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Electrophilic reactivity of coordinated cyclic π-hydrocarbons☆

Robert D. Pike [a,*], Dwight A. Sweigart [b,1]

[a] *Department of Chemistry, College of William & Mary, Williamsburg, VA 23187, USA*
[b] *Department of Chemistry, Brown University, Providence, RI 02912, USA*

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Contents

Abstract

A large number of transition metal complexes are known that contain cyclic π-hydrocarbon ligands. In many cases, coordination to the metal imparts significant electrophilic character to the hydrocarbon. In this review, the electrophilic properties of cyclic dienyl and triene complexes are examined. Featured reactions with nucleophiles include (1) single and

☆ Dedicated to Professor Ralph Pearson in appreciation of his extraordinary contributions to chemistry, in general, and inorganic chemistry in particular.

* Corresponding author. Tel.: + 1-757-2212555; fax: + 1-757-2212715.
E-mail addresses: rdpike@chem1.chem.wm.edu (R.D. Pike), dwight_sweigart@brown.edu (D.A. Sweigart)
[1] Also corresponding author. Tel.: + 1-401-8632767; fax: + 1-401-8632594.

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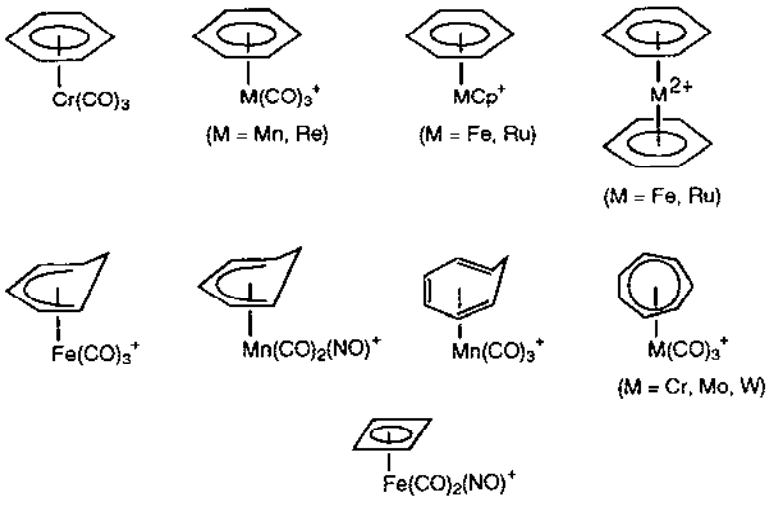
double addition to the coordinated ring, (2) substitution of a ring substituent, e.g. chloride, (3) deprotonation of the coordinated ring or a side chain, (4) ligand substitution and (5) single electron transfer. The mechanistic aspects of these reactions are discussed with regard to electrophilic and nucleophilic reactivity, regiochemistry, stereochemistry, and detailed reaction pathways. The mechanistic principles are illustrated by selected synthetic applications.

Keywords: Nucleophilic addition; π-Hydrocarbon complexes; Electrophilic complexes; Arene complexes; Cyclohexadienyl complexes

