

# Manganese(II): the black sheep of the organometallic family

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The organometallic chemistry of manganese in the +2 oxidation state is distinct from the organometallic chemistry of a 'typical' transition metal due to a significant ionic contribution to the manganese(II)–carbon bonds. The reduced influence of covalency and the 18-electron rule result in organomanganese(II) cyclopentadienyl, alkyl and aryl complexes possessing reactivity and structural diversity that is unique in organotransition metal chemistry. Recently, this unusual reactivity has resulted in a range of novel applications in selective organometallic and organic synthesis, and polymerization catalysis. This *tutorial review* summarizes key milestones in the development of manganese(II) organometallics and discusses how some of their current synthetic applications have evolved from many fascinating fundamental studies in the area.

## 1 The ionic nature of manganese(II)–carbon bonds

The first organometallic complexes of manganese(II), PhMnI and Ph<sub>2</sub>Mn, were reported by Henry Gilman in 1937, although surprisingly they were neither isolated nor characterized in any way.<sup>1</sup> The first well-defined organometallic derivative of manganese(II) was manganocene, Cp<sub>2</sub>Mn (Cp = C<sub>5</sub>H<sub>5</sub>) (I),<sup>2</sup> which was reported by Wilkinson in 1954 in the era when 'non-classical' organometallic chemistry was undergoing its genesis following the discovery and subsequent structural elucidation of ferrocene, Cp<sub>2</sub>Fe.<sup>3</sup> From the outset, manganocene was identified as being a very unusual compound due to the contrasts between its chemical and physical properties and those found generally in the family of 3d metallocenes Cp<sub>2</sub>M where M = V, Cr, Fe, Co and Ni. For example, instead of the well-known 'sandwich' metallocene structure, under ambient conditions manganocene adopts a polymeric zigzag crystal structure (Fig. 1)<sup>4</sup> more reminiscent of metal cyclopentadie-

nyls Cp<sub>n</sub>M where M = alkali metal when  $n = 1$ , M = Ca, Sr, Ba, Pb when  $n = 2$  and M = lanthanide when  $n = 3$ .<sup>5</sup>

The zigzag chain structure also results in Cp<sub>2</sub>Mn being an antiferromagnet below 432 K, the origins of which are thought to involve inter-chain interactions between Mn<sup>2+</sup> ions. This behaviour contrasts sharply with other 3d metallocenes containing unpaired electrons, which are all Curie paramagnets. Above 432 K, Cp<sub>2</sub>Mn undergoes a profound colour change from amber to pink with a concomitant change in both its structure, which adopts the more familiar molecular sandwich motif, and its magnetic response, which corresponds to Curie paramagnetism up to the high-temperature limit of the experiment. In addition to its anomalous magneto-structural behaviour, manganocene is also kinetically labile and readily hydrolysed by water and dilute hydrochloric acid, whereas other 3d metallocenes are not.<sup>2,6</sup> Cp<sub>2</sub>Mn readily forms adducts with two- or four-electron Lewis bases to result in the formation of complexes possessing formal valence electron counts of 19 or 21, showing scant regard for the ubiquitous 18-electron rule that so dominates the organometallic chemistry of the transition metals.<sup>7</sup> These observations have led to general acceptance of the manganese(II)–carbon bonds within manganocene being essentially ionic in character, and it is this fundamental property that sets manganocene and many of its derivatives apart from typical transition metal organometallics. The origins of the anomalous behaviour shown by Cp<sub>2</sub>Mn have been assigned to the enhanced stability associated with the high-spin Mn<sup>2+</sup> ion in which the 3d valence orbitals are half filled, an assertion that has recently been confirmed experimentally with evidence for highly contracted 3d orbitals using Penning ionization electron spectroscopy.<sup>8</sup>

Following the original, pioneering work of Wilkinson and subsequent studies by others, organomanganese(II) chemistry evolved at a relatively slow rate compared to the analogous chemistry of other transition metals. The cyclopentadienyl chemistry of manganese(II) has been dominated by structural and magnetic studies on simple substituent derivatives of the parent compound,<sup>9</sup> or half-sandwich analogues.<sup>10</sup> The preference of manganese(II) to engage in ionic metal–carbon

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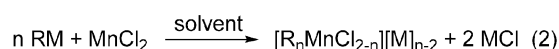
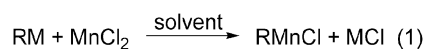
**Fig. 1** A segment of the polymeric structure of  $\text{Cp}_2\text{Mn}$  (**1**). Hydrogen atoms omitted. See ref. 4.

bonding means that it does not form stable complexes with neutral  $\pi$ -acidic ligands that rely on synergic backbonding for stability, such as olefins or carbon monoxide. Many examples of manganese(II) organometallics containing formally anionic alkyl and aryl ligands have, however, been reported and their structural properties described in detail.<sup>11,12</sup> Observations on compounds of general formula  $[\text{MnR}_2]_n$  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  $[\text{Mn}_2\text{Ph}_6]^{2-}$  (**2**), whereas lower-coordinate complexes are found in the presence of bulkier ligands such as  $[\text{MnMes}_3]^-$  (Mes = mesityl, 2,4,6- $\text{C}_6\text{H}_2\text{Me}_3$ ) (**3**).<sup>11</sup>

Although the accumulation of fundamental knowledge on manganese(II) organometallics has been underway for over half a century, it is only relatively recently that such compounds have been applied systematically to explore their potential in organometallic and metallo-organic synthesis, and the primary aim of this review is to summarize the important recent findings in the area. Particular emphasis will be placed on bimetallic compounds in which manganese(II) is combined with alkali and alkaline earth metals since systems of this type account for some of the most eye-catching developments. The applications of organomanganese(II) reagents in organic synthesis were pioneered by Cahiez and Normant in the 1970s and are now quite widespread.<sup>13</sup> The increase in their popularity in recent years has been due to the many advantages they offer over ‘conventional’ reagents such as organolithiums, Grignards, organozincs and organocuprates. However, space limitations preclude an exhaustive review of this work and the interested reader is directed to other excellent reviews on the subject.<sup>14</sup>

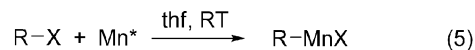
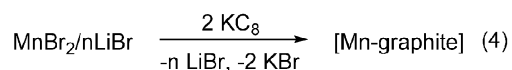
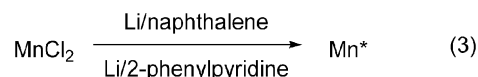
## 2 Synthesis of organomanganese(II) compounds

