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Review

Manganese tricarbonyl transfer (MTT) reagents in the construction of novel organometallic systems

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Dedicated to Professor Philip H. Rieger on the occasion of his retirement and in appreciation of his extraordinary contributions to electrochemistry and electron spin resonance spectroscopy of inorganic and organometallic systems

Contents

Abstract

Naphthalene and related conjugated polycyclic arenes readily coordinate through one carbocyclic ring to Mn(CO)$_3{}^+$. The resulting complexes, e.g., (η^6-naphthalene)Mn(CO)$_3{}^+$, function as very effective manganese tricarbonyl transfer (MTT) reagents, largely because of facile $\eta^6 \rightarrow \eta^4$ ring slippage. The MTT complexes can be used to synthesize a range of novel organometallic systems, including metal–carbonyl-capped metallocenes, and homo- and heteronuclear bimetallic naphthalene complexes. They are also the basis for the complexation and activation of benzothiophenes to desulfurization and of hydroquinones to deprotonation and self-assembly into supramolecular quinonoid coordination networks.

Keywords: Manganese; Arene complexes; Naphthalene complexes; Quinone complexes; Coordination networks; Multidecker complexes

1. Introduction

Transition metal complexes containing an arene ligand bonded in an η^6-manner have been studied for many years and constitute an important class of organometallic compounds. The most thoroughly investigated member of this class is (arene)Cr(CO)$_3$ (**1**), for which there exists an extensive body of information [1–3]. The Cr(CO)$_3$ moiety is electron-withdrawing, resulting in an electrophilically activated arene. Correspondingly, the most interesting and useful reactions of **1** are those involving the interaction of the coordinated arene with electron-rich species. In particular, nucleophilic addition, ring deprotonation, and reduction reactions are the most relevant, and some of these have provided useful new synthetic methodologies in organic chemistry.

The complex (η^6-arene)Mn(CO)$_3{}^+$ (**2**) is isoelectronic with (arene)Cr(CO)$_3$ and, as with the chromium complex, can be synthesized with a wide variety of arenes (vide infra). The positive charge on **2** results in the coordinated

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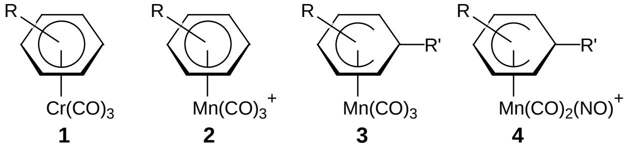


Fig. 1. Electrophilic complexes **1**–**4**.

arene ring having a greatly enhanced electrophilic character. While the complexes (arene)M(Cp)$^+$ and (arene)$_2$M^{2+} (M = Fe, Ru) also possess highly electrophilic arene ligands, the manganese system seems to be particularly suitable for synthetic applications [4]. Thus, nucleophiles can engage in addition, substitution or deprotonation reactions at the aromatic ring. In the case of the quite common nucleophile addition pathway, the initial product (**3**) can be "reactivated" by substitution of CO by NO$^+$ to afford **4**, which then undergoes a second addition to generate cyclohexadiene complexes (Fig. 1) [4,5].

The synthetic potential of (arene)Mn(CO)$_3^+$ complexes has been probed to some extent, but not nearly as much as that of the (arene)Cr(CO)$_3$ analogues. Nevertheless, results that have been published to date are very encouraging indeed and suggest that (arene)Mn(CO)$_3^+$ could be a valuable and convenient synthetic tool once the chemical properties are fully elaborated. It has already been established that an impressive range of nucleophiles will add to the ring in **2**, and that side chain deprotonations are facile, as are substitutions in chloroarene complexes [4–6]. Some of these reactions have been utilized as key intermediates in synthetic methodologies aimed at specific targets [7].

In this review the primary focus will be on the chemistry of a particular type of (arene)Mn(CO)$_3^+$ complex, namely one in which the arene is a conjugated polycyclic such as naphthalene. While this may seem like a rather pedestrian derivative on which to focus attention, it will be shown that in fact the chemistry of the (conjugated) polycyclic complexes differs from that of the monocyclic ones in fundamental and interesting ways. This differing chemical behavior, which can be traced to facile ring slippage in the polycyclics, opens the door for the synthesis of a range of novel organometallic systems (vide infra).

