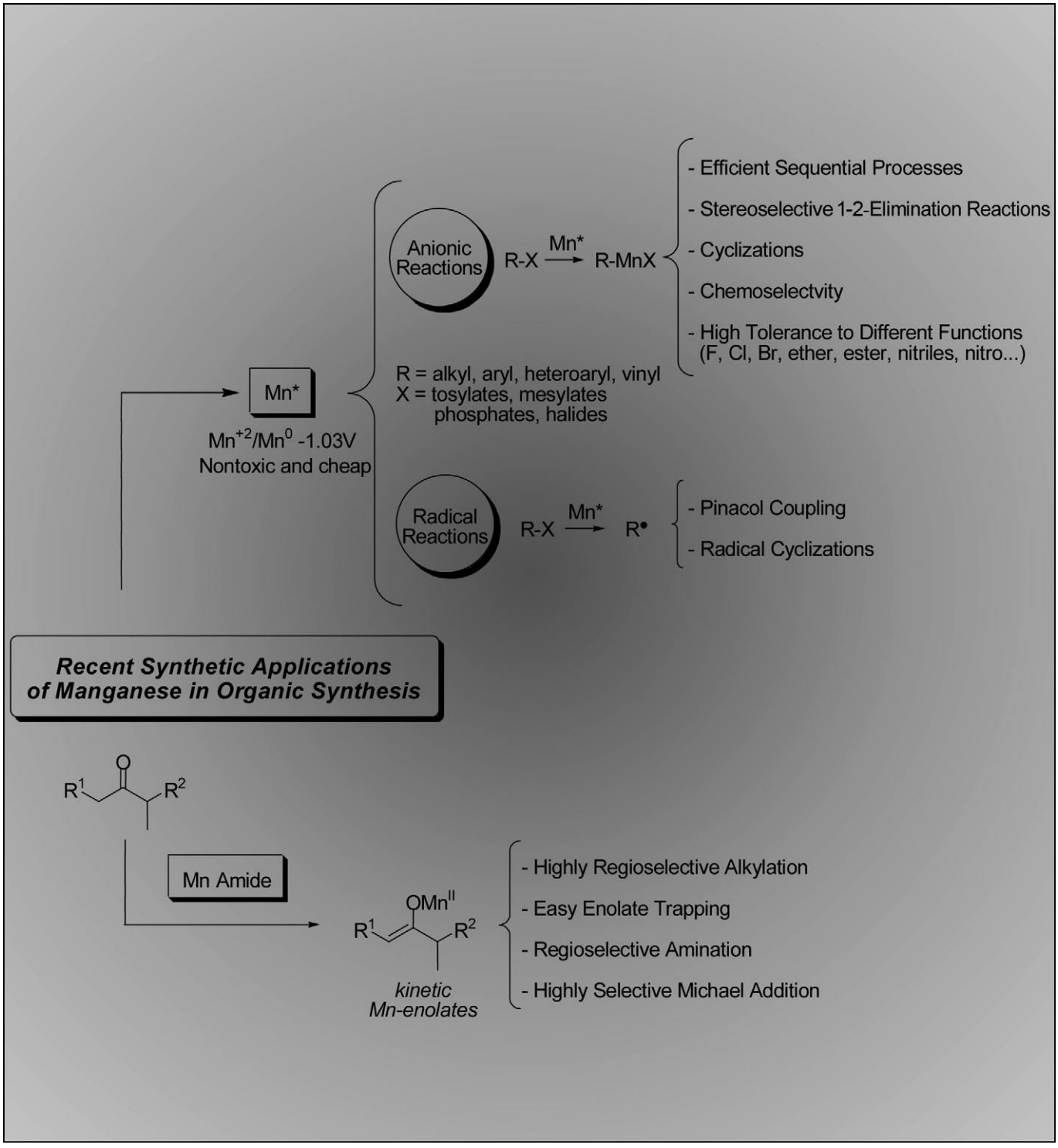
CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800796

Recent Synthetic Applications of Manganese in Organic Synthesis

José M. Concellón,* Humberto Rodríguez-Solla, and Vicente del Amo[a]



Abstract: While the organometallic compounds derived from many metals have found a broad application in organic synthesis, the use of organomanganese compounds has only recently been developed due to the passivity exhibited by commercial Mn in the direct metalation of organic compounds. In this Concept article, we highlight the potential of manganese and its organometallic compounds in organic synthesis by illustration of the studies previously reported by others and our laboratory in this field. Based on the transformations reported herein, organomanganese compounds could become important tools in the future of the organic synthesis, due to their high selectivity.

Keywords: amides · manganese · metalation · organomanganese compounds · transmetalation

Introduction

Organometallic compounds have played a decisive role in the enormous development that organic synthesis has experienced in the last century. To illustrate this affirmation we should remember the assertion of Professor Ei-Ichi Negishi in the preface of his classical book *Organometallics in Organic Synthesis*: "Today it is not only unwise but rather difficult to accomplish an efficient and selective multistep synthesis without using organometallics".[1]

However, the development of synthetic applications of organometallic reagents derived from the different metals has not been in step. While the first transformations carried out with organometallic derivatives were published at the beginning of the 20th century, involving the use of organomagnesium compounds (Grignard reagents) in organic synthesis, the use of the organomanganese compounds began in 1976.

