymmetric unit was trapped in a somewhat different state. The overall conclusion is, however, that the POX molecule replaces the coordinating water molecule at the fifth position in a side-on orientation. Binding of a POX at this position inhibits substrate binding and thus inactivates the enzyme, suggesting that position 5 is where the superoxide substrate binds during the catalysis. The POX binding site is lined by second shell residues (Tyr34, Gln143 and Trp169) which create a hydrogen bond network. It is likely that this bonding network supports proton transfer that is not just critical for catalysis, but also facilitates product release and substrate binding[24]. To conclude, enzymatic activity of the MnSOD is maintained not only by the presence of the correct metal ion at the active site but also by the presence of the second shell residues that provide the specific environment for the catalysis. These residues enable the specificity of the enzyme, which the binding site by itself is unable to provide.

An interesting observation is that in some bacterial species, the accumulation of intracellular Mn can alleviate the stress of reactive oxygen species (ROS) in a MnSOD independent and Mn concentration dependent manner[25, 26]. This has been attributed to the direct interaction between Mn^{2+} ions, imported by energy-dependent import systems (see below). Attempts to link the presence of Mn with other components (proteins, nucleic acids, phosphate ions, etc.) have not yet revealed a mechanism for free-Mn detoxification. In addition, it is not clear how unbound Mn can exist in the cell, which is certainly in opposition to other measurements showing that high intracellular concentrations of Mn^{2+} will precipitate with important anions. As will be described below, it has been shown that cyanobacteria perform uptake of large amounts of Mn into their outer membrane while all of the intracellular Mn appears to be bound to target proteins.

IV. Mn TRANSPORT IN CYANOBACTERIA

Mn^{2+} cannot freely penetrate into the intracellular compartments through the plasma membrane. Transport of Mn^{2+} is performed by a variety of proteins, depending on organism and cell type[17,27,28]. Each system has its own unique characteristics, especially the source of energy for transport: ATP in the case of ATP binding cassette (ABC) transporters[29] and P-type ATPases[17,30] or chemical gradients in the case of ZIP (Zrt and Irt related proteins)[31,32] or Nramp (natural resistance-associated macrophage protein)[27,33] transporters. All transporters require some attributes that are similar to those of the Mn dependent enzymes described above—specific Mn binding (although less specific transporters are also known) that is stable enough to promote directional movement across the membrane but that provides fast release as well. Due to the scope of this review, we will focus on one transporter system, the high-affinity Mn ABC transporter in cyanobacteria. Mn is not considered as a limiting factor for primary photosynthetic productivity (unlike Fe), however its concentration is in the low nM range in open oceans[34] and in some fresh bodies of water[35]. For comparison, the Mn concentration in standard bacterial growth media like BG11[36] or A+ [37] is in the μM range. In the analysis of Mn transport and homeostasis in cyanobacteria we should consider two conditions; the Mn deficient condition prevailing in open water bodies and the Mn sufficient condition existing for brief periods following aeolian dust depositions[38,39] and in culture media.

A. Mn Transport under Deficient Conditions: The MntABC Transporter

Transport of transition metals through biological membranes requires active transport. It is not currently known how organisms actively transport the correct ions at the proper concentrations, since at least some of the known transporters can recognize and deal with multiple ions (IRT1, for example[40]). Currently, only one transporter that exhibits both high affinity and specificity for Mn has been identified and structurally characterized—the MntABC transporter from cyanobacteria[41], a member of the ABC transporter family[42]. Transporters from this family are ubiquitous, having roles in both import and export. In bacteria, ABC transporters function mainly in transport across the plasma membrane[42] (the locations of proteins discussed in this review are depicted in Figure 2).

MntABC was identified in a mutant screen that took advantage of the glucose sensitive strain of *Synechocystis sp*. PCC 6803[43]. In this strain, only mutants with impaired photosynthetic abilities can survive on plates containing glucose in the light. This method has yielded a number of interesting mutants, including one that was mapped to the *mntCAB* operon encoding for the 3 subunits of the MntABC transporter[41]. The mutant exhibited low oxygen evolution rates and could be rescued by the addition of excess Mn. The function of MntABC mutants was further studied by ^{54}Mn transport assays[44]. A difference in the transport rate between wild type and mutant cultures was observed only under Mn deficient conditions, leading the authors to suggest that MntABC is a high affinity transporter which is expressed when Mn is scarce. As with all ABC importers, the MntABC has three components, the MntA cytoplasmic nucleotide binding domain (NBD), the MntB transmembrane permease and the MntC solute binding protein (SBP) found in the periplasmic space. The SBP recognizes and binds the substrate tightly, releasing it into the permease which transports it across the membrane. Energy for cycling the components and for the conformational changes required is provided by ATP binding to the NBD, followed by its hydrolysis and the subsequent unbinding of ADP and P_i. The question that arises is that, since the MntABC system is only expressed at very low Mn concentrations, and since similar ABC importers lack tMI specificity, how does the MntABC system ensure that it is not saturated by other tMIs (especially Zn), thus preventing Mn transport?

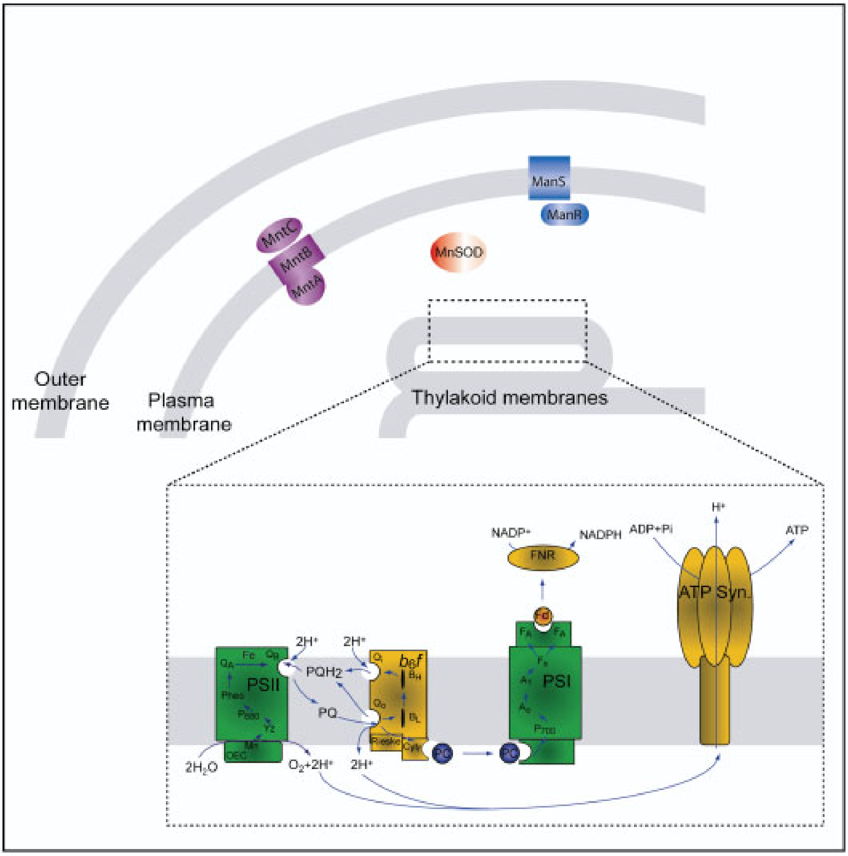

FIGURE 2. Topology of a cyanobacterial cell, the location of Mn enzymes and electron transport chain components. **Top**: Membrane architecture of a cyanobacterial cell with internal thylakoid membrane and external plasma and outer membranes. The locations of the Mn enzymes ManS/ManR, MnSOD, MntABC are noted. **Bottom**: The organization of the protein complexes involved in the electron transport chain in the thylakoid membranes of cyanobacteria, PSII, Cytochrome b_6f PSI and ATP synthase

The structure of the periplasmic binding protein, MntC, was resolved by X-ray crystallography (PDB code 1XVL), which discovered a unique and surprising feature[45]. While the overall sequence similarity with other tMI SBPs is not high (20–30%), the overall structure (Figure 3) was expected (and later found) to be quite similar to other SBPs. When phases were obtained, it was revealed that the asymmetric unit of the crystal contained two forms of the protein; two monomers contained an oxidized disulfide bond while in the third monomer the cysteines were reduced. Mn was shown to bind tightly to the protein with oxidized disulfide bond, but was released upon disulfide reduction. The existence of a redox active cysteine pair in a periplasmic solute binding protein was unexpected, and immediately hinted that this system may be under the control of other redox active components. We suggested a regulatory role for this feature, changing the protein from

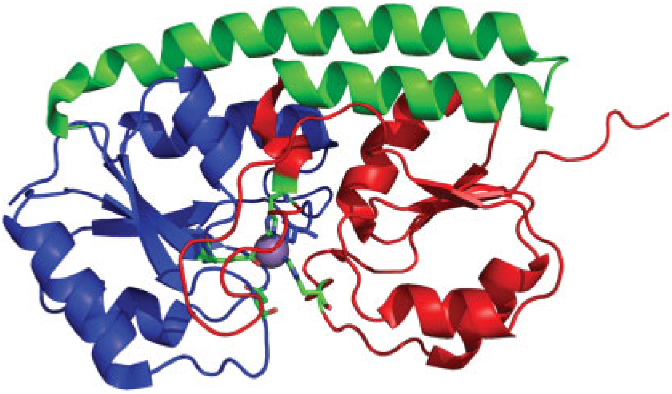

FIGURE 3. MntC (PDB code 1XVL, subunit A) with bound Mn ion (pink sphere). The protein backbone is depicted with cartoon ribbons colored from N to C termini according to the spectrum (blue to red). The active site residues are depicted in stick form

an active (facilitating transport) into an inactive state depending on the redox state of the periplasm. Support for the feasibility of such a mechanism comes from a recent work by Singh and coworkers that demonstrates the function of a plasma membrane protein involved in disulfide bond formation in the periplasmic space of cyanobacteria[46].

In the context of this review, the most important facet of the MntC structure is its ability to describe in structural terms the requirements for the differentiation between Mn and other similar ions. We have recently improved the resolution of the MntC structure to 2.7 Å and determined the structure of a site specific mutant R116A[47]. The improved structure includes additional solvent molecules in the vicinity of the Mn binding site, enabling us to provide a better description of which structural facets are required for Mn selectivity. The immediate ligands are identical to that of non-specific tMI transporters such as PsaA[48]: two histidines, a glutamic acid and an aspartic acid residue (Figure 4). These residues can potentially provide between 4 to 6 lone pair interactions with the tMI (depending on whether the acids are positioned in a bidentate or monodentate orientation). In the *S. pneumoniae* Zn/Mn binding protein, PsaA, all four ligating residues are equidistant from the tMI and the geometry is a distorted pyramid. In the *T. pallidum* Zn/Mn binding protein, TroA (in which the glutamic acid residue is replaced by a third histidine), the tMI–ligand distances are more than 0.5 Å longer and the geometry is more tetrahedral, however the Asp ligating residue may contribute two ligating oxygen atoms[49, 50]. In the *Synechocystis* 6803 Zn binding protein ZnuA, three histidine residues ligate the ion with a very tightly bound water molecule serving as the fourth ligand, in a nearly perfect tetrahedral geometry[51]. The MntC subunits with an oxidized disulfide bond hold the Mn ion very tightly with the two acid ligands at distances of less than 1.9 Å, and the two histidines at about 2.2 Å, forming a highly distorted tetrahedron. In the subunit with reduced disulfide, the two acidic residues move more than 0.5 Å away and indeed Mn is loosely bound to MntC with reduced disulfide bonds. We have analyzed the possible source of this tight binding and found a number of possible reasons. Other homologous SBPs have a conserved DPH motif preceding the two first His ligating residues that have been suggested as being important for proper positioning. In MntC the sequences are EVH and NPH, respectively. The DPH motifs are proposed to facilitate the optimal position of the two histidine tMI ligands[48], however there may be an additional role in controlling the electronic environment and thereby the pKa of the histidine Nε2 atom. Perhaps more

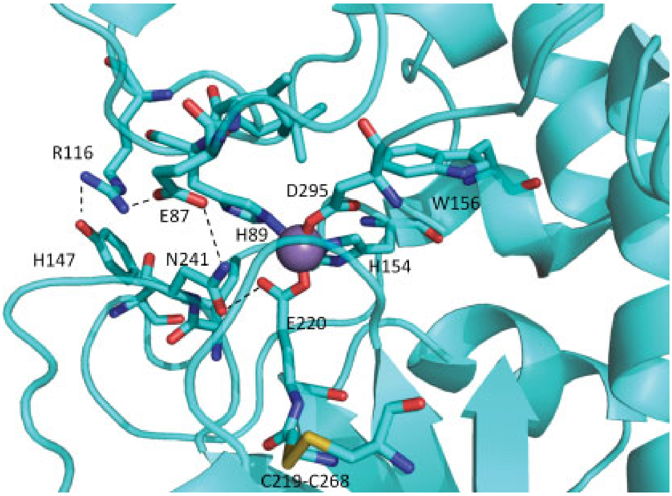

FIGURE 4. MntC active site with bound Mn ion (pink sphere). Residues important for Mn binding specificity and protein structure integrity are shown in stick figures. Black dashed lines show polar interaction network centered on Arg116, locking the proteins N and C terminal domains

important are additional second and third shell residues that are different between MntC and other tMI SBPs. The MntC second shell residues are less polar, while the third shell residues are more polar, including the potentially positively charged Arg116. This residue contributes two interesting aspects to the binding site. On the one hand, the putative exit to the active site becomes rather positive—which may repel a disbound Mn from leaving the active site (Figure 5). In addition, the Arg116 residue forms the center of a network

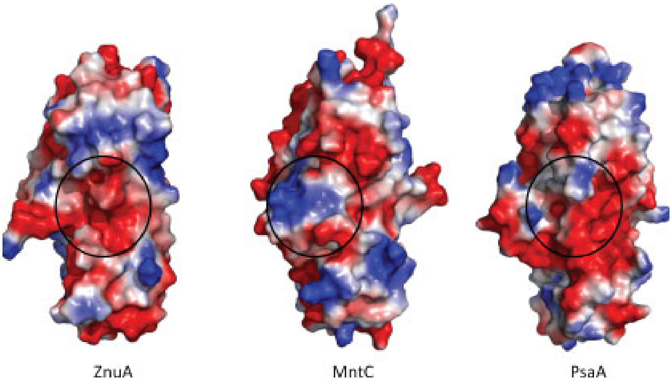

FIGURE 5. Surface electrostatic potential of three transition metal ion solute binding components of ABC transporters: ZnuA (1PQ4, left), MntC (1XVL, middle) and PsaA (1PSZ, right) tMI SPBs. All potentials are depicted at the same level with blue and red representing the positive and negative potentials, respectively. Black ovals show the general surface enclosing the tMI binding site which is about 10–12 Å deeper into the protein's interior

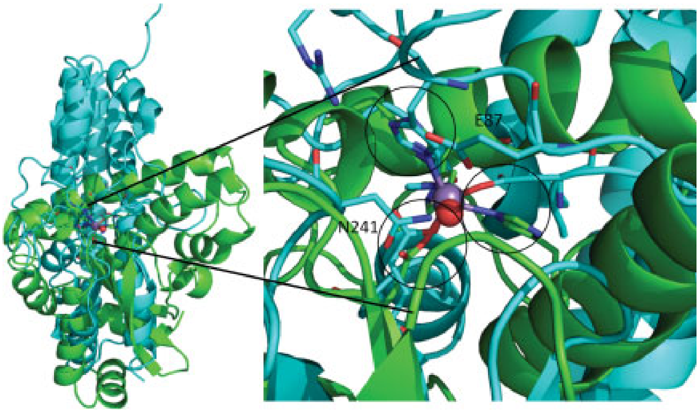

FIGURE 6. Superposition of the *E. coli* MnSOD (3K9S, green) and MntC (1XVL, cyan). Panel A shows the overall lack of similarity between the two proteins. Panel B shows an enlargement of the active site around the bound Mn ion (pink sphere). Four of the five MnSOD ligating residues overlap almost perfectly with the four ligating residues of the MntC, three of the ligating sites are identified by the black circles, with the fourth site located behind the Mn ion. The fifth MnSOD ligand is a water molecule (red sphere). In the MntC, Asn241 and Glu87 partially obstruct this position, perhaps preventing the MntC from uncontrolled activity on ROS

of contacting residues with Glu87, Tyr147 and Asn241, locking the N-terminal and C-terminal domains (Figure 4). This network extends further to the active site itself with Asn241 forming a potential hydrogen bond with the Mn ligating residue Glu219 that is immediately adjacent to the disulfide bond[45]. We recently determined the structure of the R116A mutant MntC and, as expected, the loops that surround the active site became extremely disordered, although there was still a bound tMI in the active site. Further studies will be required to determine the identity of the bound tMI in the R116A mutant. We can conclude that Mn is tightly bound to the active site and that the second and third shells of residues ensure specificity, affinity and a potential chemical controlling step that can either induce release of bound Mn, or prevent binding. The second and third shells also prevent the MntC from becoming a SOD by not providing the necessary protein environment (Figure 6).

We have recently successfully crystallized the MntB permease component of the MntABC transporter system described here. We are in the process of crystal improvement towards structure determination. We hope that this structure will reveal the mechanism of Mn unbinding from the MntC protein, and whether the permease has any novel Mn recognizing elements along the pathway of transfer through the membrane.

B. Mn Transport under Sufficient Conditions: Mn Accumulation in an Outer Membrane Bound Pool

Measurements of ^{54}Mn transport rate have clearly demonstrated that, in addition to MntABC, other transport systems function in cyanobacteria[44]. While Mn transport was severely inhibited in Δ*mntC* mutants under Mn deficient conditions, no inhibition could be measured under Mn sufficient conditions. Furthermore, the Mn uptake rate, as a function of Mn concentration, exhibited a biphasic behavior with increasing transport rates into the millimolar concentration range, both in wild type and in Δ*mntC* mutant cells. Vmax values could not be reached even in the presence of 2 mM Mn[44].

Further analysis of Mn uptake under sufficient conditions[52] found that early logarithmic growth phase *Synechcocystis* 6803 cells have the ability to bind large amounts of Mn from fresh BG11 media. Fractionation of *Synechocystis* cells indicated that most of the bound Mn is associated with the outer membrane[52] but the face of the membrane to which Mn is bound remains to be determined. X-ray absorption spectroscopy verified that this pool contains Mn^{2+} and examination of the extended X-ray absorption fine structure indicated that the Mn interacts with the membrane. However, the nature of the binding species could not be resolved using this technique[52]. Recent work from the Robinson group suggested that a protein from the cupin family, MncA, is the major Mn binding protein in the periplasm of *Synechocystis* 6803 cells[53]. The relation of this protein to Mn mass storage was not further investigated.

Release of Mn from the outer membrane pool could be achieved by incubation with EDTA at concentrations higher than 2 mM. High EDTA concentrations can poke holes in the outer membrane of Gram-negative bacteria in addition to chelating released transition metal ions[54]. Using this method it was possible to establish that in early log phase cells, an excess of *ca* 1×10^7 atoms/cell can be stored in the outer membrane bound pool, approximately 10 times the Mn concentration inside the plasma membrane. Along with the growth of the culture, Mn from the outer membrane pool is gradually utilized, thus keeping the internal Mn concentration constant[52]. This mode of transport is not affected by inactivation of MntABC proteins[52]. Maintaining a Mn concentration gradient of such large proportions requires energy. Indeed, accumulation of Mn in this outer membrane pool was found to be coupled to photosynthetic activity[52]. However, the mechanism by which photosynthetic processes in the thylakoid membrane supports Mn accumulation on the outer membrane is still unknown.

C. Mn Sensing and Regulation of Transport

In order to regulate different Mn transport pathways, cyanobacteria require a Mn sensor. Ogawa and coworkers[55] and Yamaguchi and coworkers[56] have independently identified the components of such a system. A mutant of the ManS sensory kinase was identified in a screen that utilized the *MntCAB* promoter linked to a reporter gene[55]. Microarray analysis of mutants in genes coding for two-component regulators has uncovered, in addition to ManS, the response regulator ManR[56]. The ManS/R system represses the expression of the *mntCAB* operon and its inactivation results in constitutive transcription of its mRNA. Interestingly, inactivation of either *manS* or *manR* did not significantly affect the transcription of any other genes apart from those of the *mntABC* operon[56].

The ManS protein, like many other two-component sensors, is a plasma membrane embedded protein. The sensor domain of the protein is in the periplasm and the kinase domain is in the cytoplasm[55, 56]. The topology of the protein should have an effect on its mode of sensing. Lowering the external Mn concentration will result in the depletion of the outer membrane bound pool, which will activate the ManS/R system in advance of an internal Mn deficiency.

V. Mn AND PSII FUNCTION

A. Assembly of the Mn Cluster: Sequence of Events

The assembly of the Mn_4-Ca cluster occurs for the first time during *de novo* synthesis of PSII complexes and then repeatedly throughout the photodamage repair cycle (reviewed

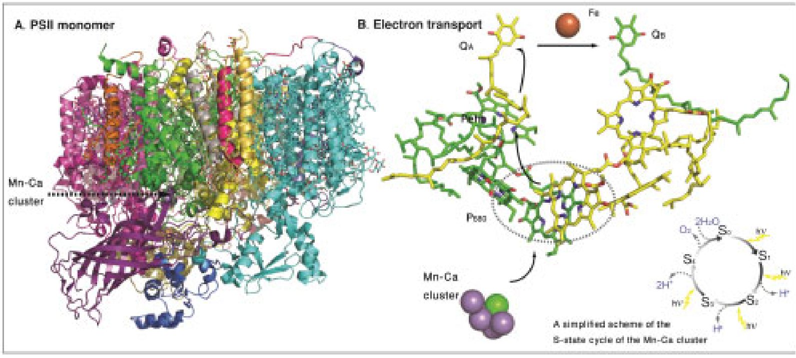

FIGURE 7. Structure of PSII and the electron transport chain within it. (**A**) Structure of a PSII monomer (based on the PDB file 3BZ1[89]). The location of the Mn-Ca cluster is indicated. (**B**) Stripped down view of the electron transfer chain cofactors. Cofactors attached to the D1 or D2 protein are colored green or yellow, respectively. The arrows represent the direction of electron transfer and a simplified scheme of the S-state cycle[90–94] is included at the bottom

in Reference 57). Considering the function of this cluster (Figure 7), it stands to reason that the assembly process will be tightly regulated and that stop-gap measures will be put into place to avoid its untimely activation. So far, two control mechanisms have been identified.

The D1 subunit of PSII protein is translated as a precursor containing a C′-terminal extension. Cleavage of the C′ terminus, a process that is catalyzed by the CtpA protease[57–59], trims the D1 to the correct size and position for contributing to the ligation of the Mn_4-Ca cluster. While the C′ terminal extension can be found in the vast majority of photosynthetic organisms, replacement of pD1 with a mature D1 does not result in any observable problems in the assembly process[60]. Nevertheless, in mixed culture competition experiments between *Synechocystis* 6803 containing either pD1 or mature D1, cells containing pD1 prevailed[60].

Psb27, a protein which is not a part of the mature photosystem, was found to be attached to monomeric PSII centers lacking Mn and extrinsic proteins[61, 62]. These complexes lacked oxygen evolution capacity and had impaired forward electron transfer on the acceptor side[63]. Studies suggest that transient Psb27-PSII assemblies play a role in the assembly and repair cycles of PSII.

Based on these studies we can suggest the following order of events: The pD1 protein is inserted into a partially assembled PSII core complex. After cleavage of its C′ terminus by CtpA, the mature D1 protein can attach the Mn cluster. It is not clear whether the cluster is assembled sequentially from the ligation of individual Mn atoms, or whether the entire complex is assembled and then transferred to PSII by a Mn chaperon. Psb27 prevents Mn attachment by associating with the lumenal side of PSII, blocking the docking sites of the extrinsic proteins[61, 62]. This prevents immature binding and interference with the sequence of the photosystem assembly process. Following the completion of the D1 processing step, Psb27 is detached[62, 64] and the extrinsic donor side proteins can bind.

A prediction for the order of binding of the donor side proteins can be derived from biochemical and structural studies. The major extrinsic protein, PsbO, is attached to the lumenal side of CP47[65–67], followed by PsbV, which binds to CP43[65–68], and PsbU, which interacts with CP43, CP47, PsbO and PsbV[69]. In *Synechcocystis* 6803 the donor side assembly process culminates with the binding of PsbQ. PSII complexes containing PsbQ were more active and stable as compared with PSII units lacking this protein[14, 64]. PsbP was found to be associated only with a fraction of PSII complexes and is not believed to be a functional component of the donor side, but rather to have a regulatory role[70].

Binding of the Mn ions and extrinsic proteins to the donor side of PSII are required but not sufficient for the function of PSII. The binding is accompanied by a series of light driven Mn oxidation events necessary for the correct functional assembly of the Mn-Ca cluster in a process termed as photoactivation[71].

B. Assembly of the Mn Cluster: Topology

The structure of cyanobacterial cells is more complex than the structure of other prokaryotic cells. On top of a periplasmatic and intracellular space, defined by the outer (OM) and plasma membrane (PM), which are common to all Gram-negative bacteria, cyanobacteria contain a third lumenal space inside the thylakoid membrane (TM). Thylakoid membranes take up a large fraction of the intracellular space, creating a maze that stands in the way of transport inside the cell[72, 73]. From an evolutionary standpoint, thylakoid membranes are considered the descendents of the photosynthetic membranes of the non-oxygenic photosynthetic purple bacteria[74]. However, while in purple bacteria the photosynthetic membranes invaginate from the plasma membrane[75], in cyanobacterial thylakoids there is no clear evidence for such a connection[72, 73].

While it is clear that PSII functions in the thylakoid membranes, there are conflicting reports as to the site of its biogenesis. Smith and Howe[76] were able to detect chlorophyll and D1 proteins in PM membranes of *Synechococcus sp*. PCC 7942. In this study, membranes were isolated by sucrose density gradient centrifugation. Using a two-phase separation technique[77], Zak and coworkers were able to detect D1, Cytochrome b_{559} and CtpA, but not CP43, CP47 or psbO in PM membranes of *Synechocystis* 6803[78]. The PSII proteins present in the PM preparation formed a complex that migrated as one band in native gels. Based on these data they suggested that the site of PSII biogenesis is in the plasma rather than in the thylakoid membrane. This hypothesis represented a departure from the accepted view of the location of PSII assembly in the chloroplast thylakoids of eukaryotic organisms[79]. In a later work using the same preparation technique[80], it was demonstrated that a limited extent of charge separation can be measured in OM partial PSII assemblies. The concentration of Mn attached to PM membranes was found to be *ca* 20% that of the TM on a chlorophyll basis[80]. The lack of stable charge separation and Mn in the PM is not surprising considering the role of the CP47 and CP43 extra-membranal loops in stabilizing the oxygen evolving complex[81]. Jansen and coworkers[82] combined the two techniques, performing sucrose gradient density centrifugation followed by two-phase separation, and were still able to detect D1, D2 and cytochrome b_{559} in PM preparations of *Synechocystis* 6803. In a recent study from the same group[83], PM right-side out and inside out vesicles were isolated from *Synechocystis* 6803. The additional fractionation step revealed heterogeneity with respect to protein distribution within the PM. D1 and pD1 were enriched in inside out as compared to right-side out vesicles on a total protein basis.

While the results of the studies mentioned above suggest a PM PSII assembly pathway, other studies did not detect chlorophyll in PM. These include work on membranes isolated by sucrose gradient centrifugation from *Synechococcus* 7942[84], *Synechocystis* 6714[85, 86], or by hyperspectral confocal fluorescence imaging of *Synechocystis* 6803 cells[87]. Peschek and coworkers[88], analyzing membrane fractions isolated from *Synechococcus* 7942 cells, could detect precursors in the chlorophyll biosynthesis pathway but very little or no chlorophyll in the PM.

These reports seem conflicting but they are not mutually exclusive. It is possible that PSII assembly takes place in different topological locations during *de novo* synthesis or during repair, when Mn concentrations are high or low or in response to other environmental cues. Any attempt to further resolve Mn transport routes and PSII assembly pathways must take into account the variability imposed by changes in the bioavailability of Mn. While it is hard to control transition metal bioavailability, and even harder to precisely control the physiological status of the cells, it is nevertheless essential that these parameters will be measured and reported so that experimental results from different growth conditions and from different cyanobacterial strains may be compared.

VI. ACKNOWLEDGMENTS

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Catalytic enantioselective reactions using organomanganese compounds

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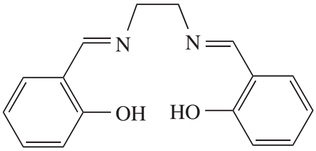
I. INTRODUCTION

Unlike some s-block and transition metals, the arsenal of the organomanganese complexes bearing Mn^{III} is defined by a limited number of structures which offer a finite list of asymmetric transformations[1]. This chapter covers the achievements made within the last quarter of a century in the area of the enantioselective reactions catalyzed by organomanganese complexes. The Mn^{III}–salen compounds are chiefly used as potent oxene- and nitrene-transfer agents in the epoxidation and aziridination reactions of C=C bonds. The scope, limitations and mechanistic studies of these processes will be discussed. An additional class of transformations performed by the Mn^{III}–salen is hydroxylation and amination of C–H bonds and oxidation of sulfides. These and other less frequently utilized methods can be found in the present chapter. Less common Mn–porphyrin and other scarcely studied complexes will be discussed as well.