2. Synthesis of (η^6-arene)Mn(CO)$_3^+$ complexes

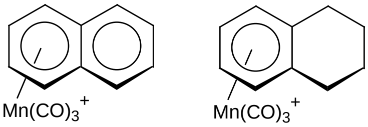
There are a number of synthetic routes to (η^6-arene)-Mn(CO)$_3^+$ complexes [8a]. The original method [8b] involves the reaction of Mn(CO)$_5$Br with the desired arene in the presence of AlCl$_3$ promoter according to Eq. (1). The solvent can be the arene itself, or an inert hydrocarbon such as cyclohexane [6c,8a]. Normally, the reaction mixture is refluxed for several hours. Alternatively, microwave heating can be used to reduce the time required [8c]. This method is satisfactory for arenes with substitutents that can withstand the harshly Lewis-acid conditions. In 1981, Pauson and co-workers [8d] proposed a milder method, in which the Mn(CO)$_5$Br is replaced with Mn(CO)$_5$ClO$_4$. The latter readily dissociates perchlorate at room temperature in the presence of arenes, initiating the generation of (η^6-arene)Mn(CO)$_3^+$. The perchlorate, Mn(CO)$_5$ClO$_4$, can be obtained by treatment of Mn(CO)$_5$Br with AgClO$_4$, or by reacting Mn$_2$(CO)$_{10}$ with HClO$_4$ [8e]. Alternatively, it is often convenient to utilize AgBF$_4$ instead, so that Mn(CO)$_5^+$BF$_4^-$ functions as the starting material. A third method for synthesizing (η^6-arene)Mn(CO)$_3^+$ involves heating Mn$_2$(CO)$_{10}$ and the arene in trifluoroacetic anhydride containing aqueous HBF$_4$ [8f]. The three methods mentioned work quite well for many arenes, but are not generally useful when the arene contains strongly electron-withdrawing substituents that exert both a minus-inductive and a minus-resonance influence, such as –C(O)R, –C(O)OR, –CN, –NO$_2$, etc. In a significant advance, Rose-Munch et al. [8g] have recently shown that (η^6-arene)Mn(CO)$_3^+$ complexes containing electron-withdrawing substituents can be synthesized by adding hydride to (η^6-chloroarene)Mn(CO)$_3^+$ to afford neutral η^5-cyclohexadienyl derivatives. This is followed by palladium-catalyzed substitution of the chloride in a Stille-type coupling to afford η^5-complexes containing the desired substituent. Hydride abstraction then generates the η^6-arene cation.

$$\mathrm{Mn(CO)_5Br + AlCl_3 + arene} \xrightarrow[-\mathrm{CO}]{\text{heat}} (\eta^6\text{-arene})\mathrm{Mn(CO)_3^+} \quad (1)$$

3. Naphthalene-based manganese tricarbonyl complexes

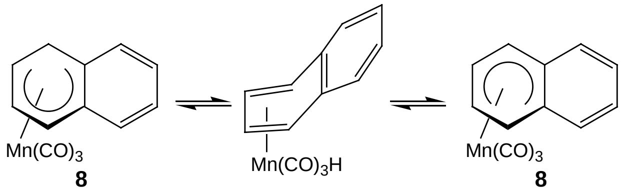
The synthesis of (η^6-naphthalene)Mn(CO)$_3^+$ (**5**) by the method indicated in Eq. (1) was first reported in 1961 [8b]. It was later determined [9], however, that the complex actually obtained was the partially hydrogenated tetralin analogue **6** (Fig. 2). The source of the hydrogen in the formation of **6** was likely adventitious water and, indeed, it was subsequently demonstrated [10] that **5** and its substituted analogues can be readily synthesized in high yield by adding Mn(CO)$_5^+$BF$_4^-$ (prepared in situ) to the naphthalene in very dry methylene chloride.

Transition metal complexes containing an η^6-naphthalene-type ligand are special in comparison to η^6-monocyclic arene complexes in that the former can show enhanced



5 **6**

Fig. 2. Naphthalene and tetralin complexes **5** and **6**.