In addition, the development of the chemistry of organomanganese reagents has been erratic, depending on the methods used for their preparation. Three methods have been used to prepare these reagents: 1) transmetalation reactions between organolithium or Grignard reagents and a salt of manganese; 2) deprotonation using a manganese amide, and 3) reaction of manganese with organic halides. Normant and Cahiez reported, in 1976, the first preparation of organomanganese reagents by treatment of organolithium or Grignard reagents with a manganese salt (generally $MnCl_2$).[2] Since then, the chemistry of organomanganese compounds prepared by a transmetalation reaction from organolithium or organomagnesium reagents has been the most reported and reviewed by Cahiez in 1995,[3] and Oshima in 1999.[4] Conversely, the synthetic applications from organomanganese compounds obtained by the second (deprotonation) and third methods (metalation of organic halides) were published later, in 1993 and 1996, respectively, and they have not been reviewed to date.

Taking into account these precedents, this Concept article covers the advances in the chemistry of organomanganese compounds obtained by using the corresponding manganese amides or manganese metal. Synthetic applications of the organomanganese reagents obtained from RLi or RMgX (from transmetalation) are not summarized herein, since the most important contributions on this area were previously reviewed. The papers published after these reviews reported generalizations of the transformations previously described.

The bibliographic information in this account has been organized in three sections. In the first, the general features in the synthesis and synthetic application of organomanganese reagents are shown. In the second part, the generation and synthetic applications of manganese enolates, prepared by treatment of carbonyl compounds with manganese amides, is described. The third section reports the most important novel work on manganese chemistry published in the last few years; initially the procedures reported for the preparation of active manganese[5] are described, followed by the synthetic applications of the organomanganese compounds obtained by direct metalation. This section finishes with some examples of sequential reactions promoted by manganese.

General Features in the Synthesis and Synthetic Applications of Organomanganese Reagents

An ideal organometallic reagent should carry out highly selective transformations, and should be obtained from a nontoxic and cheap metal with a reduction potential adequate to produce the metalation of C–halogen bonds and to reduce another organic function. Manganese and its organometallic derivatives seem to meet these requirements. The reported reactions with organomanganese reagents take place with good selectivity,[6] Mn^0 is a cheap[7] and nontoxic metal[8] with a reduction potential of the Mn^{+2}/Mn^0 system of -1.03 V[9] (between the reduction potential of Zn^{+2}/Zn^0 and Mg^{+2}/Mg^0), which is adequate to reduce an important number of organic functions. However, in contrast to other metals such as Li, Mg, Sm, or Cu the applications of manganese in organic synthesis have been hardly developed. This apparent contradiction can be easily justified by taking into account the inherent passivity exhibited by commercial Mn powder, which is coated by an outer shell of oxide.[10] This fact explains that the first preparations of organomanganese reagents were performed by transmetalation of RLi or RMgX and manganese salts, due to the inability of the man-

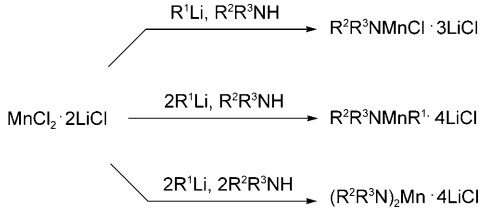
[a] Prof. J. M. Concellón, Dr. H. Rodríguez-Solla, Dr. V. del Amo
Department of Organic and Inorganic Chemistry
University of Oviedo, Julian Clavería, 7
33071 Oviedo (Spain)
Fax: (+34) 985-10-3448
E-mail: jmcg@uniovi.es

ganese metal to react directly with organic compounds. Direct metalation could only be used, when the preparation of more highly reactive manganese was reported. Initially, to overcome the lack of reactivity of manganese metal, different activation procedures were described. This active manganese allowed some transformations to be carried out that could not be performed by using commercial manganese.

Formation and Synthetic Applications of Manganese Enolates

Manganese enolates can be prepared by three different methods: 1) deprotonation employing manganese amides, 2) transmetalation from other metallic enolates, and 3) by using trialkylmanganates.

Most of the examples reported in the literature for the generation of manganese enolates require the use of different manganese amides. These bases can be prepared in THF, by reaction of an organolithium compound with a mixture of the ate complex $MnCl_2 \cdot 2\,LiCl$ and a secondary amine at room temperature. In a seminal paper, Cahiez et al. established the conditions to prepare chloromanganese amides, organomanganese amides, or manganese diamides depending on the ratio of the organolithium compounds and/or amine (Scheme 1). It is worth noting that the best



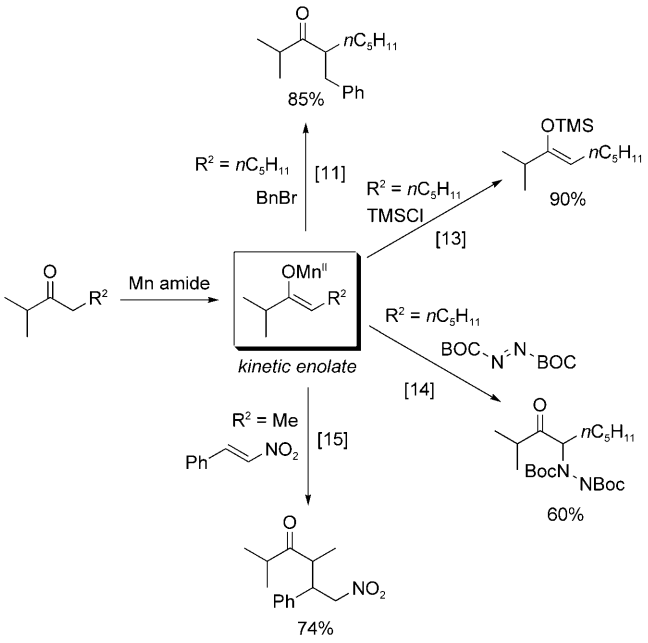
Scheme 1. Preparation of the three different type of Mn-amides.[11]

candidates for enolization processes are the manganese amides derived from aromatic amines, and in contrast to their lithium analogues these amides can be stored in THF, at room temperature, and under an inert atmosphere for several months.[11]

Later on, the same authors described the generation of manganese enolates, in high yields, by deprotonation of ketones with PhMnCl in the presence of a catalytic amount (between 7–20%) of *N*-methylaniline. In this case, a THF/sulfolane mixture is required as a cosolvent.[12]

The reactivity of manganese enolates generated from different manganese amides have been studied against electrophiles such as alkyl halides,[11] trimethylsilyl chloride,[13] azodicarboxylates,[14] and nitroolefins[15] (Scheme 2).