Although a limited diversity in the organomanganese synthetic capacity is allegedly disadvantageous, this field provides a source of intrigue and shows a potential for a multitude of applications in the synthesis of functional organic molecules possessing asymmetric cores. The availability, low environmental impact and amenability to large-scale applications make the organomanganese complexes attractive candidates for the efforts to expand the scope of their performance. Compiled information presented below is a significant opportunity to attract the attention of synthetic chemists for the future development in the field of manganese-based enantioselective methodologies.

II. MANGANESE^{III}–SALEN COMPLEXES

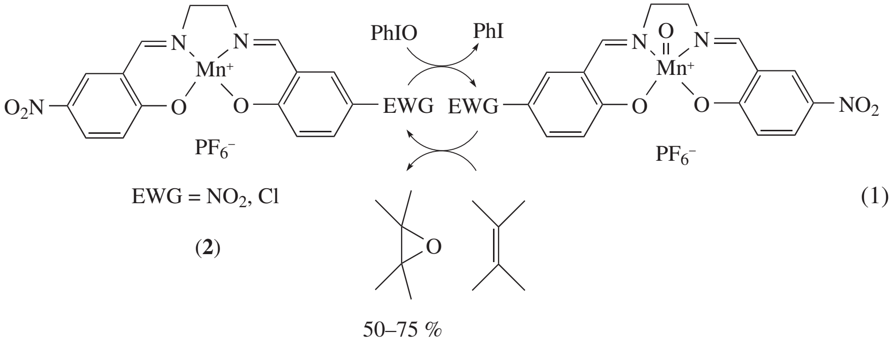
The name ‘salen’ was coined to describe a ligand core based on the *N*,*N*′-ethylenebis(salicylideneaminato) **1** (Figure 1), first prepared by Pfeiffer and coworkers by a condensation of ethylenediamine and salicylaldehyde[2].



(**1**)

FIGURE 1

It was first used in 1986 by Kochi and coworkers as a cationic manganese complex **2** for the achiral catalytic epoxidation of unfunctionalized olefins upon treatment by iodosylbenzene (PhIO) as a terminal oxidant (equation 1)[3].



EWG = NO_2, Cl

(**2**)

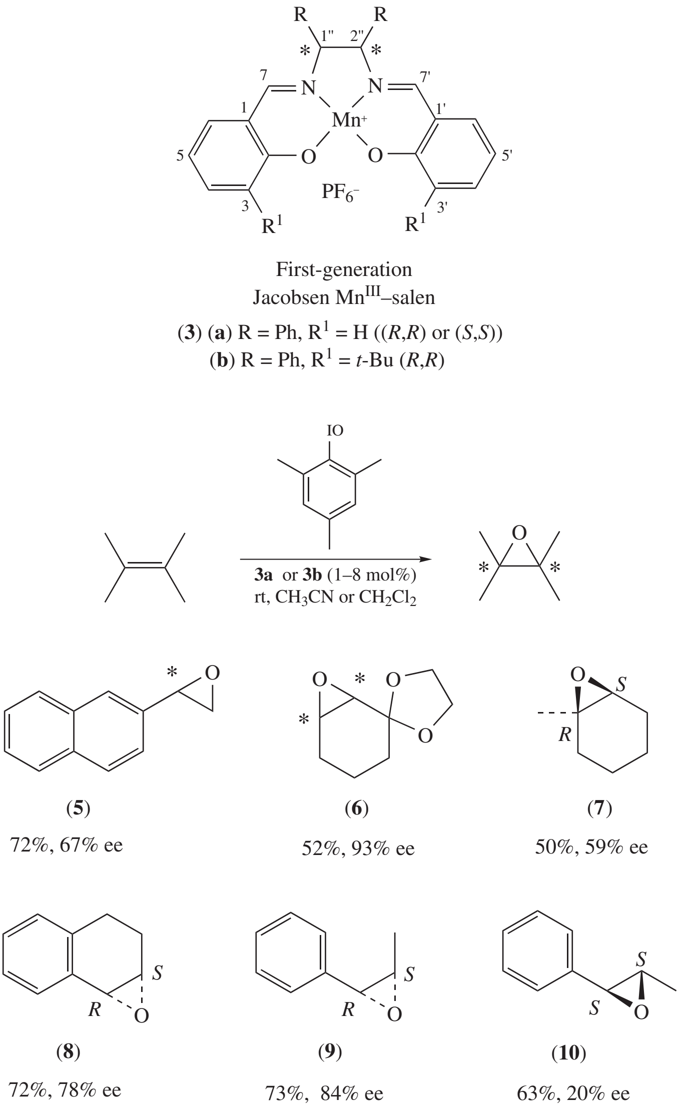
(1)

An oxo-Mn^V–salen species was suggested as a putative intermediate, thereafter detected by MS/MS study of μ-oxo Mn^{IV}–salen complexes[4]. As shown below, Kochi's seminal discovery has prompted an intensive development of asymmetric epoxidation reactions catalyzed by Mn–salen species.

A. Enantioselective Epoxidation Reactions

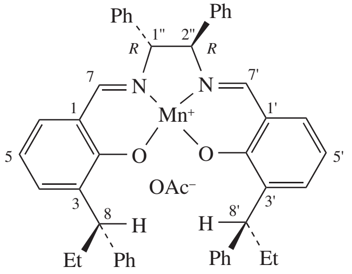
1. Historical background

Optically active epoxides are important synthetic intermediates for the synthesis of oxygen-containing natural and unnatural products[5]. The versatility of these functional groups can be realized by the stereoselective addition of various nucleophiles such as hydrides, organometallic reagents, oxygen- and nitrogen-containing species[6]. The great importance of the asymmetric epoxidation of unfunctionalized olefins lies in the fact that, unlike in the Ti-tartrate-catalyzed epoxidation of allylic alcohols[7], there is no need of the adjacent alcohol group. This practical access to simple epoxides vastly expands the substrate range and affords valuable enantiomerically enriched synthons. A single-step oxidation of olefins with electrophilic chiral oxene in mild conditions is a particularly attractive methodology, as was almost simultaneously demonstrated by the groups of Jacobsen and Katsuki in the early 1990s. Complexes **3a** and **3b**, synthesized by Jacobsen on the basis of Kochi's Mn^{III}–salen framework, possessed nearly planar geometry and one chiral subunit at the diamine backbone bearing pseudoequatorial phenyl substituents (Scheme 1)[8]. The reaction was carried out with iodosylmesitylene as a terminal oxidant and 1–8 mol% catalyst. Monosubstituted, nonconjugated disubstituted and trisubstituted prochiral olefins afforded the epoxides **5–7** in moderate to good selectivities. *cis*-Disubstituted substrates were converted to the epoxides **8–9** with higher selectivities than *trans*-β-methylstyrene, which formed an epoxide **10** in 20% ee. Remarkably, Katsuki's complex **4** differed from **3a** and **3b** only by an enantiomerically pure 1-phenylpropyl substituent at C(3) and C(3′) positions (Scheme 2)[9]. When applied on dihydronaphthalene, (*cis*)- and (*trans*)-β-methylstyrene in the presence of iodosylbenzene and 2-methylimidazole as a donor ligand, epoxides **8**, **9** and **10** were formed in



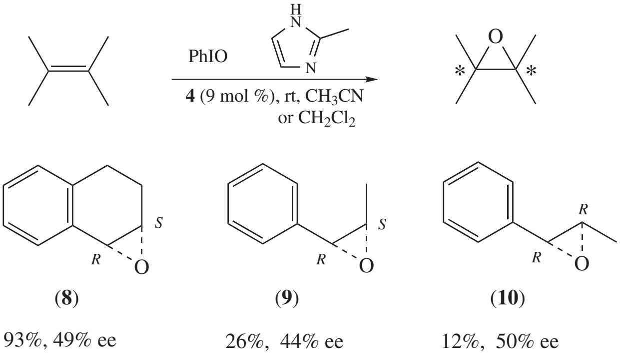
SCHEME 1

up to *ca* 50% ee respectively (Scheme 2). These very first examples of enantioselective catalytic epoxidation of simple alkenes were overwhelming and have evolved in an intensive search for modified ligands to further improve the enantiomeric outcome. Clearly, complexes **3a** and **3b**—Jacobsen's first-generation Mn–salen—are superior for *cis*-disubstituted alkenes than complex **4**. However, the dissimilarity in the selectivity was compromised thereafter by rationally designed modifications as disclosed later in this chapter.



First-generation
Katsuki Mn^{III}–salen

(**4**)

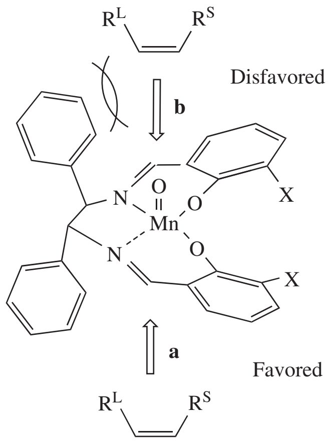


SCHEME 2

In attempt to rationalize the enantiofacial discriminations observed with complexes **3a,b** Jacobsen and coworkers suggested a 'side-on' alkene approach model **11**, where the alkene could only approach the Mn=O site from the sterically less hindered direction **a** (Figure 2). Abundant studies have been reported on porphyrin-catalyzed epoxidation wherein the side-on approach has been postulated[10]. Although no reports existed on the pathway of the oncoming olefin and its conformational orientation in respect to salen, its structural similarity to porphyrin made the side-on approach applicable. Thus, the smallest alkene group R^S is supposedly oriented toward the bulky substituent X on the phenoxide ring[11]. Approach **b** is inaccessible due to the bulky *syn* interaction between the incoming substrate and the ligand, whereas two remaining side-on trajectories are disfavored due to the phenyl and *t*-butyl substituents.

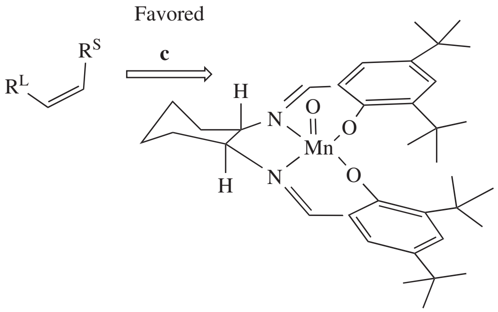
2. Jacobsen epoxidation

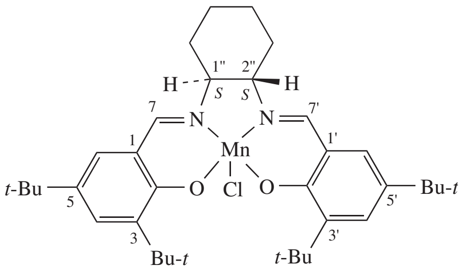
Following the model described above, the second generation of Jacobsen's ligands was designed (**12**), featuring a cyclohexyl moiety at the C1″ and C2″ diamine backbone and *t*-butyl groups at the C(5) and C(5′) positions (Figure 3)[12]. As a result, all side-on olefin accesses were now ruled out because of the steric congestion with the exception



(**11**)

FIGURE 2



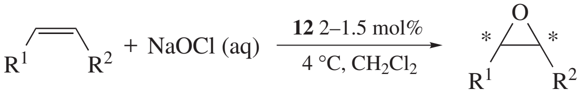


(**12**)

FIGURE 3

of approach **c**. The latter allowed better proximity between the alkene and the diamine chiral subunit and provided distinct face selectivity by the sense of unfavorable interaction between the axial hydrogen and the larger substituent.

This newly devised complex, although relatively flat, has exhibited high enantiomeric excesses with a variety of *cis*-disubstituted alkenes, especially when inexpensive common bleach NaOCl was used stoichiometrically as an oxidant (equation 2)[11, 13].



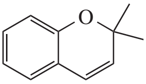
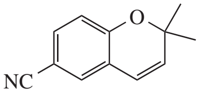
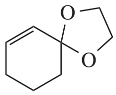
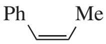
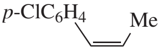
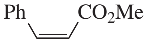
(2)

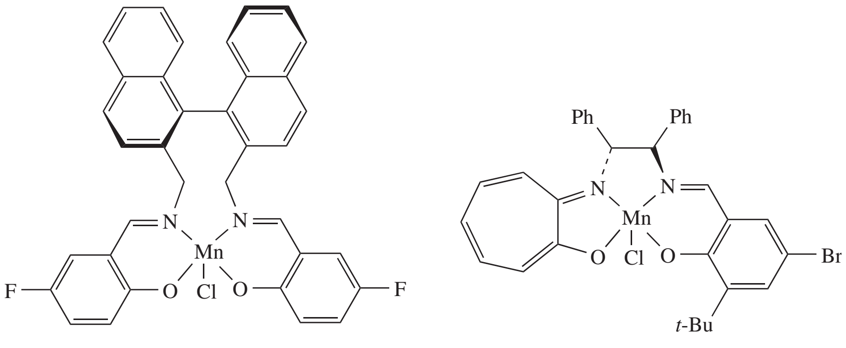
89–98 % ee

As shown in Table 1, the highest enantioselectivities are obtained for the conjugated olefins like chromenes—a bicyclic structure which recurs in a variety of natural products (entries 1 and 2). This method was further applied on different 2,2-dimethylchromene derivatives to finally obtain antihypertensive agents in enantiomerically pure form[14]. The epoxidation of *cis*-methyl cinnamate, which is a valuable precursor to optically active *erythro*-glycidic esters, exhibits higher selectivities and turnover numbers when a substoichiometric quantity of 4-phenylpyridine *N*-oxide (4-PPNO) is added[15] (entry 6). While conjugated *cis*-disubstituted olefins generally afford high enantioselectivities, simple 1,3-cycloalkadienes (except for entry 3, Table 1) show only moderate enantioselectivity with **12**[16].

In contrast to *cis* olefins, *trans*, terminal, tri- and tetrasubstituted olefins turned out to be poor substrates for this catalyst, revealing slow epoxidation and ee values below the synthetically useful values. It is generally reasoned to be so by the steric interactions which likely prevent the substrate side-on approach in the oxygen-atom transfer process

TABLE 1. Representative asymmetric epoxidation reactions catalyzed by **12** (equation 2)

Entry	Olefin	Yield (%)	ee (%)	Additive	mol% of **12**
1		72	98	none	4
2		96	97	none	3
3		63	94	none	15
4		84	92	none	4
5		67	92	none	4
6		65	89	4-PPNO (0.4 eq)	1



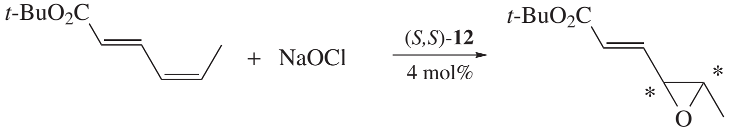
up to 86% ee

up to 83% ee

FIGURE 4

(see the model in Figure 3)[17]. In this respect, catalysts presented in Figure 4 can be alternatively used in the asymmetric epoxidation of such ‘difficult’ substrates like *trans*-β-methylstyrene by *m*-CPBA/NMO protocol at $-78\,^{\circ}$C[18]. Cr(Salen) complexes constitute a possible alternative to the epoxidation of *trans*-β-methylstyrene, reaching up to 92% ee of the corresponding *trans*-epoxide[19].

Different access to *trans*-epoxides is based on the reaction of acyclic *cis* substrates. Thus, (*Z*,*E*)-diene **13** and conjugated *cis*-enyne **15** were epoxidized by the Mn−salen catalyst (*S*,*S*)-**12** regio- and chemoselectively, respectively, with moderate to excellent enantioselectivities affording *trans* monoepoxides **14** (equation 3) and **16** (equation 4)[20].

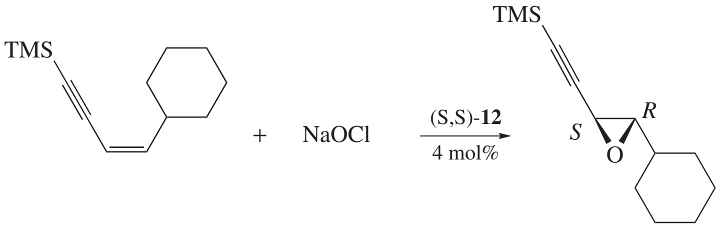


(**13**)

(**14**) 67%

trans:*cis* = 7:1
ee (*trans*) = 66%

(3)



(**15**)

(**16**) 65%

trans:*cis* = 5.2:1
ee (*trans*) = 98%

(4)

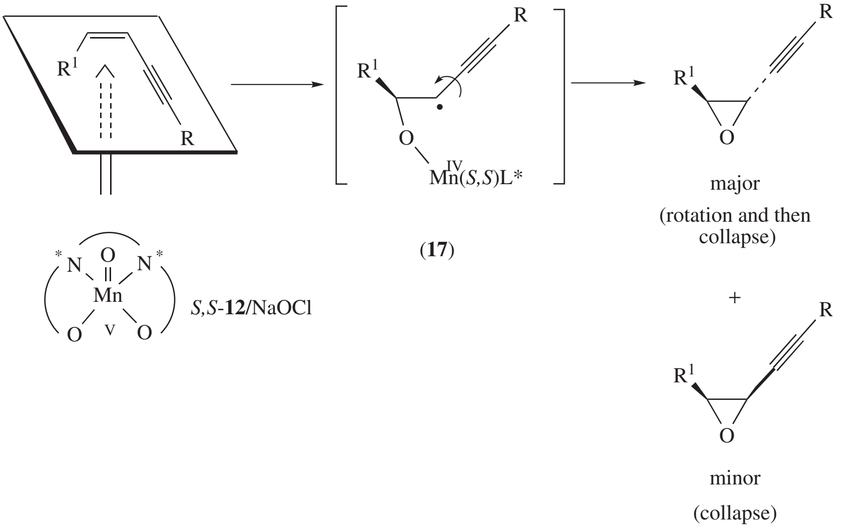


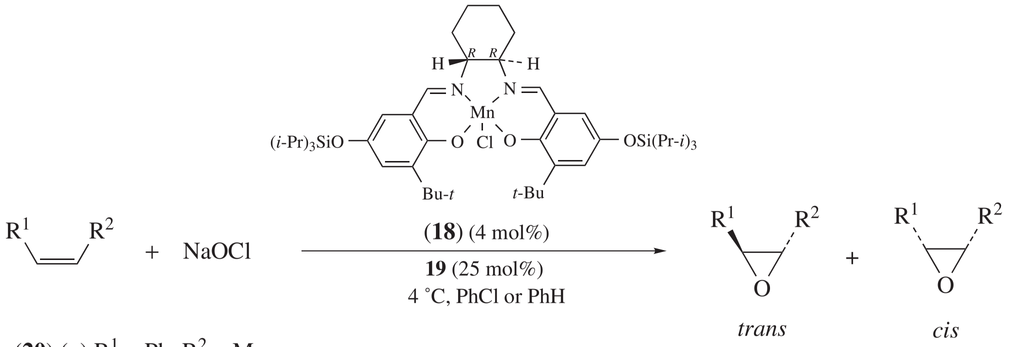
FIGURE 5

This face-selective nonstereospecific process was accredited to the stepwise oxygen transfer which involves the relatively long-lived intermediate radical or polar species **17** (Figure 5).

Yet, the general method for the preparation of *trans*-epoxides did not exist until the report of the cinchona alkaloid salts **19** used under basic conditions to diastereo- and enantioselectively epoxidize simple *cis*-alkenes **20a–d** with Mn–salen complex **18** (equation 5)[21].

The generation of both *cis*- and *trans*-epoxides from acyclic *cis*-olefins is a common phenomenon generally attributed to stepwise C–O bond formation via radical or polar intermediate species (see Figure 5)[3a, 22]. The authors have shown that chiral quaternary ammonium salt **19** induced high selectivity for the formation of *trans*-epoxides while chiral (salen)Mn complex **18** dictated the enantiomeric composition and the absolute configuration of the major epoxide products. Despite the visible effect of chiral quaternary ammonium salt, the mechanistic basis that accounts for the described selectivity in the (salen)Mn-catalyzed epoxidations remained unclear. The control over the *cis:trans* ratio in the *cis*-disubstituted olefin epoxidations can be further maintained by a properly chosen additive. Thus, when *cis* product is exclusively required, *N*-methylmorpholine *N*-oxide, used instead of **19** at −78 °C with *m*-CPBA as an oxidant, affords 98% ee in the epoxidation of *cis* β-methylstyrene[23b].

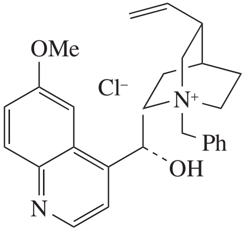
Further development of the epoxidation methods for the terminal, tri- and tetrasubstituted olefins have extended the scope of the challenging substrates pool. A protocol for rapid and nearly quantitative catalytic epoxidation of styrene and its derivatives at low temperature and homogeneous conditions has elegantly attained monosubstituted epoxides **21** in up to 86% enantiomeric excess (equation 6)[23]. The architecture of **22** differs from that of **12** by the phenyl substituents replacing the cyclohexyl on the diamine fragment, whereas both C(5) and C(5′) keep bearing bulky electron-donating groups to ensure an effective steric bulk.



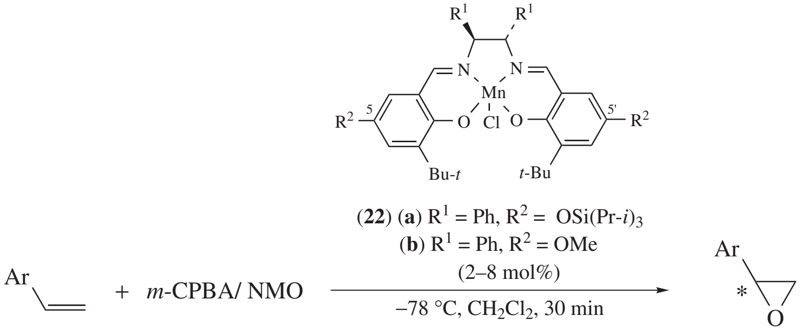
(5)

(**20**) (**a**) R^1 = Ph, R^2 = Me
(**b**) R^1 = *t*-Bu, R^2 = Et
(**c**) R^1 = Ph, R^2 = Ph
(**d**) R^1 = *p*-$MeOC_6H_4$, R^2 = CO_2Pr-*i*

R^1	R^2	*trans:cis*	ee % of *trans*
Ph	Me	95:5	81 (*S*,*S*)
t-Bu	Et	69:31	84 (n.d.)
Ph	Ph	>96:<4	90 (*S*,*S*)
p-$MeOC_6H_4$	CO_2Pr-*i*	89:11	86 (*S*,*S*)



(**19**)



(**21**) (6)

Ar	Catalyst	ee (%)	Yield (%)[a]
Ph	**22a**	86	89
p-FC_6H_4	**22a**	85	83
m-$CF_3C_6H_4$	**22a**	82	85
m-$CH_3C_6H_4$	**22b**	80	83
p-$HO_2CC_6H_4$	**22a**	72	45[b]

[a] Isolated yield.

[b] Isolated yield after conversion to the methyl ester.

By lowering the reaction temperature, an enhancement of the enantiofacial selectivity, otherwise ranging within 50–70% for terminal olefins, was achieved along with shutting down the *trans* pathway, commonly responsible for the enantiomeric 'leakage' present in this type of transformations (Figure 6).

Sodium hypochlorite was replaced in this system by the nonaqueous terminal oxidant *m*-CPBA whose uncatalyzed racemic epoxidation of styrene was circumvented by the excess of *N*-methylmorpholine-*N*-oxide (NMO). Despite this promising example, access

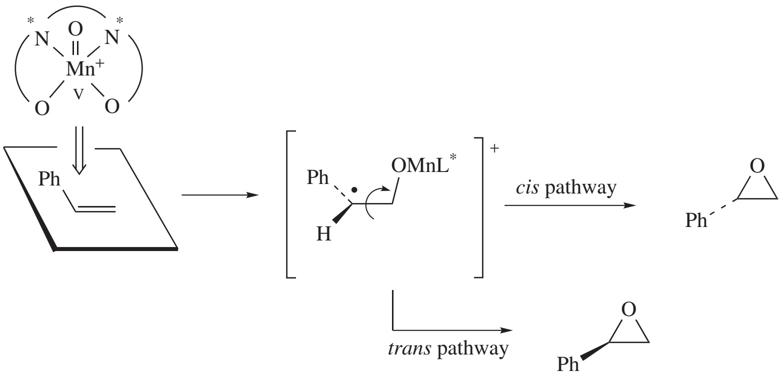
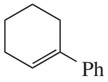
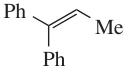


FIGURE 6

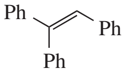
TABLE 2. Representative examples of trisubstituted olefins subjected to epoxidation reactions[a]



(**23**)



(**24**)



(**25**)

Substrate	Isolated yield	ee (%)	Epoxide configuration
23	69	93	(−)-(*S*,*S*)
24	91	95	(−)-(*S*)
25	97	92	(+)-(*S*)

[a] The epoxidations were catalyzed by 3 mmol% of (*R*,*R*,)-**12** using CH_2Cl_2 as solvent, NaOCl as oxidant, 4-PhC_5H_4NO as additive.

to terminal epoxides via epoxidation is impractical and alternative approaches have been developed for these important chiral building blocks of the modern chemical industry[24].

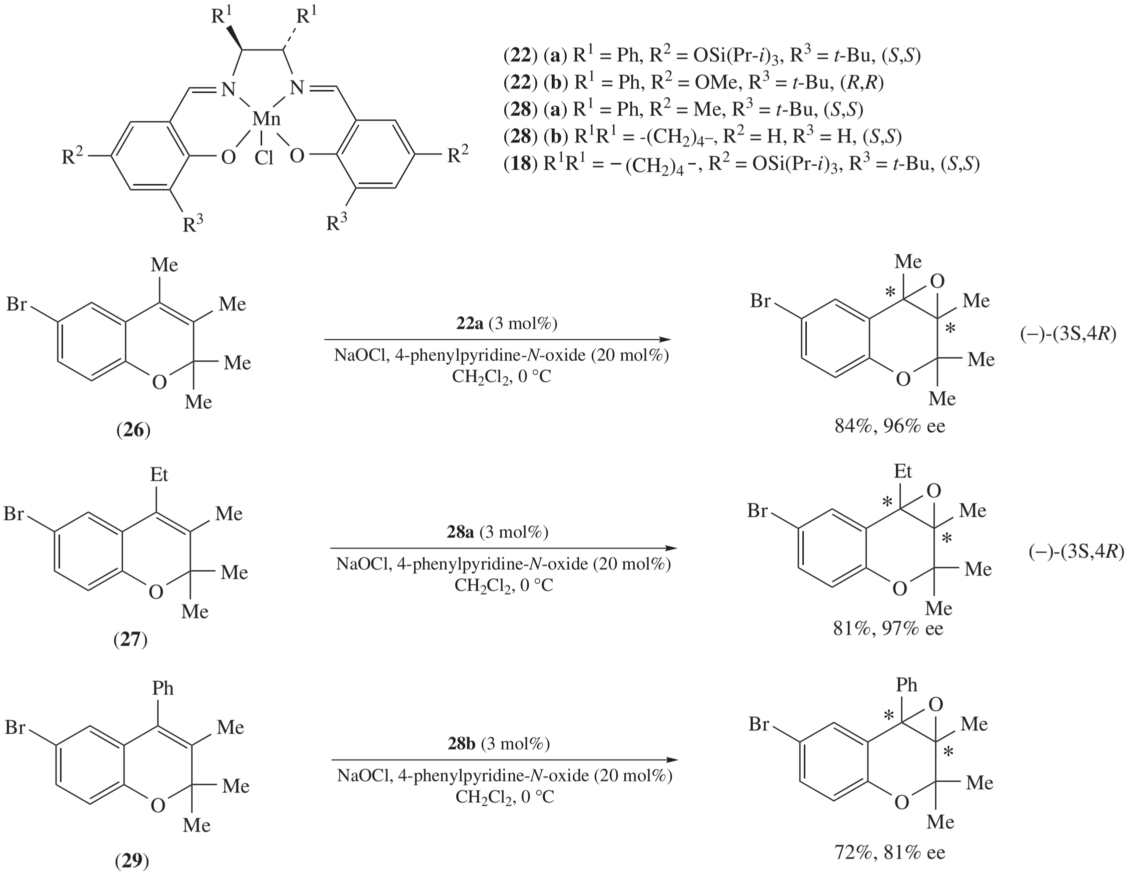
The compatibility of the (salen)Mn complexes with trisubstituted olefins was proven upon treatment of **23–25** in nonprotic solvent (CH_2Cl_2, methyl *tert*-butyl ether or EtOAc) with (*R*,*R*)-**12**, sodium hypochlorite and 4-phenylpyridine *N*-oxide (Table 2)[18, 25]. This kind of additive has been demonstrated to act as the axial ligand that binds to the Mn center *trans* to the oxo ligand, consequently supplying a profound impact on the ratios of enantiomers, reaction rate and yield[26].