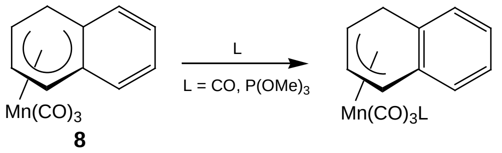
Scheme 1.

reactivity while, at the same time, being thermodynamically stable. For example, (η^6-naphthalene)Cr(CO)$_3$ and (η^6-naphthalene)RuCp$^+$ are known to undergo associative nucleophilic substitution of the naphthalene at rates orders of magnitude greater than that found for the η^6-benzene analogues [11,12]. It is thought that the naphthalene undergoes ring slippage from η^6 to η^4 as the nucleophile initially binds, and that the most important contributor to the (relative) activation energy is the change in resonance energy concomitant with this slippage. In this context, the naphthalene complexes react faster simply because the loss in resonance energy in forming the η^4-intermediate is much less than that for the monocyclic arenes. Although the η^4-intermediates are generally not observed directly, strong evidence for their viability comes from the existence of structurally characterized η^4-naphthalene chromium and ruthenium complexes obtained by two-electron reduction of η^6-presursors [12b,13,14].

We found that **5** and related polycyclic manganese complexes react within minutes or less with donor solvents, such as that indicated by Eq. (2). This great sensitivity to potential nucleophiles no doubt explains in part the historical difficulty in synthesizing **5**. The dominant role of $\eta^6 \rightarrow \eta^4$ ring slippage in Eq. (2) is evident when comparing the half-lives of the η^6-benzene and η^6-naphthalene complexes: 2 years and ca. 10 s, respectively! This rate difference expressed as an activation energy is quite close to the anticipated 40 kJ greater resonance energy loss for slippage in the benzene complex [10]. An electrochemical study of **5** shows that it undergoes a chemically reversible two-electron reduction to (η^4-naphthalene)Mn(CO)$_3^-$ (**7**). The addition of the *second* electron is quite slow, suggesting that it occurs in concert with ring slippage [15]. The anionic complex **7** is stable, and has been structurally characterized by X-ray diffraction [16].

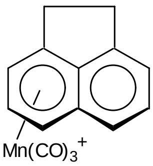
$$(\eta^6\text{-naphthalene})\text{Mn(CO)}_3^+ + 3\text{MeCN} \rightarrow (\text{MeCN})_3\text{Mn(CO)}_3^+ + \text{naphthalene} \quad (2)$$

The facile ring slippage in **5** is also manifested in related systems. For example, nucleophilic addition of hydride to **5** generates the η^5-cyclohexadienyl complex **8**, which undergoes a facile 1,4-hydride shift via an intermediate metal hydride, as shown in Scheme 1 [17]. Equally interesting is the ability of **8** to undergo an $\eta^5 \rightarrow \eta^3$ hapicity change upon the addition of monodentate ligand L (Scheme 2) [18]. Largely due to this rapid and reversible hapicity change, complex **8** is an effective catalyst for the hydrosilylation of ketones [18a].



Scheme 2.

Perhaps the most important property of the naphthalene complex **5** is its thermal stability (as a solid salt) coupled with its ready loss of the naphthalene in the presence of an appropriate nucleophile. Thus, **5** can be viewed as a reagent that can transfer the Mn(CO)$_3^+$ moiety—a manganese tricarbonyl transfer (MTT) reagent. Indeed, it was found that many (free) arenes react cleanly with **5** and related polycyclic complexes to generate (η^6-arene)Mn(CO)$_3^+$ [10]. The reaction merely requires heating the reactants in methylene chloride, and thus constitutes a very mild new synthetic procedure. The most convenient MTT reagent in terms of cost, ease of synthesis, and shelf life, is the acenaphthene complex **9**. MTT reagents can be used to synthesize (η^6-arene)Mn(CO)$_3^+$ complexes with arenes that do not contain strongly electron-withdrawing groups. In addition, they can be used to transfer Mn(CO)$_3^+$ to *metal complexes*, thus generating multimetallic systems that in some cases represent fundamentally new types of structures. The rest of this review describes some new types of organometallic systems that originate from the use of MTT reagents.



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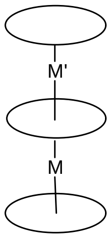
4. Uses of manganese tricarbonyl transfer (MTT) reagents

4.1. Multidecker complexes

Multidecker complexes have generated interest for many years due to the possibility of useful and novel properties that may distinguish them from monometallic complexes. Bimetallic “triple-decker” complexes **10** containing cyclopentadienyl, arene, or related hetrerocyclic π-ligands have been widely studied [19]. However, bimetallics having the general structure **11**, in which a coordinated π-ring system is “capped” with a metal carbonyl moiety are much less common and are only known with heterocyclic bridging ligands [20]. We have recently used MTT methodology to produce the first metal carbonyl capped metallocene with a strictly carbocyclic bridging ligand [21].