Ketone-based manganese enolates readily react with carbon electrophiles, leading to differently α-substituted ketones. The α-alkylation of ketones is a challenging and important reaction in organic synthesis, and to this end, differ-



Scheme 2. Alkylation and trapping of a Mn enolate.

ent metal enolates have been attempted. The main problems found during the α-alkylation of ketones are, on the one hand, the formation of polyalkylated products and, on the other hand, the poor regioselectivity observed when unsymmetrical ketones are employed. In this sense, a comparative study of the benzylation of 2-methylcylohexanone was carried out by using lithium and manganese enolates. The corresponding monoalkylated ketone was obtained with better regioselectivity and yield with the manganese enolate.[11] Thus, the reaction of manganese enolates with alkyl halides affords regioselectively monoalkylated products in high yields and at room temperature (Scheme 2). Different alkylating reagents, such as MeI, BnBr, BuI, allyl bromide, and bromoacetates, have been employed and no significant differences were observed. The best results were obtained when a mixture of THF and dimethyl sulfoxide (DMSO) or *N*-methylpyrrolidone (NMP) were used as solvent.[11] In contrast, the reaction occurs slowly and only gives moderate yields in neat THF.

Taking into account that silyl enol ethers are very versatile intermediates in organic chemistry, (*Z*)-silyl enol ethers were prepared from ketones under mild conditions by trapping the corresponding Mn enolate with TMSCl. This process took place in high yields with good stereoselectivities (*Z*/*E* 93:7→100:0) and with a good control of the regioselectivity during the enolization step in the case of unsymmetrical ketones.

The synthesis of α-hydrazino ketones (as a precursor of α-aminoketones)[16] through the electrophilic amination of Mn enolates with azodicarboxylates have also been performed in excellent yields and with very high or total stereo- and regioselectivity.[14] The employment of enantiopure *N*-sulfinyl manganese enamines afforded, after hydrolysis, α-hydrazino

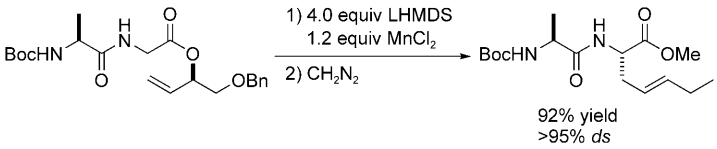
ketones with an enantiomeric excess (*ee*) ranging between 40–68%.

Since the conjugate addition of different nucleophiles to Michael acceptors is one of the most frequently used C–C bond-forming reactions, Mn enolates have also been employed in the Michael addition to nitroolefins. This study revealed that the 1,4-adducts were obtained in high yields and stereoselectivities. In the case of enolates derived from unsymmetrical ketones, this process also took place to obtain, in a regioselective manner, the kinetic adduct as the sole product.

Manganese amides mainly afford the kinetic manganese enolate (Scheme 2). Nevertheless, thermodynamic Mn enolates can also be readily achieved from the corresponding thermodynamic lithium enolate by an Li–Mn exchange reaction (using $MnCl_2$ or $MnBr_2$).[17]

Although kinetic Mn enolates can be obtained by deprotonation with Mn amides, Li–Mn exchange would be an easier way to access to the kinetic enolates, since lithium diisopropylamide (LDA) is typically utilized to this end. LDA is more usual and cheaper than Mn amides.

The Li–Mn transmetalation reaction has been applied by Kazmaier and Maier to carry out a chelate Claisen rearrangement directed toward the modification of peptides (Scheme 3).[18] These authors, after testing several metallic

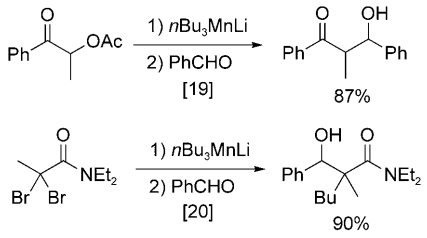


Scheme 3. Li–Mn transmetalation reaction in Claisen rearrangement.[18]

enolates, concluded that by far the best results were obtained with manganese as the enolate counterpart.

Finally, a third way for the generation of manganese enolates is employing organomanganate compounds as reducing agents. In this sense, it was found that organomanganates react with ketones, esters, and amides bearing a leaving group such acetoxy, silyloxy, or halogen[4] at the α-position, to generate enolates of the corresponding carbonyl compound. This application of the organomanganate compounds as a reductant reagent allows the regioselective generation of the corresponding enolates. Thus, enolates derived from unsymmetrical and branched ketones are available with complete regioselectivity (Scheme 4).[19]

A similar process has been described by Oshima.[20] In this case, the result of the reaction between *tert*-butyl dibromoacetate or *N*,*N*-diethyldibromoacetamide with the trialkylmanganate provided the corresponding monoalkylated manganese enolate.



Scheme 4. Mn enolate from organomanganate compounds.