Similarly to other olefin substitution patterns, only the conjugated trisubstituted systems exhibited high enantioselectivities, leaving their nonconjugated counterparts in the range of low-to-moderate ee values (e.g. 1-methylcyclohexene afforded only 40% ee upon the epoxidation process)[27]. Yet, as evidence for the synthetic usefulness of such epoxidations, such valuable chiral auxiliaries like *trans*-2-phenylcyclohexanol[28] and 1,1,2-triphenylethane-1,2-diol[29] were synthesized in >99% ee.

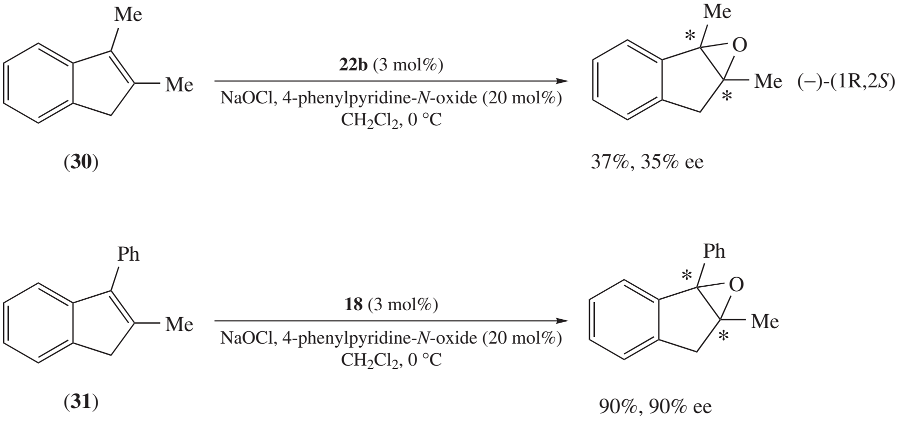
As mentioned previously, tetrasubstituted substrates have been found to undergo epoxidations in slow rates and low face selectivities. This most challenging case in the nondirected asymmetric epoxidation was partially unraveled for certain substrates and catalysts; however, no straightforward structure–reactivity correlation has been realized. Thus, rather congested chromene derivatives **26** and **27** displayed good reactivity and ee values when treated with very bulky catalysts **22a** and **28a** (Scheme 3)[30]. In contrast, good levels of enantioselection were attained in epoxidation of bulkier chromene **29** only with the unhindered catalyst **28b**[31]. To emphasize the subtleties of the chiral recognition, dimethylindene **30** could not afford reasonable ee values with any of the catalysts (**22a**, **22b**, (*S*,*S*)-**18**), whereas the more hindered phenyl-substituted derivative **31** underwent epoxidation with very high enantioselection and hindered catalyst (*S*,*S*)-**18** (Scheme 4).

Since a side-on approach (Path c, Figure 3) to a metal-oxo intermediate is not possible for the sterically hindered tetrasubstituted alkenes, high enantioselectivities nonetheless obtained in these transformations were interpreted by a top-on approach (Figure 7, path d).

Since the first report by Jacobsen and coworkers on the enantioselective epoxidations catalyzed by **12**[12], numerous structural and electronic modifications of the latter were investigated and applied (Figure 8)[32]. From the screening of the results obtained within the last two decades by Jacobsen's group and others in the asymmetric epoxidations


R^1
R^1
N
N
Mn
O
Cl
O
R^2
R^2
R^3
R^3
(**22**) (**a**) R^1 = Ph, R^2 = OSi(Pr-*i*)$_3$, R^3 = *t*-Bu, (*S*,*S*)
(**22**) (**b**) R^1 = Ph, R^2 = OMe, R^3 = *t*-Bu, (*R*,*R*)
(**28**) (**a**) R^1 = Ph, R^2 = Me, R^3 = *t*-Bu, (*S*,*S*)
(**28**) (**b**) R^{1}R^1 = -(CH$_2$)$_4$–, R^2 = H, R^3 = H, (*S*,*S*)
(**18**) R^{1}R^1 = −(CH$_2$)$_4$−, R^2 = OSi(Pr-*i*)$_3$, R^3 = *t*-Bu, (*S*,*S*)
Br
Me
Me
Me
Me
O
(**26**)
22a (3 mol%)
NaOCl, 4-phenylpyridine-*N*-oxide (20 mol%)
CH$_2$Cl$_2$, 0 °C
Br
Me
O
Me
Me
Me
O
*
*
(−)-(3S,4*R*)
84%, 96% ee
Br
Et
Me
Me
Me
O
(**27**)
28a (3 mol%)
NaOCl, 4-phenylpyridine-*N*-oxide (20 mol%)
CH$_2$Cl$_2$, 0 °C
Br
Et
O
Me
Me
Me
O
*
*
(−)-(3S,4*R*)
81%, 97% ee
Br
Ph
Me
Me
Me
O
(**29**)
28b (3 mol%)
NaOCl, 4-phenylpyridine-*N*-oxide (20 mol%)
CH$_2$Cl$_2$, 0 °C
Br
Ph
O
Me
Me
Me
O
*
*
72%, 81% ee

SCHEME 3



SCHEME 4

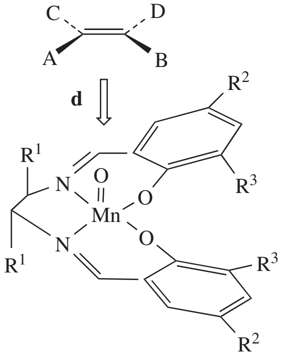
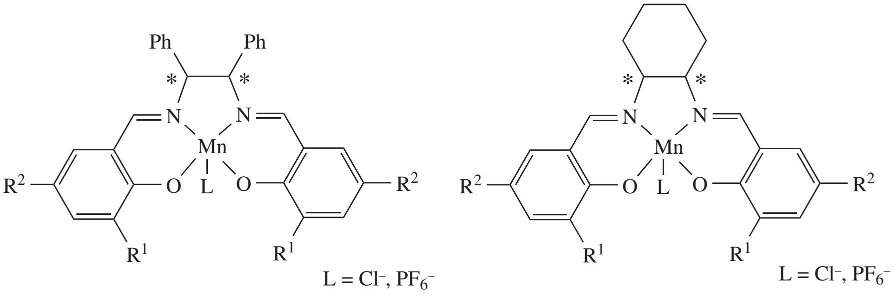


FIGURE 7

of conjugated and nonconjugated *cis*-disubstituted[12, 14, 33], mono-[23], tri-[25] and tetrasubstituted[30] olefins, complex **12** remains the most efficient catalyst, balancing between the enantioselectivity, broadness of substrates and accessibility. Its substrates scope also includes acyclic conjugated polyenes[21b], cyclic dienes[16, 34], heterocyclic enamines[35], cinnamate esters[36], enol ethers[37] and α-pinene[38]. Both enantiomers of **12** are commercially available and easily synthesized; both feature air-stability and long-period storage without appreciable decomposition.

Both steric and electronic factors are responsible for the enantiomeric selectivities exhibited by the complexes **3a**, **3b**, **12**, **18**, **22a**, **22b**, **28a**, **28b**, **32–45** presented in Figure 8, albeit no uniform relationship between the ligand architecture and the obtained ee values for a certain substrate has been delineated so far. Notwithstanding, some cases are predictable and prone to a rationalization. Thus, Jacobsen and coworkers reported on the electron tuning of the 5,5′-substituents affecting dramatically the ee values[27, 39]. It was demonstrated that 2,2-dimethylchromene was epoxidized in 22% ee when **33** was used as a catalyst, while 96% ee were obtained with **22b**. This extreme difference was rationalized



(**3a**) $R^1 = H, R^2 = H$
(**3b**) $R^1 = t\text{-Bu}, R^2 = H$
(**22a**) $R^1 = t\text{-Bu}, R^2 = OSi(Pr\text{-}i)_3$
(**22b**) $R^1 = t\text{-Bu}, R^2 = OMe$
(**28a**) $R^1 = t\text{-Bu}, R^2 = Me$
(**32**) $R^1 = t\text{-Bu}, R^2 = Cl$
(**33**) $R^1 = t\text{-Bu}, R^2 = NO_2$
(**34**) $R^1 = t\text{-Bu}, R^2 = OSi(Me)_3$
(**35**) $R^1 = t\text{-Bu}, R^2 = OSi(Et)_3$
(**36**) $R^1 = t\text{-Bu}, R^2 = OBu\text{-}i$
(**37**) $R^1 = t\text{-Bu}, R^2 = OPr\text{-}i$

(**12**) $R^1 = t\text{-Bu}, R^2 = t\text{-Bu}$
(**18**) $R^1 = t\text{-Bu}, R^2 = OSi(Pr\text{-}i)_3$
(**28b**) $R^1 = H, R^2 = H$
(**38**) $R^1 = t\text{-Bu}, R^2 = Me$
(**39**) $R^1 = t\text{-Bu}, R^2 = OMe$
(**40**) $R^1 = t\text{-Bu}, R^2 = Cl$
(**41**) $R^1 = t\text{-Bu}, R^2 = NO_2$
(**42**) $R^1 = t\text{-Bu}, R^2 = OSi(Me)_3$
(**43**) $R^1 = t\text{-Bu}, R^2 = OSi(Et)_3$
(**44**) $R^1 = t\text{-Bu}, R^2 = OBu\text{-}i$
(**45**) $R^1 = t\text{-Bu}, R^2 = OPr\text{-}i$

FIGURE 8

by the electron-donating nature of the C(5)−C(5′) groups in **22b** which allegedly stabilize the O=Mn(salen)$^+$ species, which in turn forms a more product-like TS with more specific nonbonding interactions between the substrate and the oxidant[3a,b, 40]. Computational and mass spectrometric evidence on the stability of various O=Mn(salen) species were reported and reviewed[41]. Detailed discussion on further catalyst electronic and steric tuning (Figure 8) and subsequent reactivity studies are well-presented in several reviews[42].

The most prominent examples of the epoxides obtained by the above-mentioned Jacobsen-type complexes (Figure 8) appear in Table 3. Despite the viable access to different asymmetric epoxides, the scope of this methodology is confined to conjugated substrates.

A wide variety of oxidants can be used with the Mn(salen) complexes discussed above[42c]. Several research groups have drawn attention to the fact that under some conditions the choice of the terminal oxidant can significantly influence the yield, the regio-, diastereo- and enantioselectivity[43]. It is presumed that in particular cases the oxidant nature likely dictates the structure of the active epoxidation agent(s). Sodium hypochlorite (NaOCl) solution comprises the best practical oxidant for the Jacobsen-type catalysts and is most commonly used upon basic pH[13a, 44], possessing such features as relatively low cost, environmentally benign reduction products and impact on the yield, specificity, diastereomeric and enantiomeric excesses. In case of substrate or product instability in the aqueous environment, sodium hypochlorite should be replaced by other viable options. Among a variety of other oxidants, iodosylbenzene, hydrogen peroxide, molecular oxygen and peracids are the most distinguished cases. The usefulness of iodosylbenzene is hampered by its low solubility in organic solvents, although a soluble version was also developed[45]. Schwenkreis and Berkessel have presented a protocol for H_2O_2 to be

TABLE 3. Representative epoxides obtained by Jacobsen-type Mn(salen) catalysts (1–10 mol%)

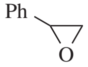
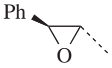
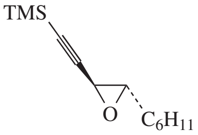
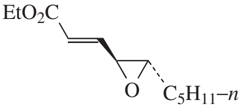
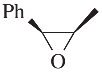
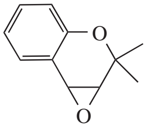
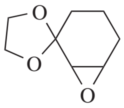
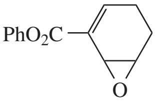
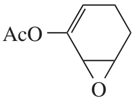
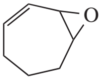
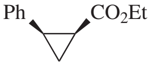
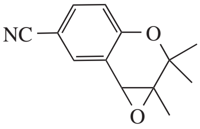
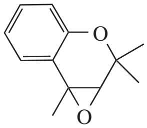
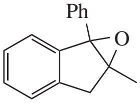
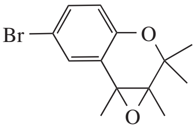
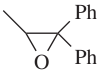
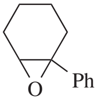
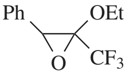
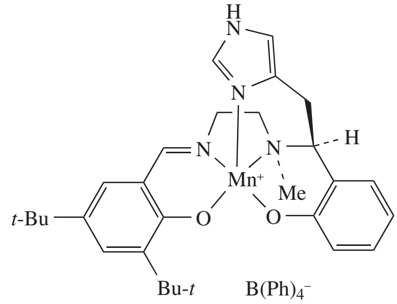
Substitution pattern	Epoxide	Catalyst	Yield (%)	ee (%)	*trans/ cis*	Reference
Terminal		**22a**	89	86	—	23
trans from *cis*-alkene		**18**	nr	81	95:5	21
		**18**	80	90	96:4	21
		**12**	65	98	5.2:1	21
		**12**	81	87	9:1	21
cis		**18**	71	98	—	3a, 12
		**12**	72	98	—	3a, 12
		**12**	63	94	—	3a, 12
Cyclic diene oxide		**12**	72	>99	—	16, 34
		**18**	32	90	—	16, 34

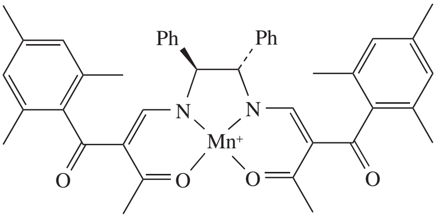
TABLE 3. (*continued*)

Substitution pattern	Epoxide	Catalyst	Yield (%)	ee (%)	*trans/ cis*	Reference
		**18**	49	70	—	16, 34
Cinnamate ester oxide		**12**	56	95–97	—	36
Trisubstituted epoxides		**12**	82	>98	—	18, 25
		**12**	51	97	—	18, 25
Tetrasubstitued epoxides		**18**	90	90	—	30
		**28a**	84	96	—	30
		**12**	91	95	—	30
		**12**	69	93	—	30
Enol ethers		**12**	50–60	80–90	—	37



(**46**)

up to 69% ee



(**47**)

up to 84% ee

FIGURE 9

employed with a biomimetic complex **46** (Figure 9) where the use of a nitrogen donor heterocycle (*N*-methylimidazole) as an additive was crucial[46, 47].

The latter is most probably coordinating to the inactive intermediary hydroperoxide species [H−O−O−Mn^{III}] to promote the heterolytic O−O bond cleavage to release the active oxo-manganese species[48]. The use of ammonium acetate with aqueous hydrogen peroxide and Jacobsen-type catalysts **12** and **28a** was reported by Pietikäinen to generate a narrow range of epoxides with enantioselectivities of up to 96%[49]. When the presence of water is undesired, an anhydrous hydrogen peroxide system comprised of either urea/H_2O_2[50] or Ph_3P/H_2O_2[51] adduct can be employed. Although epoxide yields and selectivities obtained by these strategies are comparable to those of NaOCl, higher catalyst loading and difficulty in the urea or triphenylphosphine oxide removal make this approach less attractive.

Mukaiyama and coworkers showed that molecular oxygen and peracetic acid can be used as the terminal oxidants in the asymmetric epoxidation of alkenes with Jacobsen-type Mn(salen) complexes[52]. Pivaldehyde is required in the O_2 system, affording reasonable yields and ee values (up to 92%). Interestingly, the sense of enantioface selection can be controlled by *N*-alkylimidazole—opposite product enantiomers were observed in the presence or absence of this donor ligand[53]. Furthermore, β-diketoiminato–Mn^{III} complex **47** (Figure 9) which is structurally related to Jacobsen-type catalysts has also been found to be useful in the epoxidation of simple conjugated olefins in the combination of molecular oxygen and an aldehyde[54, 55]. Electrochemical alkene epoxidation can be achieved using Mn(salen), usually with dioxygen as terminal oxidant[56].

The use of *m*-CPBA and *N*-methylmorpholine-*N*-oxide is particularly efficient in the terminal olefins epoxidation (equation 6)[23]. In addition, oxidants like $KHSO_5$[57], ammonium and phosphonium monoperoxysulfates (used for trisubstituted and *cis*-alkenes in up to 90% ee)[58], dimethyldioxirane (used for isoflavone and dimethylchromene in up to 93% ee)[59] and periodates can serve as suitable oxidants for the Jacobsen's catalysts. Accounts on less common terminal oxidants such as $Ca(OCl)_2$[60], LiOCl[61], magnesium monoperoxyphthalate, *t*-butylhydroperoxide and Oxone®[39] were also published, but none of them have surpassed the enantioselectivities, reaction rates and catalyst loadings obtained with more practical oxidants.

Although sodium hypochlorite is an ultimate oxidant for the Jacobsen complexes, in light of the long list of the available oxidants the preferred one will vary in any given case depending on substrate, reaction time, scale, cost, safety and environmental aspects.

Donor ligands play a notable role in the epoxidation process, as has been initially shown by Kochi[3a, 3c, 62]. The proposal that the added ligands, especially those containing oxygen or nitrogen, coordinate to the metal center and subsequently affect the outcome of the reaction was later expanded to a variety of effects[63]. The rate, yield, diastereo- and enantioselectivity of the reaction, as well as the catalyst stability and the conformation of the active oxidant can be influenced by the donor ligand, especially by pyridine *N*-oxides and imidazole derivatives. Pyridine *N*-oxides have been proposed to stabilize Mn(salen) species. In biphasic systems containing NaOCl as oxidant, a lipophylic *N*-oxide donor ligand assists the phase-transfer processes. Jacobsen and coworkers have noticed a consistently beneficial effect on enantioselectivity, reaction rate and product yield exhibited by 4-phenylpyridine-*N*-oxide (4-PPNO) in the case of trisubstituted olefins[25]. With PhIO as oxidant, the donor ligand monitors the competition between two different oxidizing species. With molecular oxygen and hydrogen peroxide-based systems, imidazole or carboxylates are proposed to cause the conversion of acylperoxo–($[RCO_2{-}O{-}Mn^{III}]$) or hydroperoxo–Mn(salen) ($[H{-}O{-}O{-}Mn^{III}]$) species to O=Mn(salen). Finally, *N*-methylmorpholine *N*-oxide (NMO) acts to suppress direct (achiral) epoxidation of the substrates by *m*-CPBA when it is used as terminal oxidant[36, 42c]. In conclusion, the donor ligand constitutes a very important part in the asymmetric epoxidation processes and should be chosen carefully.

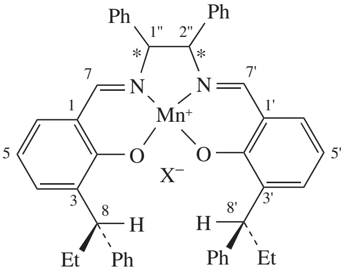
3. Katsuki epoxidation

Similarly to improvements in design and performance carried out by Jacobsen and coworkers, Katsuki has also modified the first generation catalyst **4** (Figure 10), focusing on the steric bulk of C(3)–C(3′) substituents and the stereogenic centers at C(1″), C(2″), C(8) and C(8′). Complex **48**, bearing methyl substituents at C(4) and C(4′), is a considerably better catalyst than **4** due to the C(3)–C(3′) hydrogen atoms confinement, whereas replacement of the C(8)–C(8′) phenyl groups with more bulky *t*-butylphenyl produces more effective catalysts **49** and **50**[64, 65a].

When central chirality at C(8)–C(8′) was replaced by the axial chirality as in salen complexes **51** and **52** (Figure 11), excellent results were achieved in the epoxidation of *cis*-olefins. It was assumed that phenyl substituent on the binaphthyl fragment projects toward the space above the C(2′) carbon and consequently directs the oncoming olefin[65]. Contrary to Jacobsen's olefin pathway (Figure 2, Figure 3), a side-on approach of the olefin along the N–Mn bond was postulated by Katsuki, thus facilitating the orientation of the incoming substrate bearing the larger substituent R^L away from the salen benzyl ring (Figure 11)[66]. Donor ligands were again shown to be capable of altering the enantioselectivities and yields[9c, 67].

Further rational alterations, based on the trajectory of the alkene approach, were made with **53** (Figure 12)[68]. The more readily synthesized complex **54** afforded unusually high turnover numbers of up to 9200 and ee values up to 99% in the asymmetric epoxidation of dimethylchromenes[69]. Prolonged reaction times were needed for some reactions but the unusual catalyst stability allowed its recycling and reuse[70].

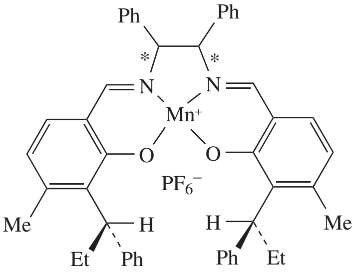
Iodosylarenes were used as a source of oxygen in many asymmetric epoxidation reactions catalyzed by Katsuki-type complexes, although soon after Jacobsen's report on bleach as a more practical reagent, the latter was also introduced to some of Katsuki's protocols.



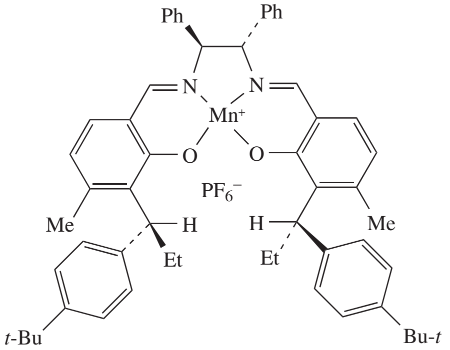
$X^- = OAc^-, PF_6^-$

(*R,R*)- or (*S,S*)-(**4**)

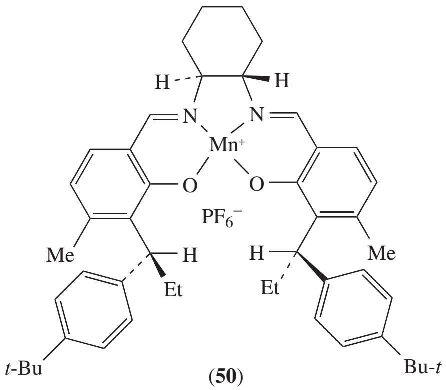
40–50% ee



(*R,R*)- or (*S,S*)-(**48**)



(**49**)

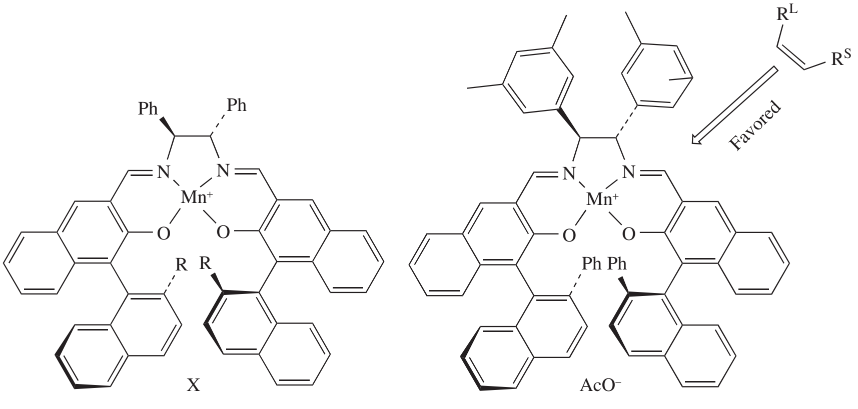


(**50**)

FIGURE 10

The role of the added donor ligands in the ee outcome was reported by Katsuki and coworkers as controversial[9c, 67]. The effects were more noticeable with PF_6^- than AcO^- as counterion. Chiral amines were shown to promote the achievement of reasonable ee values[71], whereas axially chiral 3,3′-dimethyl-2,2′-bipyridine *N*,*N*′-dioxide has improved the early reported results[72].

Transformations which exhibited the most efficient selectivities and yields upon employment of the catalysts **49–52** (2–9 mol%) are summarized in Table 4 according to the substrate type. The scope of the transformation was shown to include cyclic alkenes (entries 5, 7, 8, 10, 11, 14, 15), *cis*-conjugated alkenes (entry 4), *cis*-enynes (entries 6, 9, 12, 13), conjugated trisubtituted alkenes (entries 17–19), enol ethers (entry 22), 1,3-dicycloalkadienes (entries 1–3), and even some dialkyl-substituted *Z*-alkenes afforded moderate ee values (entry 16). As was shown earlier, *trans*-alkenes are generally poor substrates with Mn(salen) and related systems. Remarkably, Katsuki's group has

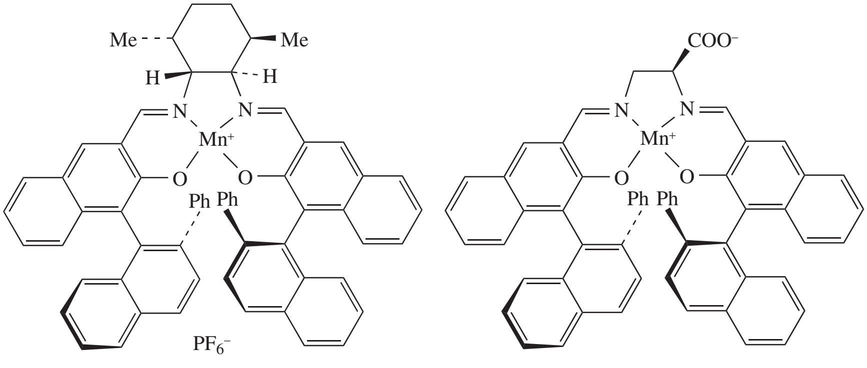


(**51**) (**a**) R = Ph
(**b**) R = Me

(**52**)

X = AcO$^-$, PF$_6^-$

FIGURE 11



(**53**)

(**54**)

FIGURE 12

developed highly enantioselective second-generation catalysts for the epoxidation of *trans*-β-substituted styrene derivatives. The choice of catalyst **55** (Figure 13) was optimal for the β-alkyl styrene derivative (Table 4, entry 20), whereas **56** (Figure 13) was best for the β-unsaturated styrene substrate (Table 4, entry 21).

The second-generation Mn(salen) catalysts introduced by Katsuki and coworkers have surpassed Jacobsen's catalysts in terms of selectivity and activity, but they are not as synthetically accessible and this is the major drawback in their extensive application.

TABLE 4. Selective examples for the asymmetric epoxidations of different alkenes catalyzed by Katsuki's Mn(salen) complexes (2–9 mol%)

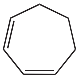
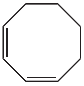
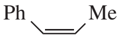
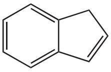
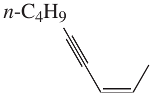
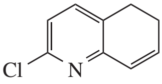
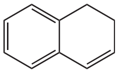
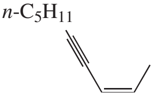
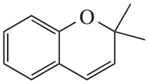
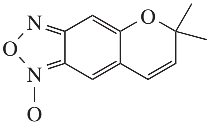
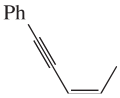
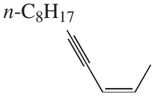
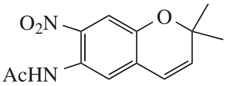
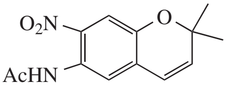
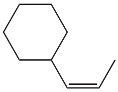
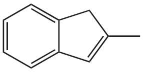
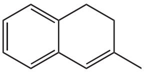
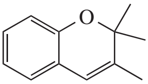
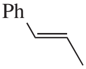
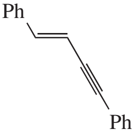
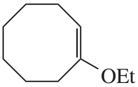
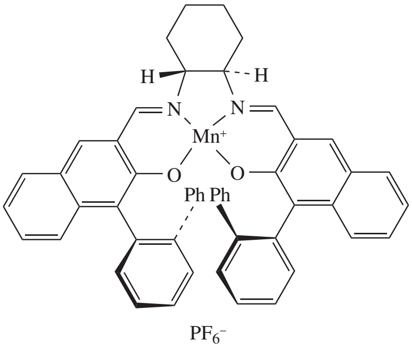
Entry	Substrate	Catalyst	Additive	Yield (%)	ee (%)	Reference
1		**52**	4-PPNO[a]	82	93	73
2		**52**	4-PPNO[a]	54	94	
3		**52**	4-PPNO[a]	40	82	
4		**49**	—[a]	36	86	64
5		**52**	—[a]	78	98	65d
6		**52**	4-PPNO[a]	80[b]	83[b]	87
7		**51a**	4-PPNO[a]	77	96	74
8		**51a**	—[a]	96	93	65b
9		**52**	4-PPNO[a]	100[b]	86[c]	87
10		**52**	4-PPNO[a]	75	99	65d
11		**52**	—[d]	72	97	65c
12		**52**	4-PPNO[a]	80[e]	96[f]	65d

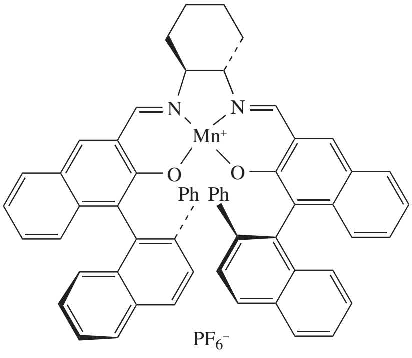
TABLE 4. (*continued*)

Entry	Substrate	Catalyst	Additive	Yield (%)	ee (%)	Reference
13		**52**	*4*-PPNO[a]	84[b]	90[c]	87
14		**52**	*4*-PPNO[a]	80	>99	65d
15		**50**	*N*-methylimidazole[g]	98	95	75
16		**52**	*4*-PPNO[a]	23	82	73
17		**52**	*4*-PPNO[a]	91	88	76
18		**52**	*4*-PPNO[d]	48	92	
19		**52**	—[a]	88	>99	
20		**55**	—[d]	77	91	77
21		**56**	—[d]	35	81	
22		**52**	—[d]	88	88	78

[a] Performed in CH_2Cl_2; NaOCl is a terminal oxidant.
[b] Product is a mixture of *cis*- and *trans*-epoxides; the ratio has not been determined.
[c] The number stands for the face selectivity.
[d] Performed in CH_3CN; PhIO is a terminal oxidant.
[e] Product is a mixture of epoxides, *trans*:*cis* = 2:1.
[f] The number stands for the ee of *trans*-epoxide.
[g] Performed in CH_3CN; H_2O_2 is a terminal oxidant.