Generally, four types of organomanganese compounds are known: organomanganese halides,  $\text{RMnX}$ , manganese diorganyls,  $\text{R}_2\text{Mn}$ , triorganomanganates,  $[\text{R}_3\text{Mn}]^-$ , and tetraorganomanganates,  $[\text{R}_4\text{Mn}]^{2-}$ . The most commonly employed synthetic route to manganese(II) organometallics is, not surprisingly, transmetalation of manganese(II) halides by a main group organometallic such as  $\text{RLi}$ ,  $\text{RMgX}$  or  $\text{R}_2\text{Mg}$ , and this method is effective when the R ligand is an unfunctionalized ‘hydrocarbyl’ such as cyclopentadienyl, alkyl or aryl, the reactions often proceeding in high yields. Manganese(II) chloride is usually the preferred starting material since it is inexpensive and useful



M = Li, MgX; solvent = thf or  $\text{Et}_2\text{O}$

**Scheme 1**



**Scheme 2**

for large-scale syntheses, although the ‘ate complex’  $\text{Li}_2\text{MnCl}_4$  is often used due to its solubility in thf (Scheme 1).<sup>13,14</sup>

An alternative method for preparing organomanganese compounds involves the action of activated manganese metal on organic halides. Several methods for the generation of activated manganese metal have been developed and the reaction with organic halides is thought to involve oxidative insertion of manganese(0) into the carbon–halogen bond (Scheme 2).<sup>15</sup> One of the main advantages of using activated manganese for preparing organomanganese(II) halides is the very high tolerance of the Mn–C bond to a wide range of functional groups, thus broadening the scope for applications of such reagents in synthesis.

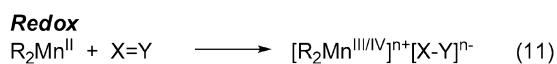
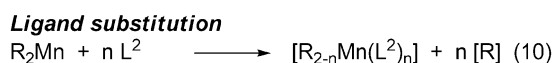
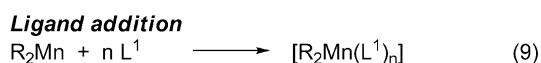
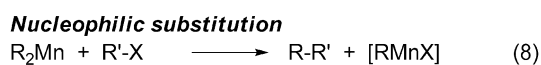
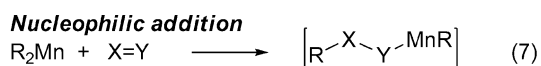
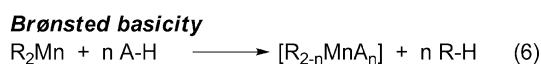
## 3 Reactivity of organomanganese(II) reagents

The reactivity of organomanganese(II) compounds arises from the presence of formally cationic  $\text{Mn}^{2+}$  ions and anionic  $\text{R}^-$  ligands. Manganese dialkyls typify the general chemical behaviour of the manganese(II)–carbon bond, which can be conveniently classified under six headings (Scheme 3).

The parentheses around each of the complexes on the right-hand side of eqn (6)–(11) in Scheme 3 mask the often complex, intriguing structures of these compounds. An important driving force behind the characterisation of many examples of organomanganese(II) compounds resulting from reactivity of these types has been the potential for creating structure–reactivity relationships that could conceivably be exploited in synthesis and this theme will be developed in the ensuing sections of the review.

### 3.1 Brønsted basicity

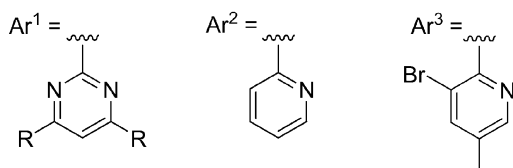
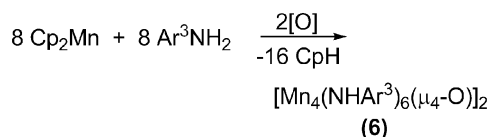
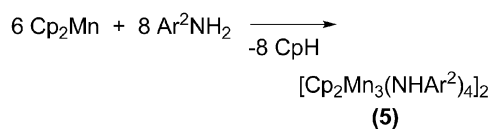
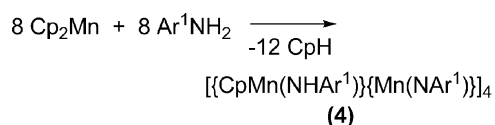
Protolytic cleavage of Mn–C bonds in organomanganese(II) bases by A–H acidic substrates (A = heteroatom) is an effective route to the formation of manganese(II) heteroatom bonds. This direct manganese(II) formation method is advantageous over the reactions of manganese(II) halides with, for example, organolithium compounds since it avoids potential complications such as solubility issues, reduction to manganese(I) and/or manganese(0), or the formation of unwanted ‘ate complexes’. The methodology is



Scheme 3

particularly useful for the formation of manganese(II) aryl-amido or -imido compounds, containing  $[ArNH]^-$  or  $[ArN]^{2-}$  ligands, respectively, from aromatic primary amine ligand precursors using manganocene as the base (Scheme 4).<sup>16</sup>

Although manganocene is air-sensitive, its use is operationally much less challenging than employing precursors such as the exceptionally air-sensitive amido compound  $[Mn(NSiMe_3)_2]$ .<sup>17</sup> Notwithstanding the general applicability of the manganocene-based synthetic methodology, the systems shown in Scheme 4 and in several related cases have unearthed a series of structurally fascinating manganese(II)-nitrogen clusters such as **4–6** (Fig. 2), a class of compound that has until recently been relatively under-investigated compared to more traditional manganese–oxygen clusters in which manganese tends to be present in its higher ( $\geq +3$ ) oxidation states. Compound **4** is particularly interesting since the primary amine has been doubly deprotonated to result in the formation