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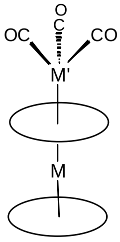

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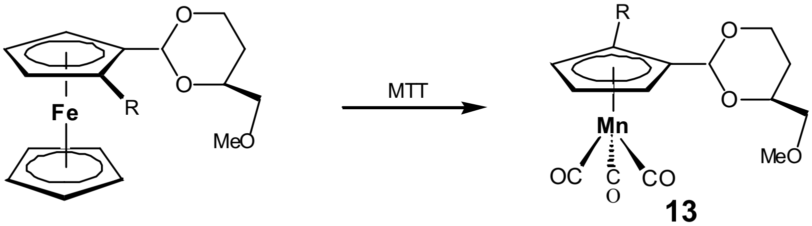
The chemistry that led to this discovery was prompted by a recent report by Chung and co-workers [22] that ferrocene undergoes ring exchange with (η^6-naphthalene)$Mn(CO)_3^+$ (**5**) according to Eq. (3). Knowing the ease with which naphthalene is displaced from **5**, these authors suggested as a possible intermediate the bimetallic species $[Cp–Fe–Cp–Mn(CO)_3]^+$, in which one of the Cp rings is coordinated to both metals. Such a species, which was not observed experimentally, could result from nucleophilic attack by an electron-rich Cp ring in ferrocene on the manganese in **5**, causing the ultimate transfer of naphthalene to the iron and Cp to the manganese. With this in mind, we tested the reaction of an MTT reagent with the more electron-rich Cp^*_2Fe, with the hope that the Cp*–Fe bond would be sufficiently difficult to break to allow detection of any bimetallic intermediate.

$$(\eta^6\text{-}C_{10}H_8)Mn(CO)_3^+ + Cp_2Fe \rightarrow CpMn(CO)_3 + (\eta^6\text{-}C_{10}H_8)FeCp^+ \qquad (3)$$

To our delight, it was found that merely refluxing equimolar amounts of **5** or **9** and Cp^*_2M (M = Fe, Ru, Os) in methylene chloride led to the air stable capped metallocenes **12** as BF_4^- salts. Ring transfer reactions as in Eq. (3) were not observed. The iron complex **12**(Fe) is green while the ruthenium and osmium analogues are orange. The X-ray structure of [**12**(Ru)]PF_6 is shown in Fig. 3. Both Cp* rings are highly planar and adopt a staggered conformation, in contrast to the eclipsed rings found in solid Cp^*_2Ru [23]. The singly coordinated Cp* ring in [**12**(Ru)]PF_6 has an average Ru–C bond length of 2.16 Å and an average C–C bond length of 1.42 Å. The corresponding distances in Cp^*_2Ru are 2.18 and 1.42 Å. The reduced electron density in the doubly coordinated Cp* ring is reflected in longer average Ru–C and C–C bonds, 2.22 and 1.46 Å, respectively. The average Mn–C bond distance to the Cp* ring is 2.18 Å, which is about 0.04 Å longer than that typical for neutral (cyclopentadienyl)$Mn(CO)_3$ complexes [24].



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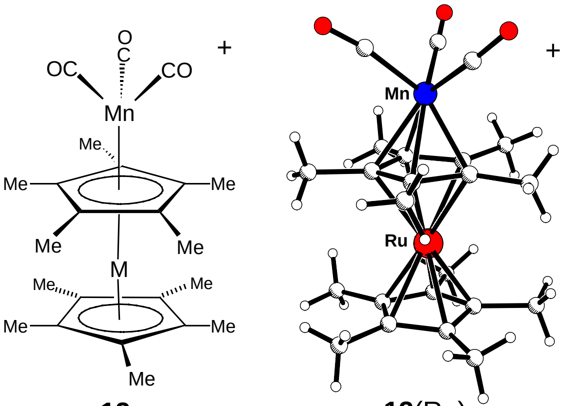
(4)



12 **12**(Ru)

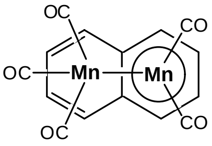
Fig. 3. Structure of capped metallocene **12**(Ru).