(**55**)



(**56**)

FIGURE 13

4. Synthetic applications

The synthetic utility of chiral Mn–salen complexes as catalysts for asymmetric epoxidation reactions has been demonstrated through several important examples. Thus, the synthesis of **57** (the phenylisoserine side chain of Taxol) was accomplished via epoxidation of *cis*-cinnamate by Jacobsen's complex **12** (Scheme 5)[13b].

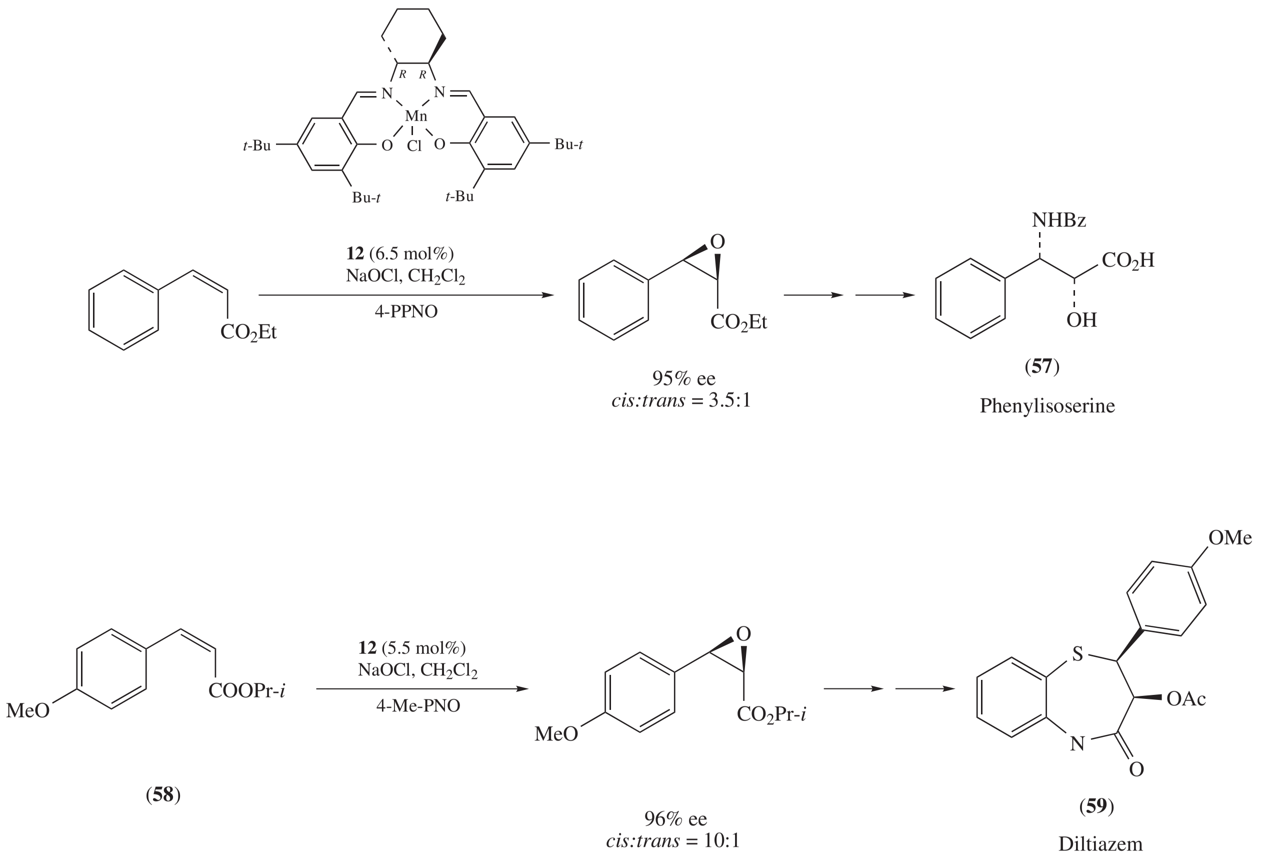
Similarly, highly stereospecific epoxidation of cis-cinnamate derivative **58** led to the calcium channel antagonist diltiazem **59** (Scheme 5)[36].

Since acyclic olefins are prone to the *cis/trans* partitioning problem, substrates which avoid the rotation are very attractive building blocks for the epoxidation process. Therefore, cyclic olefins like chromene derivatives were successfully used in the synthesis of several pharmaceutically important molecules. As shown in Scheme 6, anti-hypertensive agents cromakalim **60**, EMD-52,692 **61** and BRL 55834 **62** were easily accessed through the two-step sequence where the epoxidation is a highly selective key step[79]. The efficiency of the transformation leading to BRL 55834 is impressive as it requires the use of only 0.2 mol% of catalyst **12**.

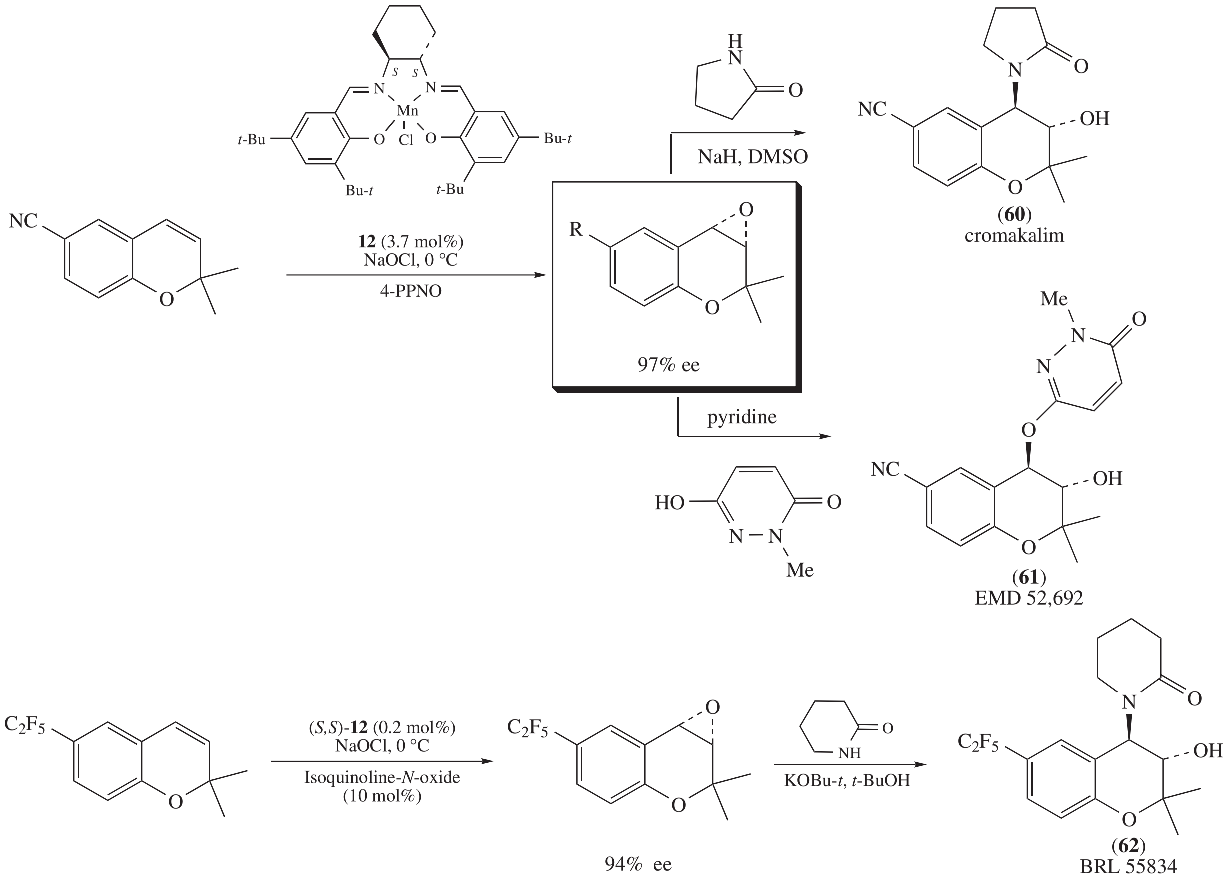
Indinavir **65**, an HIV protease inhibitor, consists of an important chiral *cis*-aminoalcohol synthon **64** which was prepared from the asymmetric epoxidation of indene, followed by Ritter reaction and hydrolysis (Scheme 7)[80]. Jacobsen's (*S*,*S*)-**12** loading was as low as 0.6 mol%, leading to the reaction completion in 15 minutes and affording isolated epoxide **63** in 88% enantiomeric purity.

A somewhat longer route to aminoindanol employs less expensive (*R*,*R*,)-**12** to transform the indene to the corresponding epoxide, which is in turn opened with ammonia and subjected to the inversion at the 2-carbon via an oxazoline intermediate[81]. The ease with which both enantiomers of **63** can be obtained in optically pure form has led to its extensive use as a chiral component in a number of processes[82].

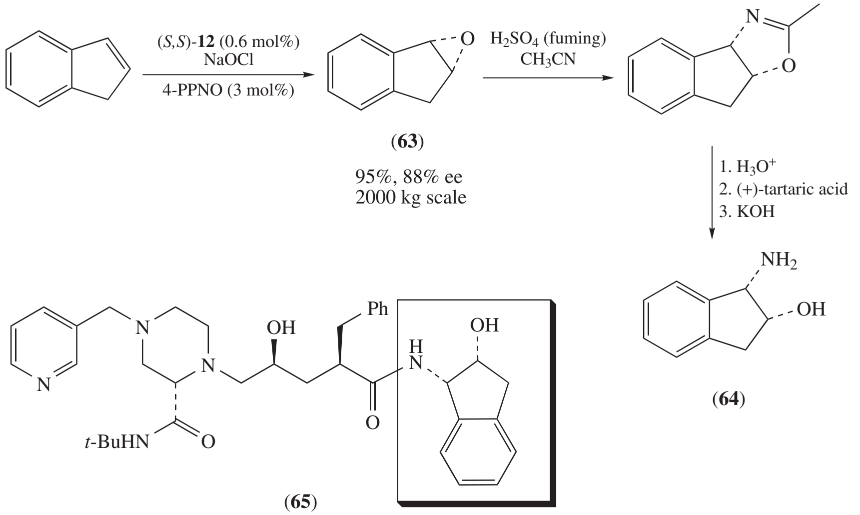
A range of other biologically active compounds has involved the asymmetric epoxidation as an important synthetic step. The list includes such notable examples as a key intermediate for the synthesis of tachykinin receptor antagonist[83], the tetrasubstituted dihydroquinoline portion of siomycin D_1 (a member of the thiostrepton family of peptide antibiotics)[84], tumorgenic *anti*-diol epoxide metabolites of benzo[*a*]pyrene[85], total synthesis of (−)-(*R*)- and (+)-(*S*)-geibalansine (quinoline alkaloid isolated from Brazilian *Zanthoxylum hyemale*)[86], total synthesis of steroidal (+)-Equilenin[87], synthesis of natural dihydropyranocoumarines (+)-decursinol and (+)-*trans*-decursidinol[88] and others[89].


t-Bu
Bu-t
Bu-t
t-Bu
R
R
N
N
Mn
O
Cl
O
12 (6.5 mol%)
NaOCl, CH$_2$Cl$_2$
4-PPNO
CO$_2$Et
O
CO$_2$Et
95% ee
cis:trans = 3.5:1
NHBz
CO$_2$H
OH
(57)
Phenylisoserine
MeO
COOPr-*i*
(58)
12 (5.5 mol%)
NaOCl, CH$_2$Cl$_2$
4-Me-PNO
O
MeO
CO$_2$Pr-*i*
96% ee
cis:trans = 10:1
OMe
S
OAc
N
O
(59)
Diltiazem

SCHEME 5


NC
t-Bu
Bu-t
Bu-t
t-Bu
Mn
Cl
O
O
N
N
S
S
12 (3.7 mol%)
NaOCl, 0 °C
4-PPNO
R
O
O
97% ee
NaH, DMSO
pyridine
HO
N
N
O
Me
(**60**)
cromakalim
NC
N
O
OH
Me
N
N
O
OH
NC
(**61**)
EMD 52,692
C_2F_5
(*S,S*)-**12** (0.2 mol%)
NaOCl, 0 °C
Isoquinoline-*N*-oxide
(10 mol%)
94% ee
NH
KOBu-*t*, *t*-BuOH
(**62**)
BRL 55834

SCHEME 6



(**63**)

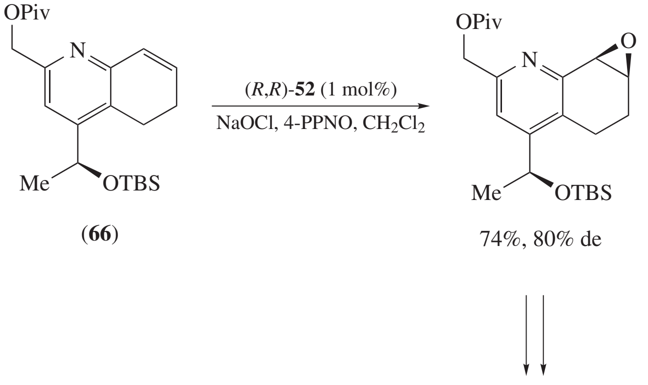
95%, 88% ee
2000 kg scale

(**64**)

(**65**)
Indinavir

SCHEME 7

The synthetic availability of Katsuki's second-generation Mn(salen) **52** remains a drawback to its widespread use notwithstanding its high efficiency. Nevertheless, it has been successfully applied to the synthesis of a variety of pheromones[90], a quinaldic acid macrocylic system[91], as well as some chiral bipyridine and biquinoline ligands[92]. In the stereocontrolled synthesis of the quinaldic acid macrocycle (part of the most complex and best characterized member of the thiopeptide antibiotics—thiostrepton[93]), an epoxidation of olefin **66** was studied under a variety of conditions. Attempts to epoxidize **66** selectively with the commercially available catalyst **12** led to low yields, poor stereoselectivity and significant C−H oxidation with subsequent aromatization. Contrary to these results, Katsuki's (*R*,*R*)-**52** (1 mol%) in conjunction with NaOCl led to selective epoxidation (equation 7).



(**66**)

74%, 80% de

(7)

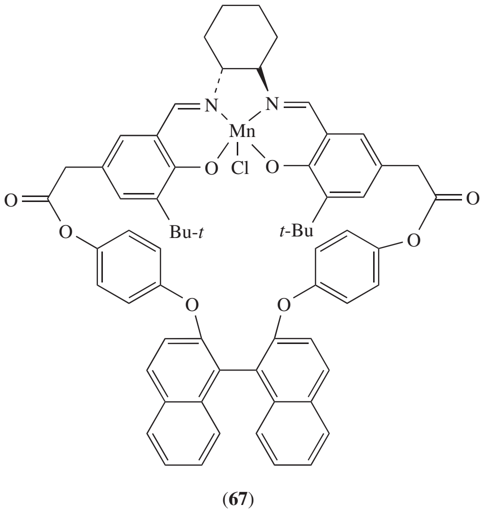
quinaldic acid macrocycle

5. Recent advances

Since the first report on asymmetric epoxidation catalyzed by Mn(salen), a range of Mn(salen)-type structures has been designed and studied[42c, 94]. Selected examples include bulky groups variations at the C(3)−C(3′) which led to moderate results[95], a monomeric Mn(salen) complex with dendritic salen ligands which did not affect the catalytic performance[96], perfluorinated Mn(salen) complexes which afforded promising results and some recyclability[97]. Catalysts suggested by Kureshy and coworkers were bearing tertiary amino side chains at C(5)−C(5′) and exhibited very high yields (>99%) and selectivities at loadings as low as 0.4 mol% with either NaOCl or urea−H_2O_2 as oxidants[98]. High ee values (up to 93%) were achieved by Murahashi's Mn(salen) complex bearing a binaphthyl strapping unit **67** (Figure 14)[99]. Similar to Katsuki-type complexes, additional chirality at the C(3)−C(3′) was attempted by Kim and coworkers furnishing a macrocyclic salen ligand which displayed only moderate activity and enantioselectivity[100]. Ahn and coworkers carried out the asymmetric epoxidation of olefins over the new sterically hindered Mn(salen) complex **68** (Figure 14), which is easier to prepare than Katsuki-type catalysts. They observed enantioselectivities as high as 96–99% for *cis*-methylstyrene and 2,2-dimethylchromene[101].

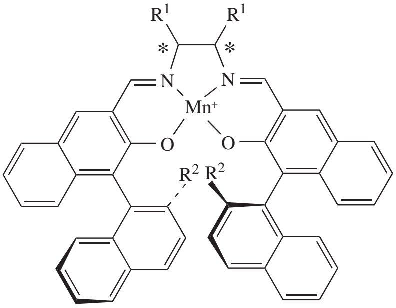
Dimeric homochiral Mn(salen) complexes **69** (Figure 15) were synthesized and used by Janssen[102], Kureshy[103], and Liu[104] and coworkers in asymmetric epoxidation of unfunctionalized olefins with a variety of oxidants, in which excellent conversions (up to 100%) and high ee values (up to 99% ee) were obtained. Upon the same catalyst loading (2 mol%), monomeric Jacobsen's version **12** has accessed the conversion of 96% and 97% ee in the epoxidation of cyano chromene.

Although the stereogenic center on Mn(salen) complexes supposedly induces the enantioselectivity in the epoxidized olefins, Katsuki and coworkers developed a new asymmetric epoxidation system built on achiral Mn complex **70** (Figure 16) and axially chiral bipyridine *N*,*N*′-dioxide[105]. High ee values and yields obtained for 2,2-dimethylchromene



(**67**)

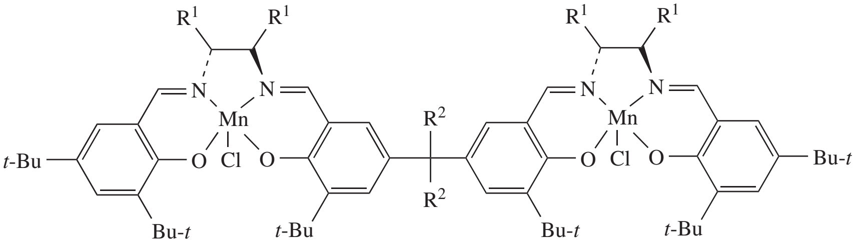
up to 93% ee



(**68**) (**a**) R^1 = H, R^2 = OCOBu-*t*
(**b**) R^1 = Ph, R^2 = OCOBu-*t*
(**c**) R^1 = Ph, R^2 = OCOMe
(**d**) R^1 = Ph, R^2 = $OSiPh_2Bu$-*t*
(**e**) R^1R^1 = -$(CH_2)_4$–, R^2 = OCOBu-*t*

96–99% ee

FIGURE 14

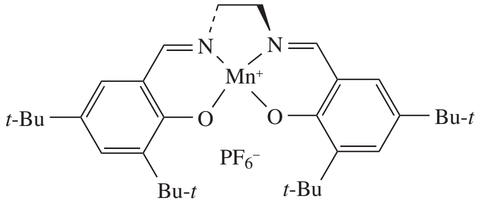


(**69**)

up to 99% ee

$R^1 = \text{-}(CH_2)_4\text{–}, R^2 = H$
$R^1 = Ph, R^2 = CH_3$
$R^1 = \text{-}(CH_2)_4\text{–}, R^2 = CH_3$

FIGURE 15



(**70**)

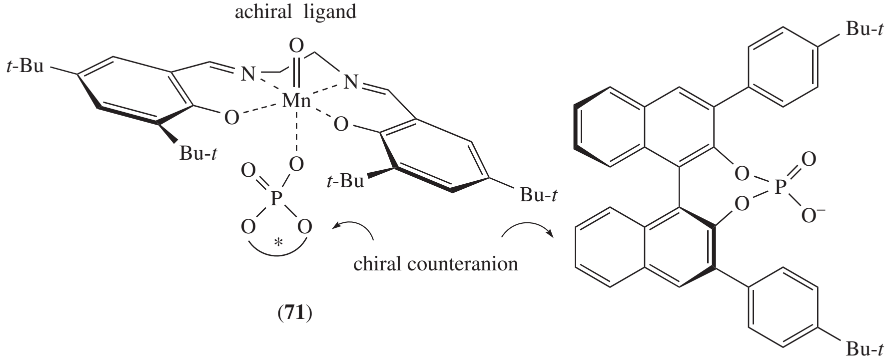
FIGURE 16

derivatives in the presence of **70** suggest a new concept of chiral modifier and its role in this type of reactions.

In their exploration of asymmetric counteranion-directed catalysis, Liao and List have designed a highly enantioselective system consisting of an achiral Mn(salen) cation and a chiral phosphate counteranion **71** (Figure 17) which has reached 99% conversion and up to 96% ee in the asymmetric epoxidation of chromenes derivatives, mono-, di- and trisubstituted olefins and *cis*-enynes with PhIO[106]. No additional neutral donor ligand was required due to the strong activity of **71**.

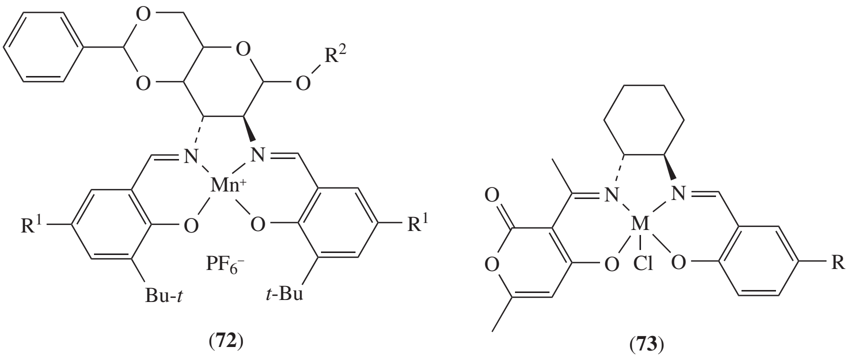
It was shown by Borriello and coworkers that the 1,2-cyclohexanediamine unit can be replaced by appropriately modified common carbohydrates like *D*-glucose or *D*-mannose without any attenuation in the catalyst activity. Up to 86% ee were attained in the epoxidation of *cis*-β-methylstyrene catalyzed by **72** (Figure 18)[107]. Good results were observed by Tang and coworkers when amino acid groups were attached to C(3)–C(3′) via an imino linkage[108].

Due to the inherent C_2-symmetry in both Jacobsen's and Katsuki's complexes, the latter are labeled 'symmetrical' catalysts, whereas 'unsymmetrical' versions of Mn(salen) (for instance **73**, Figure 18[109]) were disclosed by several groups[110–116]. The majority of the cases featured lower ee values than those obtained with 'symmetrical' catalysts; moreover, the 'unsymmetrical' Schiff-base ligands are much less accessible since the product is nearly always contaminated with various amounts of C_2-symmetric bis-imine.



(**71**)

FIGURE 17



(**72**)

R^1 = H, *t*-Bu, R^2 = Me, Bn

(**73**)

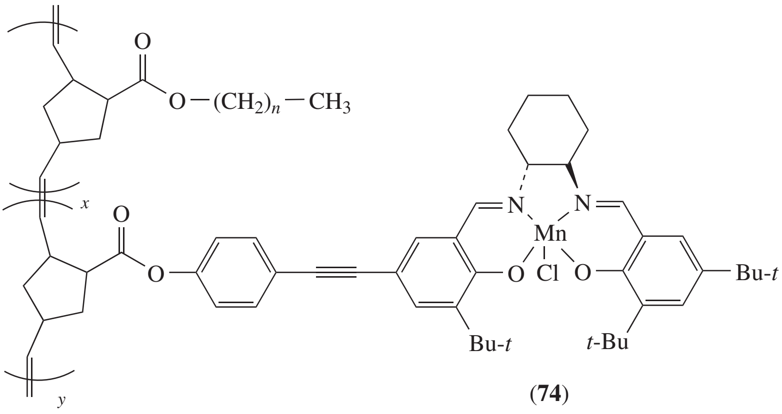
M = $Mn(H_2O)$
R = H, Cl, Me, NO_2

FIGURE 18

Changes on the diimine backbone were disclosed by Gilheany and Daly who attempted to synthesize the salen complex from enantiopure *trans*-cyclopentane and cyclobutane-1,2-diamine[117a]. Scheurer and coworkers reported the synthesis and use of Mn(salen) complexes with diimine backbone derived from L-tartaric acid[117b]. These works and other attempts at modification of the diimine fragment resulted in low ee values and, in some cases, an unclear sense of the enantioselection.

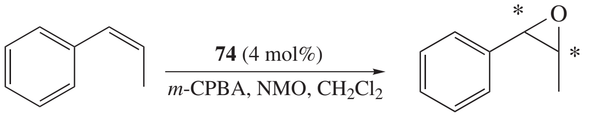
Polymer-supported Mn(salen) Jacobsen's complex **74** has shown outstanding catalytic activity and selectivities comparable to the original catalyst when applied to *cis*-β-methylstyrene (equation 8)[118]. It can be concluded that a wide variety of structural motifs have been tested on Mn(salen)-type complexes, but ultimately very few reach the results obtained with Jacobsen's and Katuski's catalysts.

As a result of a two-decades study, the salen-type ligands are nowadays included in a list of privileged ligands[119] and find broad applications within the pharmaceutical and fine chemical industries. Different nonmanganese salen frameworks (metal = Co, Cr, Y, Zn, Ti, V, Ru, Al) are employed in a wide variety of useful asymmetric processes. Since this chapter surveys the manganese complexes and their synthetic applications, reading a detailed review on the other (salen)metals is advisable[120].



(**74**)

(8)



$x/y = 1{:}1$, $x+y = 50$

100% conversion, 92% ee

6. Mechanistic aspects

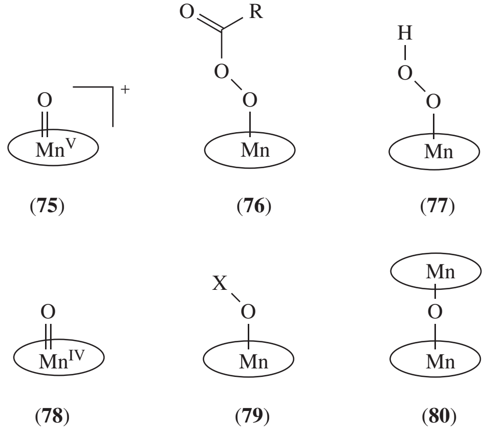
The nature of the active species and the catalytic cycle in the asymmetric epoxidation catalyzed by Jacobsen's and Katsuki's Mn(salen) complexes has attracted a great deal of interest ever since the first publications on this transformation. In conclusion to his review published in 1996[42b], Katsuki claimed that '. . .our knowledge on the structures of the catalytically active oxo Mn−salen species and their reactivity is immature. . .'. A study of Corey and coworkers on the origin of enantioselectivity in the asymmetric epoxidation of olefins is prefaced with the following remarks: '. . .the mode of oxygen transfer to the olefin has over the years become ever more controversial. . .' and '. . .the fundamental basis for its ('reaction') enantioselectivity has remained obscure'[121]. As 14 years of research separate these two publications, it is clear that there are still important mechanistic issues that need to be resolved, mainly the nature of the active oxo-manganese species, the mechanism of the oxygen atom transfer to the olefins and the factors governing the sense of enantioselectivity.