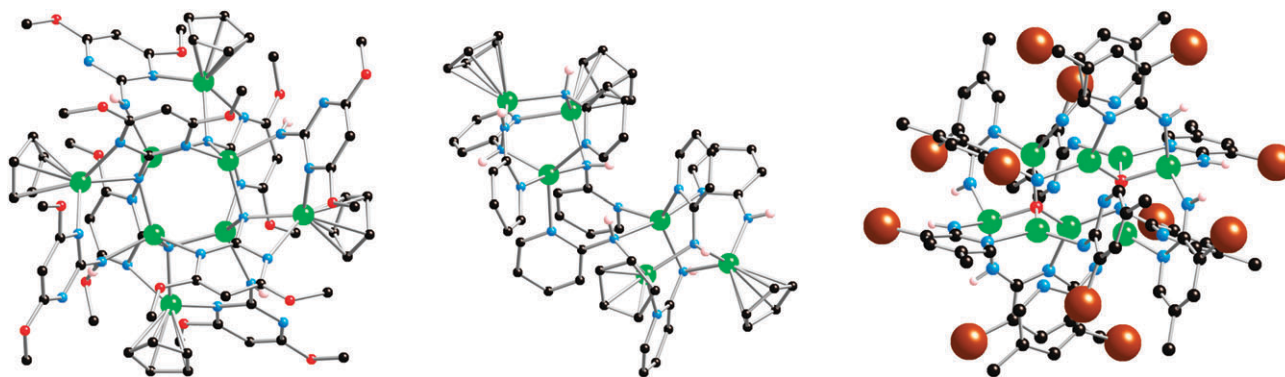
Scheme 4

of a rare manganese(II) imido compound. Also noteworthy is the clear dependence of cluster nuclearity and architecture on ligand functionality patterns and steric properties, and although the precise relationship between these properties is somewhat unpredictable the observation creates the potential to allow controlled modification of cluster shape and structure through ligand design.

Since the  $\text{Cp}^-$  ligands within manganocene are only moderately basic ( $\text{CpH}$  has  $pK_a = 15$ ) due to delocalization of the negative charge, it is not surprising that there are limitations to manganating ability of this compound. Indeed,  $\text{Cp}_2\text{Mn}$  is incapable of directly manganating arenes or even terminal acetylenes. Manganese(II) dialkyls should in principle be capable of greater reactivity towards less acidic substrates such as weak C–H acids, and several potential manganating compounds of empirical formula  $[\text{MnR}_2]$  have been known for many years.

The polymeric compound  $[\text{Mn}(\mu\text{-CH}_2\text{SiMe}_3)_2]_\infty$  (**7**)<sup>18</sup> has begun to show promise as a highly efficient manganating agent and its reactivity is especially potent when combined with alkali metal amides in the form of an alkali metal organomanganate. For example,  $[\text{Mn}(\text{CH}_2\text{SiMe}_3)_2]$  is unreactive towards both ferrocene and benzene, but when combined with lithium or sodium in  $[(\text{tmeda})\text{Li}(\mu\text{-tmp})\text{Mn}(\text{CH}_2\text{SiMe}_3)_2]$  (**8**) or  $[(\text{tmeda})\text{Na}(\mu\text{-tmp})(\mu\text{-CH}_2\text{SiMe}_3)\text{Mn}(\text{tmp})]$  (**9**) ( $\text{tmeda}$  = tetramethylethylenediamine,  $\text{tmp}$  = tetramethylpiperidine) two highly effective reagents for the direct manganating of aromatic frameworks by deprotonation are obtained. The reaction of the lithium manganate **8** with  $\text{Cp}_2\text{Fe}$  is highly efficient and results in the formation of **10** in yields of up to 83%, thus providing the first example of trisubstituted behaviour by an alkali metal ‘ate complex’ (Scheme 5).<sup>19</sup> The structure of **10** is also quite unusual, featuring three 1,1'-ferrocenediide ligands in which the  $[\text{C}_5\text{H}_4]$  ligands are eclipsed within the sandwich units. The ferrocenediide ligands bridge the two tetrahedral manganese(II) centres and two terminal tetrahedral lithium cations. Reagents that are capable of directly metallating simple aromatic molecules are a boon to the synthetic chemist yet despite its high reactivity towards ferrocene **8** is unreactive towards simple arenes such as toluene. In order to effect metallation of a simple arene using alkali metal-mediated manganation it proved necessary to vary the alkali metal to sodium and thus deprotonation of benzene by **9** affords the phenyl-bridged compound  $[(\text{tmeda})\text{Na}(\mu\text{-Ph})(\mu\text{-tmp})\text{Mn}(\text{tmp})]$  (**11**).<sup>20</sup> In the absence of  $\text{tmeda}$  chelation to sodium, regioselective 1,4-dimanganation of benzene occurs when the manganating reagent is generated using a 4 : 6 : 2 ratio of  $\text{Na} : \text{tmp} : \text{Mn}$ . The product, **12**, crystallizes as a so-called ‘inverse crown complex’, the first example of such a compound to contain a transition metal following the characterization of many inverse crowns based entirely on main group metals (Scheme 6).<sup>21</sup> However, the formation of **12** is considered somewhat more efficient than its main group counterparts due to the stoichiometric, as opposed to excess, amounts of benzene required.

An interesting application of deprotonation by a manganese(II) dialkyl involved the reactions of  $[\text{Mn}(\text{CH}_2^t\text{Bu})_2(\text{tmeda})]$  (**13**) with partially dehydroxylated silica (Scheme 7).<sup>22</sup> The extent of silica dehydroxylation increases as the silica is pre-heated at 200, 300, 500 and 700 °C, respectively, meaning



**Fig. 2** Structures of **4**, **5** and **6**. Carbon, black; nitrogen, blue; oxygen, red; manganese, green; bromine, brown. Amide hydrogen atoms shown in pink, all other hydrogens are omitted for clarity. See ref. 16 and CCDC 207481, 188030 and 188031.

that the percentage of manganese grafted onto the surface decreases concomitantly due to the presence of progressively fewer  $[\equiv\text{SiOH}]$  hydroxy groups (where  $\equiv\text{SiOH}$  denotes four-coordinate surface silicon). Of the two possible products that may result from deprotonation of surface hydroxy groups by **13**, the mono-siloxy species  $[(\equiv\text{SiO})\text{Mn}(\text{CH}_2^t\text{Bu})(\text{tmeda})]$  (**14**) and the cyclic bis(siloxy) complex  $[(\equiv\text{SiO})_2\text{Mn}(\text{tmeda})]$  (**15**), mass balance measurements and IR and EPR spectroscopies indicate that larger amounts of **15** were formed when silica dehydroxylated at lower temperatures was employed, which can be rationalized on the basis of an increasing likelihood of vicinal  $[\equiv\text{SiOH}]$  groups. With silica dehydroxylated at 700 °C, **14** is essentially the only surface product. The silsesquioxane  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}$  (**16**) is commonly used as a molecular analogue of silica supports in catalysis and its reaction with **13** was attempted with the aim of modeling the grafting of manganese onto silica surfaces. However, the only product obtained from this reaction was the bis(siloxy) compound  $[\{(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO}\}_2\text{Mn}(\text{tmeda})_2]$  (**17**), as shown by X-ray crystallography. The obvious differences between **17** and its heterogeneous parent compounds **14** and **15** highlight key differences between the nature of organometallic compounds on surfaces and in solution, and give insight into the unique catalytic reactivity that can potentially be obtained with heterogeneous catalysts.

