DALTON COMMUNICATION

The versatile chemistry of arenemanganese carbonyl complexes

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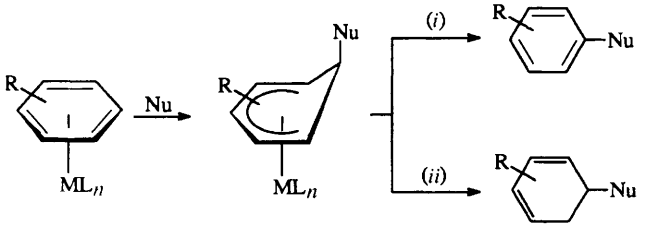
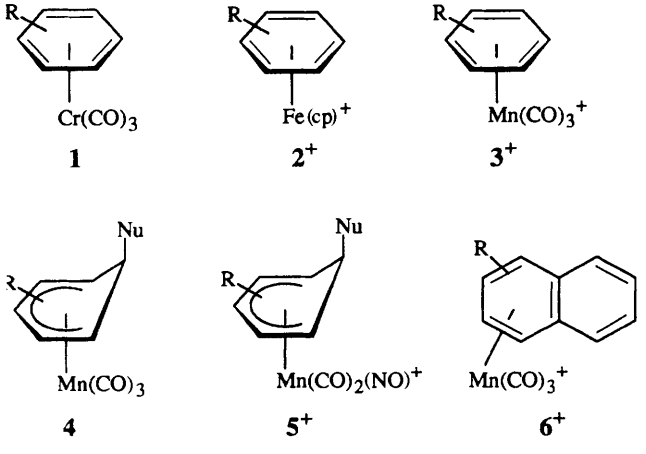
The manganese carbonyl fragment $Mn(CO)_3^+$ is easily co-ordinated to a very wide range of aromatic molecules, *e.g.* benzenes, hydroquinones, naphthalenes, indoles and benzothiophenes. The resulting air-stable [Mn(η^6-arene)$(CO)_3$]$^+$ cations are quite electrophilic, and this is the basis for much interesting and useful chemistry. Carbon-donor nucleophiles ranging from weak to strong add rapidly and regioselectively to the arene to afford thermally stable cyclohexadienyl complexes from which functionalized arenes and cyclohexadienes can be obtained after oxidative removal of the metal. Chemical reduction of [Mn(η^6-polyarene)$(CO)_3$]$^+$ with or without another metal complex present constitutes a general route to homo- and hetero-nuclear *syn*- and *anti*-facial bimetallic complexes with naphthalene-type ligands. Chemical reduction of [Mn(arene)$(CO)_3$]$^+$ (arene = η^6-benzothiophene or η^5-thiophene) leads to C–S bond cleavage and the formation of novel metallacyclic complexes of relevance to hydrodesulfurization chemistry. These and other aspects of arenemanganese carbonyl chemistry are discussed.

Arenes constitute one of the most important classes of π-hydrocarbon ligands found in organometallic chemistry. Some common examples of η^6-bonded arene complexes are shown as structures **1**–**3**$^+$. As a consequence of co-ordination to the metal, the arene ring in species such as these is electrophilically activated. Thus, nulceophiles (Nu) can react with **1**–**3**$^+$ in a number of ways, the most important of which is direct attack at the arene ring as depicted in Scheme 1. Reactions of **1** with nucleophiles have been extensively studied and useful routes to functionalized arenes and cyclohexadienes have resulted from these investigations.[1] Complexes **2**$^+$ and **3**$^+$, although less well studied than **1**, are known to react with a much wider range of nucleophiles, a fact no doubt attributable to their positive charge.[2] In order for arene complexes to be generally useful, it is necessary that (1) they are easily synthesized with a wide variety of co-ordinated arenes, (2) they react cleanly with a good range of nucleophiles, especially C-donors, and (3) the metal is easily removed at the end of the synthetic procedures. In this article we outline the chemistry of a class of compounds that nicely fulfil these requirements, namely, arenemanganese carbonyl complexes (**3**$^+$). In addition to being exceptionally versatile reagents for the chemistry depicted in Scheme 1, these manganese complexes possess a number of other intriguing properties, which are discussed below in some detail; for example, (*i*) 'reactivation' of the neutral cyclohexadienyl complex **4** by conversion into the nitrosyl analogue (**5**$^+$) allows a second nucleophilic addition; (*ii*) reduction of **3**$^+$ in the presence of a potential ligand can lead to rapid electron-transfer-catalysed carbonyl substitution; (*iii*) when the arene ligand is of the naphthalene type as in **6**$^+$ the $Mn(CO)_3^+$ moiety is readily transferred to other arenes, thereby allowing the facile co-ordination of sensitive ligands such as hydroquinones and aromatic steroids; (*iv*) controlled reduction of **6**$^+$ provides a *general* route to homo- and hetero-nuclear bimetallic complexes; (*v*) the complexes (η^6-benzothiophene)- and (η^5-thiophene)-tricarbonylmanganese(1+) undergo C–S bond cleavage upon reduction and may provide insight into hydrodesulfurization (HDS) pathways.



Scheme 1 (*i*) Oxidation; (*ii*) protonation



1 **2**$^+$ **3**$^+$ **4** **5**$^+$ **6**$^+$

Kinetic studies of nucleophilic addition to co-ordinated arenes indicate[3] (surprisingly) that the relative electrophilic reactivities do not depend on the nature of the nucleophile. This means that it is possible to quantify the ability of a transition-metal fragment to activate a co-ordinated arene. The reactivity order is: $Fe(C_6H_6)^{2+}$ (2×10^8) > $Ru(C_6H_6)^{2+}$ (6×10^6) > $Mn(CO)_3^+$ (1×10^4) > $Mn(CO)_2(PPh_3)^+$ (160) > $Fe(cp)^+$ (cp = η-C_5H_5) (1) ≫ $Cr(CO)_3$ (very small). Extremely large activating power is not necessarily desirable because the resultant arene complex may be too reactive to be easily synthesized and handled. This is the case, for example, with bis(arene)iron(2+) complexes. In contrast, the $Mn(CO)_3^+$ fragment is a good compromise; it is activating enough for most purposes while not being so much so that the arenetricarbonylmanganese(1+) complexes are prone to unwanted decomposition by solvents or by adventitious nucleophiles or reducing agents.

The $Mn(CO)_3^+$ fragment is especially versatile in that it is readily co-ordinated to a wide range of arenes, a representative list of which is provided in Table 1. The original synthetic method involved heating $Mn(CO)_5X$ (X = Cl or Br) with an

Table 1 A representative list of arenes in $[Mn(\eta^6\text{-arene})(CO)_3]^+$ complexes

C_6H_6	C_6H_5OMe	Hydroquinone
C_6Me_6	$C_6H_4(OMe)_2$-1,2	Oestrone
C_6Et_6	$C_6H_3(OMe)_3$-1,3,5	Oestradiol
$C_6H_3Me_3$-1,3,5	$(C_6H_5)_2O$	Podocarpic acid
$(C_6H_5)_2$	$(C_6H_5CH_2)_2CO$	Naphthalene
$(C_6H_5CH_2)_2$	$C_6H_5CH_2COPh$	2-Naphthol
$C_6H_5CMe_3$	$C_6H_5NMe_2$	Phenanthrene
$C_6H_5SiMe_3$	C_6H_5Cl	Indole
$C_6H_5C(Me)=CH_2$	C_6H_5Br	Dibenzofuran
Tetralin	2-Me-3-Cl-C_6H_3OMe	Thiophene (η^5)
Biphenylene	$C_6H_5Si(OCH_2CH_2)_3N$	Benzothiophene
C_6H_5OH	Catechol	Dibenzothiophene

excess of arene in the presence of $AlCl_3$ according to equation (1).[4,5] In an alternative procedure, $Mn_2(CO)_{10}$ or $Mn(CO)_5Br$

$$Mn(CO)_5X + \text{arene} \xrightarrow[AlCl_3]{\text{heat}} [Mn(\text{arene})(CO)_3][AlCl_3X] \quad (1)$$

is heated with arene in acidified trifluoroacetic anhydride solvent.[6,7] Both of these methods utilize vigorous conditions that many arenes cannot tolerate. A milder synthesis of $\mathbf{3}^+$ involves treating $Mn(CO)_5Br$ with $AgBF_4$ in CH_2Cl_2 to generate the transient $[Mn(CO)_5]^+$, which reacts with many arenes to afford moderate to good yields of $\mathbf{3}^+BF_4^-$. A detailed comparison of the relative merits and limitations of the three synthetic routes has recently appeared.[8] A fourth procedure, published in 1995,[9] utilizes tricarbonyl(η^6-polyarene)manganese(1+) as a manganese tricarbonyl transfer reagent and appears to be widely applicable (see below). An indirect method that has been useful in certain cases relies on the facile nucleophilic substitution of chloride in $[Mn(C_6H_5Cl)(CO)_3]^+$ by O-, N- and S-donor nucleophiles and has been used to generate aryl ether, aniline and aryl thioether complexes.[7,10–12]

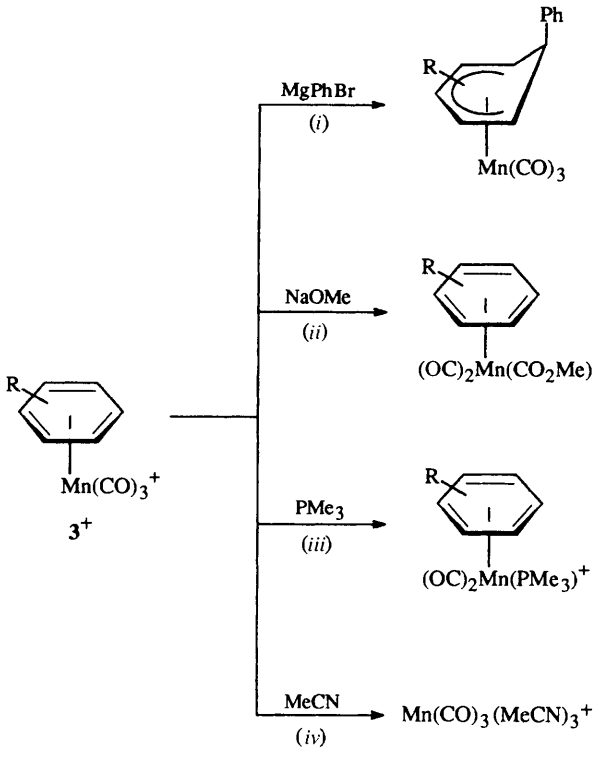
Reactions of Tricarbonyl(monoarene)manganese(1+) Complexes

A substantial amount of chemistry has been reported for complexes containing monoarenes (or unconjugated polyarenes) co-ordinated to $Mn(CO)_3^+$. In contrast, conjugated polyarenes of the naphthalene variety have only recently been successfully co-ordinated to $Mn(CO)_3^+$; the chemistry of these systems differs fundamentally from that of the unconjugated analogues and is discussed separately (see below).