From the analysis of the experimental observations obtained by different groups, the following key points can be deduced: a) conjugated olefins represent the best class of substrates for the epoxidations catalyzed by Mn(salen)[120a]; b) conjugated cyclic *Z*-1,2-disubstituted and trisubstituted olefins undergo highly enantioselective epoxidations[25]; c) acyclic conjugated *Z*-1,2-disubstituted systems frequently afford both *cis*- and *trans*-epoxides implying a radical pathway with concomitant C−C bond rotation[21c]; d) formation of *trans*-epoxide from the *cis*-substrate is enhanced by the addition of quaternary ammonium salts[21a]; e) enhancement of enantioselectivity is observed in the presence of pyridine *N*-oxides or *N*-alkylimidazole[15, 16]; f) electron-donating *para* substituents like the methoxide group on the benzene ring of the salen ligand enhance the enantioselectivity, whereas electron-withdrawing substituents like the nitro group do the opposite[27, 39]; g) the enantioselectivity of the epoxidation reaction depends on the oxidant and the axial ligand nature[42c].

The mechanism of the enantioselective epoxidation of olefins with Mn(salen) complexes as catalysts has been the object of intense discussions and keen debates. The most widely accepted scenario involves a two-step reaction, where at first a transfer of oxygen from the terminal oxidant to the $\mathrm{Mn(salen)^{III}}$ takes place to form a $\mathrm{Mn^{V}}$-oxo intermediate, followed by the oxygen transfer from the metal center to the olefin to form an epoxide. The details regarding this second step constitute fertile ground for vivid theoretical, spectroscopic and experimental explorations also today.

In addition to the $\mathrm{O{=}Mn^{V}(salen)^{+}}$ intermediate **75** (Figure 19, donor ligands omitted from some structures for clarity)[3a] which was generally accepted as a major oxygen-transfer agent from the very early stages of the mechanistic explorations, other potentially oxidizing species were proposed to be involved in the catalytic cycle under certain conditions. As described in Figure 19, the list included an acylperoxo-Mn(salen) **76**[52b], hydroperoxo-Mn(salen) **77**[75], $\mathrm{O{=}Mn^{IV}(salen)}$ **78**[122] and adducts **79**[43f, 43g] such as PhIO−Mn(salen) and ClO−Mn(salen). In addition, a μ-oxo-dimer **80** was proposed to function as a catalyst sink by Kochi and coworkers[3a]. On the basis of numerous spectroscopic[123], EPR and NMR[124] studies performed to substantiate the viability of these species, it became clear that the oxidant should be added to the reaction mixture after all the components and that the addition of donor ligand leaves only one $\mathrm{Mn^{III}}$ species for oxidation rather than several[125]. In addition, EPR spectroscopy applied to monitor the high-valence manganese intermediates detected the acylperoxo complex **76** as the last measurable species if one used *m*-CPBA as the oxidant. In the system with PhIO, the $\mathrm{O{=}Mn^{V}(salen)^{+}}$ complex **75** was the main oxygen-transferring species[41a], stocked up in the form of μ-oxo-bridged $\mathrm{manganese^{IV}}$ binuclear complexes **80**[134, 186].

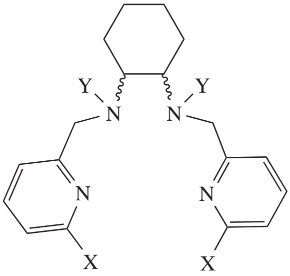
An interesting contribution for a better understanding of the nature of the oxidating species was recently made by Bryliakov and coworkers, who studied the catalytic properties of a series of chiral nonheme $\mathrm{aminopyridinylmanganese^{II}}$ complexes (Figure 20)[126].



(**75**) (**76**) (**77**)

(**78**) (**79**) (**80**)

FIGURE 19



(*S,S*) X = H, Y = Me
(*S,S*) X = Me, Y = Me
(*R,R*) X = Br, Y = Me

FIGURE 20

The above complexes were found to efficiently catalyze enantioselective olefin oxidation to the corresponding epoxides with oxidants such as peroxycarboxylic acids, alkyl hydroperoxides, iodosylarenes and others with high conversions and selectivities (up to 100%) and enantiomeric excesses (up to 79%). EPR investigations on these complexes revealed a new type of oxidant (oxomanganese^{IV} complex with a terminal oxidant) which accounts for a predominant enantioselective epoxidation pathway. Notwithstanding their nonsalen nature, these manganese complexes and their active species may prompt new investigations on the oxidizing mechanism of the Mn(salen) complexes.

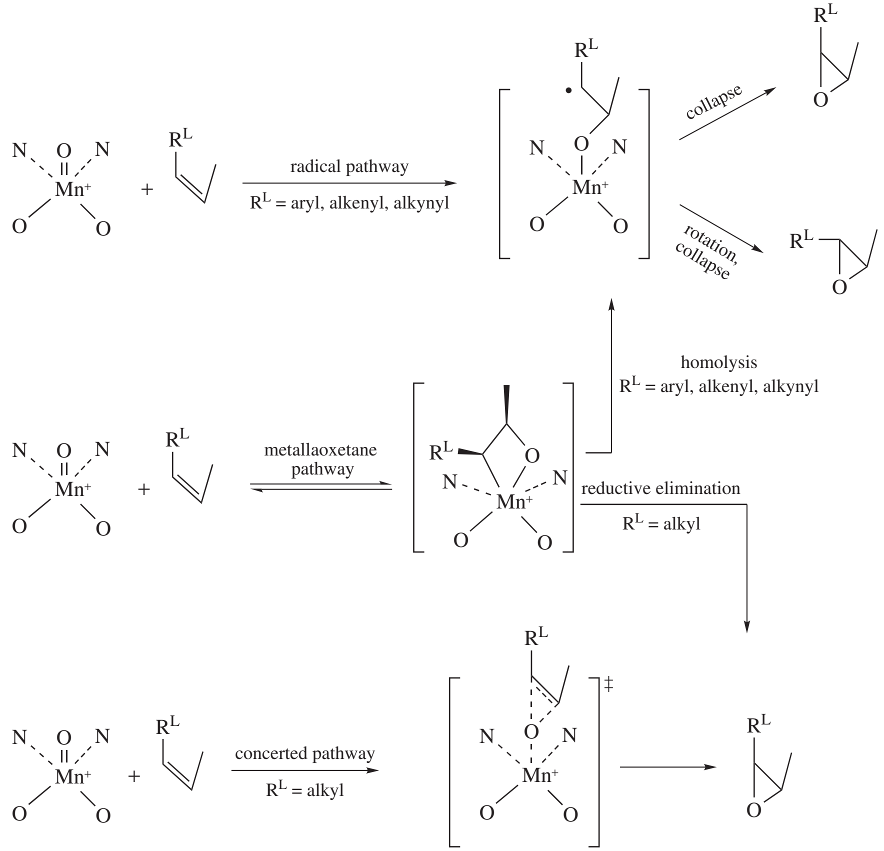
Clearly, much work has been done to elucidate the explicit nature of all the species present in the catalytic cycle of the Mn(salen) complexes; however, no consensus on this matter has been reached so far.

In the early stages of the mechanistic elucidations, three major pathways for the oxygen atom transfer from the $O{=}Mn^V(salen)^+$ species **75** to olefin were suggested: i) a stepwise radical pathway[42b], which rationalizes the nondiastereoselective reaction of conjugated *cis*-disubstituted alkenes where mixtures of *cis*- and *trans*-epoxides are formed; ii) a concerted pathway for alkyl-substituted olefins[127], for which radical intermediates would be considerably less stable; iii) a stepwise metallaoxetane pathway[128], in which the latter is reversibly formed to further break down into a radical species for the conjugated substrate or an epoxide for alkyl-substituted cases (Scheme 8).

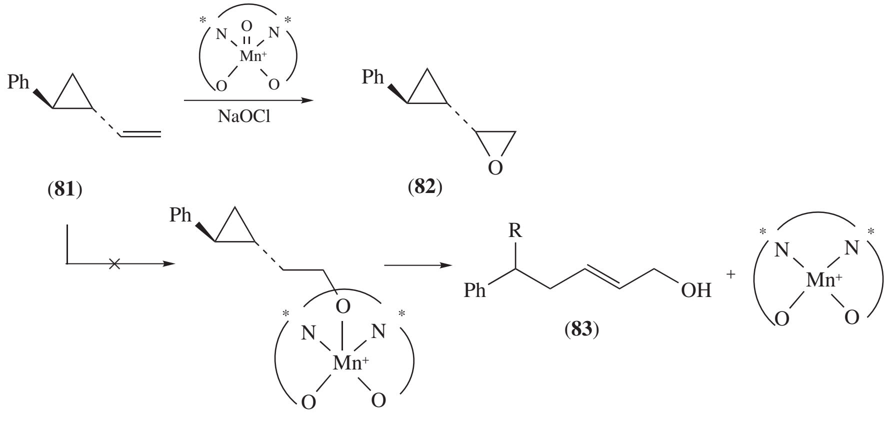
For the nonconjugated alkenes, a concerted mechanism is most likely and experiments by Jacobsen and coworkers with radical probe **81** were carried out to substantiate this claim[127]. Epoxidation of **81** with NaOCl afforded epoxide **82** and no product of cyclopropyl ring cleavage was found (Scheme 9). If a radical intermediate intervenes, a product **83** should be detected since the rate of a secondary phenylcyclopropyl radical rearrangement is very fast (above $10^{10}\ s^{-1}$)[42a].

Computational studies performed during these years of research did not completely rule out the metallaoxetane intermediate; however, a radical pathway was favored by most calculations[40, 42c, 43c, 129].

Recently, Corey and coworkers have reasonably claimed that the two pathways—radical and concerted—represent two extreme cases. In other words, provided that **75** is indeed an effective oxygen-transfer agent, a continuum of pathways is available for the formation of the two C−O bonds of the epoxide between oxygen and olefin[121]. To which extent these bonds are formed—either in a completely synchronous way or in a two-step (radical) pathway or any asynchronous scenario



SCHEME 8

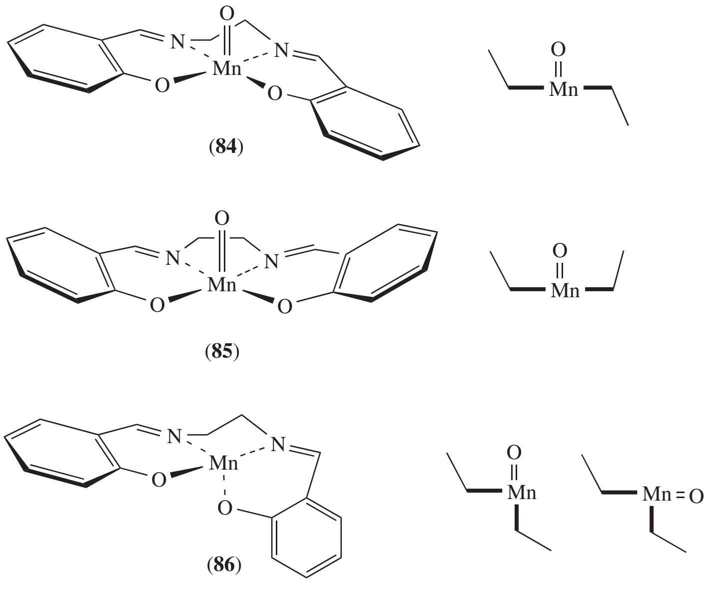


SCHEME 9

in between—strongly depends on factors like the nature of the substrate[36, 43d], the *axial* ligand[21a], oxidant[43e, 43f, 130], solvent, temperature, electronic spin issue of the d^4-(salen)Mn^{III} and d^2-(salen)Mn^{V}-oxo reagent[21a] and the degree of the ligand's nonplanarity. Corey's model proposed for the Jacobsen epoxidation of conjugated olefins with **12** implies an asynchronous two-step pathway with a substantial positive charge developing on the olefinic substrate during attack by the electrophilic oxygen.

It is generally assumed that high selectivities achieved in the epoxidation reactions by the Mn(salen) depend on the trajectory of the substrate approach to the catalyst and the conformation of the latter[11b]. The majority of the experimental and computational work has been done based on the assumption that $O{=}Mn^{V}$(salen) is the active entity in the epoxidation step. Although from the crystal structure of simple Mn^{III}(salen) complexes a relatively flat backbone was inferred[43c, 131], the hypothesis that the $O{=}Mn^{V}$(salen) complexes are flat by analogy failed to provide a satisfactory explanation for many stereochemical observations. In 1994, a slight twist noticed by Feringa and coworkers in the crystal structure of Mn^{III}(salen) was suggested as important in the oxygen-transfer step[131a]. Srinivasan and Kochi have isolated a $O{=}Cr^{V}$(salen) complex as well as its pyridine *N*-oxide adduct and unambiguously demonstrated by X-ray crystallographic analysis that the salen ligand took a nonplanar stepped conformation in both cases[132]. Contrary to that, the $O{=}Mn^{V}$(salen) species could not be isolated, therefore various nonplanar conformational modes were referred to this Mn moiety[42b, 42c, 128b, 131a, 133], of which the major three appear in Figure 21: 'stepped' or 'folded' (**84**), 'bowel-shaped' or 'umbrella' **(85)** and 'bent' **(86)**. Some researchers also propose a salicylidene ring twist which can take place in each of the conformations.

Various computational studies show a folding effect caused by a nitrogen donor axial ligand in the folded and bowel-shaped modes **84** and **85**, respectively, with consequent destabilization of the conformer, weakening and increase in the reactivity of the Mn=O



(**84**)

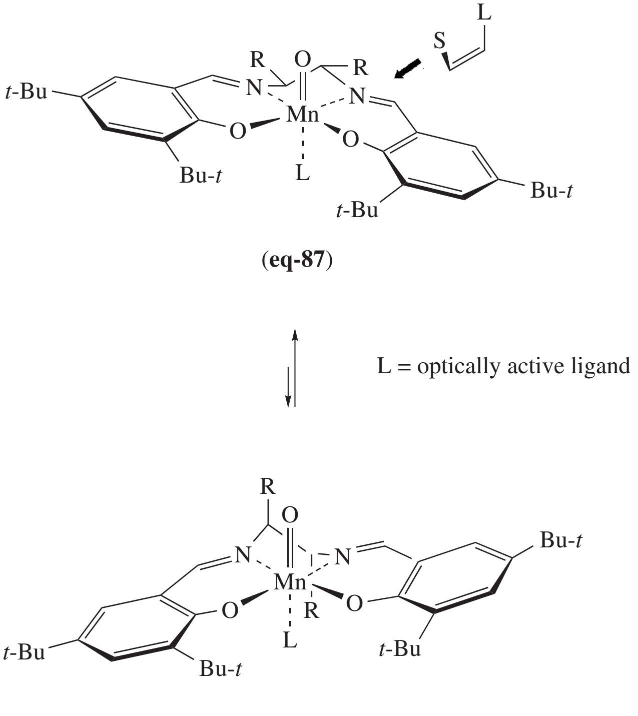
(**85**)

(**86**)

FIGURE 21

bond[133b, 134]. Cavallo and H. Jacobsen suggested that even an axial anionic ligand such as Cl$^-$ will induce folding in the complex[41c]. Khavrutskii and coworkers proposed that when oxidation is carried out with O_2/pivaldehyde in the absence of donor ligands, a 'bent' conformer **86** can arise. The reversal of enantioselection, noted in such oxidizing systems when a donor ligand was present, might be rationalized by a bent conformer which favors a different alkene approach[135].

Strong crystallographic[70, 136] and experimental evidence for the nonplanar conformation of O=Mn(salen) complexes in solution were supplied by Katsuki and coworkers. They assumed that if salen ligand takes a stepped conformation, an achiral O=Mn(salen) complex should exist as an equilibrium mixture of enantiomeric conformers. Upon the coordination of nonracemic chiral amine or amine oxide (L) at the apical position of achiral O=Mn(salen), the equilibrium should be shifted toward the diastereomer **eq-87**, in which two substituents (R) at the ethylenediamine moiety take pseudoequatorial positions (equation 9). Up to 82% ee were attained in the epoxidations performed with this kind of system, showing the reactivity bias between **eq-87** and **ax-87**[71, 72].



(**eq-87**)

L = optically active ligand (9)

(**ax-87**)

Four major approach trajectories of the olefin substrate to the oxo group of the chiral O=Mn(salen) complexes have been proposed to explain the degree and sense of enantioselectivity obtained with various catalysts (Figure 2)[11a, 128a, 131b, 137]. All of these are to a greater or lesser extent 'side-on' approaches, implying that a favorable orbital overlap takes place, similar to the porphyrins complexes[10, 17b]. Approach **a** was suggested by Jacobsen and coworkers to explain the results observed with **88**—the olefin oncoming to the oxo-metal bond occurs along the spherically less-congested pathway, placing its bulkier substituent away from the groups at C(3)−C(3′) (Figure 22, see also Figure 2 and related discussion therein)[11]. Pathway **b** was also proposed by Jacobsen, to justify the results of epoxidation when **89** is used (Figure 22, see also Figure 3 and related discussion therein)[11a, 131b]. The trajectory along the diimine bridge is favored over the other options which are blocked by the bulky substituents on C(3)−C(3′) and C(5)−C(5′). Contrary to pathways **a** and **b**, which are dictated solely by the steric repulsions, approach **c** (Figure 22, see also Figure 11), originally hypothesized by Katsuki and coworkers, involves both steric and electronic interactions as governing factors in the enantioselection[66a, 65b,c,d, 76]. They argued that pathways **a** and **b** could not account for the exceptionally high ee values obtained for *cis*-alkenes and the demand for the conjugated substrates. Therefore, pathway **c** was suggested instead, implying synergistic work of steric repulsion and repulsive $\pi-\pi$ interaction between the unsaturated substituent of an olefin (R^L = unsaturated group) and

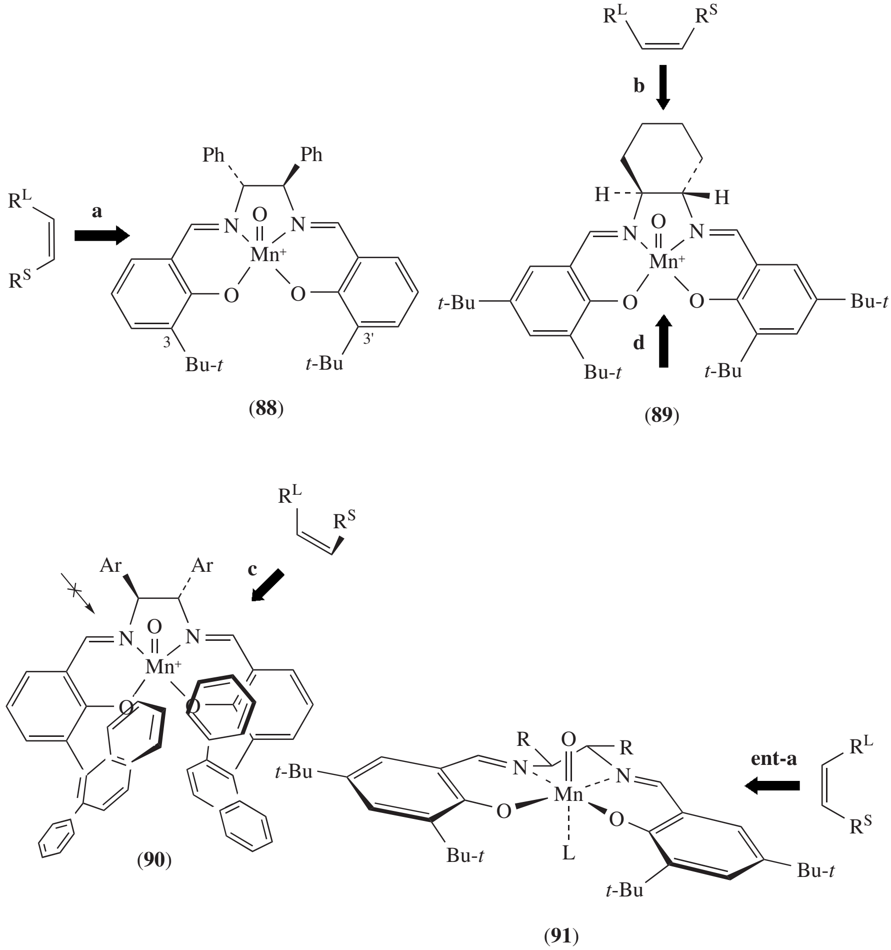


FIGURE 22

the salen ligand. Consequently, newly designed complexes **90** were developed, in which the protruding naphthyl moiety strictly orientates the incoming olefin along the approach **c**[73].

While approaches **a–c** were based on the incipient premise that the salen ligand is planar, approach **ent-a** was later constructed by Katsuki and coworkers to fit the evidence that the ligand is actually stepped (**91**, Figure 11)[128a, 138]. In such a conformation the 5,5′-substituents do not block the **ent-a** approach—this fact, along with different degrees of ligand folding, made Katsuki's second-generation ligands (**90**) more suitable for asymmetric epoxidation of different substrates and explains the results obtained for the kinetic resolutions using Mn(salen)[139], epoxidation of *trans*-alkenes[77] and oxidation of enol derivatives[37a]. While computational studies of H. Jacobsen and coworkers support the pathway **ent-a**[41b], Houk and coworkers reported an approach **d** (Figure 22), based on the fact that the crystal structures of all Mn(salen) complexes featured a twist between the planes of their salicylaldehyde-based parts[140]. Since the twists were controlled by the diimine backbone, the selectivities observed with either stilbene or cyclohexane diamine-based catalysts could be interpreted.

A kinetic study, recently performed by Norrby and coworkers on a range of methyl-substituted styrenes, rationalizes the selectivities and reaction rates by competitive 'distal' and 'proximal' approach vectors and predicts an absolute stereochemistry as a function of an alkene substitution pattern[141].

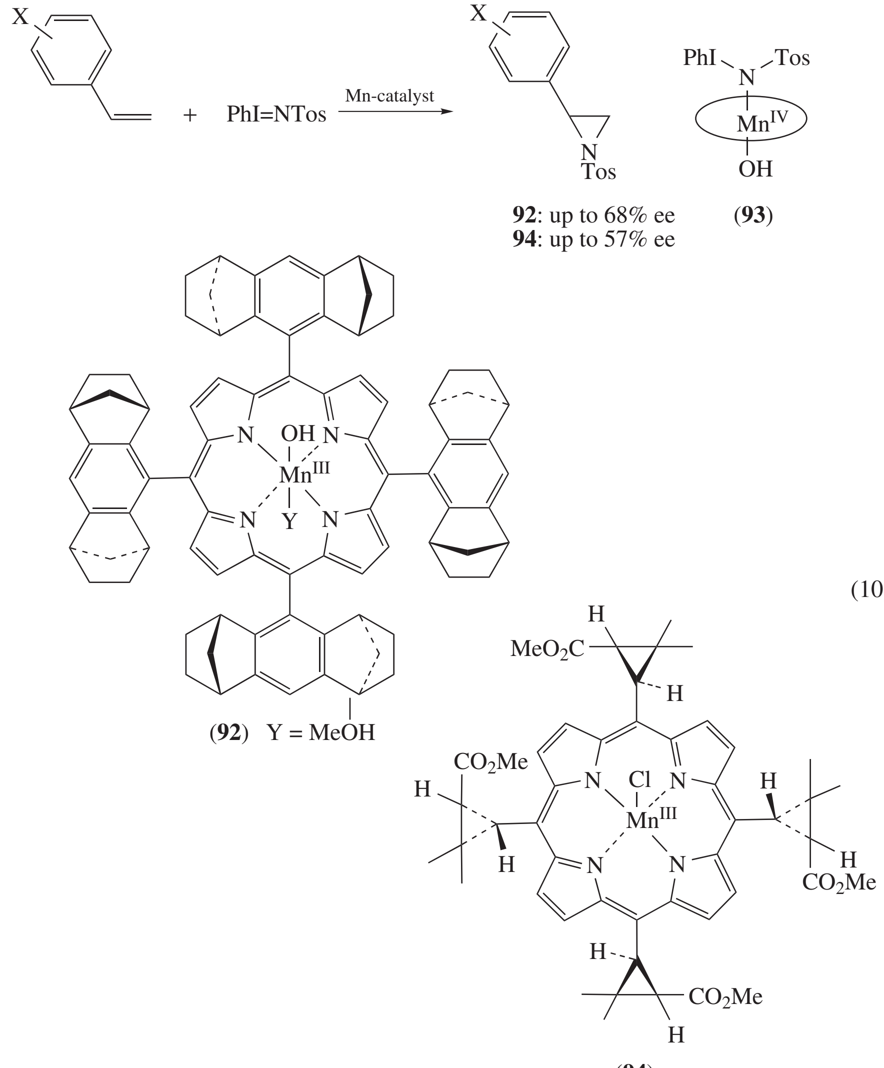
In conclusion, growing evidence for the existence of multiple oxidants and multiple competing oxidation pathways make the interpretation of the results even more intricate and leave a large scope for increased understanding of the mechanism. The balance of evidence in Mn(salen)-catalyzed asymmetric epoxidation suggests that for most complexes, the substrate approaches over the aromatic ring of the salen ligand. Clearly, the degree of nonplanarity of the O=Mn(salen) conformation plays an important role in determining the exact trajectory. For other potential oxygen-transfer entities, however, the substrate trajectory has hardly been explored.

B. Enantioselective Aziridination Reactions

Aziridines are the nitrogen analogues of epoxides and exhibit similar reactivity patterns as electrophilic reagents[142]. Highly regio- and stereoselective transformations offered by these compounds make them useful synthons for organic synthesis; moreover, their possible antitumor and antibiotic activity and other biological properties make them attractive targets in their own right[143]. Nevertheless, the scope of the synthetic methods available for the preparation of aziridines is rather narrow when compared to the diversity of existing methods for the preparation of analogous oxygenated heterocycles[144]. The asymmetric synthesis of aziridines and their applications have been reviewed recently[145]. Modern strategies of aziridines synthesis are primarily based on formal nitrene transfer to olefins or, alternatively, on carbene transfer to imines[145a, 146].

The possibility of enantioselective transfer of nitrenes to olefins by means of a transition metal catalyst first became evident from the work of Evans and coworkers. They reported that 4,4′-disubstituted bisoxazolines are excellent chiral ligands for enantioselective aziridination of aryl-substituted olefins with TosN=IPh, whereas Cu^{I} and Cu^{II} salts in MeCN appeared as the most efficient catalyst/solvent combination for nitrene transfer, affording up to 97% ee[147]. Imino-copper species in the 3+ oxidation state ($Cu^{III} = NTs$) were proposed as the key intermediate in copper-catalyzed aziridination[148].

Attempts to utilize manganese in asymmetric aziridination reactions were based on the analogous racemic transformations, performed with TosN=IPh and Mn–porphyrin catalyst, as described by Mansuy and coworkers[149]. Che and coworkers have reported the chiral version of metalloporphyrin-catalyzed aziridination[150]. The reaction of styrene derivatives with D_4-manganese^{III} porphyrin complex **92** has attained fairly good enantioselectivity (up to 68%, equation 10), and was proposed to proceed through a Mn^{IV}−PhINTos adduct **93**, as evidenced by EPR analysis.



92: up to 68% ee
94: up to 57% ee

(**93**)

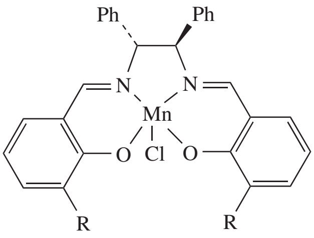
(**92**) Y = MeOH

(10)

(**94**)

Marchon and coworkers, in turn, examined a chiral Mn^{III}−porphyrin catalyst **94** and reported an ee of 57% for styrene aziridination with PhI=NTs[151].

The initial experiments to extend this chemistry to chiral Mn^{III}−salen complexes **95** (Figure 23) were carried out by Burrows and coworkers, albeit no induction was detected

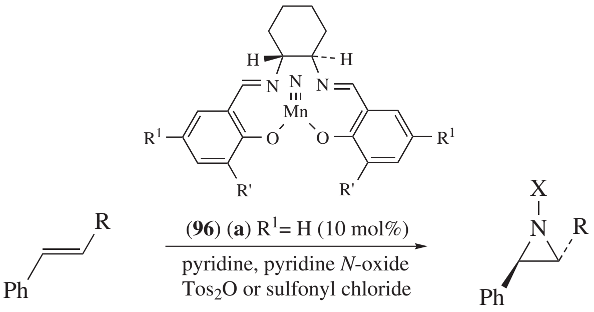


(**95**) (**a**) R = $SiMe_3$
(**b**) R = $SiMe_2Bu$-*t*

FIGURE 23

upon aziridination of styrene and β-methylstyrene[95a]. A stoichiometric aziridination procedure was then developed, using symmetric salen-derived nitridomanganese^{V} complexes, first described by Groves and Takahashi[152], and successfully exploited by Carreira and coworkers[153] for the amidation of enol ether derivatives, where aziridines are likely to be formed as intermediates.