The novel capped metallocenes **12** are remarkably stable in methylene chloride and do not react with $P(OEt)_3$ over 30 min. Similarly, a solution of **12**(Ru) in the presence of excess naphthalene was found to be unchanged after refluxing in methylene chloride overnight. Acetonitrile at room temperature slowly attacks the Mn center in **12**(Fe) to generate $FeCp^*_2$ and $(MeCN)_3Mn(CO)_3^+$, whereas **12**(Ru) slowly reacts at the Ru center to give $Cp^*Ru(MeCN)_3^+$ and $Cp^*Mn(CO)_3$. This difference in reaction pathway is likely due to easier nucleophilic attack by MeCN at the larger ruthenium center, with concomitant Cp* displacement. All three complexes **12**(Fe, Ru, Os) undergo *reversible* 1-electron reductions to afford 31-electron radicals.

In a significant application of this chemistry, and in collaboration with Prof. Y.K. Chung of Seoul National University, it was shown [25] that the reaction of **5** with planar chiral ferrocenes results in transfer of planar chirality as illustrated in Eq. (4). The cymantrene complex **13** formed with 100% *inversion*, as would be expected if a species analogous to **12** were an intermediate. (The iron-containing product is (η^6-naphthalene)$FeCp^+$.) Chiral cymantrene complexes such as **13** may be generally useful as auxiliaries in asymmetric reactions and to this end their utility was demonstrated in high yield asymmetric allylic alkylations, with enantioselectivities close to existing benchmarks [25].

4.2. Novel bimetallic systems

As stated above, **5** and analogous η^6-naphthalene-type manganese tricarbonyl complexes typically undergo two-electron chemical or electrochemical reduction to η^4-naphthalene complexes such as **7**. The facile ring slippage associated with the reduction of **5** *and* the demonstrated ease of ring slippage accompanying nucleophilic displacement of the naphthalene from **5** are related properties that were exploited simultaneously to produce truly novel *syn*-facial bimetallic complexes such as **14** and **15** [26]. The key to this synthesis is the use of only 1 eq. of reducing agent. Excess reducing agent gives the yellow anionic η^4-naphthalene complex, but when only 1 eq. is present a deeply colored material is produced in good yield. X-ray analysis of several of these products revealed them to have the remarkable structure typified by **14** and **15**. To our knowledge these were the first examples of *syn*-facial bimetallic naphthalene complexes.



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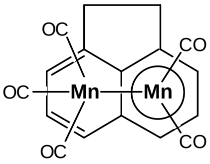

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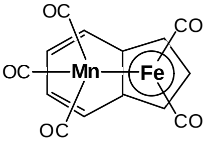
The Mn–Mn bond length in **14** is 2.9231(**7**) Å, a value close to that in $Mn_2(CO)_{10}$ [27]. Infrared spectra of **14** give no evidence for bridging carbonyls in solution. ^1H NMR spectra down to $-80\,^\circ C$ indicate that the manganese atoms in **14** are in identical environments on the NMR timescale, suggesting very rapid $\eta^4 : \eta^6 \leftrightarrow \eta^6 : \eta^4$ interconversion. Most likely this interconversion involves an intermediate with a bridging CO. Bimetallics such as **14** and **15** undergo partially chemically reversible oxidation at room temperature at a potential close to that of ferrocene. Their intense color and rather low redox potential suggest that the HOMO is Mn–Mn σ bonding. ESR spectra at 110 K support this view [26].

The formation of the *syn*-facial naphthalene bimetallics necessarily involves transfer of an $Mn(CO)_3{}^+$ moiety from one naphthalene to another, and this might be expected to occur by a rather complex mechanism. However, there is a very simple and straightforward mechanism that is strongly supported by observations. Voltammetric experiments indicate that naphthalene complexes such as **5** are reduced by two electrons at a potential about 1 V negative of the Fc^+/Fc reference couple. This means that after addition of the first electron, the second one adds *spontaneously*, most likely because of concomitant ring slippage. This observation implies that the addition of 1 eq. of a reducing agent to **5** produces as the thermodynamic product not the radical $[(\text{naphthalene})Mn(CO)_3]^0$, but rather a 1:1 mixture of starting complex **5** and the η^4-naphthalene anion. The latter is, in effect, an arene that has attached an electron-rich (anionic) metal diene fragment. Accordingly, this "arene" would be expected to easily displace naphthalene from cationic **5** present in the solution, thereby providing a simple pathway to the observed bimetallics. In accordance with this theory, it was found that combining separate solutions of $(\eta^6\text{-naphthalene})Mn(CO)_3{}^+$ and $(\eta^4\text{-naphthalene})Mn(CO)_3{}^-$ afforded $(\eta^6,\eta^4\text{-naphthalene})$-$Mn_2(CO)_5$ (**14**) in high yield [15a].