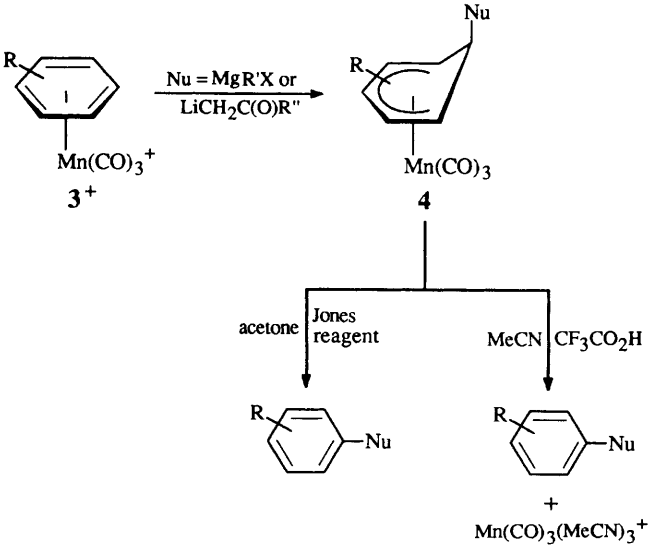
Specific examples of some of the ways complexes $\mathbf{3}^+$ can react with nucleophiles are illustrated in Scheme 2. These include (*i*) addition to the arene ring, (*ii*) addition to a co-ordinated CO, (*iii*) CO displacement and (*iv*) arene displacement. From a practical point of view it is useful to note that $\mathbf{3}^+$ rarely reacts with nucleophiles *via* single-electron-transfer or redox pathways. This is fortunate since redox processes generally lead to decomposition, a fact that plagues the chemistry of some other arene systems, notably bis(arene)iron(2+). The nucleophilic pathways in Scheme 2 are not mutually exclusive. For example, it was found[13] that PBu_3 rapidly and reversibly forms the cyclohexadienyl complex **4** (Nu = PBu_3) prior to the eventual conversion into the CO-substituted product, $[Mn(\text{arene})(CO)_2(PBu_3)]^+$. An analogous interconversion occurs with $\mathbf{3}^+$ and KCN.[14] Similarly, hydride donors in protic solvents can react with $\mathbf{3}^+$ complexes containing a heavily alkylated arene by initial attack at a CO ligand, which is then followed by migration to the arene ring.[15]

Nucleophilic addition to the arene

The most important pathway in Scheme 2 is addition to the arene and many nucleophiles are now known to react with complex $\mathbf{3}^+$ in a stereospecific manner according to pathway (*i*)

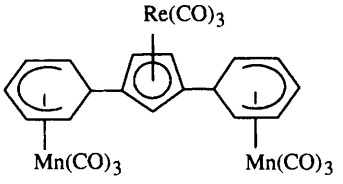


Scheme 2



Scheme 3

to give the *exo*-cyclohexadienyl products **4** which are generally quite stable thermally and can be stored indefinitely. Early work established that LiMe, LiPh and the hydride donors $NaBH_4$ and $LiAlH_4$ add to $\mathbf{3}^+$ to give **4**, although the reported yields were often moderate to poor.[5,16,17] In addition, these reactions were found to give side products resulting from attack on CO, a pathway which becomes quite significant for heavily alkylated arenes.[18] The stabilized enolate $NaCH(CO_2Et)_2$ was reported[19] to add in low yield to the arene ring in $\mathbf{3}^+$ (R = H). In another study, it was shown that the addition of cyanide ion to $[Mn(C_6H_{6-n}Me_n)(CO)_3]^+$ followed by oxidation with cerium(IV) generates free benzonitriles, $C_6H_{5-n}Me_nCN$.[14] About 1980 we became interested in examining the usefulness of $\mathbf{3}^+$ complexes for arene functionalization. It was necessary to establish the range of successful carbon-donor nucleophiles and to find a method for cleanly removing the manganese fragment from the



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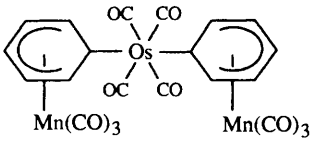

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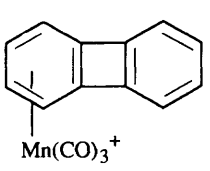
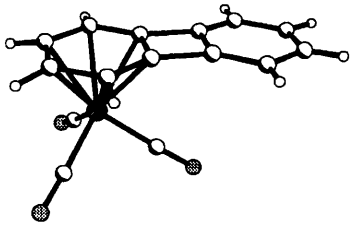
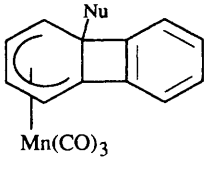


9+





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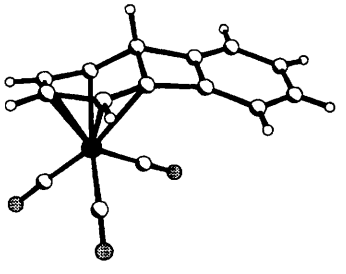


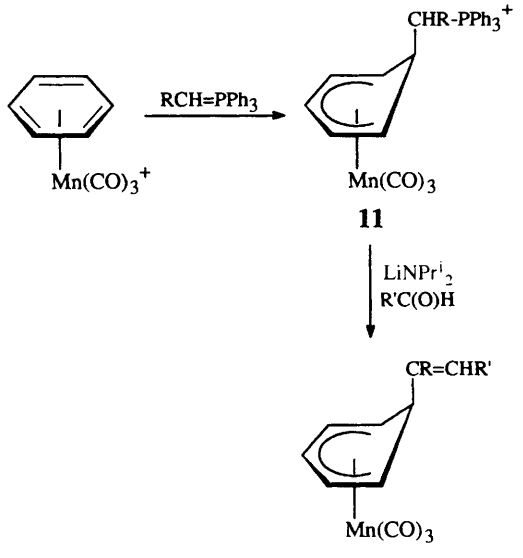
product. We found[20] that Grignard reagents and ketone enolates add rapidly and in high yield to give stable cyclohexadienyl complexes **4** according to Scheme 3. Furthermore, the metal in **4** is easily and rapidly removed by oxidation with a stoichiometric amount of Jones reagent to afford high yields of the functionalized arene. Alternatively, the functionalized arene product can be obtained by treating **4** with acid in acetonitrile. With this procedure the manganese is converted into $[Mn(CO)_3(MeCN)_3]^+$, which in principle can be isolated and recycled. Substituents R on the arene in 3^+ exert substantial directive effects in nucleophilic additions. Thus, a methoxy group, as in anisole, directs Grignard reagents and ketone enolates (and most other nucleophiles, see below) regiospecifically to a *meta* position.* Directing effects are present with other substituents (*e.g.* Cl, Me), but the regioselectivity is less marked and is dependent on the nucleophile (probably for steric reasons). When there is a choice, nucleophilic additions almost always occur at a carbon not bearing a substituent. Virtually all additions occur stereospecifically *exo* to the metal, except in certain cases with some hydride donors.[15]

Based on initial and subsequent work, it has become clear that nucleophilic addition to complex 3^+ occurs rapidly and in high yield with a good range of C-donors. The absence of decomposition resulting from single-electron transfer, the good regioselectivities observed, the thermal stability and lack of marked air sensitivity of the initial cyclohexadienyl products, and the ease of metal removal with rearomatization all point

* In contrast, ref. 17 reports that $LiAlH_4$ adds to $[Mn(C_6H_5OMe)(CO)_3]^+$ with a *meta*:*ortho* ratio of 2:1, implying only a weak preference for *meta* attack in this case.

Table 2 A representative list of nucleophiles that have been added to the arene in $[Mn(\eta^6\text{-arene})(CO)_3]^+$ to give cyclohexadienyl complexes

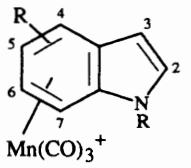
$NaBH_4$	$NaRe(CO)_5$	MgPhBr
$LiAlH_4$	$Na_2Os(CO)_4$	$NaCH(CO_2Et)_2$
$LiBEt_3H$	$AlMe_3$	$LiCH_2CO_2Bu^t$
KCN	Na(cp)	$LiCH_2C(O)CMe_3$
PBu_3	LiMe	$LiCH_2CN$
$P(OMe)_3$	LiPh	$LiCMe_2CN$
$NaPO(OMe)_2$	MgMeCl	Born-2-yl acetate enolate
$CH_2{=}PPh_3$	MgEtBr	4-Methyl-5-phenyl-3-propanoyl-1,3-oxazolidin-2-one enolate



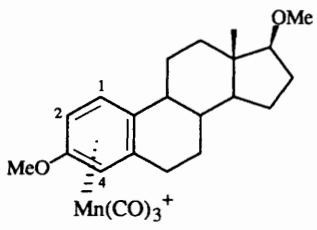
Scheme 4

to the manganese system as being superior for arene functionalization. From a practical point of view, it may be noted that nucleophilic addition to 3^+ is very easily monitored by the large shifts that occur in the IR ν_{CO} bands. A representative sample of the nucleophiles that have been added to $[Mn(arene)(CO)_3]^+$ is given in Table 2. Some rather unusual and interesting multimetallic compounds have recently been synthesized in this manner, structures **7** and **8** being two examples.[21,22] Another unusual system is (biphenylene)tricarbonylmanganese(1+) 9^+, which is atypical of 3^+ complexes in that nucleophiles attack a substituted carbon (the bridgehead) to give **10** [Nu = H, Me, $CH_2C(O)CMe_3$ or $P(OR)_3$]. This regiospecificity is probably due to a relaxation of steric constraints at the bridgehead that accompanies formation of the dienyl product, as can be seen in the structure of **10** (Nu = H).[23] Interestingly, the chemistry of 9^+ is fundamentally different from that of the naphthalene analogues, 6^+ (see below).

Manganese-mediated arene functionalization of the type in Scheme 3 has been used to synthesize antibiotic stilbenes.[24] The addition of chiral enolate nucleophiles to 3^+ has provided a route to 2-arylpropionic acids and arylglycine derivatives.[25] Asymmetric nucleophilic additions to 3^+ containing a substituent functioning as a chiral auxiliary have been reported to occur with substantial diastereoselectivity.[26] Phosphorus ylides, $RCH{=}PPh_3$, react with $[Mn(C_6H_6)(CO)_3]^+$ as shown in Scheme 4.[27] The stable phosphonium salt **11** is deprotonated with $LiNPr^i_2$ to produce an organometallic ylide, which undergoes a Wittig reaction with aldehydes as indicated. Another application of arenemanganese chemistry concerns the functionalization of the carbocyclic ring in the indole nucleus.[28] Indoles co-ordinate to $Mn(CO)_3^+$ through the carbocyclic and not the pyrrole ring, as shown in structure 12^+. Owing to the electron-rich pyrrole ring, free indoles are difficult to functionalize at the C^4 to C^7 positions by conventional methods. However, the

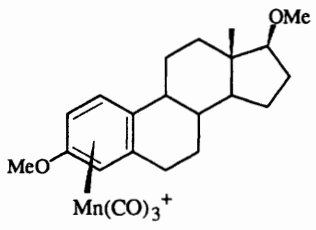


12^+



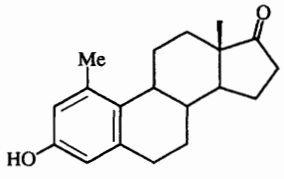
α isomer

13^+



β isomer

14^+



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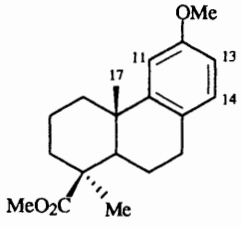

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metal in 12^+ selectively activates the carbocyclic ring to nucleophilic attack, especially at positions C^4 and C^7, so that C-donors react in good yield to give a mixture of the two isomeric cyclohexadienyl products. The selectivity for attack at C^4 *versus* C^7 can be controlled by variation of the size of the R group on the pyrrole nitrogen. For example, with $LiCMe_2CN$ as the nucleophile, an $SiPr^i_3$ group on the nitrogen effectively blocks the C^7 position so that addition occurs exclusively at C^4.