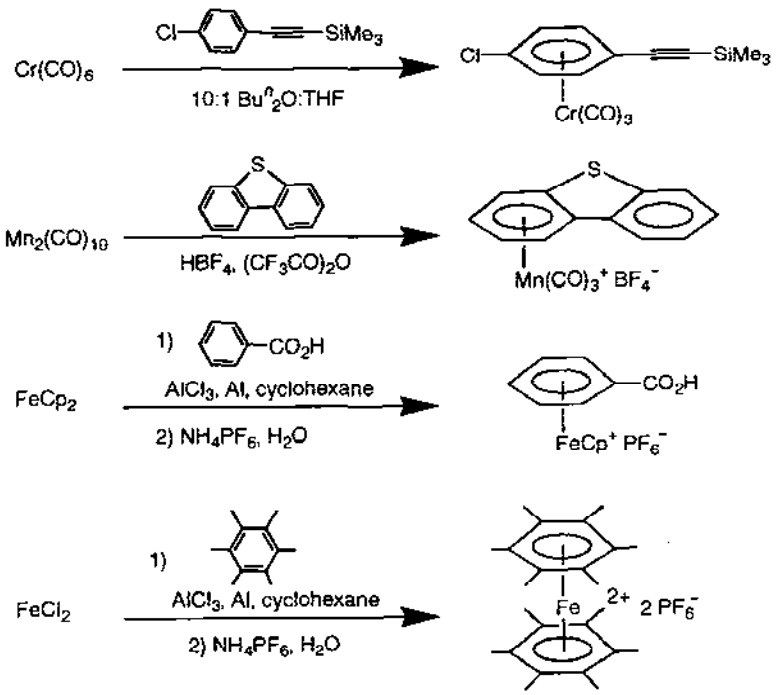
1. Introduction

The chemistry of carbon ligands coordinated to transition metals continues to attract much research. The nature and reactivity of organic ligands are influenced by transition metals in terms of redox, polarity, steric, stereochemical and regiochemical properties. During the past 20 years, a large amount of work has appeared, shedding light on the mechanistic, structural and synthetic chemistry of organometallic compounds.

In this review, we focus on the chemistry of cyclic π-trienes and π-dienyls coordinated to electrophilic transition metal fragments. The latter property is usually imparted by the presence of a cationic charge and/or carbonyl ligands. The emphasis will be upon the classes of complexes shown in Scheme 1, all of which are



Scheme 1.



Scheme 2.

subject to nucleophilic addition reactions. Since the time that one of us (D.A.S.) published a review [1] on the present topic, several related reviews have appeared. These papers cover topics which include: nucleophilic addition to manganese-coordinated arenes [2], the chemistry of arene complexes of chromium [3], iron [4–6] and ruthenium [7,8], and polymetallated hydrocarbon complexes lacking metal–metal bonds [9]. Comprehensive Organometallic Chemistry II, published in 1995, contains useful reviews of nucleophilic attack on dienyl complexes [10] and nucleophilic addition [11], ring lithiation [12], and side chain activation [13] of arene complexes.

2. Chemical reactivity of cyclic π-hydrocarbon complexes

Several metal fragments are available for π-coordination of aromatics, as shown in Scheme 1. The complexes vary not only in reactivity, but also in the ease of initial preparation. Representative syntheses for several compounds are shown in Scheme 2. The $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes may be prepared, for most arenes, either directly from $[Cr(CO)_6]$ or from $[Cr(CO)_3L_3]$ (L = NH_3, py, or MeCN) [14]. The $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes are synthesized from the reactive intermediate $[Mn(CO)_5]^-$, which is itself prepared by halide abstraction from $[Mn(CO)_5X]$

using $AlCl_3$ or Ag(I) or, alternatively, by direct oxidation of $[Mn_2(CO)_{10}]$ with strong acid in trifluoroacetic anhydride [15,16]. As a milder route to either the chromium [17] or the manganese [18] arene complexes, polycyclic aromatics can be coordinated and exchanged under mild conditions for other arenes. The $[Mn(CO)_3]^+$ fragment is particularly electron-deficient and does not tolerate strongly electron-withdrawing arene substituents such as nitro and α-keto groups [15].

The $[(\eta^6\text{-arene})FeCp]^+$ complexes are prepared from ferrocene or $[CpFe(CO)_2Cl]$ by ligand exchange in the presence of $AlCl_3$ [4], while the ruthenium analogues are produced similarly from ruthenocene or under milder ligand exchange conditions from $[CpRu(NCMe)_3]^+$ [7]. Analogously, the syntheses of $[(\eta^6\text{-arene})_2M]^{2+}$ complexes differ for iron [6,19] and ruthenium [8,20]. The iron complexes must be prepared using $FeCl_3$ or $FeCl_2$ and generally cannot tolerate sensitive functionalities. The ruthenium species are formed under mild conditions by halide abstraction from $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ or by ligand exchange from $[(\eta^6\text{-arene})Ru(OH_2)_3]^{2+}$. The cyclohexadienyl complexes of $[Fe(CO)_3]$ are made from arenes which are first reduced to dienes by Li/NH_3, then metallated using $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$, and finally, converted to the dienyl by H^- abstraction using Ph_3C^+ [19].