Preparation and Synthetic Applications of Active Manganese

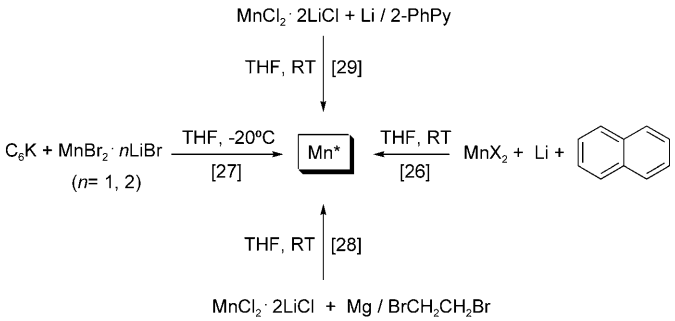
As proof of the low reactivity of the commercial Mn, the first, and sole paper reporting the use of commercial Mn in a direct metalation reaction was published on 1989 by Cahiez.[21] In this pioneering paper, Barbier-type additions of allyl bromide to various ketones were performed by using ethyl acetate as the solvent (no reaction took place in THF) at 60 °C and in high yields. Commercial Mn showed its passivity towards aldehydes, methylketones, or methallyl bromide and the corresponding alcohols were obtained only in very low yields. The yields of these reactions were increased by performing the same reactions in the presence of 0.1 equiv of $ZnCl_2$ at 60 °C. In addition, the use of $ZnCl_2$ also permitted the reaction to be carried out using allyl chlorides or bromoacetates as starting materials, and THF as solvent. Finally, high chemoselectivity was shown in the Barbier reactions of manganese reagents with ketoesters, ketoacetals, or ω-chloroketones.

Other additives to enhance the reactivity of commercial manganese have been published. The Barbier allylation of carbonyl compounds and Reformatsky-type reactions were performed with commercial powdered manganese in the presence of catalytic amounts of Me_3SiCl and $PbCl_2$.[10] We developed the first reported β-elimination reaction promoted by commercial manganese in the presence of stoichiometric amounts of Me_3SiCl as the sole additive to synthesize (*E*)-α,β-unsaturated esters with complete stereoselectivity from 2-bromo-3-hydroxyesters.[22]

Iodine has also been used for Mn activation in the Barbier reaction of allyl bromide with aldehydes and ketones in THF at reflux.[23] The manganese obtained from the reduction of $MnCl_2$ with $LiAlH_4$ could be used to metalate allyl bromides. The addition of the organomanganese reagents so obtained to aldehydes afforded the expected alcohols in good yields.[24] Sonication, which has been extensively used to accelerate heterogeneous reactions, was ineffective to activate manganese. When Barbier reactions were performed with Mn under sonication, Wurtz coupling products were exclusively obtained instead of the corresponding Barbier products.[25]

Thus, it can be concluded that only a partial and insufficient increase of the reactivity of the commercial Mn^0 was achieved by means of additives, since by using commercial Mn/additive systems only the metalation of the most reac-

tive C–halogen bonds (allyl or carbonyl α-halogenated compounds) could be achieved. In this sense one of the most important contributions for the development of the synthetic applications of manganese was the development of four different procedures to obtain active manganese, allowing the metalation of a broad range of C–halogen bonds and other organic functions (Scheme 5). Accordingly, Rieke reported



Scheme 5. Synthetic procedures to obtain active manganese.

the preparation of active manganese on 1996, utilizing the reaction of anhydrous $MnCl_2$ with lithium in a solution of a catalytic amount of naphthalene in THF at room temperature.[26] $MnBr_2$ and MnI_2 can be also used to prepare Rieke Manganese (Mn*), the Mn* obtained from MnI_2 being less reactive.

During the same year, Fürstner reported another elegant preparation of active manganese, called Mn-graphite, by reduction of the soluble ate complex $MnBr_2{\cdot}n\,LiBr$ ($n=1,2$) with the potassium graphite intercalation compound C_8K in THF.[27]

Later on, in 1998, Oshima published another alternative method to prepare active manganese by reduction of $MnCl_2{\cdot}2\,LiCl$ with magnesium turnings (previously activated with 1,2-dibromoethane) for 24 h at room temperature.[28]

Finally, Cahiez reported in 1999 an improvement of the method reported by Rieke. Thus, $MnCl_2{\cdot}2\,LiCl$ was reduced with lithium, by using 2-phenylpyridine (instead of naphthalene) as the electron carrier. Two advantages were evident from this method: elimination of the excess of active Mn with 1,2-dibromoethane before the reaction with electrophiles is not necessary and the 2-phenylpyridine is more easily removed, in comparison to naphthalene, during an acidic workup.[29]

After the appearance in the literature of the aforementioned procedures for preparation of active manganese (Scheme 5), the number of contributions reporting new synthetic applications of this metal have increased. Now, we summarize the synthetic applications of organomanganese obtained by direct metalation. This information has been organized as follows: firstly, transformations involving anionic intermediates, arranged by the type of active manganese, are shown, followed by the radical transformations promoted by manganese. This section finishes reviewing the sequential reactions promoted by manganese.

In the seminal paper in which Rieke described for the first time the preparation of its active manganese (Mn*), a synthesis of ketones in good yields by reaction of primary, secondary, and tertiary alkyl bromides with Mn* and further addition of benzoyl chloride was reported. The synthesis of ketones demonstrated the usefulness of the Rieke manganese to metalate the former halides.[26]

Later on, the same authors generalized this synthesis of ketones using aryl bromides[30] and bromothiophenes.[31] The formation of the corresponding organomanganese reagents and the subsequent cross-coupling reactions with acid chlorides under mild reaction conditions afforded the corresponding ketones. The organomanganese obtained from bromothiophenes also underwent cross-coupling reactions with aryl iodides. In addition, it is worth noting that the selective monometalation of 3,4-dibromothiophene followed by its reaction with an electrophile, afforded a monosubstituted bromothiophene. A second treatment of this bromothiophene with Mn*, followed by the reaction with a different electrophile provided unsymmetrically 3,4-disubstituted thiophenes.