It appears from initial work that arenemanganese chemistry may be useful for the functionalization of aromatic steroids and related natural products. Thus, 3,17-di(methyl ether)oestradiol co-ordinates to manganese to form nearly equal amounts of α and β isomers (13^+ and 14^+).[29] Nucleophiles add to the β isomer regiospecifically *meta* (C^1) while a distribution of C^1, C^2 and C^4 additions occurs with the α isomer, as illustrated in Fig. 1. This difference in selectivity is related to tripodal carbonyl interactions with the steroidal backbone. A simple example of the utility of this chemistry is the facile conversion of the steroid oestrone into 1-methyloestrone **15** in an overall 42% isolated yield by the following sequence of steps: protection of the ketone group in oestrone, complexation of $Mn(CO)_3^+$, addition of MgMeCl to the C^1 position, and deprotection of the ketone. This procedure is easily accomplished in about ten hours and, due to cost considerations, is an attractive alternative to purchasing the product (oestrone, $10 per g; 1-methyloestrone, $45 per 5 mg; Steraloids Inc., Wilton, NH). Manganese-mediated reactions analogous to those with the aromatic steroids have been applied to the dimethylated derivative of podocarpic acid **16**, an abundant diterpenoid resin acid available in high purity from the New Zealand rimy and kahikatea trees. It is of substantial interest as a possible precursor to other diterpenes and C-ring aromatic steroids.[30] The ion $Mn(CO)_3^+$ co-ordinates to the α and β faces of **16** in a nearly 1:1 ratio and activates the aromatic ring to attack by a good range of nucleophiles to afford cyclohexadienyl complexes.[31] The α isomer is attacked regiospecifically at the *meta* position (C^{14}) but the β isomer adds nucleophiles with the regioselectivity *ortho* (C^{13}) > *meta* (C^{14}) ≫ *ortho* (C^{11}). Normally, attack at a site *ortho* to an OMe substituent is rare in 3^+ complexes unless steric factors intervene. In the case of the β isomer of tricarbonyl(podocarpic acid)manganese(1+), X-ray structural studies[31] clearly indicate that the steric interaction of relevance is between Me-17 and a carbonyl ligand, as illustrated in Fig. 2. The key to understanding this is the observation that the CO tripodal orientation in all manganese cyclohexadienyl complexes examined to date is such that one CO eclipses the saturated carbon; this must be the electronically favoured conformation. Fig. 2 shows the structure of a β-*meta* and a β-*ortho* product. For electronic reasons, the former, but not the latter, is forced to position a CO close to Me-17; the resulting steric contact is manifested in a slightly bent Mn–C–O angle (173°). In effect, there is a balance between electronic factors (favouring *meta* to OMe) and steric factors (favouring *ortho*). The α isomer does not impose steric constraints to attack at either site and, accordingly, the position *meta* to OMe is overwhelmingly favoured.

Non-nucleophilic bases such as $LiNPr^i_2$, KH or $KOBu^t$ may deprotonate appropriate arene substituents in 3^+ complexes. For example, base converts $[Mn(C_6H_5OH)(CO)_3]^+$ into the oxocyclohexadienyl complex **17**, which then undergoes sequential nucleophilic and electrophilic addition to form **18**.[32] Oxidative removal of the metal from **18** produces *ortho*-substituted arenes. Of more general synthetic utility is the discovery[33] that single and double deprotonation of $[Mn(C_6Me_6)(CO)_3]^+$ and related species proceeds smoothly to give 'benzyl' (**19**) and 'xylylene' (**20**) complexes. Electrophilic reagents (H^+, Br_2, PhCOCl, CCl_4, $MeOSO_2CF_3$, *etc.*) react with **19** and **20** by simple combination as well as radical pathways to generate new arene complexes.

Double nucleophilic addition

Most hydride donors react with complex 3^+ to produce cyclohexadienyl complexes **4**; however, very strong donors, such as $LiBEt_3H$, undergo a 'double addition' according to Scheme 5.[34] The diene anion **21** is protonated to the cyclohexenyl complex **22**, which contains an agostic three-centre two-electron C–H···Mn bond. Oxidation of **21** with oxygen liberates the free cyclohexadiene. The addition of a C-donor nucleophile to **4** would constitute overall double addition to a co-ordinated arene and provide a direct route to disubstituted cyclohexadienes. This approach is limited by the weak electrophilicity of **4**, with the result that many convenient nucleophiles (stabilized enolates, ketone enolates, Grignard reagents, *etc.*) do not react. However, strong nucleophiles do react with **4** in one of two ways. The hard bases LiMe and LiPh attack a CO ligand in **4** to give acylmetalates **23**.[35] Acid induces migration of the R′ group to the *endo* face of the cyclohexadienyl ring to afford mixtures of isomeric cyclohexenyl complexes analogous to **22**, from which cyclohexadienes can be obtained after decomplexation from the metal. Strong ester, nitrile and sulfur-stabilized lithium carbanions add directly to the ring in **4** to give transient anionic tricarbonyl(cyclohexadiene)manganate(1−) species that react with oxygen to afford good yields of *cis*-disubstituted cyclohexadienes.[36]

The dienyl ring in complex **4** can be rendered receptive to nucleophiles of varying strengths, including fairly weak ones, by 'reactivating' the complex *via* treatment with a nitrosonium salt, *e.g.* $NOBF_4$. This affords the cationic nitrosyl analogue 5^+, which turns out to be more electrophilic than $[Mn(arene)(CO)_3]^+$ and reacts with nucleophile Nu′ to give the diene **24**. The overall transformation $3^+ \longrightarrow 4 \longrightarrow 5^+ \longrightarrow 24$ amounts to double nucleophilic addition to an arene to yield functionalized cyclohexadiene complexes.[37] When the second nucleophile (Nu′) is hydride high yields of diene complex **24** are obtained;

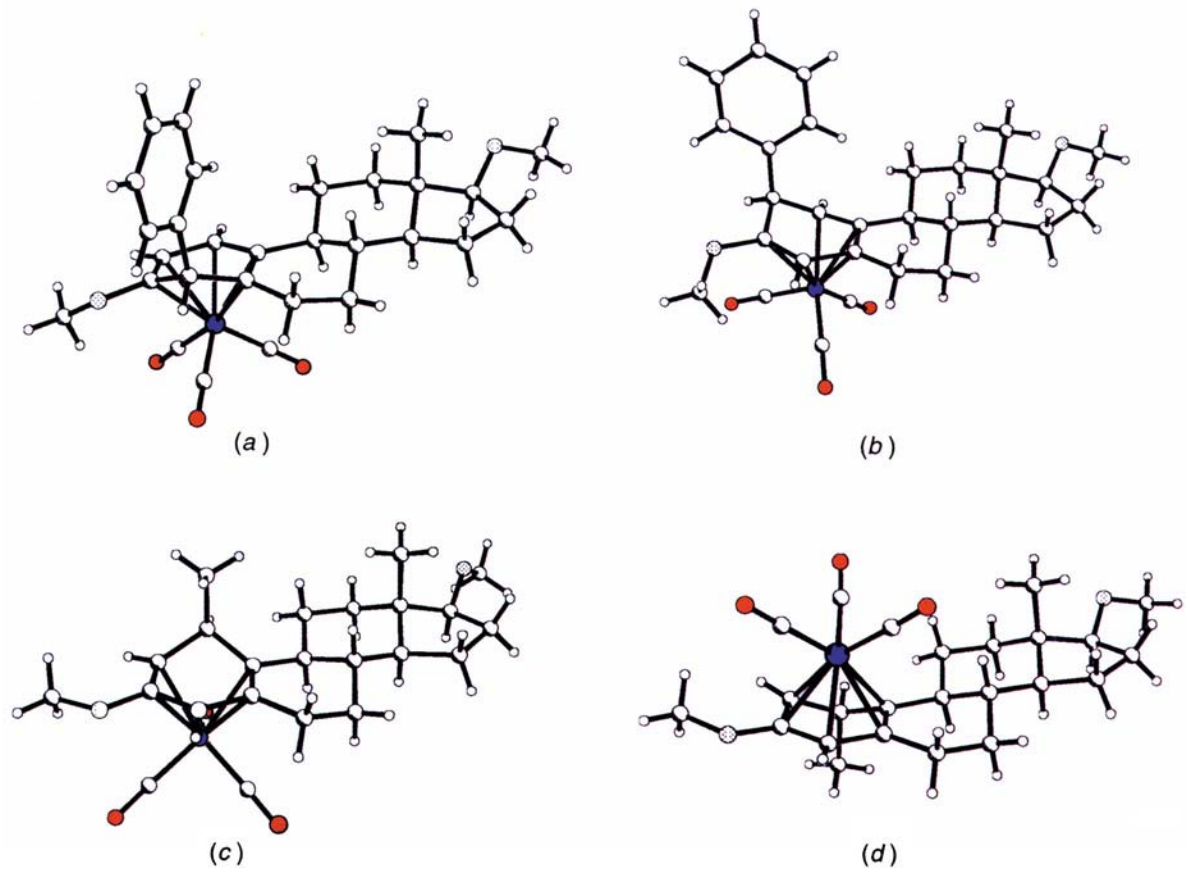


Fig. 1 Cyclohexadienyl products obtained from nucleophilic addition to tricarbonyl(oestradiol dimethyl ether)manganese(1+). The nucleophile, its position relative to the OMe group, and the position of the metal are as follows: (*a*) Ph, *o*-C^4, α; (*b*) Ph, *o*-C^2, α; (*c*) Me, *m*-C^1, α; (*d*) Me, *m*-C^1, β

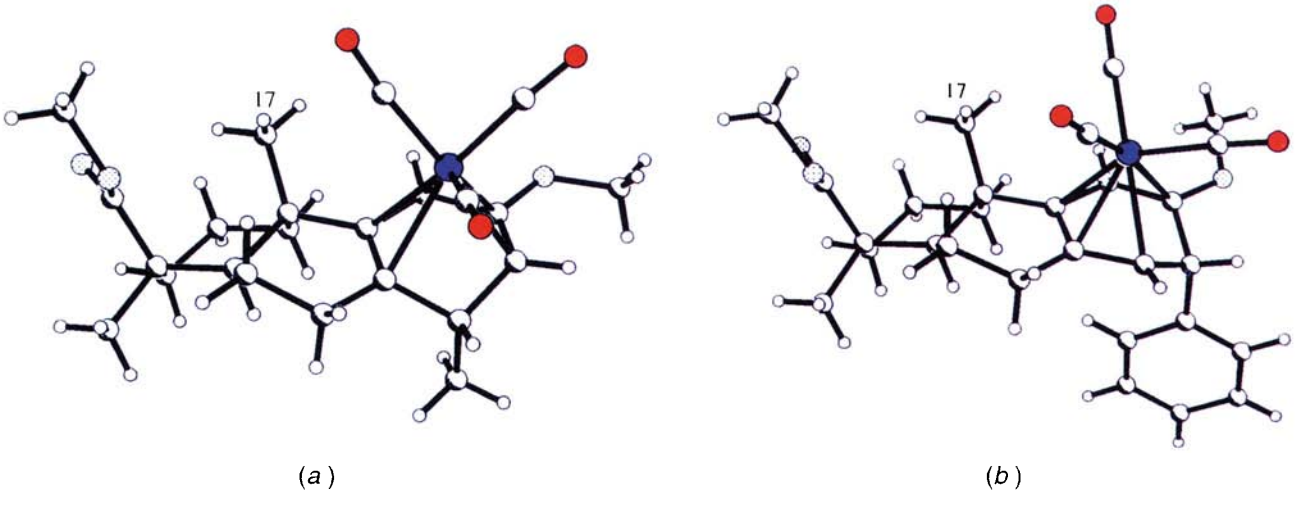
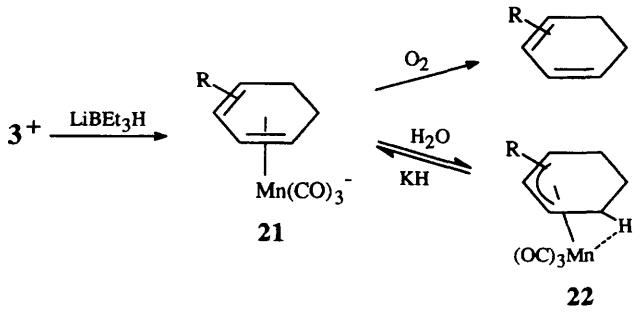


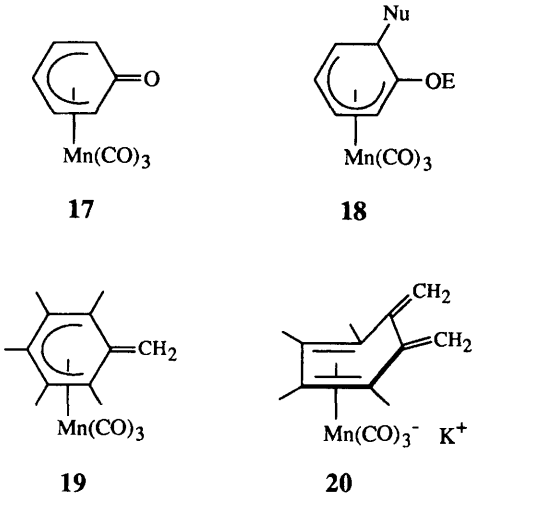
Fig. 2 Structures of two cyclohexadienyl complexes obtained from nucleophilic addition to tricarbonyl(podocarpic acid)manganese(1+). The nucleophile and its position relative to the OMe group are as follows: (*a*) Me, *m*-C^{14}; (*b*) Ph, *o*-C^{13}