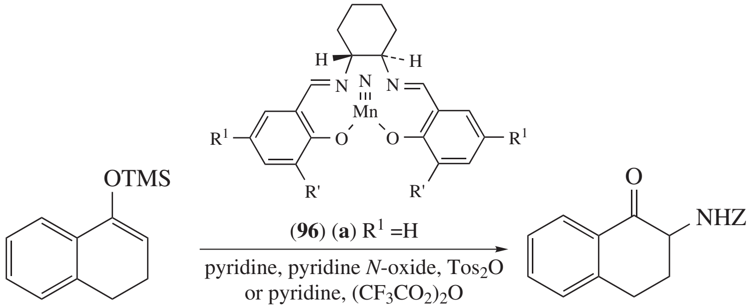
Finally, the asymmetric version of the above reaction was developed by Komatsu, where a chiral 1,2-diaminocyclohexane based nitridomanganese **96a** was used[154]. It reacted with olefins in the presence of *p*-toluenesulfonic anhydride Ts_2O, trifluoroacetic anhydride $(CF_3CO)_2O$ or sulfonyl chlorides to afford substituted aziridines in yields ranging from 50% to 87% and enantioselectivities reaching up to 96% (equation 11). The reaction was stereospecific with β-methylstyrene. When acid chlorides were used instead of sulfonyl chlorides as initiators, the reaction afforded oxazolines, presumably via intermediate aziridines in yields ranging from 53% to 85%. Enantioselectivity for the oxazoline formation was high (up to 92%) in the case of *trans*-disubstituted styrenes, but much lower with α-methylstyrene, *cis*-disubstituted styrenes and with styrene itself.



R = C_6H_{11}, X = $SO_2CH_2CH_2SiMe_3$: 62%, 93% ee
R = *i*-Pr, X = Tos: 53%, 94% ee
R = *i*-Pr, X = $COCF_3$: 53%, 96% ee
R = Me, X = $COCF_3$: 72%, 85% ee

(11)

This transformation was applied on silyl enol ether **97** aiming at a directed asymmetric amination. The amination, which is presumed to take place via an aziridine intermediate[147c, 153c, 155], proceeded smoothly with Ts_2O to afford the *N*-tosylated α-aminoketone **98** in 76% yield and 48% ee (equation 12)[154c]. Improved enantiomeric excess was obtained upon addition of TFAA[153a], whereas the yield has dropped under these conditions, suggesting that the additives used for the generation of the imido complex **96a**[152a] might control its performance in the aziridination.

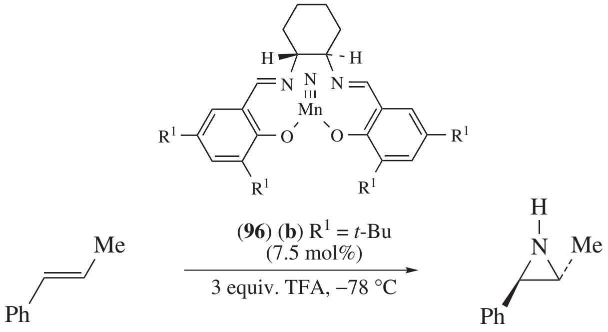


(12)

(**97**) (**98**)

Z = Tos, 0.1 equiv of (**96a**): 76%, 48% ee
Z = CF_3CO, 2 equiv of (**96a**): 58%, 79% ee

The chiral salen–manganese^V nitride complexes may also be activated by Brønsted or Lewis acids such as trifluoroacetic acid (TFA) or BF_3. In this case, olefin aziridination proceeds to the unprotected aziridine. For instance, *trans*-β-methylstyrene **99** reacted at −78 °C in the presence of **96b** and 3 equivalents of TFA to afford **100** in 91% ee, albeit in a low yield (20%, equation 13.)[156]

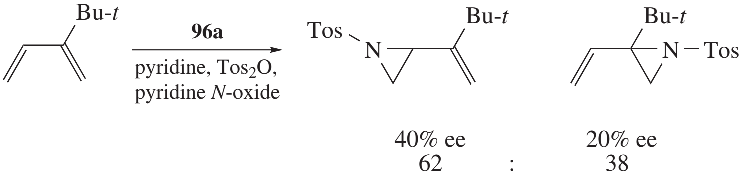


(13)

(**99**) (**100**)

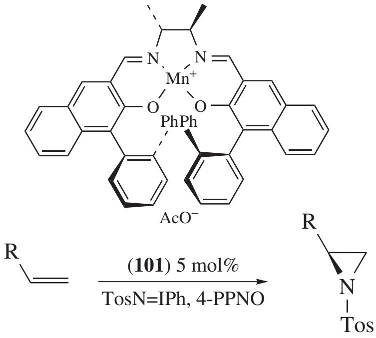
20%, 91% ee

Nitridomanganese complex **96a** was also used for the selective 1,2-addition to conjugated dienes[154b, 157]. The reaction, shown in equation 14, provided the first reagent-controlled asymmetric aziridination of conjugated dienes, although enantioselectivities were only low to moderate (20–40% ee).



(14)

Catalytic asymmetric Mn-catalyzed aziridination utilizing an optimized salen complex **101** has been developed by Katsuki and coworkers, attaining up to 94% ee for aziridination of styrene derivatives with TosN=IPh (equation 15)[78, 158]. The presence of catalytic quantities of 4-phenylpyridine-*N*-oxide was required to obtain high enantioselectivities. The architecture of **101** was designed based on the assumption that, contrary to the oxo-Mn species, the imino-manganese species, which comprises a putative active catalyst, bears a substituent on its nitrogen atom. Katsuki has reasoned that the size of the substituents at the ethylenediamine moiety of **101** directs the orientation[139a, 159]. Unfortunately, this protocol is limited to styrene derivatives.



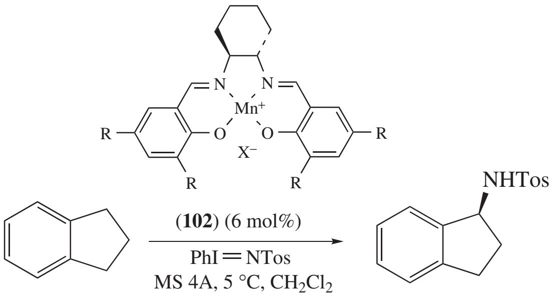
(15)

R = Ph, 76%, 94% ee
R = p-ClC_6H_4, 70%, 86% ee
R = p-MeC_6H_4, 75%, 81% ee

As can be inferred from the above, methods to introduce chiral nitrene to olefins have realized sufficient enantioselectivities upon manganese catalysis; however, development of new approaches is indispensable. Further research should focus on broadening the substrate scope and development of the approaches into synthetically interesting methodologies.

C. Enantioselective C−H Bond Amination Reactions

Nitrenoid species can be inserted into active C−H bonds at benzylic or allylic positions competitively to aziridination[160]. Amination becomes the dominant reaction if a ligand bearing electron-withdrawing groups is used as the catalyst, thus enhancing the electrophilicity of the intermediary imino metal species[161]. Mn(salen) complexes **102a–f** possessing different electron-withdrawing groups as substituents were tested in the asymmetric C−H amination of indane at 5 °C in dichloromethane (equation 16)[161a].



(16)

(**102**) (**a**) R = H, X = PF_6, 18%, 6% ee
(**b**) R = F, X = PF_6, 37%, 5% ee
(**c**) R = Cl, X = PF_6, 59%, 41% ee
(**d**) R = Br, X = PF_6, 63%, 44% ee
(**e**) R = I, X = PF_6, 44%, 26% ee
(**f**) R = Br, X = Cl, 12%, 23% ee

The results witnessed a complex relationship between the nature of the substituents and the yield and enantiomeric excess, bromo-substituted complex **102d** being the catalyst of choice. Under the optimized conditions (−40 °C, 1,1,2,2-tetrachloroethane), a moderate to good level of enantioselectivity was obtained for benzylic and allylic C−H aminations upon the use of **102d** (Figure 24).

D. Asymmetric Oxidation of C−H Bonds

Catalytic asymmetric oxidation of alkanes is one of the important yet challenging topics in view of synthetic and industrial aspects[162]. The capability of Mn(salen) to catalyze

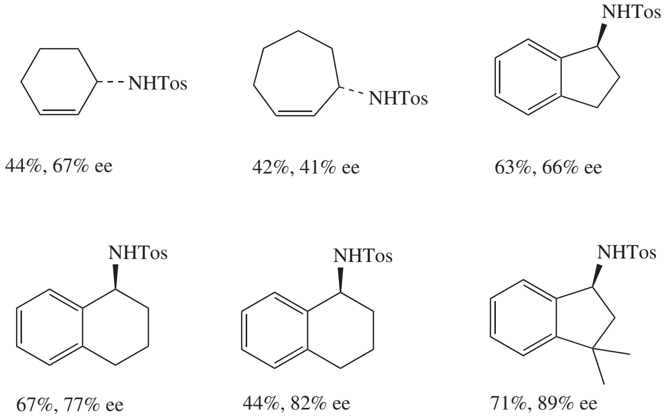


FIGURE 24

C−H hydroxylation reactions was first demonstrated by Kochi and coworkers in 1986[3a]. Interestingly, a Mn(salen) linked to a steroid substrate has successfully catalyzed a regioselective intramolecular C−H hydroxylation[163]. These studies have revealed salens' aptitude as catalyst for C−H bond oxidation, which subsequently resulted in applications described below.

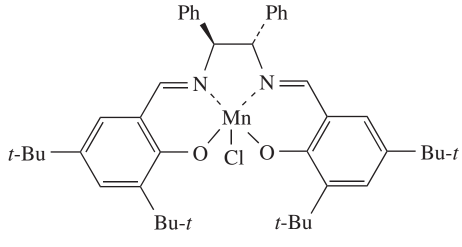
1. Asymmetric hydroxylation of C−H bonds

In 1994, Larrow and Jacobsen reported that the kinetic resolution of racemic dihydronaphthalene oxide and its derivatives with complexes such as **103** (Figure 25) proceeded in moderate reaction ratios. On the contrary, $k_{\text{fast}}/k_{\text{slow}}$ of racemic 1,2-epoxy-3,3-dimethyl-3,4-dihydronaphthalene has reached a relative reaction rate of 28, which was rationalized by the stereoelectronic effect displayed in this benzylic oxidation[164]. Namely, a selective oxidation of an axial benzylic C−H bond by oxo-manganese species stems from the presence of the epoxide ring which fixes the substrate conformation.

This observation served as a basis for the oxidation of the benzylic C−H bond of 1,1-dimethylindane, studied by Katsuki and coworkers[165]. Catalysts **12** and **104**, contrary to their performance at the epoxidation reactions, afforded only poor enantioselectivity in the benzylic oxidation process (Scheme 10).

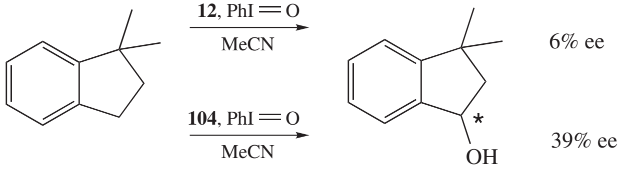
Since the oxidation reaction has presumably a radical character[166], rapid dissociation of the radical intermediate from the manganese ion and further formation of the nonchiral radical species diminishes the enantioselectivity. Solvent of higher viscosity like chlorobenzene had created a stronger cage surrounding the substrate–reagent complex, therefore delaying the radical decay and improving the enantiomeric outcome up to 61% ee[164]. Better results were obtained upon construction of complexes **105a, b**, which possess a *t*-butyldiphenylsilyl group (Scheme 11)[78, 159]. Although the yields are still poor, the enantiomeric excess of the resulting alcohols improved as the reaction proceeded, since the minor enantiomer of the alcohols was oxidized to ketones preferentially ($k_{\text{minor}}/k_{\text{major}} = 2.6–5.0$).

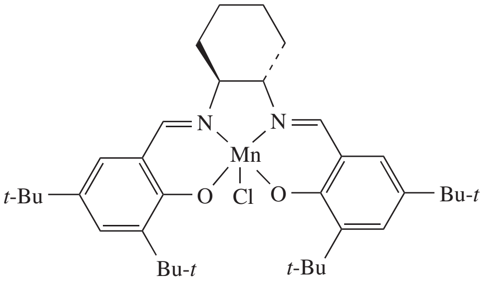
Optically active ketones bearing a stereogenic center at the α-position can be obtained by the asymmetric oxidation of alkanes as was shown by Murahashi and coworkers[167]. 2-Methyl-1,3-diphenylpropane **106a** was desymmetrized by the catalyst **107** and iodosylbenzene to afford a corresponding chiral ketone in 22% ee (Scheme 12). The electronic effect at the *para* position of **106** is not expressed in this transformation, as can be deduced from the oxidation of **106b** and **106c**. Cyclic substrate **108** afforded the corresponding ketone with a quaternary carbon in 14% ee[168].



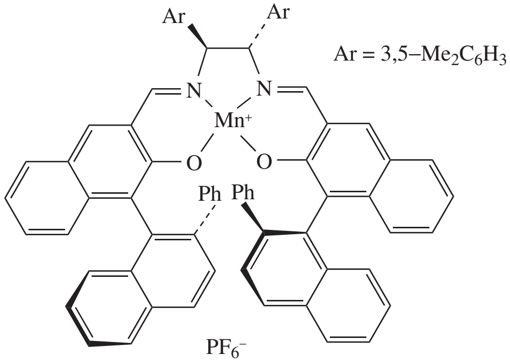
(**103**)

FIGURE 25





(**12**)



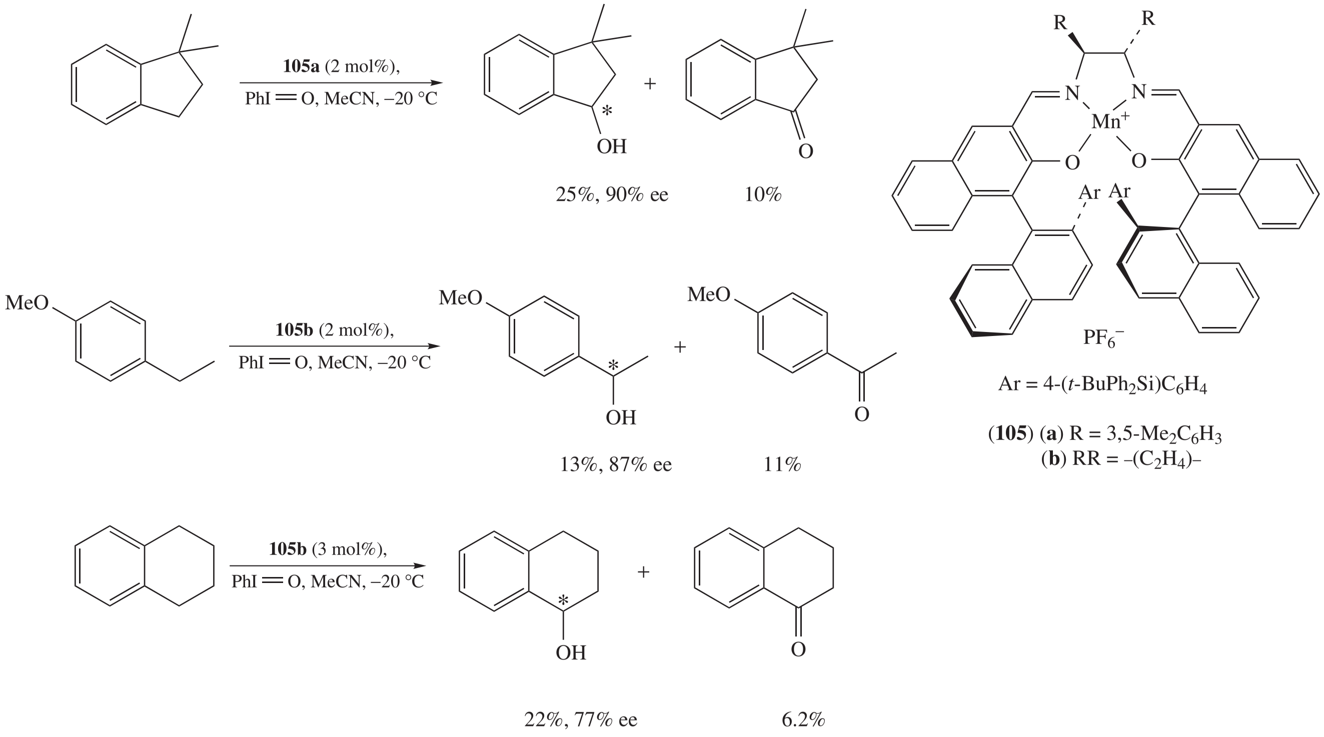
(**104**)

SCHEME 10

2. Asymmetric oxidation of silyl enol ethers and enol acetates

The catalytic oxidation can also be applied to the α-C−H oxidation of silyl enol ethers and enol acetates to afford the corresponding optically active ethers. Reddy and Thornton have reported the asymmetric oxidation of silyl enol ether using complex **109** as a catalyst, giving a mixture of α-hydroxy ketones **110** and their trimethyl silyl ethers **111** (equation 17)[169]. The enantioselectivity of the reaction varied in accordance with the substrate used from 15% to 62% ee (Table 5).

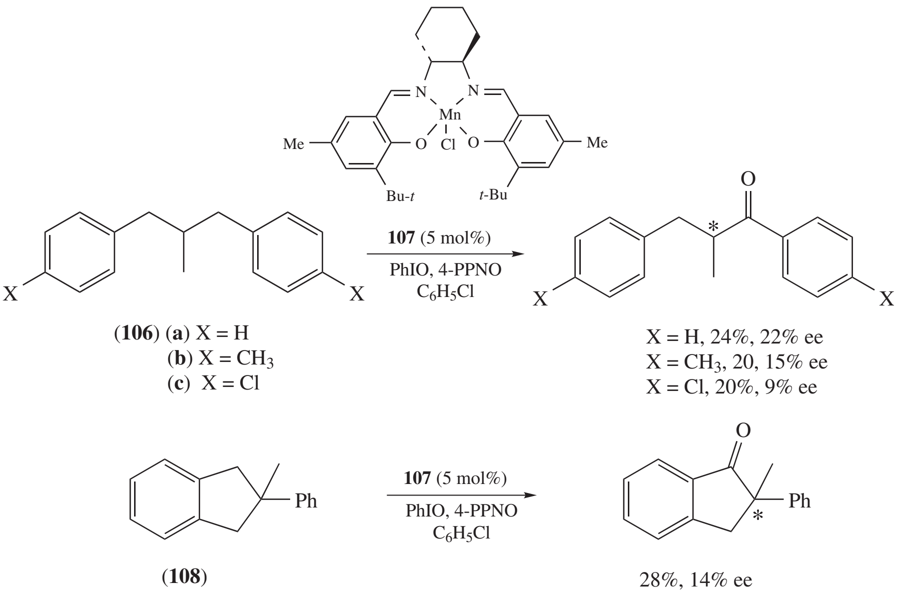
Oxidation of enol acetates using **112** as a catalyst proceeds with moderate to good enantioselectivity (Scheme 13)[42a].



Ar = 4-(t-$BuPh_2Si)C_6H_4$

(**105**) (**a**) R = 3,5-$Me_2C_6H_3$
(**b**) RR = –(C_2H_4)–

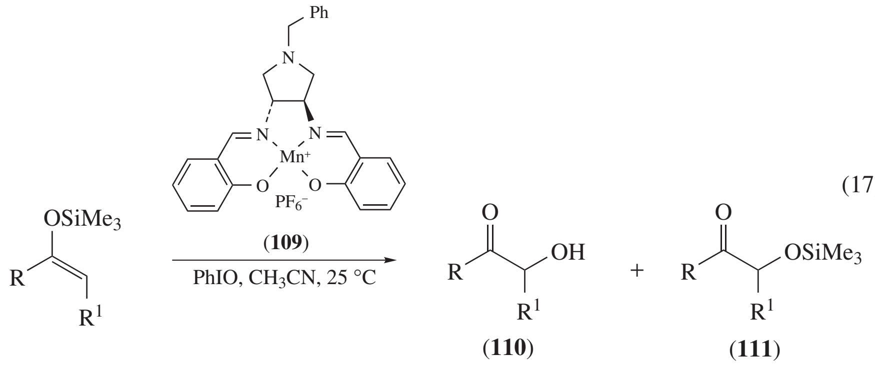
SCHEME 11



SCHEME 12

3. Desymmetrization of meso- and prochiral substrates

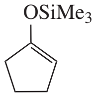
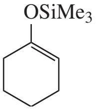
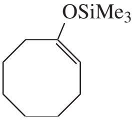
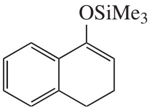
Study of the kinetic isotopic effect had indicated that Mn(salen)-catalyzed oxidation of heterocycles proceeds through one-electron transfer[170]. This finding makes such complexes expedient for the oxidative desymmetrization of *meso*-heterocycles[171], since hydrogen atom abstraction makes these compounds chiral and radical decay does not affect the enantioselectivity of the reaction.



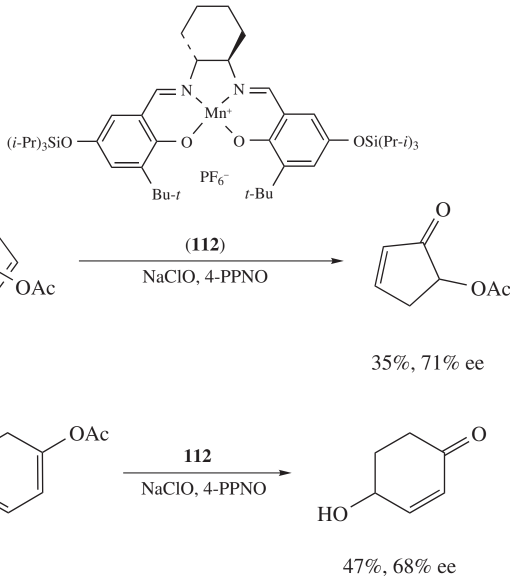
(17)

Indeed, desymmetrization of *meso*-tetrahydrofurans proceeded with high enantioselectivity when (R,R)-complex **56** was used as catalyst (Scheme 14)[172]. Functional groups such as acetonide and ester tolerate the reaction conditions.

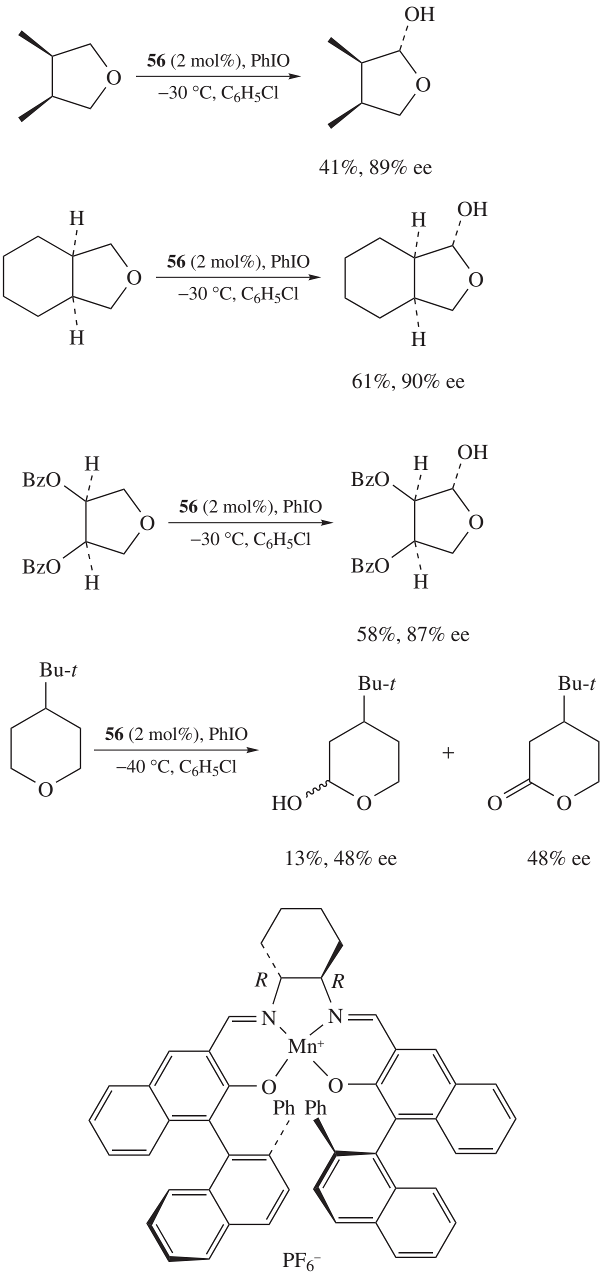
TABLE 5. Asymmetric oxidation of silyl enol ethers (equation 17)

Entry	Substrate	Yield (%)[a]	Ratio (**110**:**111**)	ee (%)[b]
1		70	2.6:1	30
2		78	1.4:1	51
3		68	0.8:1	15
4		72	0.8:1	62

[a] Total yield of **110** and **111**.
[b] Total ee of **110**.



SCHEME 13

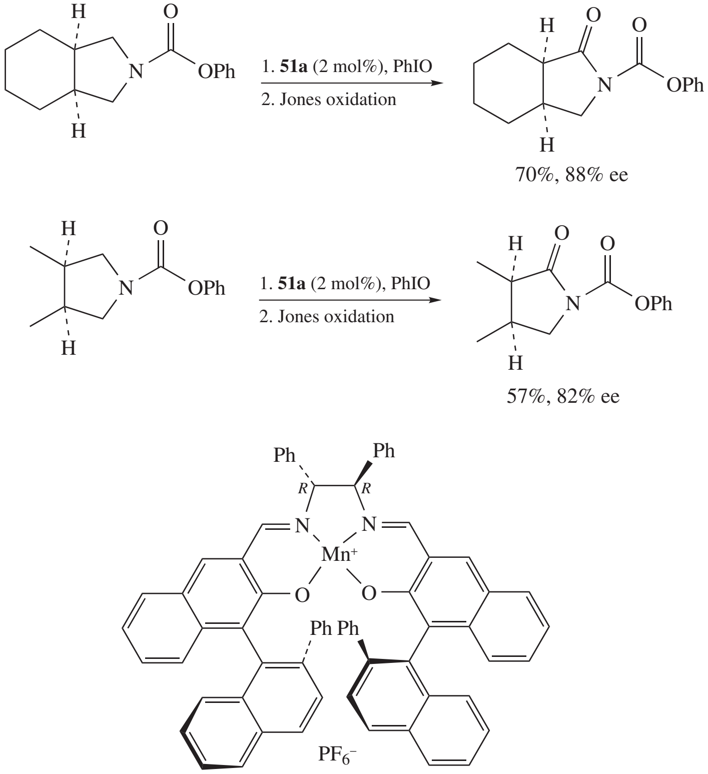

OH
O
56 (2 mol%), PhIO
−30 °C, C6H5Cl
41%, 89% ee
H
H
61%, 90% ee
BzO
BzO
58%, 87% ee
Bu-t
HO
−40 °C, C6H5Cl
+
13%, 48% ee
48% ee
R
R
N
N
Mn+
Ph
Ph
PF6−

(**56**)

SCHEME 14

On the other hand, oxidation of prochiral 4-(*t*-butyl)tetrahydrofuran was slow and less selective. Study on the kinetic isotope effect of this transformation indicated a single electron transfer from the *n*-orbital on the oxygen atom to the oxo species and subsequent proton transfer[173]. The chair conformation of the 4-(*t*-butyl)tetrahydrofuran benefits little from the HOMO (C−H σ bond)−SOMO (singly occupied *n*-orbital) interaction, which is essential for the proton transfer. It is also noteworthy that the (*R*,*S*)-diastereomer of complex **56** is a poor catalyst for the oxidation of the heterocycles, contrary to its good performance in the asymmetric epoxidation. This fact suggests different mechanistic pathways for the epoxidation and C−H oxidation catalyzed by Mn(salen) complexes.

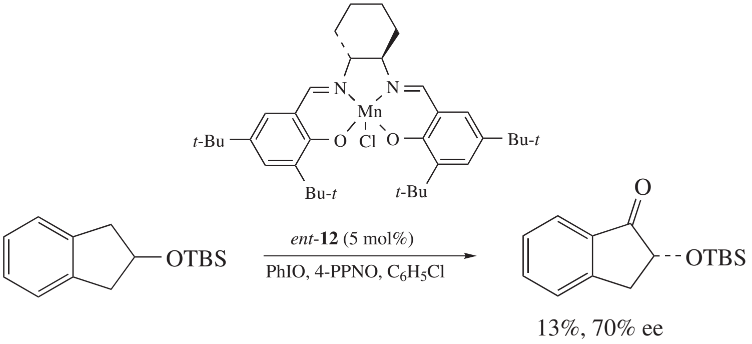
Desymmetrization of *meso*-pyrrolidines was also effected by using (*R*,*R*)-Mn(salen) **51a** as a catalyst (Scheme 15)[174]. The enantioselectivity of this reaction was dependent on the *N*-protecting group, while the phenoxycarbonyl has emerged as the most appropriate substituent. This reaction has also been considered to proceed through an electron transfer pathway, since the hydroxylation of the C−H bond occurs in preference to epoxidation.