Aromatic amides were also prepared by reaction of aryl bromides with Mn* followed by treatment with phenyl isocyanates.[30] While the use of a transition-metal catalyst was necessary in both reactions of arylmanganeses with benzoyl chloride and thienylmanganese with aryl iodides; the reaction of arylmanganeses with phenyl isocyanates and thienylmanganese with benzoyl chloride did not require catalysis.

Benzylic manganese reagents were also accessed by treatment of functionalized benzyl halides (bromide or chloride) with Rieke manganese (prepared from $MnCl_2$ or MnI_2) at room temperature. The subsequent reactions proceeded in yields ranging from good to excellent with several electrophiles (acid chlorides, esters, aldehydes, ketones, benzyl halides or di-*tert*-butyl azodicarboxylate).[32]

Interestingly, the access to organomanganese reagents was extended to the metalation of organic functions other than organic halides, such as primary and benzyl tosylates, mesylates, or phosphates. These metalations took place readily at room temperature and the obtained manganese derivatives were allowed to react with different electrophiles, such as acid chlorides, aldehydes or ketones, affording the expected products in good to high yields.[33] Taking into account that tosylates, mesylates, or phosphates are readily prepared from alcohols, this new route to organomanganese reagents increases the synthetic applications of manganese and to prove the synthetic usefulness of this method; resorcinolic lipids have already been readily prepared.[33]

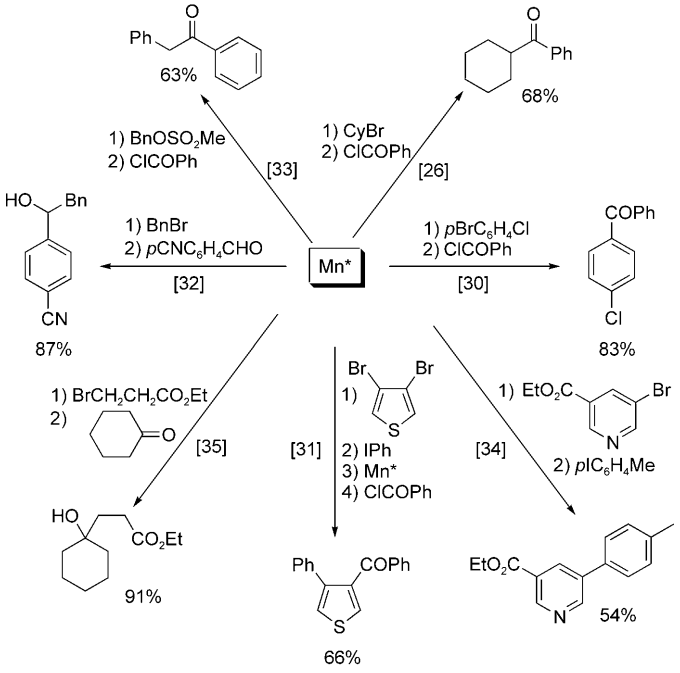
The synthesis of heteroaryl manganese reagents was also reported by the direct metalation of pyridine, thiophene, or furan derived bromides with Rieke manganese. Their reaction with benzoyl chloride, aryl iodides, or vinyl bromides gave the expected cross-coupling products in good yields under mild reaction conditions. It is worth noting that ester and cyano groups were tolerated by the active manganese, and in addition, some transformations could not be performed using other methods; for example, Friedel–Crafts acylations cannot be carried out on the pyridine ring.[34]

Hydroxy esters were readily prepared in good to high yields by the Reformatsky reaction of α-haloesters, α-halolactones, and alkyl halides with a remote ester group and subsequent reaction with aldehydes and ketones.[35] The formation of organomanganese reagents from alkyl ω-haloesters illustrates that the presence of the C–Mn bond is tolerated by an important number of organic functions, such as ester, ether, nitro, nitrile, F, Cl or Br, in contrast to other C–metal bonds.

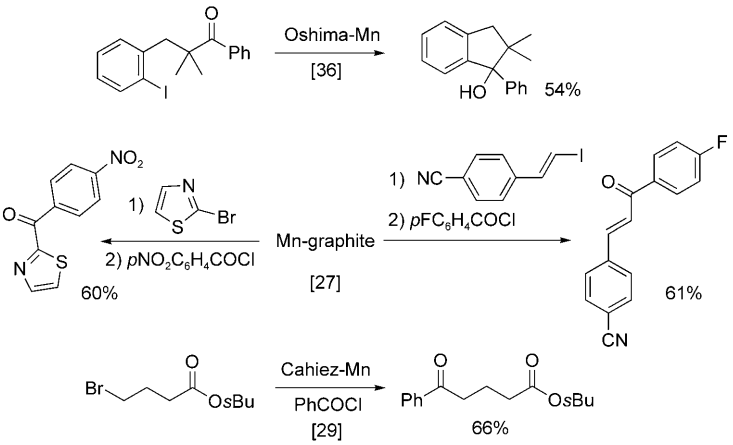
Representative examples of the anionic transformations promoted by Rieke manganese[26,30–35] have been included in Scheme 6.