This mechanism suggests that heteronuclear bimetallics may be formed by the reaction of **5** with appropriate metal complexes having a "free" arene ring available. An example of this chemistry is indicated by structures **16** and **17**, which were formed by adding a reducing agent to a solution of **5** containing $(\eta^5\text{-indenyl})Fe(CO)_3{}^+$ and $(\eta^6\text{-naphthalene})FeCp^+$, respectively. The *syn*-facial structure obtains for **16** while **17** has a zwitterionic *anti*-facial structure. The *anti*-facial geometry is probably a consequence of the iron center not possessing an easily dissociable two-electron ligand. The conclusion from this work is that the ability of complexes such as **5** and **9** to function as MTT reagents provides a general route to homo- and heteronuclear bimetallics of fused-ring systems.



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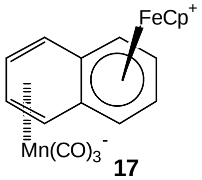

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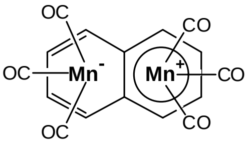
The *anti*-facial bimetallics made with MTT reagents are generally highly polar (zwitterionic) and the *syn*-facial bimetallics are relatively nonpolar. Interestingly, the nonpolar *syn*-facial **14** reacts rapidly with CO in the presence of catalytic amounts of an oxidizing agent to break the Mn–Mn bond and afford zwitterionic **18**. The *syn*-facial structure is maintained in **18** by virtue of a large bending (46°) of the η^4-diene plane from the η^6-ring. Interestingly, the conversion **14** → **18** is readily reversible, and this allows for potentially significant applications in catalysis [28].



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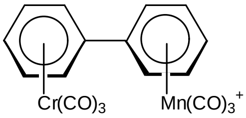
Finally, it is interesting to note that MTT reagents can be utilized for the synthesis of multimetallic complexes such as **19** and **20** [29]. The only requirement for the synthesis of a multimetallic of this type is a metal complex containing an arene ring that is sufficiently electron-rich to coordinate to the $Mn(CO)_3{}^+$ moiety from the MTT reagent.



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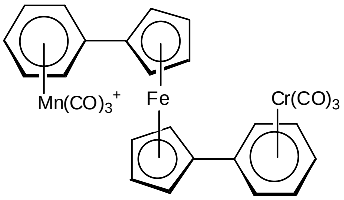

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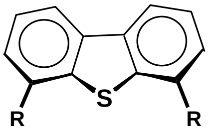
4.3. C–X bond cleavage in heterocycles

MTT reagents have played an indirect role in the activation of C–S bonds in dibenzothiophenes (DBTs) and benzothiophenes (BTs). Using MTT reagents, the $Mn(CO)_3^+$ fragment can be readily attached to the arene rings in variously substituted DBTs and BTs, as in complex **21** [15a,30]. It was subsequently found that the manganese fragment had the effect of activating the C–S bonds in the adjacent heterocyclic thiophenic ring to cleavage by the insertion of mild metal nucleophiles to give metallacyclic complexes such as **22**. Thus, the C–S bonds are activated by “precoordination” of the manganese fragment and this is termed “remote activation” because the transition metal is attached to a part of the molecule remote from the bond to be broken. The chief advantage of this approach is that it permits the use of mild and conveniently synthesized reagents to break the required bond, usually in a regioselective manner. This strategy can produce remarkable and in some cases unprecedented levels of activation for a variety of bond types (C–C, C–O, C–S, C–Se, N–H).