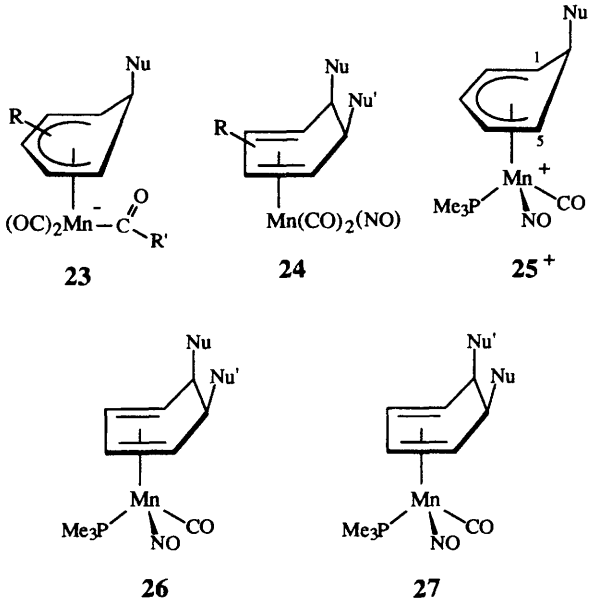
this procedure has been used to synthesize the sesquiterpene (+)-juvabione.[38] Decomplexation of the diene from **24** can be accomplished with a variety of oxidizing agents. Carbon-donor nucleophiles (Nu′) generally give poor yields of **24** due to interfering redox pathways, although certain donors (LiPh, LiMe) attack $\mathbf{5}^+$ at a CO ligand to give acyl species that spontaneously decompose to *trans*-disubstituted cyclohexadienes.[35,39] The role of redox pathways in the addition of C-donors to $\mathbf{5}^+$ is diminished by replacing a CO ligand with a phosphine. Thus, stabilized enolates react with $\mathbf{25}^+$ to give good yields of *cis*-disubstituted cyclohexadiene complexes.[40] Owing to the chiral metal centre in $\mathbf{25}^+$, positions C^1 and C^5 are chemically inequivalent and nucleophilic addition produces the diastereomers **26** and **27**, which have been separated and structurally characterized for the combination Nu = Ph, Nu′ = $CH(CO_2Me)_2$.[41] The diastereoselectivity for C^1 *versus* C^5 attack in $\mathbf{25}^+$ is only modest, but the fact that the diastereomers are separable means that this chemistry provides a route to enantiometrically pure *cis*-disubstituted cyclohexadienes, provided the original cation, $\mathbf{25}^+$, can be resolved.

Most nucleophiles add in a stereospecific *exo* manner to $[MnR(CO)(NO)L]^+$ (R = cyclohexadienyl), yielding a *cis*-disubstituted diene as in **24**. Surprisingly, however, hydride donors add stereospecifically *endo* regardless of the nature of L

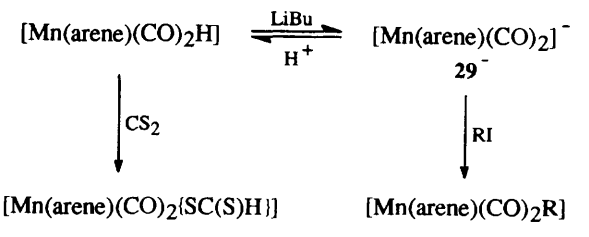


Scheme 5





or the hydride donor. Hydride addition is also *endo* with the rhenium analogues and with manganese cycloheptadienyl analogues. A mechanistic study[39] of this reaction indicated that hydride initially attacks a CO ligand to generate a formyl intermediate, which transforms to a metal hydride species prior to migration to the *endo* side of the cyclohexadienyl ring. Direct migration of H^- from the formyl group to the ring does not occur. The metal hydride intermediate is thought to have a bent nitrosyl in order to maintain an 18-electron count at the metal. When no CO ligand is present, as in [Mn(C_6H_6Ph-*exo*-6)-



Scheme 6

(NO)(dppe)]$^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$), hydride attacks in an *exo* fashion.

Chemistry of [Mn(monoarene)(CO)$_2$L]$^{n+}$ (L ≠ CO)

A variety of arenemanganese complexes are known for which one of the CO ligands is replaced. A phosphine or phosphite readily substitutes for a CO in **3**$^+$, under photolytic conditions or *via* treatment with Me_3NO in the presence of PR_3, to give [Mn(arene)(CO)$_2$(PR_3)]$^+$ **28**$^+$.[13,42,43] As would be expected, **28**$^+$ shows reduced arene-ring electrophilicity in comparison to its tricarbonyl precursor. A recent study shows that electrophiles (E^+) react with [Mn(arene)(CO)$_2$(CN)] by bonding to the nitrogen according to equation (2).[44] The electrophiles that were used

$$[Mn(arene)(CO)_2(CN)] + E^+ \longrightarrow [Mn(arene)(CO)_2(CNE)]^+ \quad (2)$$

in this reaction include alkyl triflates (trifluoromethanesulfonates), which produce stable isocyanide complexes. The interesting bimetallic [Mn(arene)(CO)$_2$(CN)–Mn(CO)$_5$] is the product of the reaction with [Mn(CO)$_5$]$^+$. The halides [Mn(arene)-(CO)$_2$X] (X = Cl, Br or I), made by photolysis of **3**$^+$ in the presence of NaX, are useful precursors to other complexes.[42,45] Equations (3) and (4) are two examples; the complex [Mn(C_6-

$$[Mn(C_6Me_6)(CO)_2I] + NaBH_4 \longrightarrow [Mn(C_6Me_6)(CO)_2H] \quad (3)$$

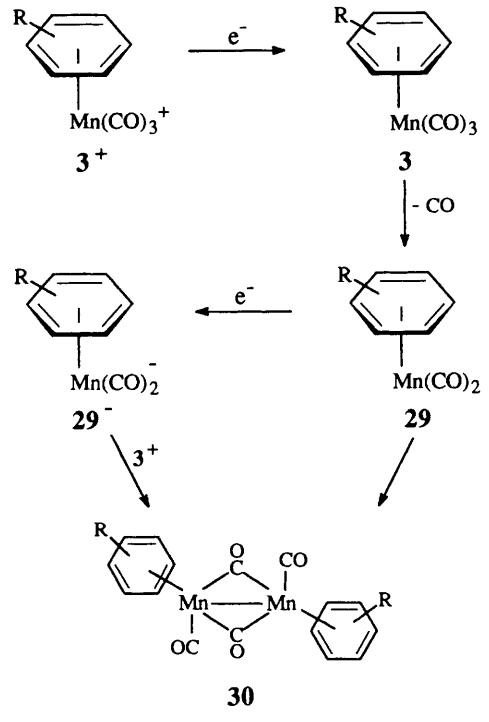
$$[Mn(C_6Me_6)(CO)_2Br] + LiMe \longrightarrow [Mn(C_6Me_6)(CO)_2Me] \quad (4)$$

Me_6)(CO)$_2$H] was the first isolable η^6-arene metal carbonyl hydride.[45] It, as well as its C_6H_6 analogue, is quite stable and only reluctantly does the hydride ion undergo formal migration to the arene ring by a mechanism that is not understood.[46,47] As shown in Scheme 6, the hydride inserts CS_2 to give dithioformate complexes.[48] Deprotonation gives the carbonyl anion **29**$^-$, which is readily alkylated to [Mn(arene)-(CO)$_2$R].[46] In a most interesting reaction, **29**$^-$ was found to react with [Mn(arene)(CO)$_3$]$^+$ to give the dimeric species **30** (see below).[15]

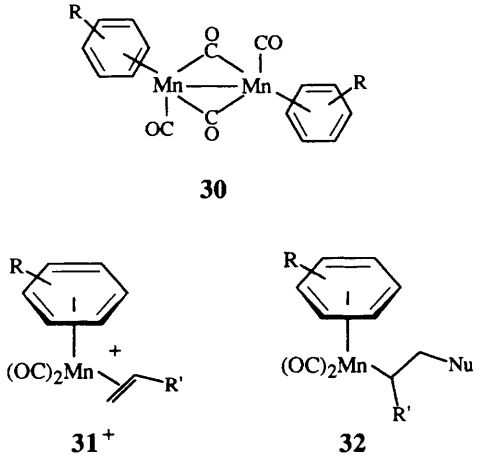
Addition of Me_3NO to complex **3**$^+$ in tetrahydrofuran (thf) affords the purple [Mn(arene)(CO)$_2$(thf)]$^+$, which is a convenient precursor to other complexes because the thf is easily replaced by a variety of ligands.[49,50] For example, alkenes displace the thf to form **31**$^+$, which in turn has significant synthetic potential because nucleophiles react rapidly at the alkene to produce high yields of alkyl complexes **32**. There is the possibility of arene functionalization by this route if the alkyl moiety can be induced to migrate to the arene.[46]

Electron-transfer chemistry of [Mn(monoarene)(CO)$_3$]$^+$

The chemical and electrochemical reduction of complex **3**$^+$ has been examined by several groups, with results that are quite variable. The reduction of [Mn(C_6Me_6)(CO)$_3$]$^+$ **33**$^+$ with the dihydronaphthylide $KC_{10}H_8$ and of [Mn(C_6H_6)(CO)$_3$]$^+$ **34**$^+$ with Na–NH_3 is reported[15,51] to form the dimer **30**; the same product



Scheme 7



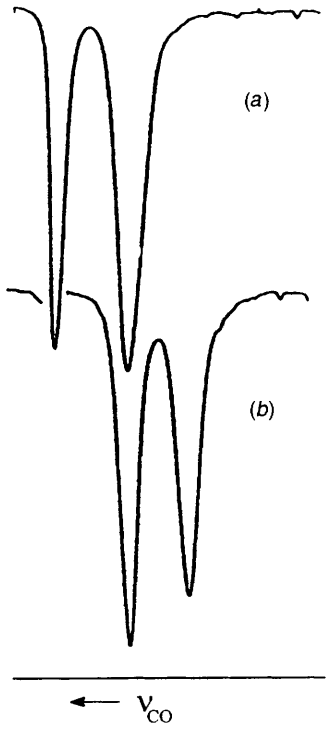
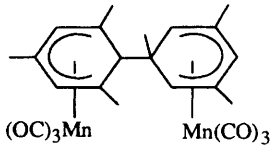
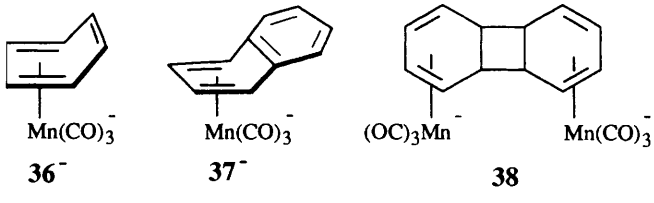


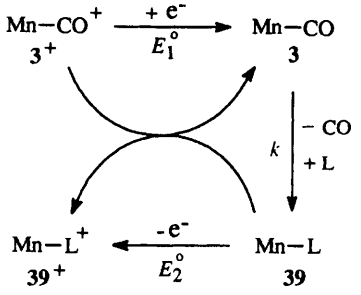
Fig. 3 The IR spectrum of 1 mmol dm^{-3} $[Mn(C_6Me_6)(CO)_3]^+$ and 1.5 mmol dm^{-3} $P(OBu)_3$ in CH_2Cl_2. Spectrum (*a*) is before and (*b*) after a current supplied 0.03 equivalent of electrons; (*b*) corresponds to $[Mn(C_6Me_6)(CO)_2\{P(OBu)_3\}]^+$