(**51a**)

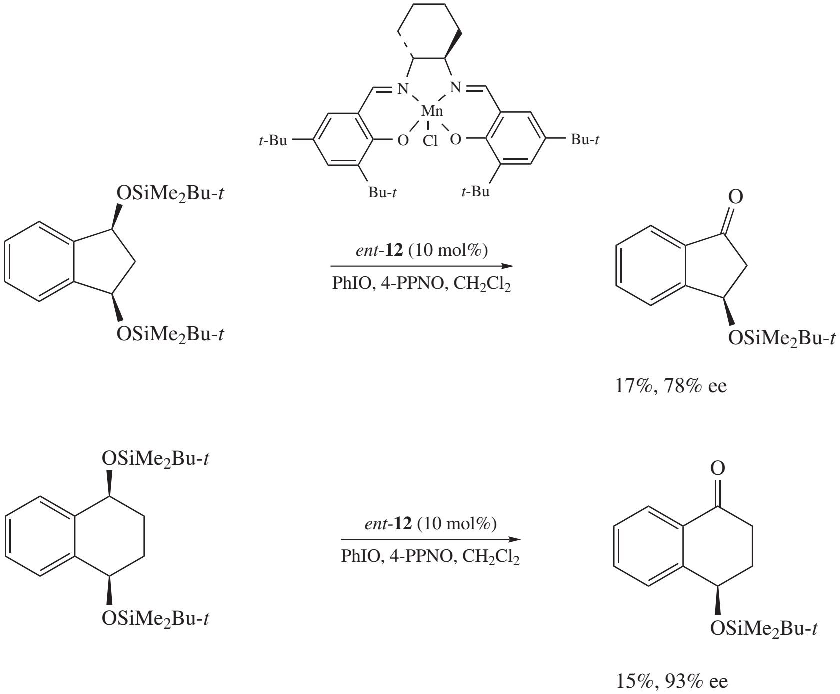
SCHEME 15

Murahashi and coworkers also explored desymmetrization of prochiral TBS ether of 2-hydroxyindane using Mn(salen) *ent*-**12** as a catalyst (equation 18)[175].

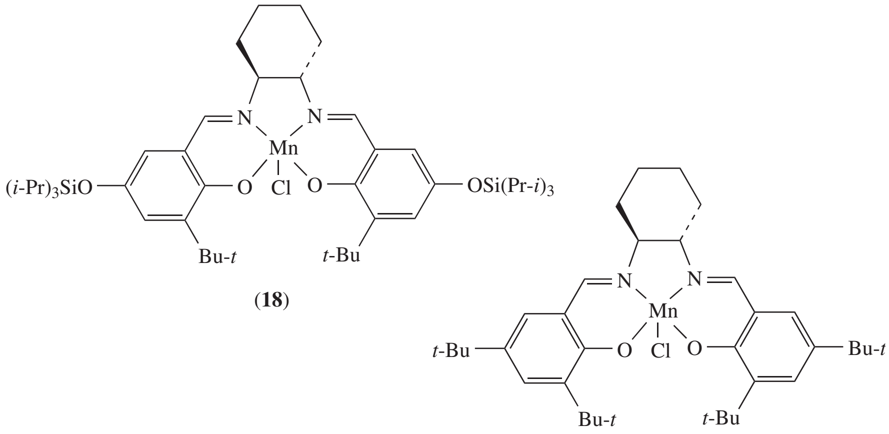


(18)

Symmetrical 1,3- and 1,4-disilyl ethers were also subjected to the oxidation with concomitant desymmetrization and formation of optically active *β*- and *γ*-silyloxy ketones (Scheme 16)[168].

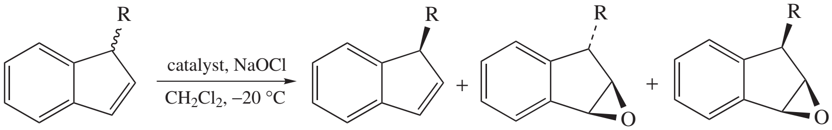


SCHEME 16

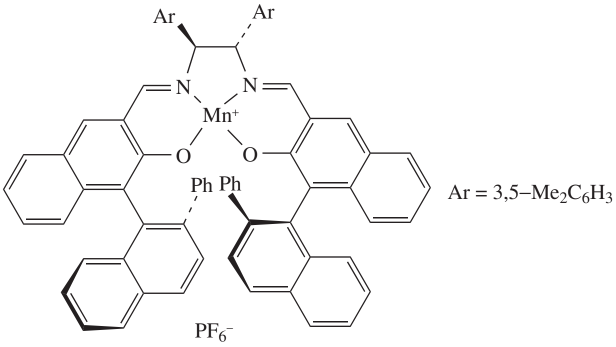


(**18**)

(**12**)



	recovered (**A**)	*trans* (**B**)	*cis* (**C**)
R = Me, **104**, $k_{fast}/k_{slow} = 2.6$	13%, 82% ee	55%, 98% ee	32%, 93% ee
R = Me, **12**, $k_{fast}/k_{slow} = 4\text{-}5$	75%, 22% ee	20%, 82% ee	5%, 85% ee
R = *i*-Pr, **104**, $k_{fast}/k_{slow} = 7.5$	10%, 100% ee	79%, >99% ee	11%, 67% ee
R = *i*-Pr, **12**, $k_{fast}/k_{slow} = 4\text{-}5$	93%, 6% ee	6%, 35% ee	1%, 64% ee



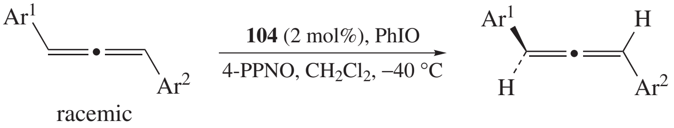
(**104**)

SCHEME 17

4. Kinetic resolution

It is generally assumed that a catalyst used for enantioselective transformation can also serve as a good catalyst for kinetic resolution of the corresponding racemic substrate. Since Mn(salen)s constitute excellent catalysts for asymmetric epoxidation of prochiral *cis*-olefins, racemic *cis*-olefins are expected to undergo epoxidation in an enantiomer-differentiating fashion. Thus, epoxidation of racemic 2,2-dialkylsubstituted chromenes has been examined with complex **18** (Scheme 17), at −78 °C, however only a moderate level of enantiomer differentiation was attained ($k_{\text{fast}}/k_{\text{slow}} = 2.7-9.3$)[176]. Similarly, racemic 1-alkylindenes exhibited modest enantiomer-differentiation ($k_{\text{fast}}/k_{\text{slow}} = 2.6-7.5$) when subjected to the epoxidation by catalysts **12** and **104** (Scheme 17)[139a]. Despite such a moderate result, the enantiomeric excess of the fast-reacting isomer was high, especially when sterically congested complex **104** was used.

This catalyst was also successfully applied in the enantiomer-differentiating oxidation of racemic aryl-substituted allenes (equation 19)[177].



Ar^1 = Ph, Ar^2 = Ph, $k_{fast}/k_{slow} = 18$

Ar^1 = Ph, Ar^2 = p-ClC_6H_4, $k_{fast}/k_{slow} = 21$

(19)

As shown in Figure 26, two incoming enantiomers **A** and **B** are well differentiated by Mn(salen) **104**, since the C(3)-substituent (Ar^2) of enantiomer **A** is directed toward the catalysts thus inducing stronger steric repulsion than enantiomer **B**.

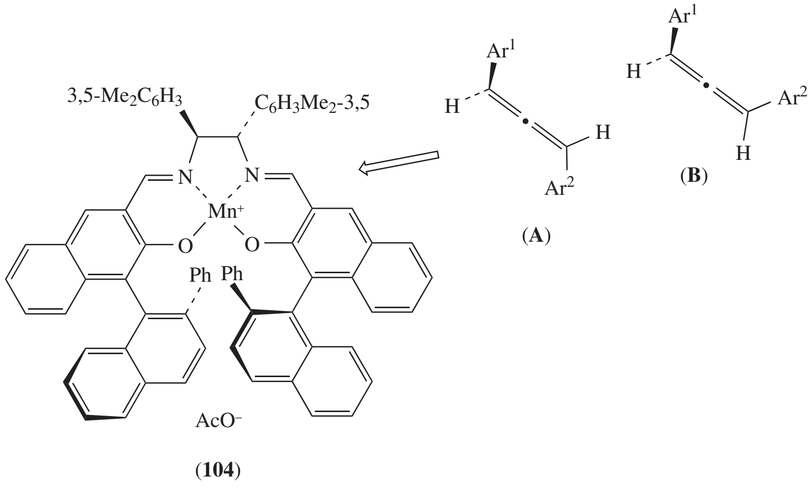
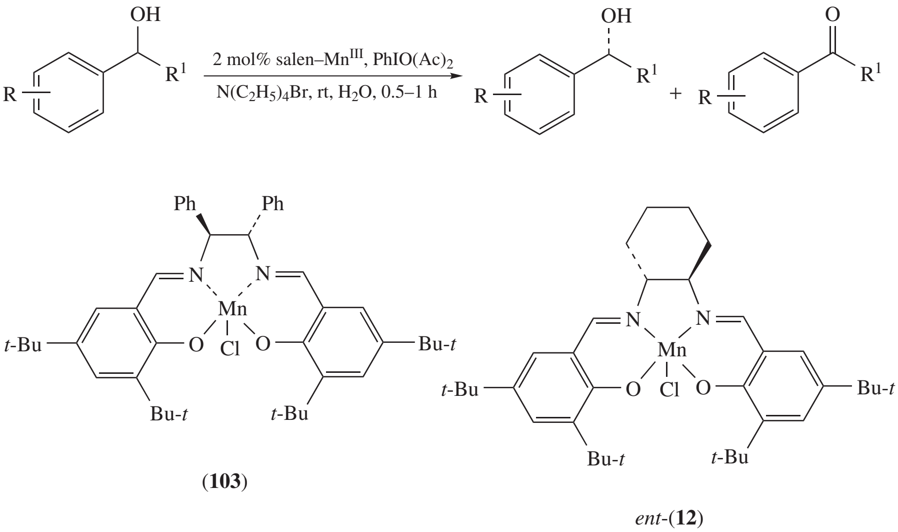


FIGURE 26



(**103**)

ent-(**12**)

SCHEME 18

A method for the enantioselective kinetic resolution of secondary alcohols in the presence of catalysts *ent*-**12** and **103** was discovered and studied by Xia and coworkers (Scheme 18)[178]. The reaction conditions included water and phase-transfer catalyst $N(C_2H_5)_4Br$, while steric hindrance at the 5,5′-positions of the Mn(salen) complex appeared as favorable for the enantiomeric outcome. The substrate scope evaluation revealed that *para*-substituted α-methylbenzyl alcohols are generally good substrates for oxidative kinetic resolution with high k_{rel} values (Table 6, entry1–3)[179]. However, when the R^1 group of the substrate is changed from methyl to ethyl, the enantioselectivity decreases sharply (Table 6, entry 6). The electronic cooperation between the catalyst and substrate has a strong influence on the enantioselectivity of the reaction. It becomes evident from the efficiency of the catalyst **103** in case of α-methylbenzyl alcohol and 1-phenyl-2-propanol versus complex *ent*-**12** which performs more efficiently for the substrates with substituents on the aromatic ring.

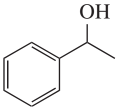
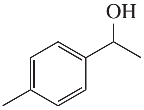
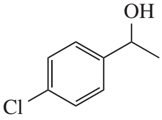
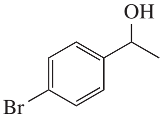
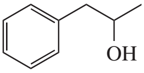
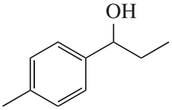
E. Sulfide Oxidation and Amidation Reactions

1. Enantioselective formation of S–O bond

Chiral sulfoxides constitute useful auxiliaries in asymmetric synthesis and products with biological properties containing chiral sulfinyl groups[180]. In 1984, the group of Kagan and Modena discovered that titanium^{IV} isopropoxide-diethyltartrate based systems are apt to asymmetrically oxidize prochiral sulfides by alkylhydroperoxides[181]. A catalytic version of this transformation was later developed and remains nowadays one of the most applied methodologies for the asymmetric sulfoxidation. However, low turnover numbers, complexity and expensiveness of the method prompt the search for other transition metals based catalysts.

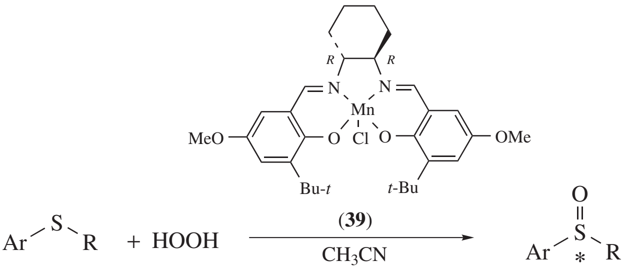
In 1992, Jacobsen and coworkers reported on Mn(salen) complexes as effective catalysts for the oxidation of sulfides[182]. An optimal reaction system includes unbuffered hydrogen

TABLE 6. Asymmetric kinetic resolution of secondary alcohols (Scheme 18)

Entry	Substrate	Catalyst	Conversion (%)	ee (%)	k_{rel}[a]
1		**103**	62.5	88	8.9
2		*ent*-**12**	78	51	51
3		*ent*-**12**	61	98	18.2
4		*ent*-**12**	66	97	11.3
5		**103**	60	80	7.7
6		*ent*-**12**	65	5.4	1.1

[a] k_{rel} rate of fast-reacting enantiomer/rate of slow-reacting enantiomer

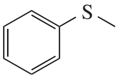
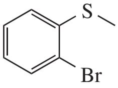
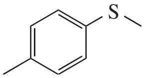
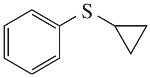
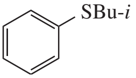
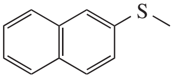
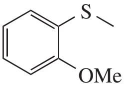
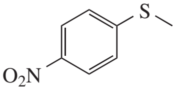
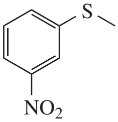
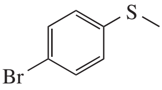
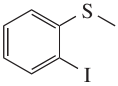
peroxide as the stoichiometric oxidant, acetonitrile as solvent and 2–3 mol% of complex **39** (equation 20). As Table 7 shows, this efficient transformation in terms of isolated yields (84–95%) reaches only moderate enantiomeric excesses (up to 68% ee, entry 2).



(20)

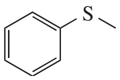
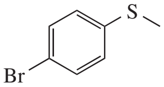
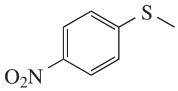
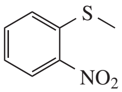
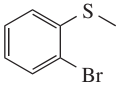
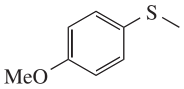
Katsuki and coworkers have shown that methoxylated second-generation catalyst **104** enhances the enantioselectivity remarkably in the oxidation of sulfides with PhIO

TABLE 7. Asymmetric oxidation of prochiral sulfides by (*R*,*R*)- or (*S*,*S*)-**39** (equation 20)

Entry	Sulfide	Catalyst	Yield (%)[a]	ee (%)	Configuration
1		(*R*,*R*)-**40**	90	47	*S*-(−)
2		(*R*,*R*)-**40**	80	68	*S*-(−)
3		(*R*,*R*)-**40**	95	42	*S*-(−)
4		(*R*,*R*)-**40**	84	40	*S*-(−)
5		(*R*,*R*)-**40**	94	43	*S*-(−)
6		(*R*,*R*)-**40**	84	46	*S*-(−)
7		(*S*,*S*)-**40**	94	34	*R*-(+)
8		(*R*,*R*)-**40**	86	66	*S*-(−)
9		(*S*,*S*)-**40**	84	63	*R*-(+)
10		(*S*,*S*)-**40**	93	56	*R*-(+)
11		(*S*,*S*)-**40**	93	65	*R*-(+)

[a] Isolated yields based on sulfide.

TABLE 8. Asymmetric oxidation of prochiral sulfides by **104** and **105** and PhI=O as an oxidant

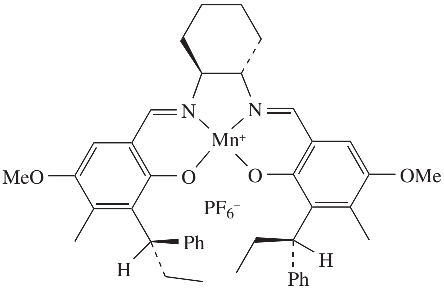
Entry	Sulfide	Catalyst	Yield (%)	ee (%)
1		**104**	76	63
2		**105**	60	84
3		**104**	63	75
4		**104**	67	86
5		**104**	51	90
6		**105**	90	94
7		**104**	74	88
8		**104**	45	40

(Figure 27, Table 8, entries 1, 3–5, 7–8)[42a, 183]. Even better ligand efficiency (up to 2 mol%) and enantiomeric excesses were reached upon sulfoxidation with methoxylated catalyst **105** (Figure 27, Table 8, entries 2, 6)[184].

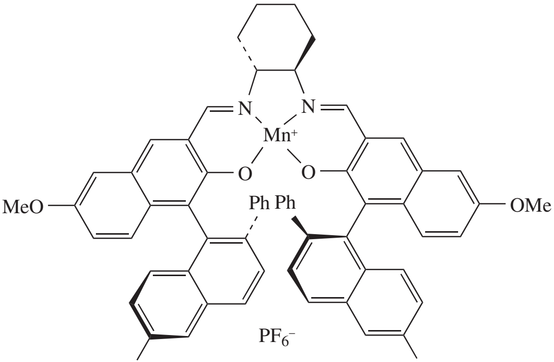
Extended mechanistic studies on the manganese-catalyzed oxidation of sulfides by Rajagopal and coworkers showed that different mechanisms operate in case of PhIO and H_2O_2[185]. In particular, Mn(salen)−PhIO oxidations showed clear second-order kinetics, first order each in the oxidant and substrate. The proposed mechanism implies the formation of the reactive manganese^{V} oxo species **106** (Figure 28), which was confirmed by electrospray ionization tandem mass spectrometry (ESMS)[186] and NMR studies[187]. On the contrary, the oxidations performed by H_2O_2 proceed via a rate-determining step of the sulfide oxidation by the reactive manganese^{III} hydroperoxo species **107** (Figure 28).

Mukaiyama and coworkers described a family of β-oxoaldiminatomanganese^{III} complexes like **108**, which oxidize sulfides with molecular oxygen in the presence of pivaldehyde (Figure 29)[188]. Only 2 mol% of the catalyst were required to reach 70% ee in excellent yields and nearly no overoxidation to sulfones. In the mechanistic study performed by Bryliakov and coworkers, acylperoxo manganese^{III} complex Mn(salen)^{III} (OOCOR) emerged as the actual oxidant[189].

In 2003, a manganese(II)−Schiff base/H_2O_2 **109** was published by Fontecave and coworkers (Figure 29) as an asymmetric oxidizing system which is able to convert methyl *p*-nitrophenyl sulfide to the corresponding sulfoxide in up to 62% ee[190]. When perchlorate

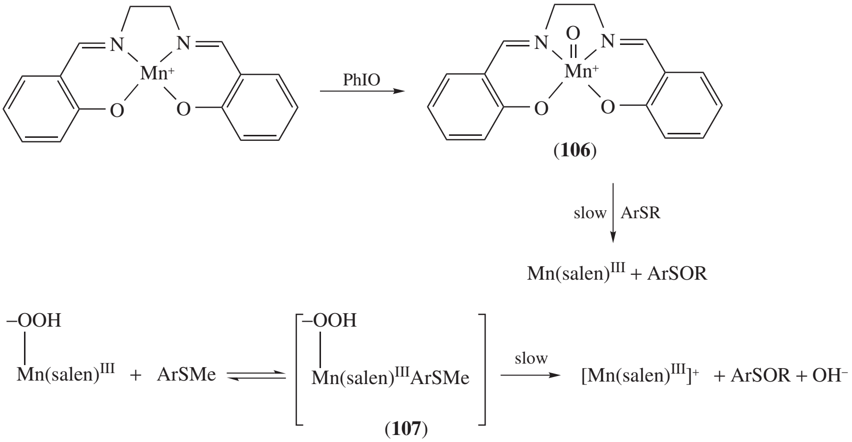


(**104**)



(**105**)

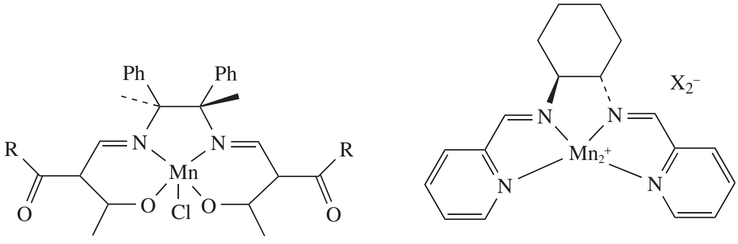
FIGURE 27



(**106**)

(**107**)

FIGURE 28



(**108**) (**109**)

$X^- = ClO_4^-$, acac$^-$

FIGURE 29

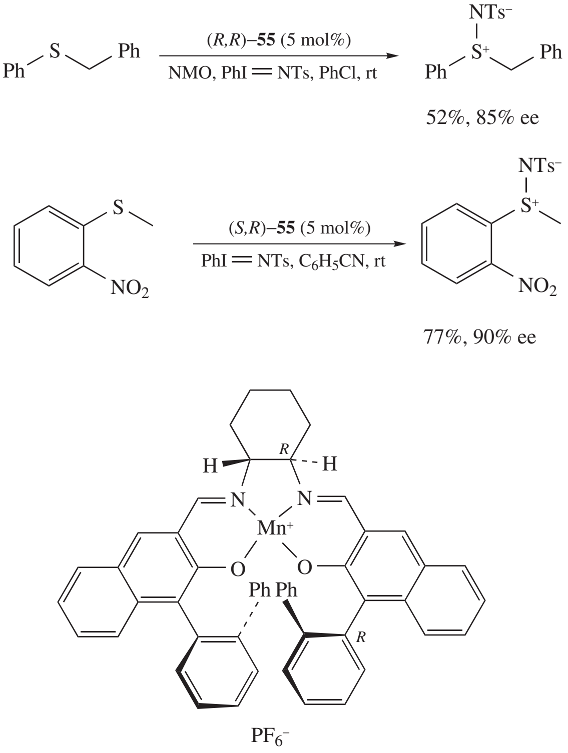
counterion was replaced by acetylacetonate, an inversion in the absolute configuration of sulfoxide was noted.

2. Enantioselective formation of S–N bond

Sulfimides are synthetic equivalents of sulfoxides and are expected to be efficient chiral auxiliaries, albeit their use in organic synthesis has been limited by the lack of enantioselective synthetic protocols[191]. Following Uemura and coworkers' report on the imidation of alkyl aryl sulfides with a chiral copper^{I}-bis(oxazoline) complex[192], optically active second-generation Mn(salen)s turned out to be good catalysts for enantioselective sulfimidation (Scheme 19)[193]. Interestingly, a choice of the proper catalyst was substrate-dependent. Namely, imidation of alkyl aryl sulfides was efficiently catalyzed by (*R*,*R*)-**55** in the presence of *N*-methylmorpholine *N*-oxide (NMO) in chlorobenzene, while that of methyl *o*-nitrophenyl sulfide required (*S*,*R*)-**55** in benzonitrile. The active species of the above transformations were defined by the analysis of the reaction based on the Eyring equation[193b]. Thus, imino Mn species are responsible for the imidation of alkyl phenyl sulfide with (*R*,*R*)-**55** in the presence of NMO, whereas Mn–PhI=NTs adduct is believed to imidate methyl *o*-nitrophenyl sulfide when (*S*,*R*)-**55** is used.

F. Formation of Cyanohydrin

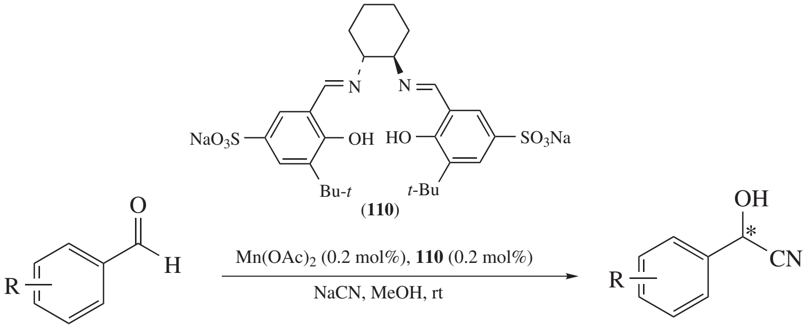
The cyanohydrin formation reaction is one of the fundamental carbon–carbon bond-forming processes in organic chemistry[194]. Optically active cyanohydrins can be used as versatile synthons to form a wide variety of important chiral compounds such as α-amino acids, α-hydroxycarboxylic acids, β-aminoalcohols, vicinal diols and α-hydroxy ketones[195]. Catalytic systems generated from transition metals were developed and successfully applied in the asymmetric trimethylsilylcyanation of aldehydes[196]. Enzymes and peptides also constitute excellent tools for the catalytic addition of HCN to aldehydes, providing high enantiomeric excess[195]. Nevertheless, difficult handling of trimethylsilyl cyanide and the volatility of hydrogen cyanide stimulate efforts to search for different, easily-manipulated systems for this reaction. One of the applications of the Mn(salen) chemistry was demonstrated by Zhou and coworkers, who reported asymmetric cyanohydrin formation from aldehydes, performed with sodium cyanide and catalyzed by *in situ*-generated sulfonato manganese–salen complex under mild reaction conditions[197].



(**55**)

SCHEME 19

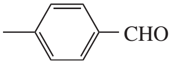
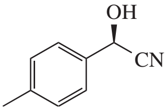
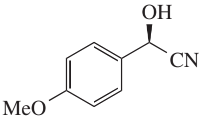
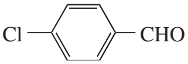
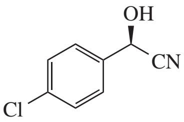
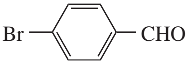
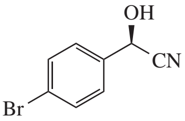
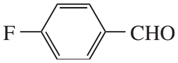
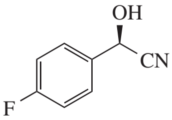
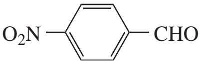
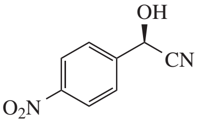
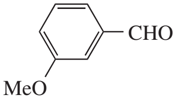
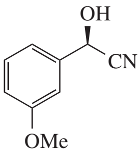
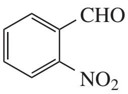
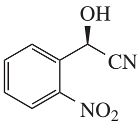
Schiff base ligand **110** exhibited the best results when applied with 0.2 mol% of $Mn(OAc)_2$ and sodium cyanide in methanol on benzaldehyde and its derivatives (equation 21).



(21)

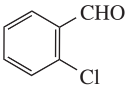
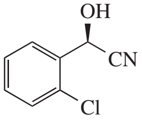
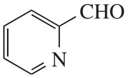
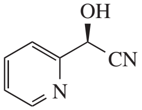
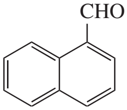
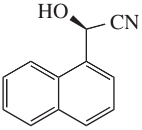
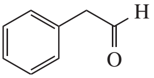
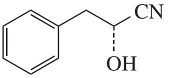
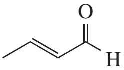
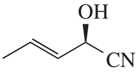
As Table 9 indicates, substituent position inflicts greater influence on the results than the electronic effects. For instance, both 4-methylbenzaldehyde and 4-nitrobenzaldehyde

TABLE 9. Asymmetric formation of cyanohydrins from aldehydes (equation 21)

Entry	Substrate	Product	Yield (%)	ee (%) (configuration)
1			67	97 (*R*)
2			45	91 (*R*)
3			68	>99 (*R*)
4			55	98 (*R*)
5			65	83 (*R*)
6			60	93 (*R*)
7			54	89 (*R*)
8			42	66 (*R*)

(*continued overleaf*)

TABLE 9. (*continued*)

Entry	Substrate	Product	Yield (%)	ee (%) (configuration)
9			44	81 (*R*)
10			69	95 (*R*)
11			56	>99 (*R*)
12			35	38 (*R*)
13			68	12 (*R*)

afforded 97% and 93% ee respectively (Table 9, entries 1 and 6), whereas 2-nitrobenzaldehyde gave only 66% ee (Table 9, entry 8). The highest enantioselectivities of 99% were obtained for 4-chlorobenzaldehyde and α-naphthaldehyde (Table 9, entries 3 and 11, respectively). Aliphatic substrates, however, are not suitable for this catalytic system (entries 12 and 13).

III. MANGANESE^{III}–PORPHYRIN COMPLEXES

A. Introduction

A great deal of attention dedicated for the last two decades to the synthesis and asymmetric applications of metal(salen) complexes was preceded by extended studies on the metalloporphyrins and their asymmetric reactions[94, 198]. Along with such common features as electronic structure and catalytic activity, porphyrins differ from salen ligands in structure, since the peripheral carbon atoms of porphyrins are all sp^2, while salen ligand bears two sp^3 carbon atoms. The latter can be replaced with asymmetric carbon atoms, thus providing stereogenic centers which reside in proximity to the metal center so rendering salens a promising chiral template. Indeed, in a retrospective view, salen ligands have proved to be more efficient and selective catalysts for the oxo transfer reactions than their porphyrin analogues[42a].