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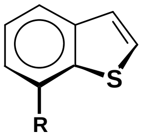

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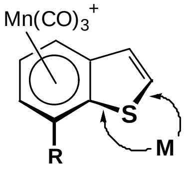

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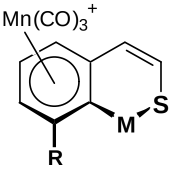


22

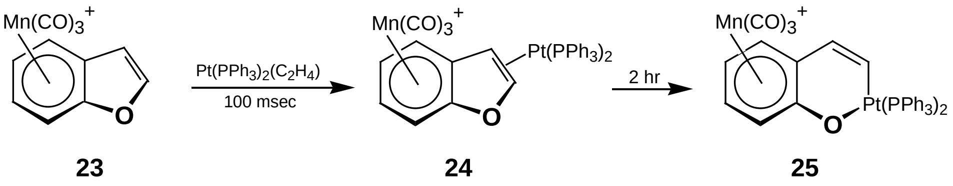
The activation of C–S bonds in BTs and DBTs is important because these and other stable conjugated heterocyclic molecules constitute major pollutants in crude petroleum. The combustion of fuels containing these species contributes significantly to environmental pollution through the release of sulfur oxides. For this and other reasons, crude petroleum is treated with hydrogen to remove sulfur as H_2S, generally with a heterogeneous catalyst, in what constitutes the largest industrial chemical reaction in the world [31]. Thiophenic molecules such as benzothiophene and dibenzothiophene are of special concern because their alkylated derivatives are difficult to desulfurize by present technology and, as a consequence, much of the fossil fuel sulfur contamination can be traced to these species. Proposed US government regulations to take effect in the near future will require deep cuts in sulfur content in gasoline and diesel fuels and this, in turn, will require substantial improvements in “deep” hydrodesulfurization (HDS) technology. In effect, this means finding better ways to desulfurize alkylated thiophenes.

Coordination of $Mn(CO)_3^+$ to the carbocyclic rings in BTs and DBTs allows the C–S bonds to be cleaved in seconds at room temperature by nucleophiles as mild as $Pt(PPh_3)_2(C_2H_4)$. Alternatively, the bonds may be cleaved by mild reducing agents. Remarkably, even 4,6-dimethyldibenzothiophene, about the most intractable sulfur-containing species in petroleum, undergoes the cleavage reaction in seconds! Once a nucleophile inserts into a C–S bond to give a metallacycle like **22**, the sulfur atom becomes much more nucleophilic, and can be attacked and subsequently removed by appropriate electrophiles (e.g., H^+).

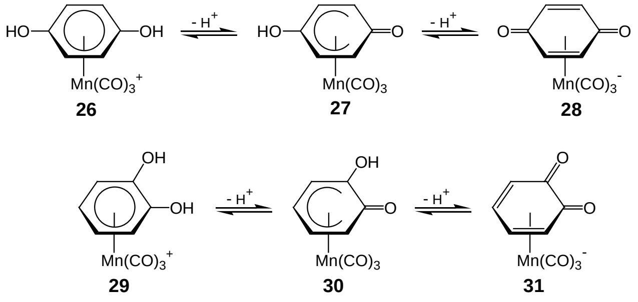
The remote activation protocol for C–S activation was successfully applied to the more difficult problem of C–O activation in benzofuran [32]. As indicated in Scheme 3, the coordinated benzofuran **23** reacts with the mild nucleophile $Pt(PPh_3)_2(C_2H_4)$ to rapidly form an η^2-(C=C) intermediate **24**, which slowly converts to insertion product **25**. The same mechanism holds for benzothiophene, except that the weaker C–S bond is much more rapidly cleaved. The use of the “remote activation” methodology to cleave strong C–O bonds like that in benzofuran may point the way to better hydrodenitrogenation (HDN) catalysts, an area of major technological importance.

4.4. Quinone π-complexes as organometalloligands

An especially interesting example of the use of an MTT reagent is in the high yield synthesis of π-bonded η^6-hydroquinone and η^6-catechol manganese complexes [33]. The transition metal chemistry of π-bonded hydroquinones is little developed due to difficulty in synthesis and/or instability [34]. Furthermore, hydroquinones have a strong propensity to bind through the oxygen atoms rather than through the π-system [35]. Nevertheless, η^6-hydroquinone, resorcinol, and catechol π-complexes of



Scheme 3.

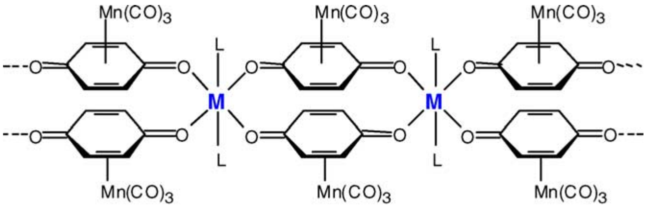


Scheme 4.