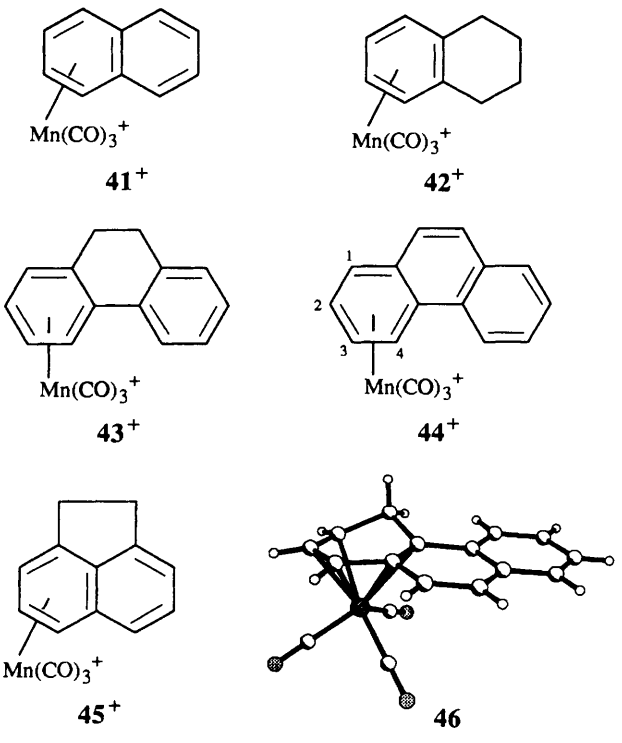


results when 33^+ is treated with $[Mn(C_6Me_6)(CO)_2]^-$. An electrochemical study, supported by infrared-OTTLE (optically transparent thin-layer electrode) experiments and digital simulations, established that the reduction of 3^+ (arene = C_6Me_6, $C_6H_3Me_3$-1,3,5, C_6H_6) in CH_2Cl_2 also leads to **30**; the mechanism shown in Scheme 7 was proposed.[52] In this mechanism the 19-electron radical **3** dissociates a CO to give the 17-electron **29**, from which the dimer **30** can form by direct coupling or by initial (spontaneous) reduction to the 18-electron 29^- and reaction with the starting material, 3^+. Treatment of $[Mn(C_6H_3Me_3$-1,3,5$)(CO)_3]^+$ with $AlEt_3$ was found to lead to reduction as well as simple addition of an ethyl group to the ring.[53] In this case, however, the reduction product was shown to be the bis(cyclohexadienyl) bimetallic complex **35**, or an isomer thereof. In another study, reduction of 34^+ with $KC_{10}H_8$ in thf at −78 °C produced the slipped η^4-C_6H_6 complex 36^-, which proved difficult to isolate due to facile exchange with the naphthalene coproduct to afford the more stable η^4 analogue 37^-, the structure of which was verified by X-ray diffraction.[54] Reduction of 34^+ with $K[C_{10}H_6Bu^t_2$-2,6] or with $KC_{10}H_8$ under certain circumstances led to the tetrahydrobiphenylene complex **38**.[55] It is proposed that **38** is formed from 34^+ *via* reduction of an initially generated bis(cyclohexadienyl) dimer analogue to **35**, which itself, in MeCN as the solvent, is the product of the reaction of 34^+ and 36^-. The conclusion from all of these studies is that the product(s) obtained when 3^+ cations are reduced depends markedly on the reaction conditions (reducing agent, solvent, temperature, *etc.*).

When a P-donor such as $P(OBu)_3$ or PPh_3 is present, the coupling, dimerization and ring-slippage reaction pathways that occur when complex 3^+ is reduced are short circuited in favour of an electron-transfer-catalysed substitution to give $[Mn(arene)(CO)_2(PR_3)]^+$ 39^+.[52] For example, Fig. 3 shows that the application of a reducing current for a few seconds (corresponding to 0.03 equivalent of electrons) is sufficient to quantitatively convert $[Mn(C_6Me_6)(CO)_3]^+$ (*a*) into the substitution product $[Mn(C_6Me_6)(CO)_2\{P(OBu)_3\}]^+$ (*b*). A trace of a chemical reducing agent may be used to effect the same substitution. The relevant electron-transfer-catalysed mechanism for this chemistry is outlined in Scheme 8. In this mechanism reduction of Mn–CO$^+$ 3^+ to the 19-electron Mn–CO greatly facilitates dissociatively activated substitution to afford Mn–L **39**.[56] As expected, Mn–L is more easily oxidized than is Mn–CO ($E_1^\circ > E_2^\circ$), and this means that Mn–L will be spontaneously oxidized to Mn–L$^+$, either at an electrode surface and/or homo-



Scheme 8



geneously *via* reaction with Mn–CO$^+$. Either way, a catalytic cycle results, the success of which depends on the conversion of Mn–CO into Mn–L being rapid.

A comparison of manganese and rhenium with respect to electron-transfer-induced carbonyl substitution has been reported.[52] The behaviour of [Re($C_6H_3Me_3$-1,3,5)$(CO)_3$]$^+$ **40**$^+$ was found to differ fundamentally from that of the manganese analogue. Thus, **40**$^+$ is reduced in a chemically reversible two-electron step that is not affected by the presence of a P-donor ligand. An analysis of electrochemical results indicates that **40**$^+$ is reduced to the 19-electron **40**, which then undergoes a (relatively) slow and spontaneous second reduction as the arene slips to η^4 bonding. From this one can infer that the rate of dissociation of CO in the 19-electron complexes [M(arene)$(CO)_3$] is in the order Mn ≫ Re.

Reactions of Tricarbonyl(polyarene)manganese(1+) Complexes

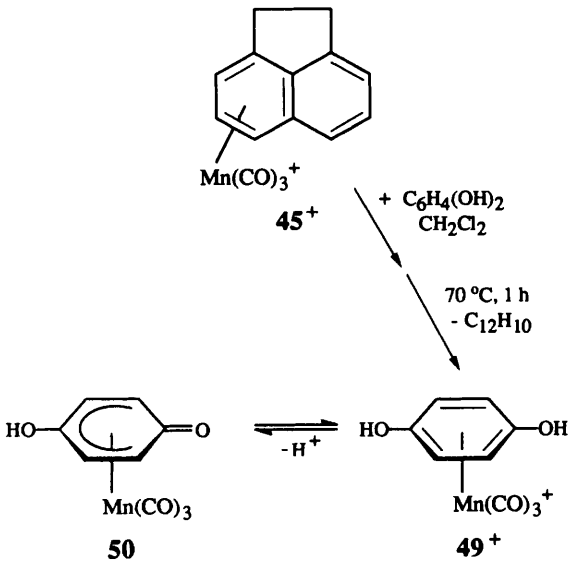
In analogy to monoarenes, one would anticipate that conjugated fused-ring polyarenes such as naphthalene and phenanthrene could be co-ordinated to $Mn(CO)_3^+$ without any particular difficulty. However, for the most part this turns out not to be the case. For example, all of the synthetic methods mentioned above that are successful with monoarenes failed with naphthalene, with at most a trace of the desired product **41**$^+$ being identified.[8,57] Interestingly, the attempted synthesis of **41**$^+$ using the $AlCl_3$–$Mn(CO)_5Br$ method in equation (1) produced only the hydrogenated (tetralin) complex **42**$^+$; similarly, attempted co-ordination of phenanthrene led to **43**$^+$ rather than **44**$^+$ as the primary product. We recently found, however, that polyarenes can be co-ordinated to $Mn(CO)_3^+$ in good yields by the $AgBF_4$–$Mn(CO)_5Br$ method (see above) provided all reagents and glassware are thoroughly dried and contact with donor solvents is avoided.[9] Thus, the phenanthrene complex **44**$^+$, as well as a series of naphthalene analogues, were prepared in yields of 70–90% and found to be stable in the solid state under N_2. The acenaphthene complex **45**$^+$, which is easily and inexpensively made, was found to be a particularly useful reagent in subsequent reactions (see below). The polyarene complexes undergo clean nucleophilic addition reactions in a regioselective manner with a range of C- and H-donors.[58] For example, the mild hydride donor [NBu_4][BH_3(CN)] adds to **44**$^+$ at the C^4 and C^1 positions in a ratio of 2:1 and combined yield of 92%; the C^4 addition product is shown as structure **46**.

The complexes with naphthalene-type ligands as well as those with η^6-benzothiophene, dibenzothiophene and dibenzofuran ligands (see below) undergo ready displacement with donor solvents.[9] Equation (5) shows the reaction with

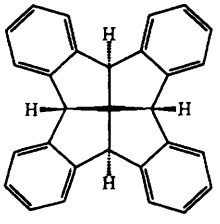
$$[Mn(polyarene)(CO)_3]^+ + 3\ MeCN \longrightarrow [Mn(CO)_3(MeCN)_3]^+ + polyarene \quad (5)$$

acetonitrile. Half-lives at 25 °C in CH_2Cl_2 containing 1.0 mol dm^{-3} MeCN are in the order: polyarene = naphthalene (1 min) < acenaphthene (2 min) < phenanthrene (50 min) ≤ benzothiophene (55 min) < dibenzothiophene (250 min). It is possible to compare this reactivity to that found[13] for the analogous reaction of [Mn(C_6H_5Me)$(CO)_3$]$^+$ **47**$^+$ which is calculated to have a half-life of *ca.* 4 years! This reactivity difference most likely is due to easier $\eta^6 \longrightarrow \eta^4$ ring slippage in the polyarene complexes, which accompanies associative attack by MeCN at the metal. A similar interpretation has been presented to explain the rate of arene displacement by P-donors from [Cr(arene)$(CO)_3$] complexes, which also follows the reactivity order arene = naphthalene > phenanthrene ≫ benzene.[59] The important reactivity factor is the change in resonance energy (ΔRE) upon the $\eta^6 \longrightarrow \eta^4$ ring slippage. It follows the order: benzene (84 kJ) > phenanthrene (59 kJ) > naphthalene (44 kJ). Indeed, the rough assumption that changes in ΔRE are completely responsible for the relative reactivity of **41**$^+$, **44**$^+$ and **47**$^+$ predicts a half-life order that closely approximates the observed reactivities.

The ease with which the polyarene complexes undergo arene displacement by donor solvents suggested that they would be effective at transferring the $Mn(CO)_3^+$ moiety to other arenes, *i.e.* they would function as manganese tricarbonyl transfer reagents. (In analogy, naphthalene- and *N*-methylpyrrole-tricarbonyl chromium are known to function as chromium tricarbonyl transfer reagents.[60]) Indeed, it was found that simply heating **41**$^+$ or **45**$^+$ for about 1 h in dichloromethane containing only a slight excess of any of a number of arenes leads to clean substitution and liberation of the polyarene. Not surprisingly, the ease of $Mn(CO)_3^+$ transfer from the polyarene complexes to an arene correlates with the rate of reaction with MeCN, equation (5). With respect to the yield and time of reaction, any of the naphthalene-type complexes are excellent $Mn(CO)_3$ transfer reagents. However, when the cost of the presursor polyarene and the ease of complexation to $Mn(CO)_3^+$ are considered, 1-methylnaphthalene and acenaphthene are the reagents of choice. One can speculate that chiral $Mn(CO)_3$ transfer reagents such as (binaphthol)tricarbonylmanganese(1+) may allow enantioselective π complexation of appropriate arenes.[61] The important point to note is that the synthesis of [Mn(arene)$(CO)_3$]$^+$ complexes *via* $Mn(CO)_3$ transfer reagents constitutes an exceptionally mild procedure and



Scheme 9



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can be utilized to co-ordinate arenes that fail to react satisfactorily by other available methods (see above) due to the presence of sensitive functional groups or for other reasons. Examples include many phenylacetylenes, phenols, anilines and certain aromatic steroids,[7] as well as centropolyindans such as fenestrindan **48**.[62]

An especially interesting example of the use of an $Mn(CO)_3$ transfer reagent is in the high-yield synthesis of hitherto unavailable π-bonded η^6-hydroquinone (and catechol) manganese complexes, as outlined in Scheme 9.[63] In general, the transition-metal chemistry of π-bonded hydroquinones and 1,4-semiquinones is little developed, a fact attributable to difficulty in synthesis and/or high reactivity. In the case of catechol and 1,2-semiquinones, metals almost always bind *via* the oxygens and not the π network. It was found, however, that hydroquinone and catechol give stable π complexes with $Mn(CO)_3^+$ when treated with an $Mn(CO)_3$ transfer reagent. Furthermore, these complexes are readily deprotonated to afford the π-semiquinone analogues. Repeated attempts to grow X-ray-quality crystals of $\mathbf{49}^+BF_4^-$ were unsuccessful. However, an acetone solution of $\mathbf{49}^+BF_4^-$ containing a small amount of HBF_4 (to suppress dissociation to **50**) deposited well formed crystals of $\mathbf{49}^+_2SiF_6^{2-}$ over a period of several months at −20 °C. This presumably resulted from the action of HBF_4 on the glass container to produce a continuous supply of SiF_6^{2-} anions at low concentration, a necessary condition for crystal growth because $\mathbf{49}^+_2SiF_6^{2-}$ is virtually insoluble in acetone. The most interesting structural feature is the strong hydrogen bonding that exists between each OH group and an F atom. Four of the six F atoms in each SiF_6^{2-} are strongly hydrogen bonded; the other two are not because there are not enough donors. The extensive hydrogen-bonding network effectively dictates the beautiful structural pattern shown in Fig. 4[63] and accounts for the insolubility in acetone (the BF_4^- salt is quite soluble).