The manganese obtained according to the other methods (Oshima, Fürstner, or Cahiez) have also been used to promote different transformations. Selected examples of them are shown in Scheme 7. The Oshima manganese[28] was used to promote the addition of allyl bromides, aryl halides, α-halo esters, lactones, ketones, or amides to various aldehydes, ketones, or aryl iodides or bromides affording the expected adducts. The reaction of a ketone bearing an iodoaryl moiety provided the corresponding dihydroindene derivative (Scheme 7). All these transformations were performed by treating the mixture of the organic halide and the electrophile with manganese (Barbier methodology), except the reactions with aryl halides, in which the arylmanganese reagent was previously prepared and later treated with the electrophile.[36]

Manganese-graphite[27] was employed for the efficient metalation of primary, secondary, allyl, aryl, alkenyl, and heteroaryl (pyridinyl, thiophenyl) halides. The functionalized organomanganese compounds obtained were efficiently trapped with aldehydes, anhydrides, acid chlorides, or aryl halides. A range of functional groups remained unaltered in the starting materials.[27]



Scheme 6. Synthetic applications of Rieke manganese.



Scheme 7. Synthetic applications of active manganese other than Rieke's.

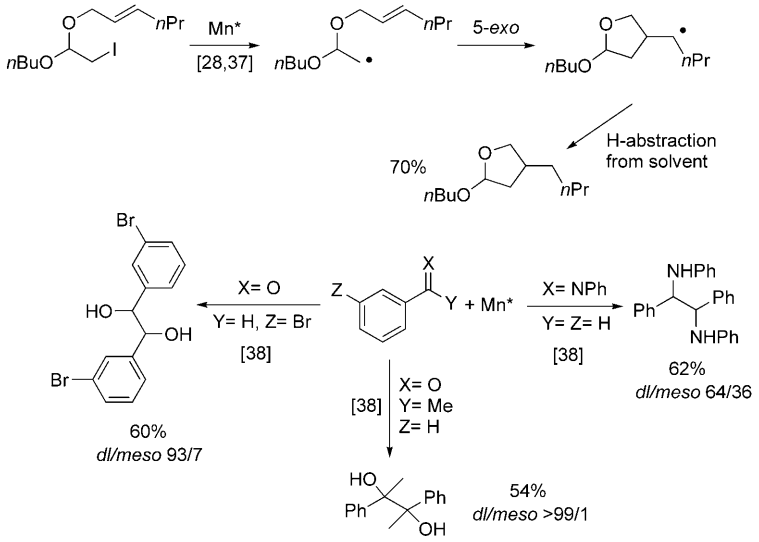
Interestingly, Cahiez manganese[29] demonstrated its chemoselectivity in the synthesis of functionalized organomanganese reagents, such as those derived from ω-bromo esters.

Anionic mechanisms have been proposed to explain the aforementioned Mn*-mediated transformations. Nevertheless, the Mn* can also promote other transformations that take place through radical intermediates. Selected examples of these transformations are shown in Scheme 8. Thus, Oshima reported the radical cyclization of 2-iodo or bromoethanal, allylic, propargylic, or allenylic acetals. A mechanism was proposed to justify the observed results.[28,37]

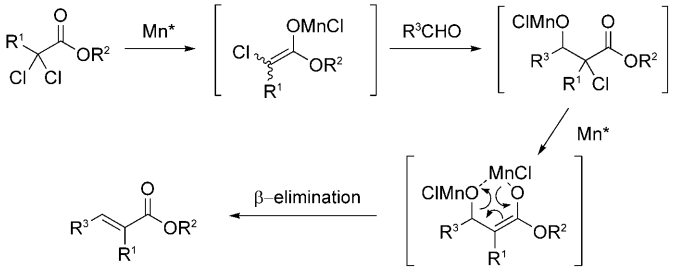
Rieke manganese (from MnI_2) could be also used as a single-electron donor in organic synthesis. Thus, reductive dimerization of aryl aldehydes, aryl ketones, and aldimines afforded the corresponding 1,2-diols and vicinal diamines at room temperature and in good yields. The diastereoselectivity was poor except for aryl ketones. The coupling reaction displayed tolerance to the presence of several functional groups on the aromatic ring, including the bromine, chlorine, cyano, and methoxy groups.[38]

Sequential reactions are those in which multiple carbon–carbon or carbon–heteroatom bonds are formed, in a sequence of events without the isolation of any intermediate. These synthetic methods held enormous potential in organic synthesis, due to their enormous simplicity and because considerably less time, effort, and material are required to obtain organic compounds when compared with more traditional multistep procedures. An important requirement is that the yield and selectivity for each individual reaction in a multistep sequence must be exceedingly high to avoid the generation of complex product mixtures. Consequently, only a select group of reagents (for example, SmI_2)[39] may be suitable for sequential processes.

Active Mn has also been successfully utilized to promote sequential reactions. In the first report, the synthesis of α,β-unsaturated esters with total *E* selectivity and in high yields is reported. This process, promoted by active manganese (Cahiez method),[29] took place from the reaction of dichloroesters with a variety of aldehydes through an aldol-type re-



Scheme 8. Radical reactions promoted by active manganese.



Scheme 9. Mechanistic proposal for the aldolic/elimination sequential reaction promoted by active manganese.