2.1. General reaction pathways

Each of the complexes shown in Scheme 1 is rendered electrophilic by the presence of a metal group and each is therefore subject (to varying degrees) to reactions with nucleophiles. The wide range of known reaction pathways is illustrated in Scheme 3, using $[(\pi\text{-arene})Mn(CO)_3]^+$ as a representative electrophile. Generally speaking, these reactions fall into three categories: (1) inner sphere electron transfer (resulting in nucleophilic substitution or addition), (2) outer sphere electron transfer (generating radical products), and (3) proton transfer. Reactivity of all three types tends to follow a single overall trend which depends on the relative electrophilicity of the various organometallic complexes.

2.2. Nucleophilic substitution reactions

Cyclic π-polyene ligands coordinated to electrophilic metal fragments are subject to nucleophilic displacement reactions. A requirement for this reactivity is the presence of a suitable leaving group (sometimes referred to as the nucleofuge). Substitution reactions are of significant synthetic interest because the product retains electrophilic character, allowing for further transformations. Thus, for example, conversion of cationic $[(\eta^6\text{-}C_6H_5Cl)ML_n]^+$ generates cationic products, $[(\eta^6\text{-}C_6H_5R)ML_n]^+$. The latter are subject to nucleophilic addition reactions (see Section 2.4). Alternatively, multiple substitution reactions may be carried out. The enhancement of reactivity imparted by the metal fragment, ML_n, toward nucleophilic substitution [21,22] generally parallels that of nucleophilic addition [1]: $[Cr(CO)_3] < [Mo(CO)_3] \ll [FeCp]^+ < [Mn(CO)_3]^+$. Fluoroaromatics are more reactive toward substitution than chloroaromatics [21,22].

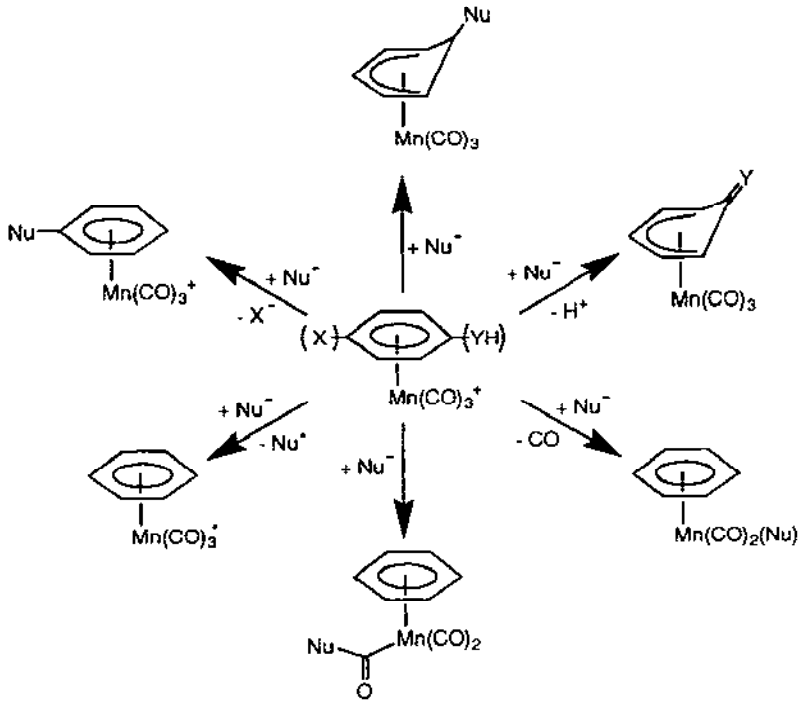
By far the most intensively studied systems have been the complexes of the $[FeCp]^+$ (and, to a lesser extent, the $[RuCp]^+$) fragment, Eq. (1).

$$[(\eta^6\text{-}C_6H_5Cl)FeCp]^+ + Nu^- \rightarrow [(\eta^6\text{-}C_6H_5Nu)FeCp]^+ + Cl^- \quad (1)$$