The electrochemistry of the polyarene complexes $\mathbf{6}^+$ differs

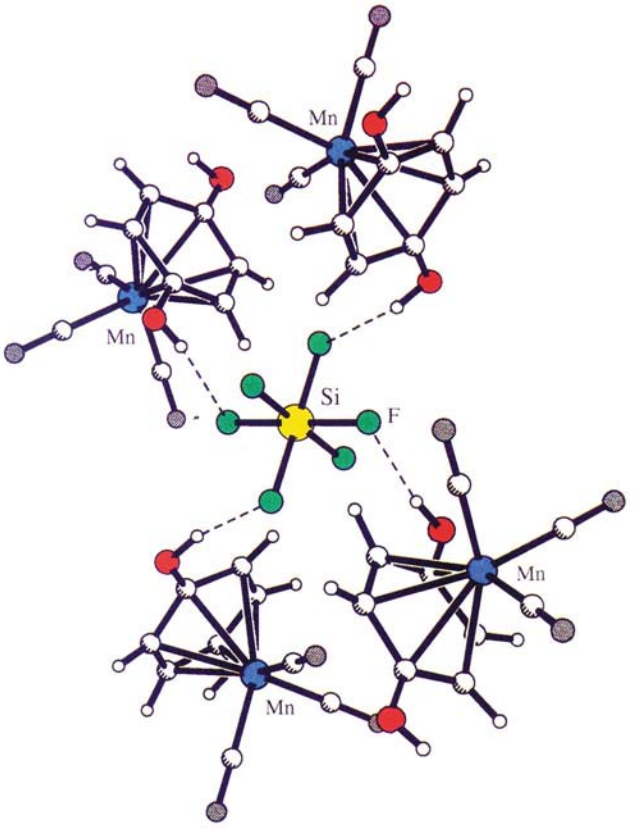


Fig. 4 The hydrogen-bonding network present in $[Mn\{C_6H_4(OH)_2\text{-}1,4\}(CO)_3]_2[SiF_6]$ $\mathbf{49}^+$

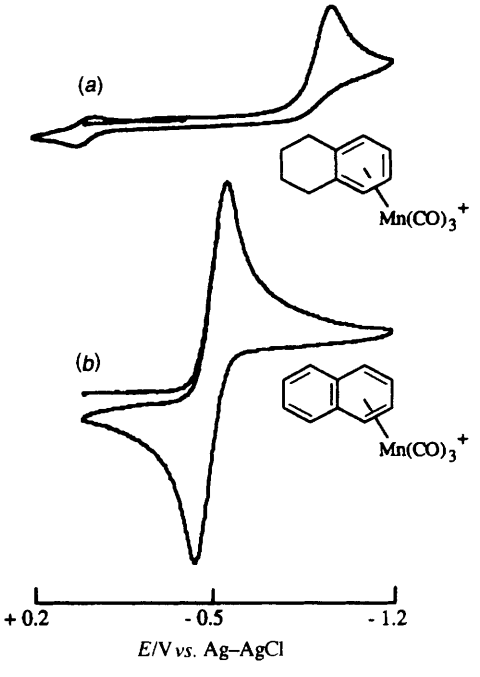


Fig. 5 Cyclic voltammograms of (*a*) 1.0 mmol dm^{-3} tricarbonyl(tetralin)manganese(1+) $\mathbf{42}^+$ and (*b*) 1.0 mmol dm^{-3} tricarbonyl(naphthalene)manganese(1+) $\mathbf{41}^+$ in CH_2Cl_2–0.10 mol dm^{-3} $NBu_4^nPF_6$ at 25 °C. The scan rate was 0.50 V s^{-1} and the potentials are relative to ferrocene, $E_{\frac{1}{2}} = 0.52$ V

fundamentally from that of the monoarene analogues $\mathbf{3}^+$, as illustrated in Fig. 5.[64] Thus, whereas $\mathbf{3}^+$ complexes generally suffer one-electron irreversible reductions [Fig. 5(*a*)], $\mathbf{6}^+$ undergo chemically reversible two-electron reductions to afford η^4-diene complexes analogous to $\mathbf{37}^-$ [Fig. 5(*b*)]. The much easier

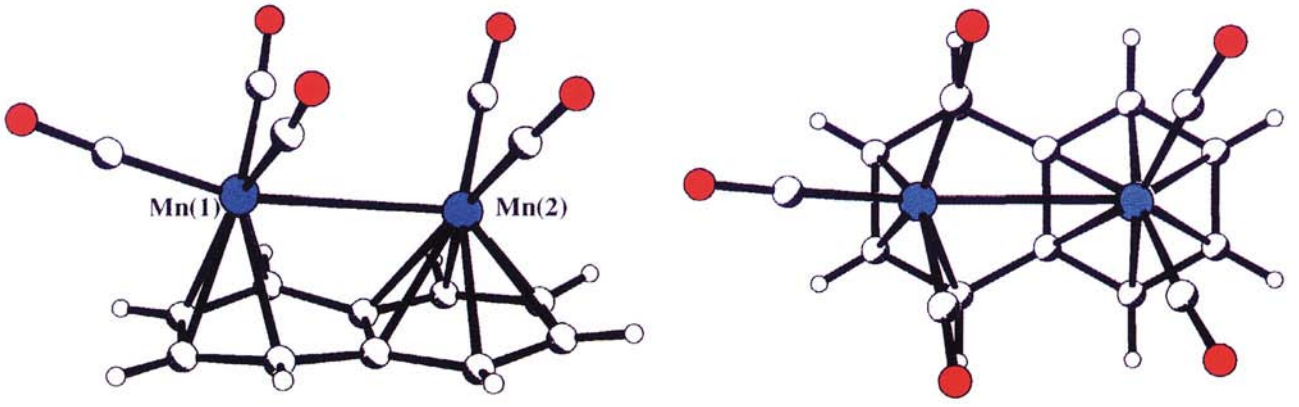
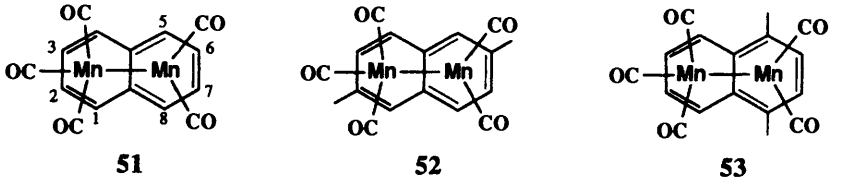
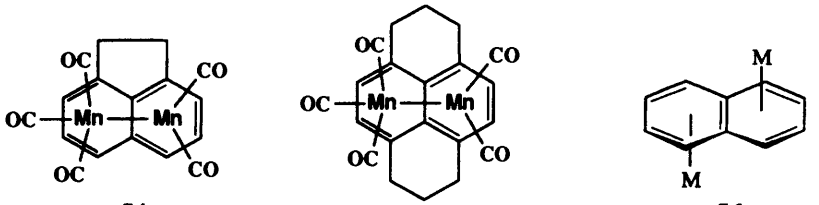


Fig. 6 Two structural views of the bimetallic naphthalene complex **51**

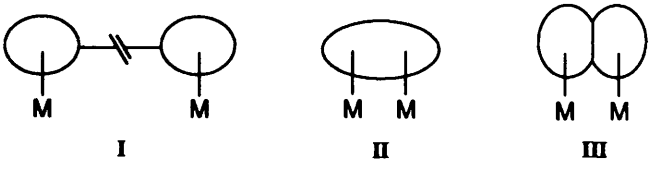


51 **52** **53**



54 **55** **56**

Scheme 10

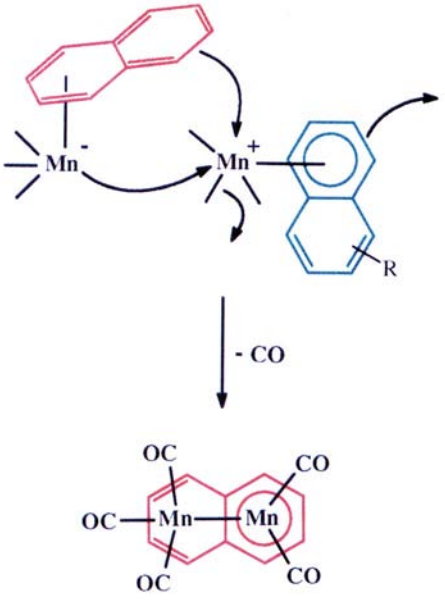


I **II** **III**

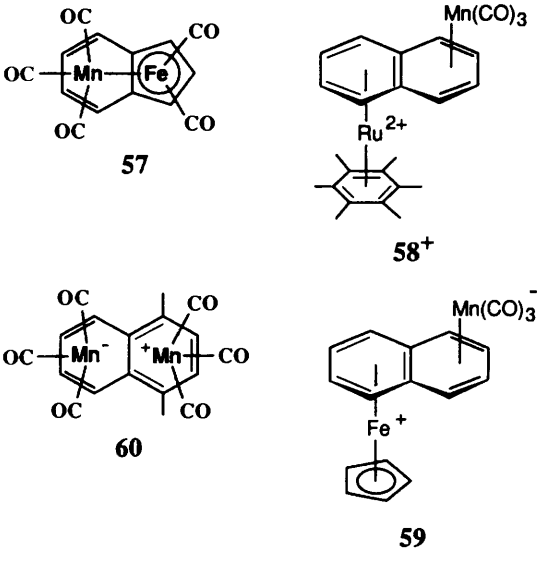
Fig. 7 Three generic types of bimetallic complexes. Each type can have the metals in a *syn* or *anti* conformation

$\eta^6 \longrightarrow \eta^4$ ring slippage in the polyarene complexes clearly is responsible for this contrasting behaviour. Chemical reducing agents such as cobaltocene, when present in excess, also convert $\mathbf{6}^+$ into slipped η^4-diene complexes. However, when only 1 equivalent of cobaltocene (or other reducing agent) is used, the chemistry is very different: instead of the yellow η^4-diene, the major product is a deeply coloured ('black') material. Spectroscopic and X-ray diffraction studies showed the black reduction products to be novel *syn*-facial bimetallic η^4:η^6-naphthalene complexes, *e.g.* **51**–**55**.[65] To our knowledge these are the first examples of this type of naphthalene complex. Fig. 6 gives two structural views of **51**. The Mn–Mn bond length is 2.9231(7) Å, a value close to that in $Mn_2(CO)_{10}$.[66] Infrared spectra of **51**–**55** give no evidence for bridging carbonyls in solution. The ^1H NMR spectra down to −80 °C indicate that the manganese atoms in **51** (as well as **52**, **54**, **55**) are in identical environments on the NMR time-scale. For example, hydrogens $H^{2,3}$ and $H^{6,7}$ in **51** give a single resonance, as do the two methyls in **52**, suggesting very rapid η^4:$\eta^6 \longleftrightarrow \eta^6$:$\eta^4$ interconversion (Scheme 10). It is likely that this interconversion involves an intermediate with a bridging CO. The bimetallics **51**–**55** undergo partially reversible oxidation at 25 °C at a potential close to that of ferrocene. Their intense colour and the rather low redox potential suggested that the highest occupied molecular orbital (HOMO) is Mn–Mn σ bonding and this was confirmed by the ESR spectrum at 110 K of the hexahydropyrene bimetallic **55**.