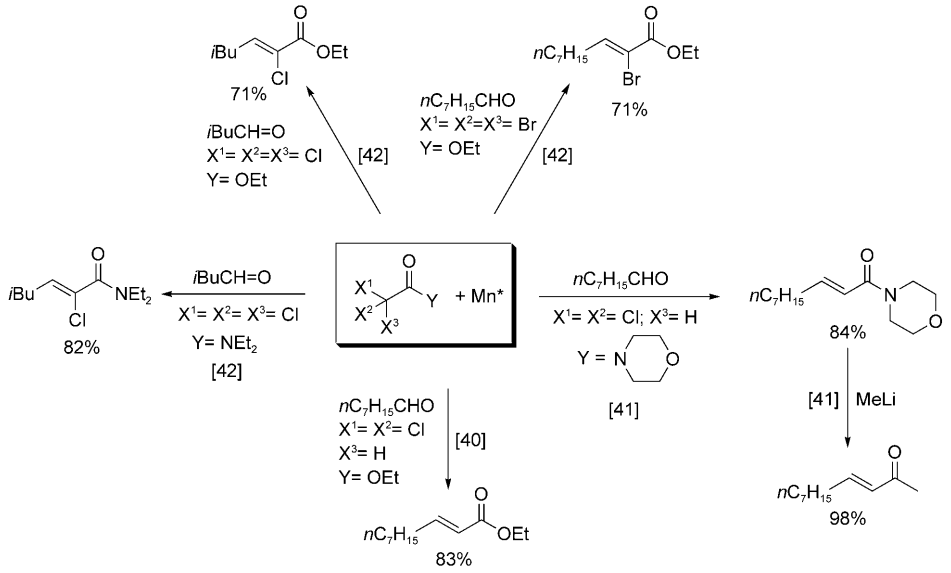
action in the first step, followed by a β-elimination reaction in the second. The total *E* selectivity was explained by a cyclic transition state that is formed by the coordination of manganese with two oxygen atoms (Scheme 9).

This sequential reaction was general and di- or trisubstituted C–C double bonds could be formed. A comparative study of these results with those previously obtained by using SmI_2 in the same sequential reaction, revealed that the best results were obtained when active manganese was used.[40] This sequential reaction was later generalized, and (*E*)-α,β-unsaturated amides were also prepared with complete selectivity from dichloroamides and a variety of aldehydes. In addition, the unsaturated amides obtained could be readily and efficiently transformed into ketones, aldehydes, or carboxylic acids without loss of the diastereoisomeric purity of the C–C double bond (Scheme 10).[41]

(*Z*)-α-Halo-α,β-unsaturated esters (fluoro, chloro, or bromo) and chloro amides were also available with complete *Z* selectivity through a similar sequential reaction from trihaloesters or amides and various aldehydes. The unsaturated amides or esters were readily transformed into ketones, carboxylic acids, or haloallylic alcohols.[42] Representative examples of these sequential reactions are included in Scheme 10. Thus, taking into account that the simplicity, speed, and the use of readily available and cheap starting materials are some of the features required in an ideal synthesis, these sequential methods constitute an advantageous alternative to obtain (*E*)- and (*Z*)-α-halo-α,β-unsaturated esters or amides, and is also a method of choice for preparation ketones, carboxylic acids or haloallylic alcohols.

Conclusion

In an effort to find highly efficient transformations, organic chemists have developed organometallic reagents derived from different metals. In particular, the development of the chemistry of the organomanganese reagents has been relatively scarce to date. This fact is surprising, taking into ac-



Scheme 10. Sequential reactions promoted by active manganese.

count that manganese is a nontoxic, cheap metal and with a reduction potential adequate to reduce many organic functions. However, due to the passivity of commercial manganese, the late publication of procedures to obtain active manganese has delayed the development of the synthetic applications of this metal in organic synthesis. After the publication of the various methods to prepare active manganese, the number the synthetic applications of this metal have increased.

The synthetic transformations presented in the previous sections clearly show the versatility and efficiency of manganese and its organomanganese derivatives in organic synthesis. The selectivities achieved with the employment of manganese are comparable to, or—in many cases—higher than those obtained with the more traditional metals. Thus the transformations promoted by manganese are highly selective, and it is possible to prepare organomanganese derivatives bearing different functional groups. Some reactions mediated by manganese take place with high or total regioselectivity; for example, the alkylation of manganese enolates. In the few reported transformations in which stereochemical aspects are involved, the reactions take place with high stereoselectivity; for example, in the β-elimination reactions or the synthesis of silyl enol ethers. The high selectivity of the organomanganese reagents, which have been reported recently, together with the previously known properties of manganese (nontoxicity, low price, and the adequate reduction potential) allow the prediction of an important increase of its employment in organic synthesis in the next few years. Special growth should be present in the use of manganese in the field of those transformations that are required to take place with high stereoselectivity. Thus, organomanganese compounds could become an important type of organometallics in the future of the organic synthesis.

Acknowledgement

We thank the Ministerio de Educación y Ciencia (CTQ2007-61132) for financial support. J.M.C. thanks his wife Carmen Fernández-Flórez for her time. H.R.S. thanks Ministerio de Educación y Ciencia for a Ramón y Cajal Contract (Fondo Social Europeo). Our thanks to Euan C. Goddard (University of Oxford) for his revision of the English.