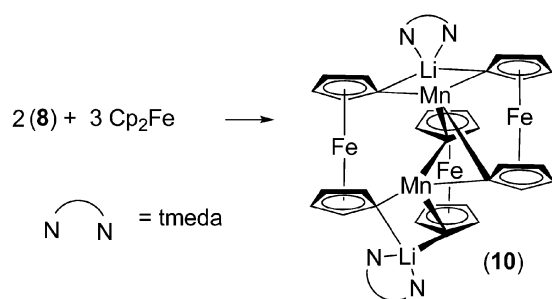
### 3.2 Lewis acid–base behaviour: addition of nucleophiles to $\text{MnR}_2$ and addition of $\text{MnR}_2$ to electrophiles

Due to the presence of both an electrophilic  $\text{Mn}^{2+}$  cation and nucleophilic  $\text{R}^-$  ligands, organomanganese(II) reagents exhibit

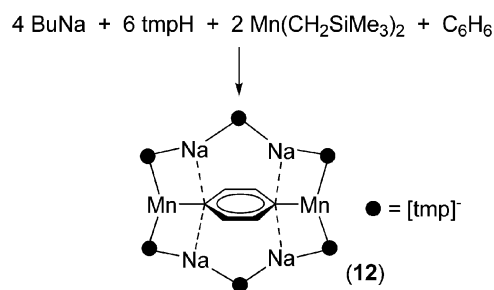
some very interesting reactivity towards Lewis bases and Lewis acids.

Reports describing the nucleophilic addition of monodentate (L) and bidentate (L–L) Lewis bases such as (di)amines and (di)phosphines to manganese are legion and such reactions frequently result in compounds of general formula  $[(\eta^5\text{-Cp})_2\text{Mn}(\text{L})_n]$  ( $n = 1, 2$ ) or  $[(\eta^5\text{-Cp})_2\text{Mn}(\text{L}-\text{L})]$ , *i.e.* simple adducts in which the  $\eta^5$ -bonding of the Cp ligand is maintained but with slight tilts relative to the perpendicular axis.<sup>7</sup> In some cases, slippage of the Cp rings is observed,<sup>23</sup> as with the addition of sterically demanding *N*-heterocyclic carbene (NHC) ligands to  $\text{Cp}_2\text{Mn}$  to form **18** and **19** (Scheme 8).<sup>24</sup> Lewis bases such as thf and phosphines also form simple adducts with manganese dialkyls such as  $[\text{Mn}(\text{CH}_2\text{SiMe}_3)_2]$ ,<sup>25</sup> and the addition of a gallium(I) analogue of an NHC ligand affords the interesting ion-contacted complex **20** with a Ga–Mn bond distance of 2.6658(10) Å (Scheme 9).<sup>26</sup>

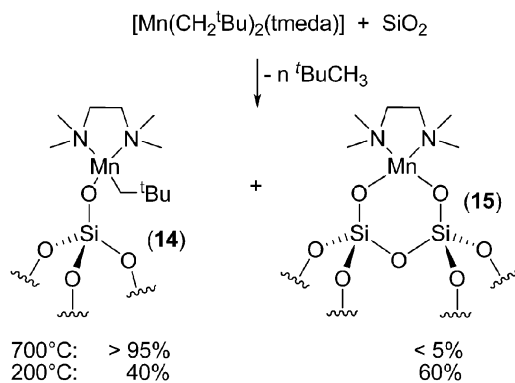
Of increasing importance are the reactions of manganese(II) dialkyls with unsaturated *N*-donors such as  $\alpha$ -diimines and 2,6-diiminopyridines due to the application of these ligands in olefin polymerization and the growing popularity of manganese(II) catalysts (see section 4). By analogy to the highly successful ( $\alpha$ -diimine)-nickel(II) and pyridyldiimine-iron(II) catalysts,<sup>27</sup> attempts were made to prepare manganese(II) complexes of types **21**, **23** and **25** and, therefore, develop novel polymerization catalysts based on manganese(II) (Scheme 10). However, the polar character of the Mn–C bonds in the putative complexes **21**, **23** and **25** means that they may in fact undergo rearrangement *via* a series of intramolecular nucleophilic additions of the R group across the unsaturated components of the *N*-donor ligands. In the case of  $\text{MnR}_2$



Scheme 5



Scheme 6



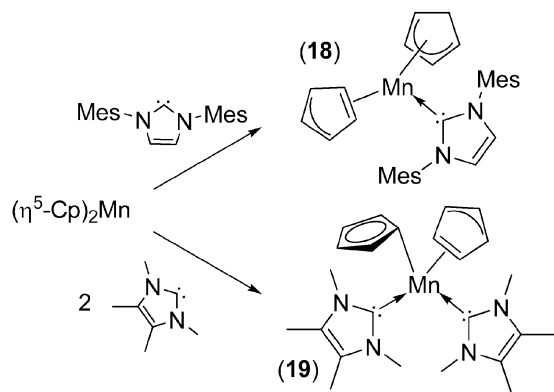
Scheme 7

complexes of 2,6-diiminopyridine ligands, migration of an R ligand to the 4-position of the pyridyl ring occurs with concomitant reduction of the metal to manganese(I) (**22**). Subsequent cleavage of the ligand from manganese can be effected to produce the free ligand and hence a novel route to 4-substituted 2,6-diiminopyridines.<sup>28</sup> In the case of diimine adducts of MnR<sub>2</sub>, **23** and **25**, the fate of the complex is strongly dependent on the steric properties of the imine nitrogen aryl substituent such that **23b** is stable with respect to rearrangement whereas **23a** rearranges to give an unusual dimanganese amido-imine complex (**24**). Complex **25** (Dipp = 2,6-diisopropylphenyl) rearranges *via* a [1,3]-shift mechanism to give complex **26**.<sup>29</sup>