Bimetallic organometallic complexes have been of interest because of their potentially useful physical and chemical properties related to metal–metal interactions and electron delocalization, both of which are more difficult (or impossible) to mimic with monometallic complexes. Applications related to conductivity, non-linear optical behaviour, and certain types of catalysis are most often cited. The three generic types of bimetallic complexes are illustrated in Fig. 7. Type **I** has the metals co-ordinated to separate π-hydrocarbon rings, which are attached directly together or are separated by a spacer. In this arrangement the metals can be *syn*- or *anti*-facial. In the former case there may be a direct metal–metal interaction, whereas in the latter there is at most an indirect metal–metal interaction. Type **II** bimetallics have the metals bound (*syn* or *anti*) to the same π-hydrocarbon ring. In type **III** systems the metals are bound to adjacent fused rings. Examples[67–69] in this class include complexes with pentalene-, azulene-, indenyl- and naphthalene-type ligands, with the most numerous containing an indenyl ring system.[68] By comparison, bimetallic complexes with naphthalene-type ligands are rare and those known previously[70] have the *anti*-facial conformation **56**.

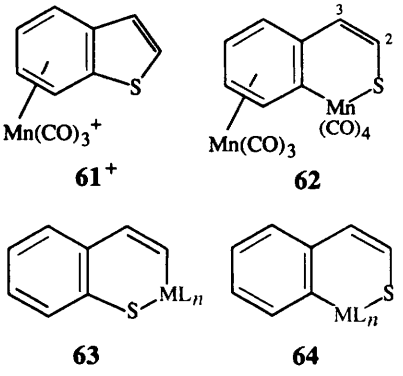


Scheme 11 Possible mechanism of formation of *syn*-facial bimetallics



The formation of the *syn*-facial bimetallic naphthalene complexes **51**–**55** necessarily involves the transfer of an $Mn(CO)_3^+$ moiety from one naphthalene to another, and one might guess that this occurs *via* a rather complex mechanism. In fact, the mechanism appears to be straightforward and is predicated on two related aspects of the chemistry of **6**$^+$: (1) the polyarene readily slips from η^6 to η^4 when reduced or when attacked by a nucleophile and (2) the polyarene is easily displaced by monoarene nucleophiles. Addition of an excess of reducing agent merely converts **6**$^+$ into the anionic η^4-diene complex (*e.g.* **37**$^-$). However, the thermodynamic product after addition of only 1 equivalent of reducing agent is a 1:1 mixture of **6**$^+$ and the η^4-diene. As Scheme 11 shows, the η^4-diene is, in effect, an arene that happens to have an attached electron-rich metal diene fragment. From the chemistry discussed above one would expect the arene end of the η^4-diene readily to displace the polyarene from **6**$^+$ and thereby provide a pathway to the observed *syn*-facial bimetallics. In accordance with this, the addition of a solution of the η^4-diene to a separate solution of **6**$^+$ (R = H) gives the bimetallic **51**.

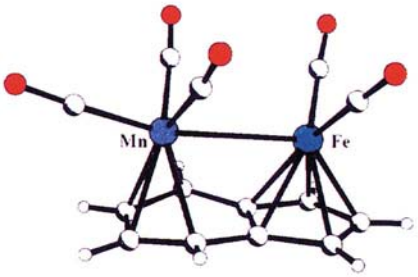
Scheme 11 suggests that *hetero*nuclear bimetallics may be formed by the reaction of **6**$^+$ with appropriate metal complexes that have a free arene ring available. Thus, reduction of a mixture of **6**$^+$ and tricarbonyl(η^5-indenyl)iron(1+) results in complex **57**.[65] Reduction of mixtures of **6**$^+$ with $[Ru(C_{10}H_8)(C_6Me_6)]^{2+}$ and with $[Fe(C_{10}H_8)(cp)]^+$ affords bimetallics **58**$^+$ and **59**, respectively, which adopt an *anti*-facial structure. It appears from the available structures[58] (Fig. 8) that **58**$^+$ and **59** are prevented from forming an M–Mn bond and being *syn*-facial because of the steric congestion that would result and because the ruthenium and iron centres do not possess a two-electron ligand that can readily dissociate. The above results indicate that the ability of **6**$^+$ to function as a facile manganese tricarbonyl transfer reagent provides a general synthetic route to homo- and hetero-nuclear bimetallic complexes of fused-ring systems which, in the absence of steric constraints, adopt a *syn*-facial structure.



An interesting aspect of the *anti*-facial bimetallics is their highly polar nature, with the formal charges being (Ru^{2+}, Mn^-) for **58**$^+$ and (Fe^+, Mn^-) for **59**. The *syn*-facial manganese bimetallic **53** is relatively non-polar, but in the presence of an atmosphere of CO the Mn–Mn bond is broken upon the addition of a catalytic amount of oxidizing agent to afford the zwitterion **60**. Scheme 12 illustrates this *reversible* transformation. Complex **60** retains the *syn*-facial structure, which is made possible by a large bending (46°) of the diene (η^4) plane from the η^6 ring.[58] Trimethylamine oxide effects the conversion of **60** back into **53** by attacking and removing a CO ligand. More significantly, **60** can also be converted into **53** by adding a stoichiometric amount of the reducing agent cobaltocene.

C–S bond activation in thiophenes and benzothiophenes

In analogy to the chemistry of the naphthalene-type complexes described above, it was anticipated that reduction of the easily synthesized heterocyclic complex (η^6-benzothiophene)tricarbonylmanganese(1+) **61**$^+$ would give a *syn*-facial η^4:η^5 or η^6:η^3 bimetallic. However, it was found[70] that reduction of **61**$^+$ under an atmosphere of CO affords a high yield of bimetallic **62**, which contains an $Mn(CO)_4$ moiety inserted into the S–C (aryl) bond of benzothiophene. This insertion reaction is particularly interesting because of a possible relationship to the enormously important field of catalytic hydrodesulfurization (HDS).[71] A large amount of HDS research has focused on the problem of sulfur removal from thiophenic molecules, especially benzothiophene and dibenzothiophene, because these are difficult to desulfurize and are, for this reason, relatively abundant in fossil fuels. A key step in HDS is cleavage of the S–C bonds, and it is postulated that this is facilitated by precoordination of a metal in the catalyst to the sulfur, followed by insertion into the S–C bonds.[72–74] With benzothiophene several metal fragments have been inserted into the S–C (vinyl) bond to give **63** (M = Fe, Ru, Rh, Ir or Pt). However, complex **62** is the only example of metal insertion into the S–C (aryl) bond of benzothiophene to give a complex of type **64**. [Recently, it was found that Rh(η-C_5Me_5)(PMe_3) can insert into the S–C (aryl) bond in 2-methylbenzothiophene (but not in benzothiophene).[75]] Why, then, is it the S–C (aryl) bond that is cleaved when **61**$^+$ is reduced? The metal in **61**$^+$, being η^6-co-ordinated to the carbocyclic ring, may function selectively to weaken the S–C (aryl) bond, or the role of the metal may be to make pos-



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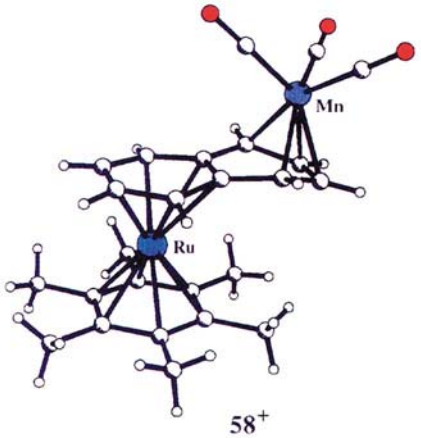

58^+

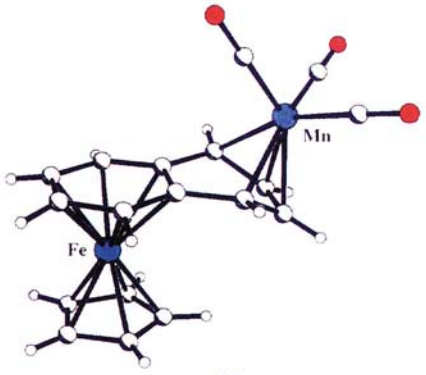

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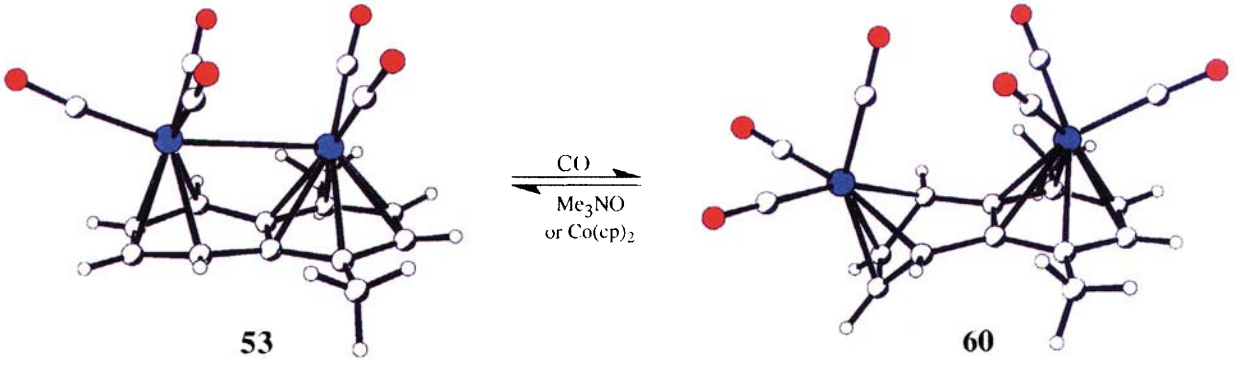
Fig. 8 Molecular structures of heteronuclear bimetallics **57**, **58**$^+$$BF_4^-$ and **59**



53 60

Scheme 12 Redox-promoted interconversion between *syn*-facial $\eta^4:\eta^6$-dimethylnaphthalene dimanganese carbonyl complexes

sible the formation of a *syn*-facial bimetallic intermediate upon reduction, thereby positioning the second metal for subsequent insertion into the S–C (aryl) bond. In a more general sense, it may be that S–C (aryl) bond cleavage in benzothiophene *requires* initial co-ordination of a metal to the carbocyclic ring. Indeed, one pathway for the catalytic desulfurization of benzothiophene may involve simultaneous co-ordination of the carbocyclic and the thiophenic rings prior to insertion into an S–C bond. In any case, the possible significance of η^6 precoordination of benzothiophene in heterogeneous HDS reactions should be kept in mind.

The crystal structure of complex **62** is illustrated in Fig. 9.[70] The neutral molecule is, in effect, a zwitterion with the $Mn(CO)_3$ unit bearing a formal +1 charge while the inserted manganese atom is formally −1. The most significant structural feature of **62** is the non-planarity of the metallacyclic ring. The inserted Mn and C^3 atoms are essentially coplanar with the highly planar carbocyclic ring. However, atoms C^2 and S are 0.53 and 1.05 Å, respectively, above this plane. The position of the sulfur shows that it is not conjugated with the π network and it would, therefore, be expected to be nucleophilic; the formal negative charge on the adjacent manganese atom would serve to enhance such behaviour. Thus, the sulfur in **62** is rapidly and cleanly methylated by methyl triflate to give **65**$^+$ and is oxidized to the dioxide by dimethyldioxirane. Hydrogenation of **62** at 300 psi (*ca.* 2068 kPa) and 100 °C for several hours cleaves the Mn–C bond to afford **66**.