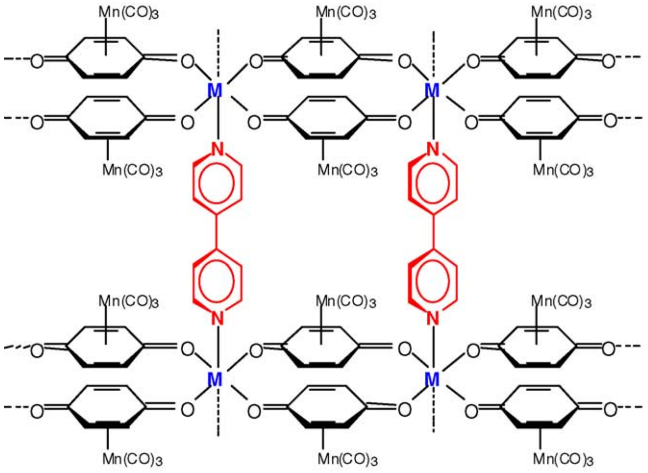
$Mn(CO)_3^+$ are thermally stable species and undergo interesting reactions. For example, complexes **26** and **29** are easily deprotonated to afford η^5-semiquinone and η^4-quinone derivatives (Scheme 4) [33,36]. The semiquinone **27** exists in linear polymeric arrays in the solid state with a structure dictated by strong intermolecular hydrogen bonding. By comparison, the catechol analogue **30** exists as discrete hydrogen-bonded dimers.

The anionic η^4-quinone complexes **28** and **31** have been shown to function as good ligands towards transition metals by σ-binding through the oxygen atoms [37,38]. Accordingly, we term complexes **28** and **31** "organometalloligands". The catecholate **31** functions as a chelating ligand and with divalent metal ions forms complexes $[M(31)_2(L_2)]$ ($M =$ Mn, Cd, Co; $L_2 =$ phen, 2,2′-bipy, 2 py). The electron-sink nature of the manganese carbonyl moiety combined with the redox active nature of quinones make these complexes interesting in the context of "redox tautomerization" [35], meaning that they may show a dynamic electronic environment (oxidation state) at the metal M that self-adjusts to changes in the binding properties of the non-quinonoid ligand L.

In contrast to the discrete complexes formed by organometalloligand **31**, the quinone complex **28** is geometrically prevented from chelating a metal ion and instead functions as a bifunctional ligand to form supramolecular coordination networks. These consist of metal ions, called nodes, connected by organometalloligand spacers. The whole assembly is termed a metal organometallic coordination network (MOMN) [38]. As an example, in DMSO **28** reacts to form the 1-D MOMN **32**. By using a bifunctional organic spacer as the axial ligand, the 1-D "string" polymers in **32** can be tied together to give the 2-D MOMN **33**. With suitable experimental conditions, it is possible to construct 3-D MOMNs similar to **33** that contain 2-D quinonoid planes connected by the bipyridine spacers. Many types of architectures can be constructed with organometallic quinonoid spacers, some of which may be useful in guest-host chemistry, electron transfer initiated reactions, and catalysis. Significantly, it appears that the architectures can be rationally designed based upon the coordination number, oxidation state, and geometrical requirements of the metallic nodes that link the organometalloligands [38].



MOMN 32 **(M = Mn, Co, Ni, Cd; L = DMSO, py)**



MOMN 33

5. Conclusions

It has been shown that (η^6-naphthalene)$Mn(CO)_3^+$ and related conjugated polycyclic arenes function well as manganese tricarbonyl transfer reagents. The chemistry of these complexes is dominated by very facile $\eta^6 \rightarrow \eta^4$ ring slippage that occurs upon reduction or upon associative nucleophilic attack. This is the basis for the use of MTT reagents to synthesize other (η^6-arene)$Mn(CO)_3^+$ complexes. Two examples are the complexation and activation of benzothiophenes to desulfurization and of hydroquinones to deprotonation and self-assembly into coordination networks. The MTT reagents can transfer the $Mn(CO)_3^+$ moiety to generate novel metal–carbonyl-capped metallocenes. Electron transfer reactions of MTT reagents are the basis for a generalized synthesis of homo- and heteronuclear η^6,η^4-bimetallic naphthalene complexes.

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