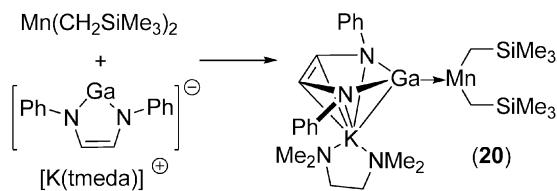
Complex **23b** demonstrates that manganese dialkyls can form stable adducts with unsaturated N-donor ligands, but the observations on **21**, **23a** and **25** do suggest that a certain degree of caution should be exercised when attempting to apply such ligands in the organometallic chemistry of manganese(II) alkyls, although these observations are not entirely surprising given that [Mn(CH<sub>2</sub><sup>t</sup>Bu)<sub>2</sub>]<sub>4</sub> and [Mn(CH<sub>2</sub>CMe<sub>2</sub>-Ph)<sub>2</sub>]<sub>2</sub> are known to react readily with unsaturated organic substrates such as isocyanates and isocyanides by a nucleophilic addition mechanism.<sup>30</sup>

### 3.3 Addition of main group cyclopentadienides to Cp<sub>2</sub>Mn

A range of compounds of general formula [Cp<sub>3</sub>Mn]<sup>-</sup> with s-block metals as the counter cation is well known and particularly interesting from a structural perspective. The first reported examples of tris(cyclopentadienyl)manganates were

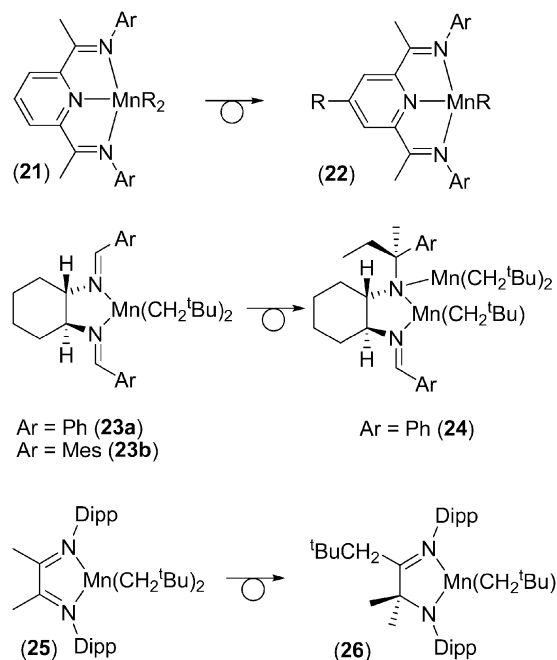


Scheme 8

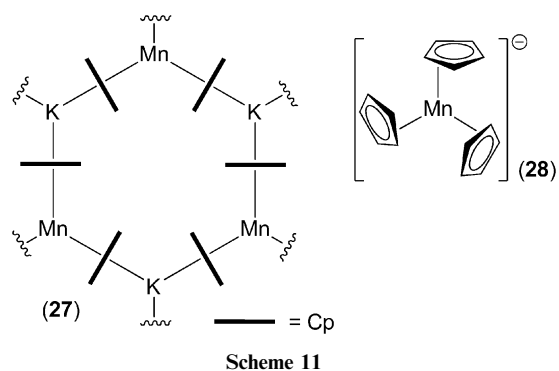


Scheme 9

the ion-contacted complex [(η<sup>2</sup>-Cp)<sub>3</sub>MnK(1.5thf)] (**27**) and the ion-separated analogue [(η<sup>2</sup>-Cp)<sub>3</sub>Mn]<sub>2</sub>[Mg(thf)<sub>6</sub>], [(**28**)] [Mg(thf)<sub>6</sub>], which were synthesized by addition of [CpK(thf)<sub>2</sub>] and Cp<sub>2</sub>Mg, respectively, to Cp<sub>2</sub>Mn in thf solvent.<sup>31</sup> The three-fold symmetry of the [(η<sup>2</sup>-Cp)<sub>3</sub>Mn]<sup>-</sup> anion in **27** and the bridging interactions to the potassium cations result in a crystal structure containing hexagonal [(μ-Cp)Mn(μ-Cp)K]<sub>3</sub> rings that fuse together to afford an infinite honeycomb lattice, a relatively rare structural type in organometallic chemistry (Scheme 11). Alternatively, the structure of **27** can be regarded as consisting of [(η<sup>5</sup>-Cp)<sub>3</sub>K]<sup>2-</sup> anions coordinating to Mn<sup>2+</sup> cations, in which case **27** contains the first example of a tris(cyclopentadienyl)alkali metal complex. The structure of **28** shows separated [(η<sup>2</sup>-Cp)<sub>3</sub>Mn]<sup>-</sup> anions, yet despite the sharp contrasts in bulk structures of **27** and **28** the Mn–C bonding with the two [(η<sup>2</sup>-Cp)<sub>3</sub>Mn]<sup>-</sup> anions is essentially identical, being in the range 2.361(1)–2.405(4) and 2.351(5)–2.392(6) Å, respectively. Furthermore, **27** and **28** show identical, temperature-dependent effective magnetic moments, μ<sub>eff</sub>, in the range 5–300 K, whereby spin crossover between the S = 3/2 and S = 5/2 states of the Mn<sup>2+</sup> ion accounts for the increasing value of μ<sub>eff</sub> as the temperature is raised. The reason for the difference in the structures of **27** and **28** is due to the hard Lewis acidic character of Mg<sup>2+</sup> and the somewhat softer character of K<sup>+</sup>, although the reason for the apparent persistence of a [(η<sup>2</sup>-Cp)<sub>3</sub>Mn]<sup>-</sup> hapticity were not