When the reduction of complex **61**$^+$ is carried out under N_2 in the presence of 1 equivalent of a phosphite $P(OR)_3$ (R = Me or Et) a bimetallic is formed that is analogous to **62**, except that $Mn(CO)_3\{P(OR)_3\}$ instead of $Mn(CO)_4$ is inserted into the S–C (aryl) bond. This product is also obtained in comparable yield when **62** is treated with $P(OR)_3$. Both synthetic methods give predominantly the facial isomer, as illustrated in Fig. 10 for the $P(OEt)_3$ complex.[70] The chiral sulfur atom in the phosphite complexes reacts with methyl triflate to give a diastereomeric

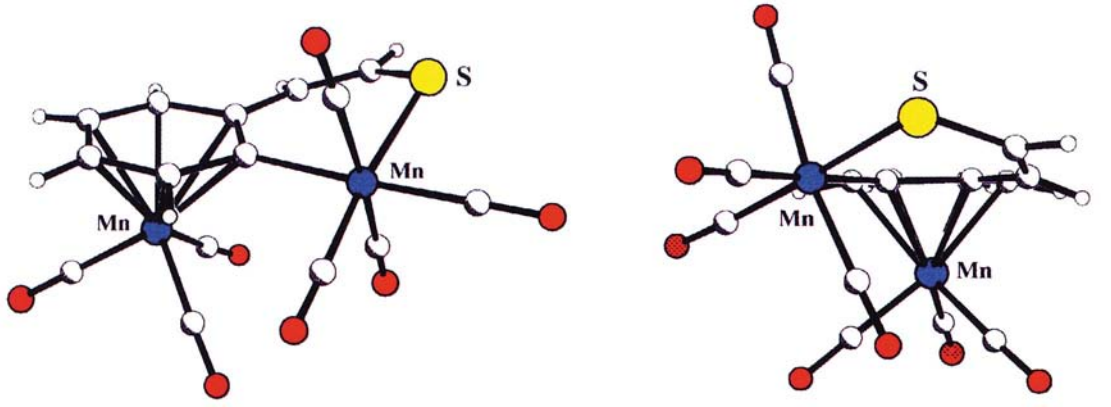


Fig. 9 Two views of the bimetallic benzothiophene insertion complex **62**

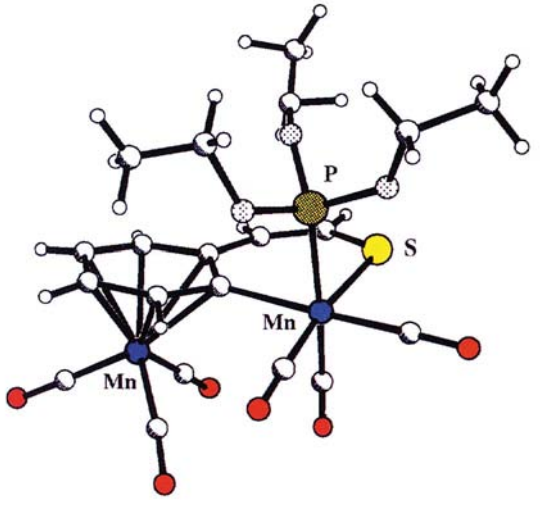
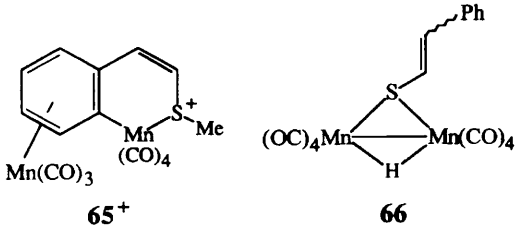


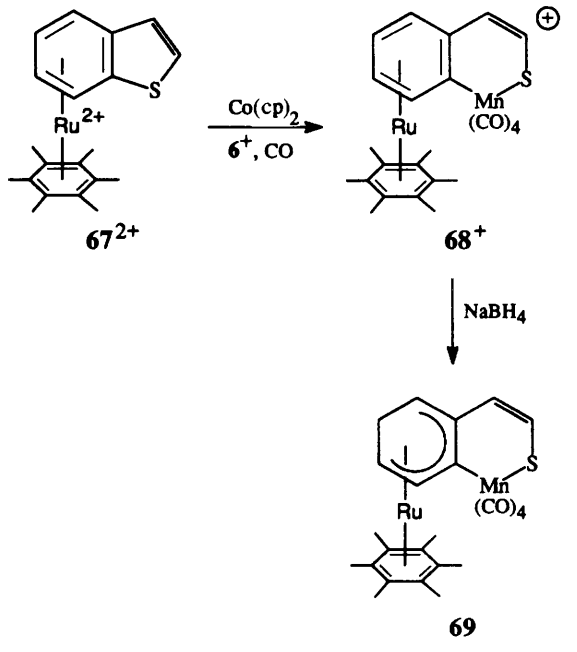
Fig. 10 Product of carbonyl substitution by $P(OEt)_3$ in complex **62**



mixture of *exo* and *endo* addition products that over a period of hours in solution isomerize to a single diastereomer. In contrast, **65**$^+$ is formed as a single diastereomer on the NMR timescale.

Insertion into the S–C (aryl) bond of benzothiophene also occurs when $[Ru(\eta^6\text{-}C_8H_6S)(C_6Me_6)]^{2+}$ **67**$^{2+}$ is reduced under CO and in the presence of a manganese tricarbonyl transfer reagent **6**$^+$. As Scheme 13 shows, this reaction leads to insertion of $Mn(CO)_4$ into **67**$^{2+}$ to afford the cationic metallacycle **68**$^+$. Single crystals of **68**$^+$ suitable for X-ray diffraction could not be grown, but it was possible to verify that S–C (aryl) bond cleavage had occurred by determining the structure of the product of hydride addition (**69**), which is shown in Fig. 11.[76]

Manganese-mediated activation of the S–C bonds in thiophene has recently been observed.[58,70] As with the benzothiophene complex **61**$^+$, reduction of $[Mn(\eta^5\text{-}C_4H_4S)(CO)_3]^+$ **70**$^+$ under CO leads to insertion into an S–C bond. The bimetallic product **71** has the metallacyclic ring π-bonded (η^5) through C^2–C^3–C^4–C^5–S to an $Mn(CO)_3$ moiety (Fig. 12).[70] As a consequence of this π bonding, and in contrast to the situation with **62**, the C_4S segment of the metallacyclic ring is highly planar, and the sulfur atom in **71** is not substantially nucleophilic. Bimetallic insertion products analogous to **71** are formed by reduction of (η^5-2,5-dimethylthiophene)- and (η^5-2-methylthiophene)-tricarbonylmanganese(1+); the reaction of the latter cation occurs regiospecifically to afford **72**. Reaction of bimetallic thiophenic complexes such as **71** and **72** with H_2 results in cleavage of the σ Mn–C bond and formation of a



Scheme 13

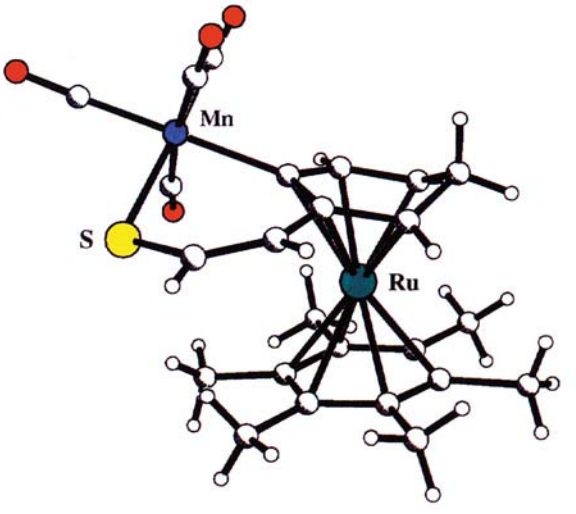


Fig. 11 Structure of the heterobimetallic benzothiophene complex **69**

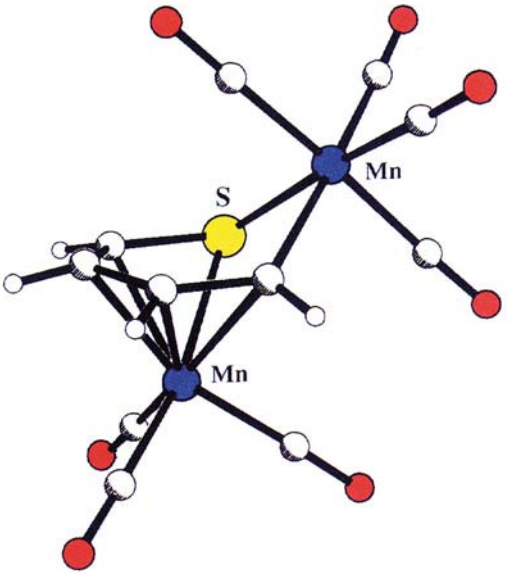


Fig. 12 Structure of the bimetallic thiophene complex **71**

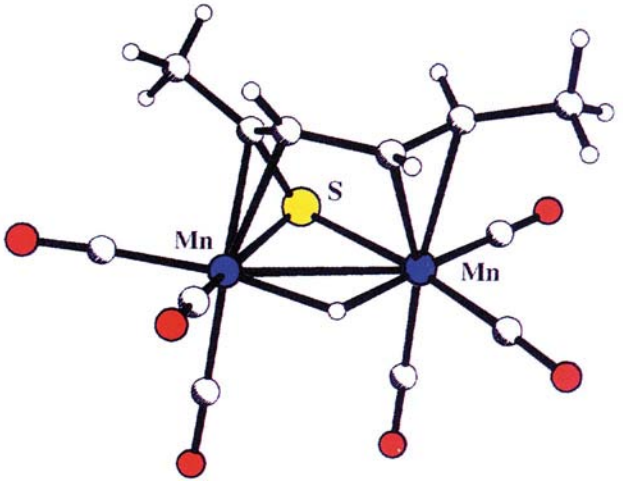
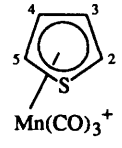
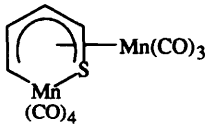


Fig. 13 Structure of the product (**73**) of hydrogenation of $[Mn(\eta^5\text{-}C_4H_2SMe_2\text{-}2,5)(CO)_3]^+$



70$^+$



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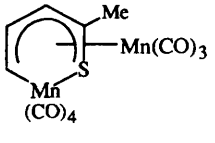

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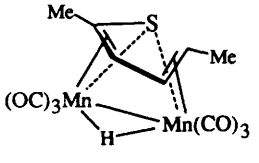

73

complex containing a co-ordinated diene thiolate, an Mn–Mn bond, and a bridging hydride ligand. For example, hydrogenation of the bimetallic derived from reduction of $[Mn(\eta^5\text{-}C_4H_2SMe_2\text{-}2,5)(CO)_3]^+$ yields complex **73**, the structure of which is shown in Fig. 13. Most interestingly, the bimetallic structural unit $Mn_2(H)(SR)$ in **73** was also found in **66**, and is similar to structures suggested to occur with heterogeneous HDS catalysts.[77]

It is apparent from the above discussion that manganese-mediated activation and desulfurization of thiophenes and benzothiophenes is a promising field of study. The availability and low toxicity of manganese are particularly attractive features of this chemistry. The results to date point to an important role for electron transfer in C–S bond activation and research is underway aimed at effecting catalytic desulfurization based on manganese.

Conclusion

It is hoped that this Perspective helps to demonstrate to the reader that manganese arene chemistry has many interesting and useful applications. The ease with which a very wide range of arenes and aromatic heterocycles can be co-ordinated to $Mn(CO)_3^+$ to give air-stable electrophilic $[Mn(arene)(CO)_3]^+$ complexes is the foundation upon which subsequent reactions are based. Applications of this chemistry include (1) facile nucleophilic addition to and functionalization of monoarenes and polyarenes, (2) double nucleophilic addition to arenes to afford disubstituted cyclohexadienes, (3) a general route to homo- and hetero-nuclear *syn*- and *anti*-facial bimetallic complexes with naphthalene-type ligands, and (4) C–S bond activation in thiophenes and benzothiophenes, with possible relevance to catalytic HDS.

Acknowledgements

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