An ever-growing interest toward porphyrins was initially stimulated by the comprehensive work performed on the oxo transfer enzyme cytochrome P-450[199], which is known to catalyze the mono-oxygenation of various compounds, both biotic and exobiotic, with high stereo- and regioselectivity under mild conditions[200]. Much effort was devoted to the study of the function of P-450 bearing an iron–porphyrin complex as its active site[201]. The P-450-catalyzed oxo transfer reaction was proposed by Groves and Nemo to proceed through an oxoheme catalytic intermediate[10]. Furthermore, Groves and coworkers reported in 1979 that simple iron^{III} porphyrins are good models for the reaction site of cytochrome P-450 and that they are readily oxidized to the active cationic oxoiron^{IV}–porphyrin species by their treatment with iodosylbenzene[202]. It should be noted that in the epoxidation of simple olefins catalyzed by this system, *cis*-olefins reacted much faster than *trans*-substrates. This substrate specificity has been explained by assuming that an olefin approaches the oxo-metal bond from its side parallel to the porphyrin ring. The proposed side-on approach is now widely accepted for the metalloporphyrin- and metallosalen-catalyzed epoxidation.

Many metalloporphyrin complexes have been synthesized since then, among them iron$^{(III)}$[203], manganese$^{(III)}$[204], ruthenium$^{(IV)}$[205] and molybdenum[204, 206] porphyrins have been found to be efficient catalysts for the epoxidation of simple olefins and the oxidation of sulfides. Chiral groups have been attached to porphyrins, aiming at systems that might give high enantioselectivities and turnover numbers. Supplementary consideration lies in the nature of oxidants and metals[207]. Of three metal complexes with the same chiral porphyrin ligand, much better results were obtained with iron and ruthenium than with manganese.

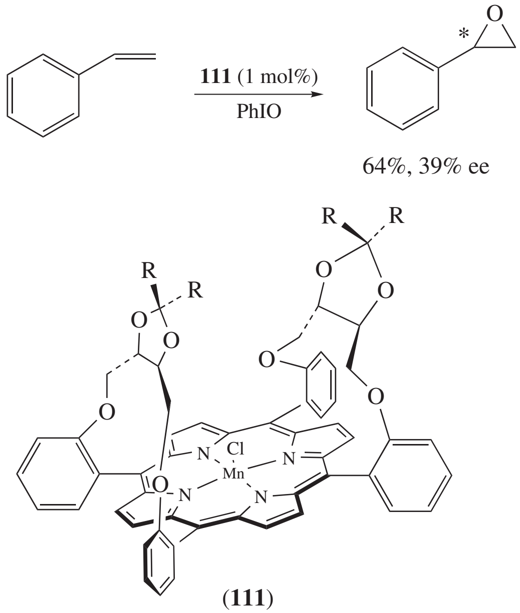
B. Enantioselective Epoxidation Reactions of Manganese Porphyrins

In natural hemoproteins, the protein chain present in the vicinity of the metal ions controls the substrate access to the active site. Thus, if one wants to mimic the natural enzyme, special care has to be dedicated to the design of the superstructure of the model in order to accurately control the substrate approach to the metal center. Numerous chiral porphyrin structures appeared during the last twenty-five years but only a few were very successful in enantioselective epoxidation catalysis. Their structural types can be divided into two major groups: single-faced protected and bis-faced protected porphyrins. Collman and coworkers contributed most significantly to the development of single-faced protected porphyrins[17b]. Thus, they have designed a threitol-strapped manganese^{III} porphyrin **111**, which catalyzed epoxidation of styrene in 64% yield and 39% ee with PhIO as oxidant; ee values reaching 59% were measured for the epoxidation of *cis*-β-methylstyrene (equation 22)[208].

The same group has also designed a strapped version of porphyrins **112**, with a bridge spanning the center of the macrocycle. The catalyst shows moderate to good enantioselectivities in the epoxidation of a wide range of olefins with PhIO in the presence of 1,5-dicyclohexylimidazole (Scheme 20)[208]. The substituted imidazole in this reaction is presumably coordinated to the unhindered face of the complex **112** and the reaction occurs on the strapped face.

Various organic bases can act as blocking agents for the unhindered face to force the incoming substrate to interact with the chiral pocket (Figure 30)[94].

Inoue and coworkers have demonstrated as well that axial ligation is important for effective asymmetry transfer during the alkene epoxidation catalyzed by single-faced chiral porphyrins[209]. Complex **113**, endowed with facial chirality by introducing a strap, shows remarkable improvement in the enantioselectivity of the styrene epoxidation reaction when imidazole is present (Scheme 21).



(**111**)

R = Me, Ph

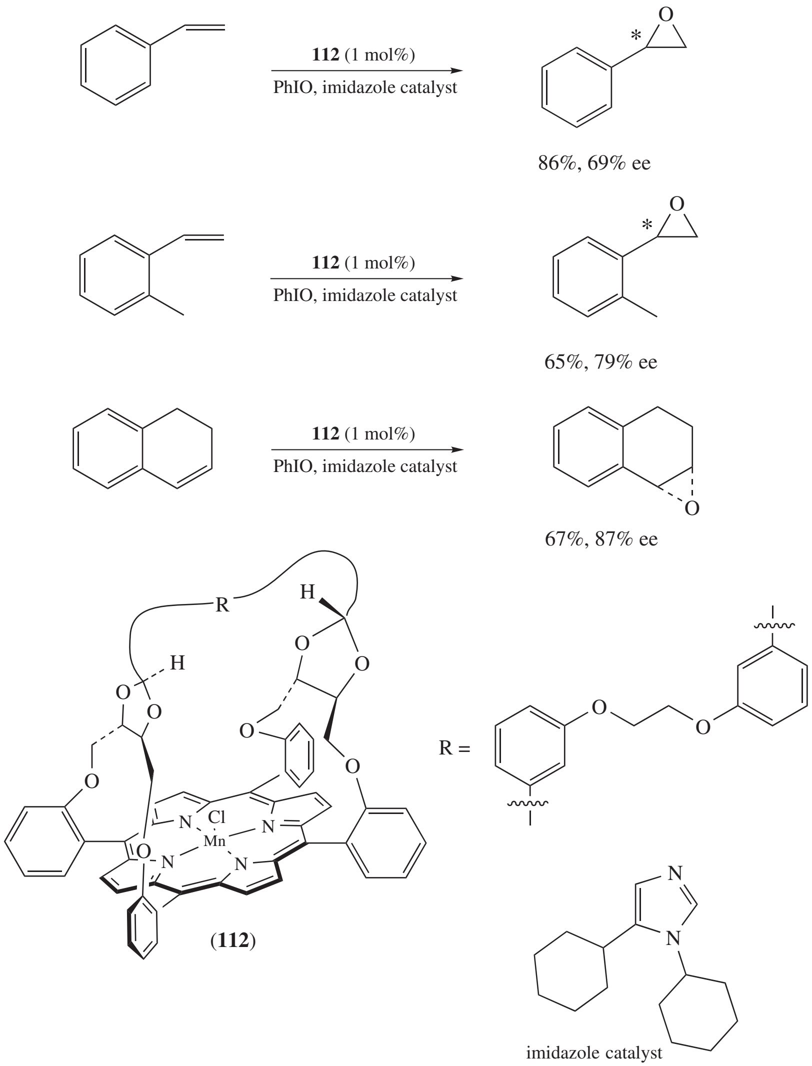
(22)

The group of double-faced porphyrins is divided in two subgroups: the bis-faced picket porphyrins and the bis-faced ansa porphyrins[210]. $\alpha,\beta,\alpha,\beta$-Tetrakis-(2′-camphanylamidophenyl)porphyrin **114** (Figure 31), synthesized by Paolesse and coworkers, is among the bis-faced picket-type porphyrins which exhibited some enantioinduction in the epoxidation of styrene with PhIO (Table 10, entry 1)[211]. The authors suggested that low enantiomeric excess could be ascribed to the difficult access of the substrate to the catalytic center.

Another representative of the bis-faced picket porphyrins is a D_4-chiral **115** (Figure 31) which furnished good optical yields in the epoxidation of *cis*-β-methylstyrene with NaOCl in the presence of 4-*t*-butylpyridine (Table 10, entry 2)[212]. Identically, (*S*)-(−)-styrene oxide was obtained in 52% ee (entry 3). The complex was recovered and used in the next reaction batch to afford identical results. Chang and coworkers have demonstrated that the use of multifarious organic bases is beneficial: *cis*-β-methylstyrene was epoxidized in 86% ee by oxone ($KHSO_5$) and **115** when 4-(*N*,*N*-dimethylamino)pyridine was used (versus 43% ee with no base additive)[213].

Kodadek and coworkers also prepared the D_4-symmetric porphyrin **116** (Figure 31) which has formed styrene oxide in 70% yield and 70% ee when LiOCl was used as oxidant in the presence of 1,5-dicyclohexylimidazole in a phase transfer system (Table 10, entry 4)[214]. In parallel, epoxidation of α-methylstyrene afforded the corresponding epoxide in 65% ee (entry 5).

Porphyrin **117** (Figure 31), synthesized by Groves and coworkers, belongs to the bis-faced ansa groups. Its manganese complex afforded only moderate selectivity and poor yield when applied on the epoxidation of styrene (Table 10, entry 6)[166].



SCHEME 20

The scope of the manganese(porphyrin)-catalyzed epoxidation is still limited, and there is room for improvement in their enantioselectivity. Chiral synthesis of such ligands is not facile in many cases, and the nature of the active site and the influence of the geometry of the porphyrin ring on the differentiation of the prochiral faces should be thoroughly modeled and studied. Yet, metalloporphyrin in general demonstrates an advantage in its

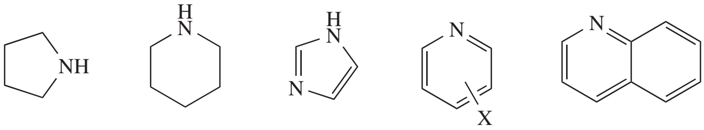
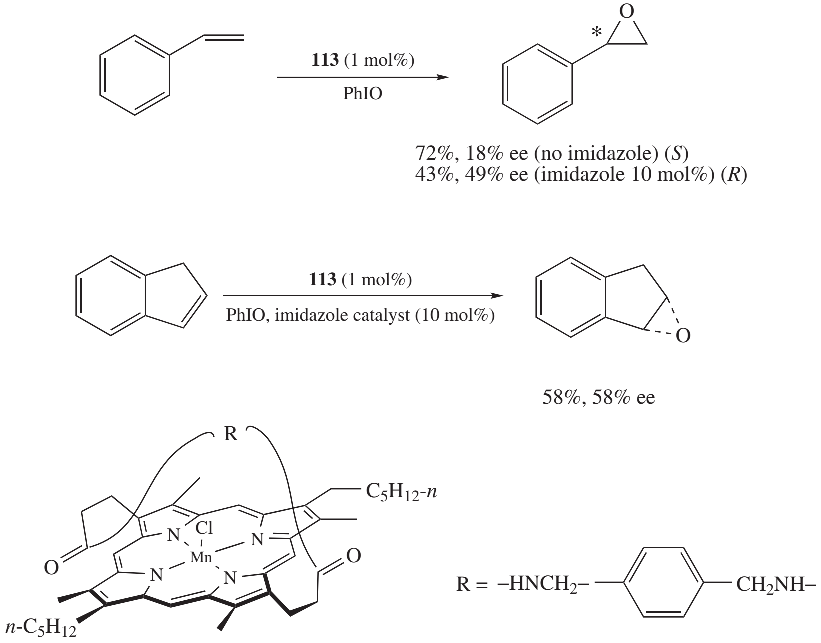


FIGURE 30



(**113**)

SCHEME 21

robustness against various terminal oxidants, especially when the ligand bears electron-withdrawing substituents. In addition, high turnover numbers exceeding thousands have been realized in porphyrin-catalyzed epoxidations[27].

C. Asymmetric Nitrogen Transfer to Hydrocarbons

The epoxidation[17b], aziridination and cyclopropanation[215] of alkenes and the hydroxylation[216] and amidation[161b, 161c] of saturated C−H bonds are among the most common hydrocarbon-functionalization reactions mediated by a metalloporphyrin. These processes are widely believed to proceed by oxygen-, nitrogen- and carbon-atom transfer from oxo-, imido- and carbene-metalloporphyrin active species, respectively. The utility of the metalloporphyrin catalysts has been extended to asymmetric synthesis and the catalytic

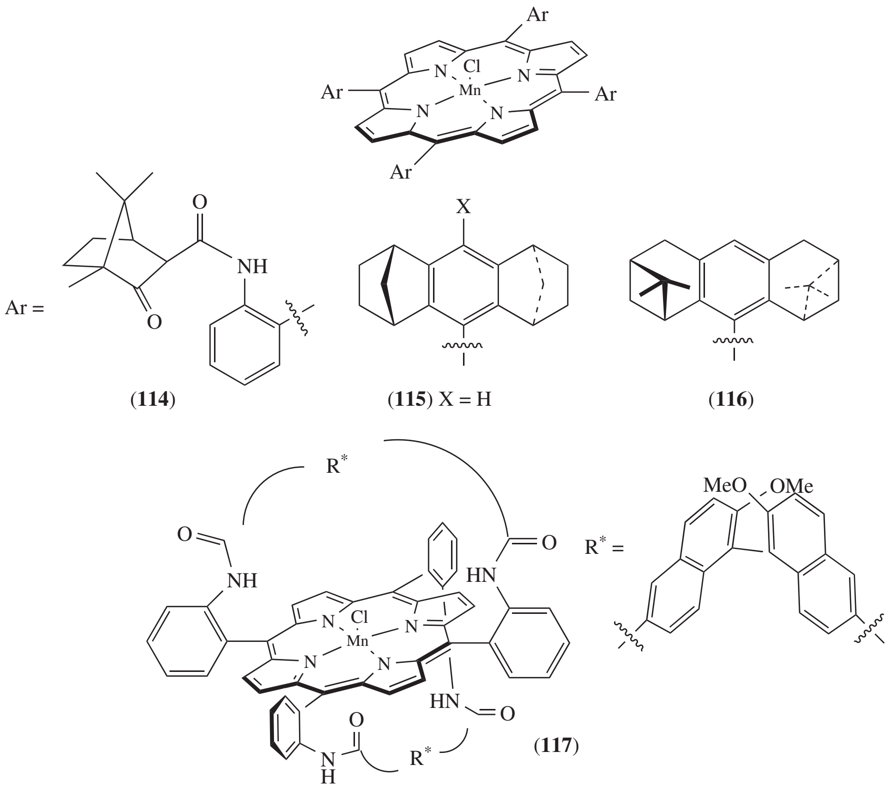


FIGURE 31

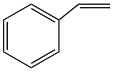
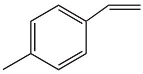
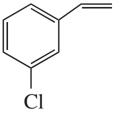
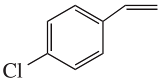
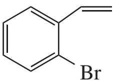
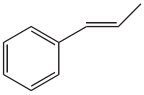
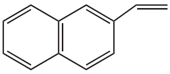
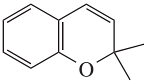
TABLE 10. Asymmetric epoxidation of styrene and its derivatives using different Mn(porphyrins) (Figure 31)

Entry	Catalyst	Substrate	Configuration	Yield (%)	ee (%)
1	**114**	Styrene	nd	51	20
2	**115**	*cis*-β-methylstyrene	(*S*)-(−)	90	76
3		styrene	(*S*)-(−)	90	52
4	**116**	Styrene	(*R*)-(+)	70	70
5		α-methylstyrene	(*R*)	91	65
6	**117**	Styrene	(*R*)-(+)	21	36

behavior of the chiral complexes toward oxygen- and carbon-atom transfer to hydrocarbons has been thoroughly investigated. Yet, little is known about the catalytic properties of a chiral metalloporphyrin for asymmetric hydrocarbon-functionalization reactions by nitrogen-atom-transfer processes.

Che and coworkers have reported on chiral Mn−porphyrin complex **92** which catalyzes the aziridination reaction of aromatic alkenes with iminoiodane PhI=NTs in up to 57%

TABLE 11. Asymmetric aziridination of aromatic alkenes by **92** (equation 23)

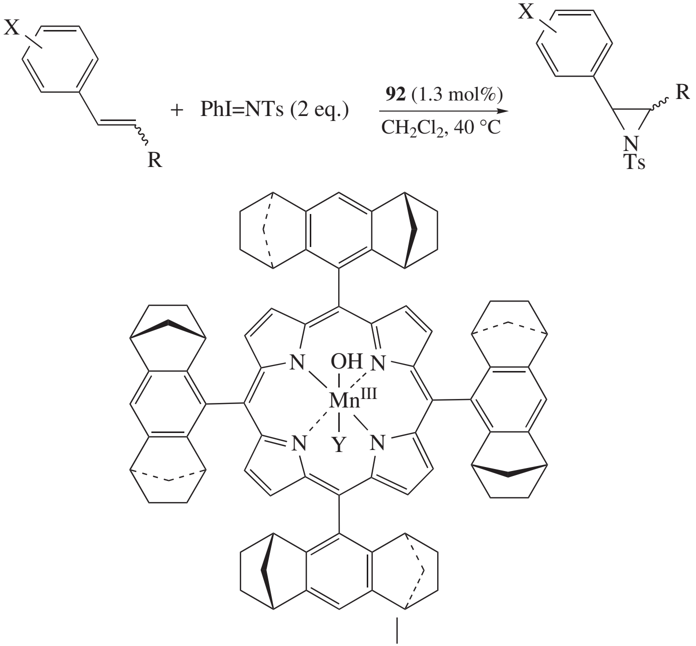
Entry	Substrate	Yield (%)[a]	ee (%)
1		78	47
2		76	44
3		91	40
4		93	50
5		75	57
6		81	11
7		94	56
8		73	5

[a] Yield of isolated product based on the amount of the substrate consumed.

ee, 94% yield and 1160 turnovers for styrene (equation 23, Table 11)[150b]. This is the first manganese porphyrin complex known to catalyze asymmetric nitrogen transfer to hydrocarbons. In the preliminary work by the same authors, the reactions were conducted using $\geq$20-fold excess of substrate, which hampered the determination of substrate conversion (equation 10)[150a].

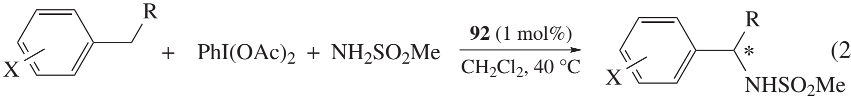
The same authors have applied complex **92** to the amidation reaction of saturated C−H bonds with $PhI(OAc)_2$ and NH_2SO_2Me to produce the *N*-substituted methanesulfonamides in up to 56% ee and 92% yield (equation 24, Table 12).

Complex **92** was also used in a diastereoselective amidation of steroid **118** (equation 25).



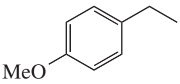
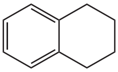
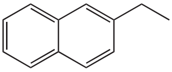
(23)

(**92**) Y = MeOH

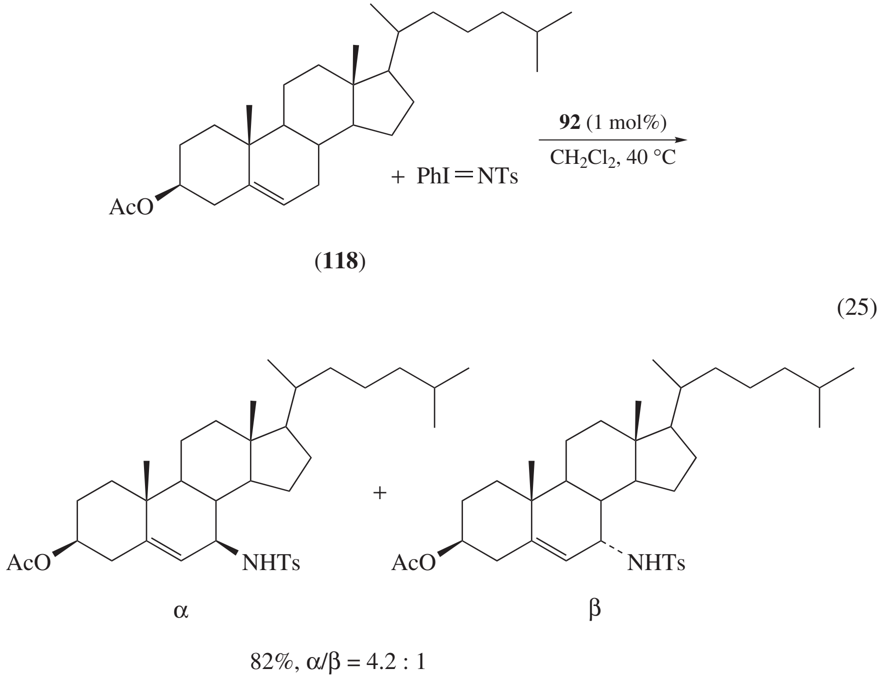


(24)

TABLE 12. Asymmetric amidation of benzylic hydrocarbons by **92** (equation 24)

Entry	Substrate	Yield (%)[a]	ee (%)
1		78	47
2		76	44
3		91	40

[a] Yield of isolated product based on the amount of the substrate consumed.



(**118**)

(25)

α

β

82%, α/β = 4.2 : 1

Despite a wide proposal of metal-imido species as the active intermediate in metal-complex catalyzed nitrogen-atom transfer reactions with iminoiodanes, isolation or direct observation of such intermediates remains a challenging task in most cases. No imidomanganese porphyrins have been detected in the reactions of iminoiodanes with complex **92**. Some useful insight into the mechanism of asymmetric nitrogen-atom transfer reactions were obtained for Ru(porphyrin) catalyst[150b].

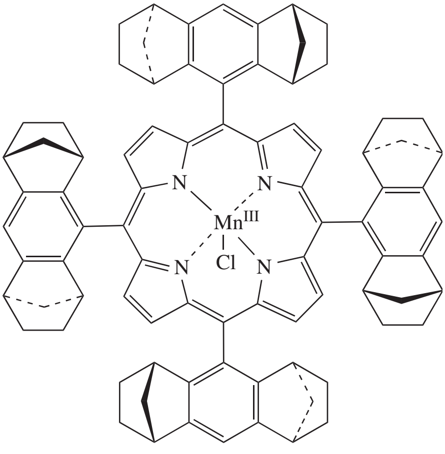
D. Enantioselective Oxidation of Sulfides

Examples of asymmetric oxidation of sulfides by Mn(porphyrin) catalysts are scarce and no significant ee values have been achieved so far[180]. Halterman and coworkers oxidized methyl *o*-bromophenyl sulfoxide with 68% ee using manganese^{III} tetraphenylporphyrin complex **119** (Figure 32)[217].

IV. OTHER MANGANESE COMPLEXES AND THEIR REACTIONS

A. Manganese^{III}–Corrole Complexes

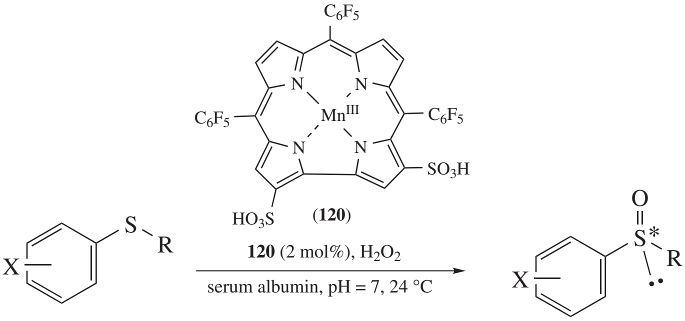
Manganese–corrole complexes have received much attention in the exploration of their aptitude as oxidizing catalysts[218]. A representative case when these complexes are used in asymmetric sulfide oxidation reactions was reported by Gross and coworkers[219]. Thus, manganese corrole **120** was found to spontaneously form tightly bound noncovalent conjugates with human serum albumin (HSA). This finding led to a consequent asymmetric



(**119**)

FIGURE 32

catalysis in a biomimetic fashion, implementing the metal complex in the catalytic oxidation and the protein for a chiral environment. The oxidation was performed with hydrogen peroxide and only 2 mol% of **120**-albumin conjugates (equation 26).



(26)

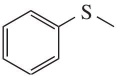
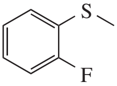
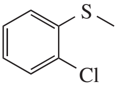
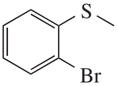
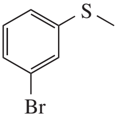
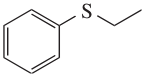
As Table 13 indicates, enantiomeric excess of up to 68% along with yields as high as 98% were reached upon oxidation of different benzylic sulfoxides with four kinds of conjugates, based on different albumin sources.

It was shown that the albumin source has a highly profound effect on the enantiomeric outcome, whereas the catalysis itself is controlled by the metalocorrole species. Interestingly, Mn(corrole) is far superior to Fe(corrole) species in terms of enantioselectivity, chemical yield and stability of the catalyst.

B. Manganese-substituted α-Carbonic Anhydrase

Combination of proteins and metals might create useful catalysts which, unlike their organic analogues, do not require complex synthesis and optimization. Proteins create

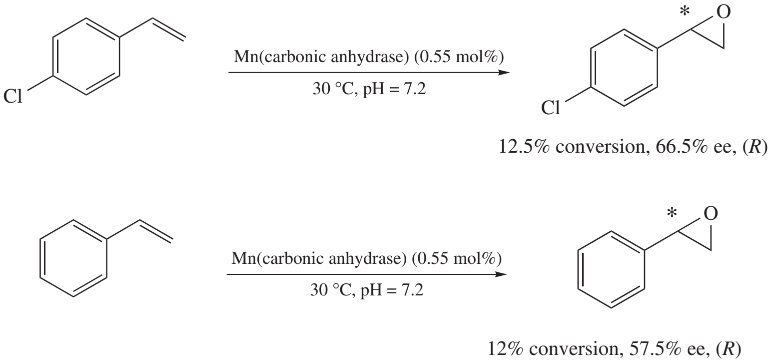
TABLE 13. Asymmetric oxidation of sulfides by **120** and different albumin sources (equation 26)

Entry	Substrate	Albumin source[a]	Yield (%)	ee (%)	Configuration
1		RSA	90	55	*S*
2		BSA	76	68	*S*
3		PSA	98	65	*S*
4		SSA	40	61	*S*
5		SSA	30	60	*S*
6		RSA	28	61	*S*
7		RSA	90	49	*S*

[a] BSA = bovine serum albumin, PSA = pig serum albumin, RSA = rabbit serum albumin, SSA = ship serum albumin.)

complex chiral surfaces that can orient unfunctionalized substrates and impart high stereoselectivity, including enantioselectivity, in the asymmetric nonphysiological reactions[220]. One of the attempts to implement the concept of metalloprotein involved in the organic reaction is based on the carbonic anhydrase and manganese conjugate. Carbonic anhydrases, also known as carbonate dehydratases, are zinc metalloproteins that catalyze the reversible hydration of carbon dioxide to bicarbonate. The best studied carbonic anhydrases are the bovine and human α-carbonic anhydrases, which are able to bind larger substrates than carbon dioxide[221]. Quite recently, the replacement of zinc active-site from carbonic anhydrase with manganese^{II} by dialysis was carried out in an attempt to form a metalloprotein catalyst for asymmetric epoxidation reaction of olefins with hydrogen peroxide[222]. As shown in Scheme 22, *p*-chlorostyrene and styrene were epoxidized in 66.5% and 57.5% ee respectively with only 12.5% and 12% conversion.

Several factors responsible for low conversion values were proposed. Thus, the ESI-MS spectrum of Mn−carbonic anhydrase complex shows no clear protein peak after 16 hours of reaction. Presumably, radical intermediates generated during catalysis cause the degradation of the protein[223].



SCHEME 22

V. SUMMARY AND FUTURE PERSPECTIVES

The use of organometallic reagents in organic synthesis has become routine over the last few decades, both on the laboratory scale and as an important industrial tool. When economic and environmental aspects are of major significance, inexpensive and toxicologically benign organomanganese compounds, competent in catalyzing asymmetric transformations, are especially appealing. Studies on salen-catalyzed epoxidation began in the search for a stereoselective oxo transfer reaction comparable to the biological process catalyzed by cytochrome P-450. Twenty five years after the first report by Kochi on the achiral epoxidation of olefins catalyzed by manganese–salen species, great achievements were made in the field of asymmetric epoxidations. In fact, Jacobsen's and Katsuki's Mn(salen) complexes and their performance in the epoxidation reactions constitute the most prominent and successful use of organomanganese compounds in asymmetric processes. Asymmetric nitrogen-atom transfer, C−O bond formation and sulfoxidation are also in the list of Mn(salen) specialties. It is important to underscore that the mechanistic aspects of the above processes have not yet received an unambiguous and solid picture, not to mention a confined class of substrates prone to these processes. Unfortunately, non-salen organomanganese reagents which emerged recently have not surpassed the yields and enantiomeric excesses attained in the Mn(salen)-catalyzed transformations. Therefore, the arsenal of the existing catalysts, processes and substrates demands a substantial expansion. We hope that this chapter provides a fair platform for further explorations in the field.

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