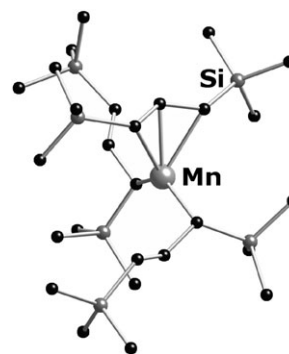


Scheme 10



immediately obvious from this study. Indeed, an entire family of  $[(\eta^2\text{-Cp})_{3-n}(\eta^2\text{-Cp}')_n\text{Mn}][\text{M}]$  anions ( $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$ ;  $n = 0, 1, 2, 3$ ;  $\text{M} = \text{K}$  or  $\text{Mg}$ ) is known<sup>32</sup> yet neither these compounds nor the related network structure of  $\{[(\eta^2\text{-Cp})_3\text{Mn}\}\{\text{Cs}([18]\text{crown-6})\}$  (29)<sup>33</sup> were able to shed light on the apparent persistence of the  $3\eta^2$  hapticity of the Cp ligands. A study employing density functional theory implied that  $3\eta^2$  should be the most stable arrangement of Cp ligands for high-spin  $\text{Mn}^{2+}$ , but also that other hapticities were only higher in energy by several  $\text{kcal mol}^{-1}$ .<sup>33</sup> These calculations are broadly consistent with observations made in the attempted synthesis of the dinuclear derivative  $[\text{Cp}_2\text{MnCpMnCp}_2]$ : combining  $\text{Cp}_2\text{Mn}$  with 0.5 equivalents of  $\text{CpLi}$  in the presence of [12]crown-4 results not in the formation of the desired compound  $[\text{Cp}_3\text{Mn}_2][\text{Li}([12]\text{crown-4})_2]$  but does instead afford crystals of  $[\text{Cp}_3\text{Mn}][\text{Li}([12]\text{crown-4})_2]$  (30) in which the unit cell contains five unique  $[\text{Cp}_3\text{Mn}]^-$  anions with hapticities of  $3\eta^2$  (twice),  $2\eta^2\eta^3$  (twice) and  $2\eta^2\eta^5$ , suggesting that crystal packing forces do play some role in determining the precise nature of the interaction between manganese(II) and cyclopentadienyl ligands.<sup>32</sup>

Closely related to the tris(cyclopentadienyl)manganate anions is the tris(allyl)manganate  $[\text{Mn}\{\eta^3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}\{\eta^3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}][\text{Li}(\text{thf})_4]$ , (31) $[\text{Li}(\text{thf})_4]$ , featuring the first example of non-cyclopentadienyl  $\pi$ -coordination by an organometallic ligand to manganese(II) (Fig. 3).<sup>34</sup> Despite transition-metal allyl complexes having been known for over 40 years, it was not until 2004 that this ligand was applied successfully in the chemistry of manganese(II). Geometry optimizations of the anion **31** and its 'parent' anion  $[\text{Mn}\{\eta^x\text{-(C}_3\text{H}_5)_3\}]^-$  (32) (where  $x$  denotes mixed hapticity of the ligands) in the  $S = 5/2$  spin state of manganese(II) revealed that the steric influence of the silyl substituents on ligand hapticity is minimal and that the  $2\eta^1\eta^3$  arrangement is the preferred arrangement of ligands in both **31** and **32**.<sup>35</sup> Natural Population Analysis (NPA) and Wiberg Bond Index (WBI) calculations on **31** and **32** revealed ionic bonding between manganese(II) and the  $\eta^3$ -allyl ligand whereas the  $\eta^1$ -allyl ligands feature polar covalent Mn–C bonding. Interestingly, when **31** and **32** are geometry-optimized with manganese in the  $S = 3/2$  state, not only are the hapticities of the ligands modified to  $\eta^12\eta^3$  but all the Mn–C bonds possess a greater degree of covalency. According to theory, the  $S = 1/2$  of manganese(II) is a relatively high energy spin configuration in both **31** and **32** but the  $S = 5/2$  and  $3/2$  states are quite close in energy, hence they may couple through spin–orbit coupling to



**Fig. 3** Structure of the anion **31**. Hydrogen atoms omitted. See ref. 34 and CCDC 231180.

generate a spin-admixed state. Attempts at synthesizing **32** have so far been unsuccessful, with reductive elimination of manganese being the apparent outcome. This observation suggests that the stability of **31** can be attributed in large part to kinetic factors associated with bulky silyl substituents, which contrasts to the stability of manganese(II) cyclopentadienyls, where steric stabilization is not a stringent requirement.

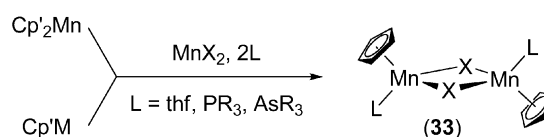
### 3.4 Nucleophilic substitutions

The lability of the cyclopentadienyl ligands in manganocene and some of its simple derivatives is a general feature of the chemistry of these compounds that has been put to effective use in synthesizing new complexes in which one or both of the Cp ligands may be displaced by nucleophiles.<sup>36</sup> A useful route to manganese(II) half-sandwich complexes combines manganocenes with manganese(II) halides in the presence of Lewis bases such as thf, phosphines or arsines according to Scheme 12.

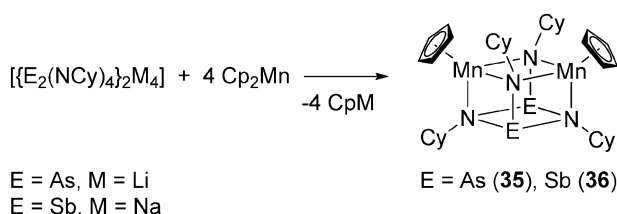
Monocyclopentadienyl compounds of manganese(II) tend to adopt ligand-bridged structures (*e.g.* **33**) in the solid state which can be preserved in solution, although paramagnetic NMR spectroscopy has revealed that ligand dissociation and scrambling is possible.<sup>10,37</sup> Dicyclopentadienylmanganese(II) complexes have general utility as soluble sources of manganese(II), suggesting that a range of complexes of this ion should be readily accessible in organic solvents, avoiding problems with solubility often encountered with manganese(II) halides. For example, replacement of both Cp ligands in  $\text{Cp}_2\text{Mn}$  by the tripodal tris(2-pyridyl) ligand  $[\text{MeAl}(2\text{-py})_3]^-$  occurs smoothly in thf solvent to afford the bimetallic complex  $[\{\text{MeAl}(2\text{-py})_3\}_2\text{Mn}]$  (**34**).<sup>38</sup>

Addition of nucleophiles such as alkali metal amides and imides can lead to the formation of manganese(II) cage compounds (Scheme 13).