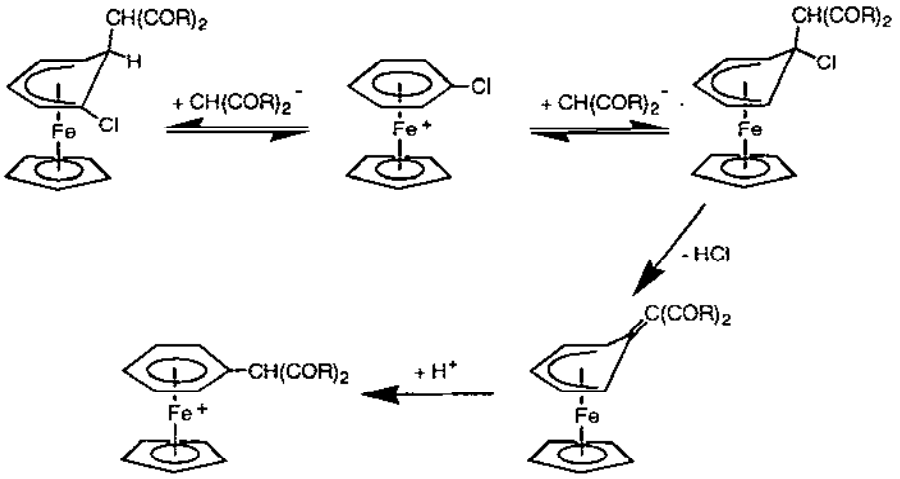
Since the first description of this reaction by Nesmeyanov [23,24], a vast arsenal of relatively soft anionic nucleophiles, including amides, enolates, thiolates, nitroalkyls, alkoxides, and many others, have been brought to bear on it [6,25–29]. Although the chloro group is more commonly used, the nitro group is similarly effective as a nucleofuge [30–32]. The tethered aryloxy group can also serve as a leaving group when $[(\eta^6$-dibenzofuran)$FeCp]^+$, or similar oxygen-bearing heterocyclic complex, is reacted with a nucleophile [33,34].

The probable mechanism of nucleophilic substitution of chloride by a stabilized carbanion is shown in Scheme 4 [35]. The initial and, typically, reversible addition of the nucleophile occurs at the *ortho* position. In the case of hard carbanions and even some ketone-enolates, the *o*-chlorocyclohexadienyl product is isolated [36–39]. Nucleophile migration can produce the *ipso* attack product, which is isolated through the loss of HCl (or release of Cl^- when the nucleophile cannot deprotonate).

Abd-El-Aziz [40,41] and Pearson [42,43] have reacted $[(\eta^6$-chlorobenzene)$MCp]^+$ (M = Fe, Ru) with dinucleophiles to prepare a variety of bridged bimetallic

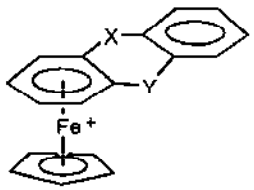


Scheme 3.



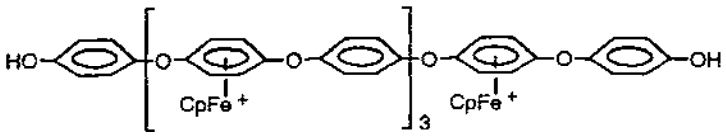
Scheme 4.

complexes. For example, the reaction with hydroquinone in the presence of base affords the *p*-diether complex $[CpFe(\eta^6\text{-}C_6H_5\text{–}O\text{–}C_6H_4\text{–}O\text{–}\eta^6\text{-}C_6H_5)FeCp]^{2+}$. Several studies have been carried out using dichlorobenzene complexes. Either mono- or disubstituted products can be realized from the reaction with simple nucleophiles [6,40,44]. The use of dinucleophiles allows for ring closure or the formation of oligomers. The *o*-dichlorobenzene complex of $[FeCp]^+$ reacts with 1,2-disubstituted aromatics bearing the appropriate heteroatom substituents to produce fused ring heterocyclic complexes of type (**1**) [45–47].