[1] E. Negishi, *Organometallics in Organic Synthesis*, Wiley, New York, **1980**.
[2] "Organomanganous Reagents": J. F. Normant, G. Cahiez, in *Modern Synthetic Methods, Vol. 3* (Ed.: R. Scheffold), Springer, Berlin, **1983**, 173–216.
[3] G. Cahiez, *An. Quim.* **1995**, *91*, 561–578.
[4] K. Oshima, *J. Organomet. Chem.* **1999**, *575*, 1–20.
[5] To see a review regarding the synthesis and synthetic applications of various active metals: A. Guijarro, C. Gómez, M. Yus, *Trends Org. Chem.* **2000**, *3*, 65–91.
[6] The reactions promoted by manganese present different types of selectivities. Thus, most of the transformations were compatible with the presence of several functional groups.[21,22,27–30,32–38,40–42] Other reactions can be carried out with starting materials highly prone of suffering enolization.[22,40–42] The reported β-elimination reactions take place with complete or high diastereoselectivity.[22,40–42]]
[7] Aldrich catalogue (2007–2008): powder manganese (325 mesh): 250 g = 37 €.
[8] No special precaution is required due to the low toxicity of manganese and manganese salts obtained after the aqueous workup of organomanganese reactions; see reference [3].
[9] Electrochemical redox potential: Mn^{+2}/Mn^{0} −1.03 V; *Handbook of Chemistry and Physics*, 62nd ed., CRC, Boca Raton, FL, **1982**.
[10] K. Takai, T. Ueda, T. Hayashi, T. Moriwake, *Tetrahedron Lett.* **1996**, *37*, 7049–7052.
[11] a) G. Cahiez, B. Figadère, P. Cléry, *Tetrahedron Lett.* **1994**, *35*, 3065–3068; b) G. Cahiez, K. Chau, B. Blanchot, *Org. Synth.* **1999**, *736*, 239–244.
[12] G. Cahiez, M. Kanaan, P. Cléry, *Synlett* **1995**, 191–192.
[13] G. Cahiez, B. Figadère, P. Cléry, *Tetrahedron Lett.* **1994**, *35*, 6295–6298.
[14] G. Dessole, L. Bernardi, B. F. Bonini, E. Capitò, M. Fochi, R. P. Herrera, A. Ricci, G. Cahiez, *J. Org. Chem.* **2004**, *69*, 8525–8528.
[15] G. Micheletti, S- Pollicino, A- Ricci, G. Berionni, G. Cahiez, *Synlett* **2007**, 2829–2832.
[16] J. M. Concellón, H. Rodríguez-Solla, *Curr. Org. Chem.* **2008**, *12*, 524–543.
[17] a) M. T. Reetz, H. Haning, *Tetrahedron Lett.* **1993**, *34*, 7395–7398; b) G. Cahiez, K. Chau, P. Cléry, *Tetrahedron Lett.* **1994**, *35*, 3069–3072.
[18] S. Maier, U. Kazmaier, *Eur. J. Org. Chem.* **2000**, 1241–1251.
[19] M. Hojo, H. Harada, H. Ito, A. Hosomi, *J. Am. Chem. Soc.* **1997**, *119*, 5459–5460.
[20] R. Inoue, H. Shinokubo, K. Oshima, *J. Org. Chem.* **1998**, *63*, 910–911.
[21] G. Cahiez, P.-Y. Chavant, *Tetrahedron Lett.* **1989**, *30*, 7373–7376.
[22] J. M. Concellón, H. Rodríguez-Solla, V. del Amo, *Synlett* **2006**, 315–317.
[23] T. Hiyama, M. Sawahata, M. Obayashi, *Chem. Lett.* **1983**, 1237–1238.
[24] T. Hiyama, M. Obayashi, A. Nakamura, *Organometallics* **1982**, *1*, 1249–1251.
[25] B. Pugin, A. T. Turner, *Adv. Sonochem.* **1990**, *1*, 81–118.
[26] S.-H. Kim, M. V. Hanson, R. D. Rieke, *Tetrahedron Lett.* **1996**, *37*, 2197–2200.
[27] A. Fürstner, H. Brunner, *Tetrahedron Lett.* **1996**, *37*, 7009–7012.
[28] J. Tang, H. Shinokubo, K. Oshima, *Synlett* **1998**, 1075–1076.
[29] G. Cahiez, A. Martin, T. Delacroix, *Tetrahedron Lett.* **1999**, *40*, 6407–6410.
[30] S.-H. Kim, R. D. Rieke, *Synth. Commun.* **1998**, *28*, 1065–1072.
[31] a) S.-H. Kim, R. D. Rieke, *Tetrahedron Lett.* **1997**, *38*, 993–996; b) S.-H. Kim, X. Wu, R. D. Rieke, *J. Org. Chem.* **1997**, *62*, 6921–6927.
[32] S.-H. Kim, R. D. Rieke, *J. Org. Chem.* **1998**, *63*, 6766–6767.
[33] a) S.-H. Kim, R. D. Rieke, *Tetrahedron Lett.* **1999**, *40*, 4931–4934; b) S.-H. Kim, R. D. Rieke, *J. Org. Chem.* **2000**, *65*, 2322–2330.
[34] R. D. Rieke, Y. Suh, S.-H. Kim, *Tetrahedron Lett.* **2005**, *46*, 5961–5969.
[35] Y. Suh, R. D. Rieke, *Tetrahedron Lett.* **2004**, *45*, 1807–1809.
[36] H. Kakiya, S. Nishimae, H. Shinokubo, K. Oshima, *Tetrahedron* **2001**, *57*, 8807–8815.
[37] J. Tang, H. Shinokubo, K. Oshima, *Tetrahedron* **1999**, *55*, 1893–1904.
[38] R. D. Rieke, S.-H. Kim, *J. Org. Chem.* **1998**, *63*, 5235–5239.
[39] For reviews of SmI_2-promoted sequential reactions, see: a) G. A. Molander, C. R. Harris, *Tetrahedron* **1998**, *54*, 3321–3354; b) G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307–338.
[40] J. M. Concellón, H. Rodríguez-Solla, P. Díaz, R. Llavona *J. Org. Chem.* **2007**, *72*, 4396–4400.
[41] J. M. Concellón, H. Rodríguez-Solla, P. Díaz, *J. Org. Chem.* **2007**, *72*, 7974–7979.
[42] J. M. Concellón, H. Rodríguez-Solla, P. Díaz, *Org. Biomol. Chem.* **2008**, *6*, 451–453.

Published online: August 27, 2008