In the structures of **35** and **36**,  $[\text{CpMn}]$  units have been incorporated into the framework of pseudo-cubane cluster



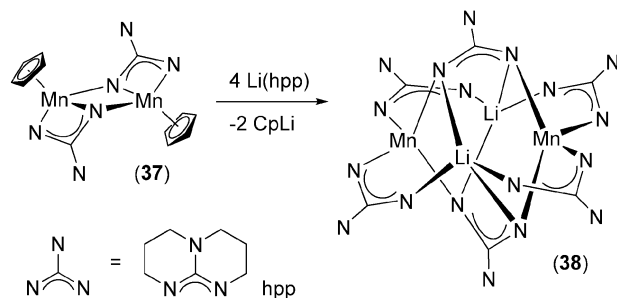
**Scheme 12**



Scheme 13

and were the first examples of a paramagnetic ion to be complexed by a ligand based on heavy p-block elements.<sup>39</sup>

Manganocene is particularly prone to substitution of the Cp ligands by organolithiums and the outcome is often the formation of ligand-bridged dimers,  $[CpMn(\mu-L)]_2$  in the solid-state where L = amide, acetylide and arenide.<sup>40</sup> Sequential replacement of both ligands in  $Cp_2Mn$  occurs when the lithium salt of hexahydropyrimidopyrimidine (hpp) is added in the appropriate stoichiometry. After substitution of one Cp ligand by  $[hpp]^-$  the familiar dimeric structural motif is observed in **37**, but upon displacement of the second Cp ligand by  $[hpp]^-$  an unusual lithium manganate cage (**38**) is formed (Scheme 14).<sup>41</sup>

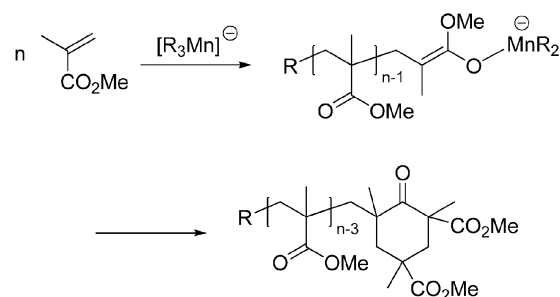


Scheme 14

#### 4 Organomanganese(II) catalysts for olefin polymerizations

In the context of organometallic catalysis, manganese(II) has made very little impact in comparison not only to other transition metals but also to manganese in other oxidation states. However, there are now signs that manganese(II) organometallics have the potential to provide viable alternatives to the many established catalysts for the polymerization of functionalized and unfunctionalized olefins.

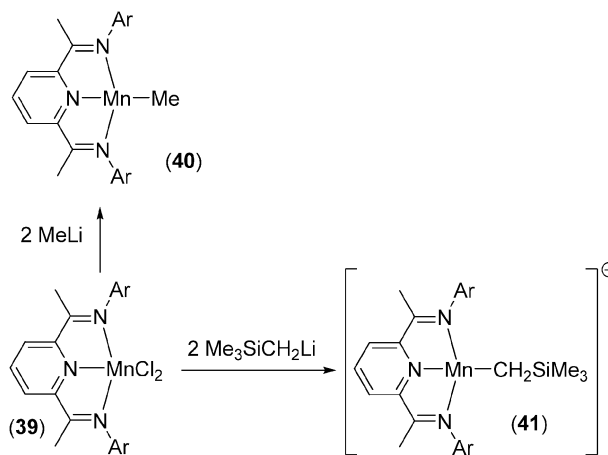
Alkali metal organomanganates  $[R_3Mn][M]$  (R = Me, *n*Bu, Ph; M = Li, K) are capable of initiating the polymerization of methyl methacrylate (MMA) to poly(methyl methacrylate)s (PMMA) in high yield according to Scheme 15.<sup>42</sup> Typically, one R group is found on the  $\alpha$ -terminus of the PMMA, demonstrating that polymerization is initiated as a result of nucleophilic attack by one R group on MMA and that the other two R ligands remain coordinated to manganese throughout the reaction. The six-membered rings at the  $\omega$ -terminus are indicative of back-biting within the manganese enolate intermediates. A dependency of PMMA tacticity



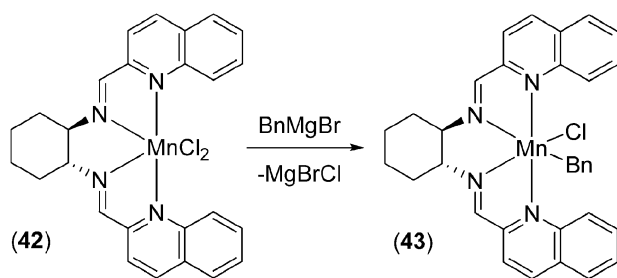
Scheme 15

(*mm:mr:rr*) on the steric requirements of the initiating ligand R was apparent, introducing the possibility of controlling polymer stereochemistry through a judicious choice of organomanganese catalyst. The addition of  $t\text{Bu}_3\text{Al}$  to the polymerization reaction in varying Al : Mn ratios allowed a degree of control over PMMA molecular weights and polydispersity to be exerted.

Manganocene polymerizes ethylene to high molecular weight, linear polyethylene in the presence of methylalumoxane (MAO) or  $\text{Et}_2\text{AlCl}$  co-catalysts, albeit with low activities, although an enhancement of activity occurred when using an  $\text{MgCl}_2$ -supported catalyst.<sup>43</sup> Propylene cannot be polymerized by  $Cp_2Mn$ . In the same study, both  $\text{MgCl}_2$ -supported  $[Mn(\text{acac})_3]$  and  $[Mn(\text{salen})\text{Cl}]$  were shown to polymerize both ethylene and propylene and since this work levels of interest in organomanganese(II) catalysts for ethylene polymerization have steadily grown. Manganese(II) complexes of the well known 2,6-diiminopyridine ligands that have proven to be so effective in iron(II)-mediated catalysis are surprisingly inactive towards ethylene polymerization in the presence of co-catalysts.<sup>44</sup> Complex **39** is isomorphous with the Fe(II) analogue yet its catalytic inactivity is thought to be due either to the high-spin  $d^5$  configuration hindering alkylation by MAO or to some inherent instability of the manganese-alkyl entity. The latter situation was shown to be more likely through some elegant reactivity studies of **39** with stoichiometric amounts of simple organolithiums (Scheme 16). In forming **40** from the reaction of **39** with  $\text{MeLi}$ , the metal is reduced to manganese(I), yet when  $\text{Me}_3\text{SiCH}_2\text{Li}$  is employed the square planar manganese(0) complex **41** is instead formed. The formation of



Scheme 16



Scheme 17

**41** is thought to involve a process in which alkylation/dealkylation of the pyridyl ring occurs in a manner similar to the rearrangement mechanism of **21** (Scheme 10).

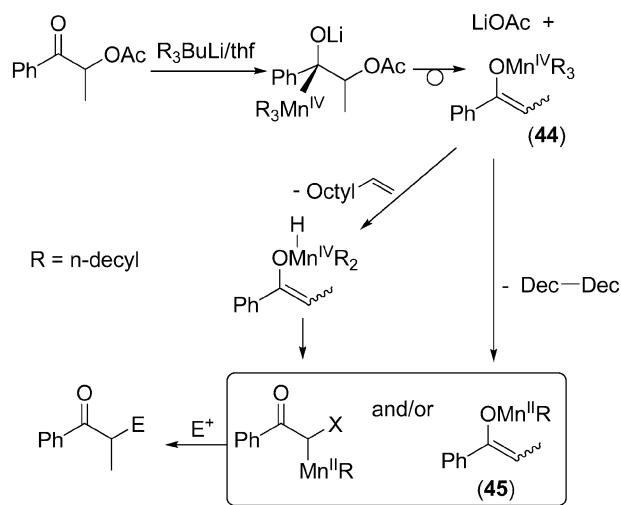
Application of a parallel screening method to 16 *N*-donor chelate ligands complexed to MnCl<sub>2</sub> allowed identification of a new family of complexes for ethylene polymerization.<sup>45</sup> In general, tetradentate imine ligands (e.g. as in **42**) or two bis(imine) ligands, in which a C<sub>2</sub> bridge separates the donor atoms and the coordination geometry is distorted from octahedral, are capable of generating manganese(II) coordination environments that are conducive to ethylene polymerization with MAO. Because of the importance of manganese(II) alkyls as likely intermediates in ethylene polymerization reactions with *N*-donor ligands, benzyl complexes such as **43** were synthesized (Scheme 17).

Only monobenzylated complexes can be isolated even if **42** is treated with an excess of BnMgCl, which is thought to be due to the bulk of the *N*-donor ligands preventing approach of a second benzyl group. The polymerization activities of **42** and related compounds were quite high compared to other manganese(II) catalysts, but they are still significantly less active than complexes of these ligands with other metals such as iron(II). However, this area is still very much in its infancy and a general summary of the work described in this section suggests that interest in the area will continue to grow.

## 5 Exploiting redox properties in synthesis

The ionic bonding within organomanganese(II) compounds leads to obvious comparisons being made between them and organometallic derivatives of the group 1, 2, 11 and 12 metals. These comparisons are particularly poignant in light of the widespread application of main group organometallics in organic synthesis as alkylating agents and the general recognition that manganese(II) could provide useful alternatives in this setting. One aspect of the chemistry of manganese that is not available to, say, lithium, magnesium and zinc, is the rich redox chemistry of the transition metal. Although applications of the redox chemistry of manganese(II) in synthesis have not been developed extensively, reports are emerging that suggest electron transfer reactions could be combined with the 'main group-like' chemistry of manganese(II) to result in a range of new organomanganese(II) synthetic reagents.<sup>14b</sup>

Enolates are amongst the most valuable and versatile intermediates in organic synthesis. Manganese(II) enolates are well known and they were first synthesized using transmetallation reactions of lithium enolates with manganese(II) chloride (see

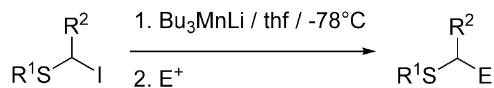


Scheme 18

Scheme 1).<sup>46</sup> Alkali metal manganates such as [R<sub>3</sub>Mn][Li] (R = <sup>n</sup>Bu, <sup>n</sup>Dec) (**43a**, **43b**) are able to generate manganese enolates with a degree of regiocontrol *directly* from ketones bearing a leaving group in the  $\alpha$ -position by acting as formal two-electron reducing agents (Scheme 18).<sup>47</sup>

A mechanism was proposed to account for the generation of the manganese(IV) enolate (**44**) by oxidative addition of the ketone to **43b** followed by reductive elimination to afford a manganese(II) enolate (**45**), which can then be used in aldol reactions and alkylations, the latter being specific for the monoalkylation product. A similar methodology has been applied to the generation of thiomethylmanganese(II) reagents, presumably of empirical formula [PhSMn<sup>IV</sup>R<sub>3</sub>] (**46**), directly from the reaction between thiomethyl iodides and **43a**, thus offering a useful alternative route to thiomethyl anions (Scheme 19).<sup>48</sup> The reactions of **46** with allyl bromides resulted in the formation of but-3-enyl(phenyl)sulfanes in good yield, although improvements in yield are obtained on addition of CuCN. Thiomethylmanganese reagents only react with  $\alpha,\beta$ -unsaturated ketones by 1,4-addition in the presence of CuCN and also only react with aldehydes in the presence of BF<sub>3</sub>·OEt<sub>2</sub>. If **43a** and BF<sub>3</sub>·OEt<sub>2</sub> are mixed in advance, the reaction of the thiomethyl anion-containing species with aldehydes is unaffected and gives the aldol product in good yield, suggesting that **43a** and BF<sub>3</sub>·OEt<sub>2</sub> are compatible with each other. The mixed manganate–BF<sub>3</sub>·OEt<sub>2</sub> reagent is also capable of manganoating acetals for subsequent use in alkylation reactions.<sup>49</sup>

Only a brief summary of some of the interesting applications of alkali metal manganates as reducing agents in organic synthesis has been given here. From a pragmatic point of view, it can be said that manganates are versatile reagents capable of effecting many different transformations and that their popularity will probably increase in due course. However, it is quite apparent that current mechanistic information



Scheme 19



to account for the way in which these compounds react is not available in any definite form and highlights a major challenge for structural and synthetic chemists: by studying the coordination chemistry of manganese-containing intermediates in synthesis a deeper knowledge of these compounds will become available which promises ultimately to lead to further insightful applications in a broad range of settings.

## 6 Conclusions

This review has attempted to show that the essence of synthetic chemistry with organomanganese(II) compounds is diversity, and that this diverse reactivity is unique within organotransition metal chemistry due to predominantly ionic manganese(II)–carbon bonding. The range of structures adopted by manganese(II) organometallics is fascinating and has provided much of the major impetus for work in the area. Over half a century since the first systematic studies began, the manganese(II)–carbon bond is still providing a source of intrigue and, as the field continues to evolve, is beginning to show potential for a multitude of applications in areas such as the synthesis of functional organic molecules, polymerization catalysis and cluster chemistry. Equally appetising is the work that remains to be done, and as the discussion of selected applications of manganate reagents in synthesis has suggested, there are significant opportunities for developing synergistic relationships between structural inorganic chemistry and organic synthesis, for the mutual benefit of chemists with ‘traditional’ backgrounds in those areas, and it is anticipated that this aspect will provide some of the major future developments.

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