1 X,Y = O, S, NH

Two industrial groups have demonstrated the polymerization reactions of $[(\eta^6\text{-}p\text{-}C_6H_4Cl_2)RuCp^{\ddagger}]^+$ ($Cp^{\ddagger} = Cp$ or Cp^*) with aromatic oxygen- and sulfur-based dinucleophiles, producing poly(phenylene oxide) and poly(phenylene sulfide) polymers bearing $[Cp^{\ddagger}Ru]$ groups [48,49]. One polyether, derived from $Me_2C(p\text{-}C_6H_4OH)_2$ (bisphenol A) and the *p*-dichlorobenzene ruthenium complex, showed a M_n value of 6170 by gel permeation chromatography after demetallation [48]. Abd-El-Aziz has extended the concept of substitution polymerization by developing controlled step-wise oligomerization reactions [50,51]. The key to his work is the use of monosubstitution reactions of the dichloroaromatic complexes to produce synthetically-useful fragments, such as **2**, **3**, and **4** (Scheme 5). These have been used to synthesize monodisperse, soluble oligomers having up to 69 aromatic rings and 35 $[CpFe]^+$ groups.



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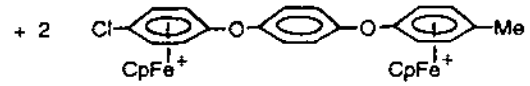

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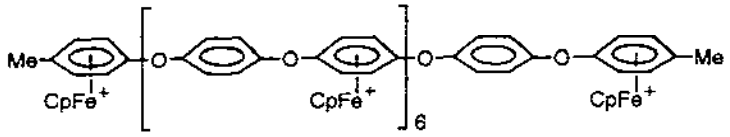

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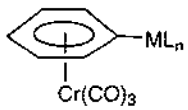
Scheme 5.

Less substitution work involving $[(\pi\text{-arene})Cr(CO)_3]$ and $[(\pi\text{-arene})Mn(CO)_3]^+$ has been carried out. The fluorobenzene, chlorobenzene and dichlorobenzene complexes of chromium tricarbonyl have been successfully reacted with thiolates, amines, hydride, and carbanions to give substitution products [52–60]. Mechanistic studies have revealed that nucleophile attack at non-*ipso* positions (similar to that shown in Scheme 1) also takes place in the chromium system [47,61]. Nucleophile migration again results in the isolation of the substitution product. Aryl ether monomers have been synthesized from $[(\pi\text{-}p\text{-}C_6H_4Cl_2)Cr(CO)_3]$ and aryl oxides; however, the second nucleophilic substitution was found to be greatly retarded by the aryloxy substituent [62]. Bimetallic complexes, **5**, have been generated through aromatic substitution when $[(\eta^6\text{-}C_6H_5X)Cr(CO)_3]$ (X = F, Cl) has been treated with organometallic nucleophiles: $ML_n = [Fe(CO)_4]^{2-}$, $[M(CO)_5]^-$ (M = Cr, W), and $[Cp'Fe(CO)_2]^-$ [63–67]. Several researchers have reported that methoxy and amino groups can act as nucleofuges during reactions with hydride or carbanions [68–71]. In several instances, the unusual remote (*meta* or *para*—so-called *tele*) displacement of the nucleofuge is reported (vide infra).



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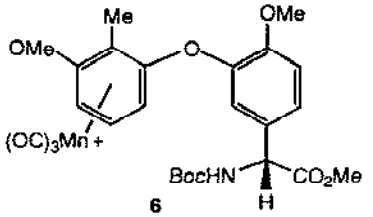
The initial investigations of nucleophilic substitution reactions involving $[(\eta^6\text{-chloroaromatic})Mn(CO)_3]^+$ were carried out by Pauson during the 1970s [72].

Since that time, a few synthetic applications of this chemistry toward the preparation of diaryl ethers have appeared [73–75], including **6**,



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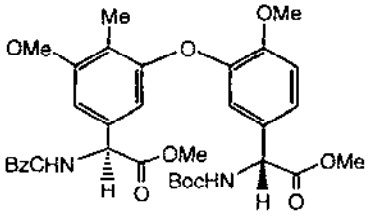
an intermediate in the synthesis of protected ristomycinic acid, **7** [75].



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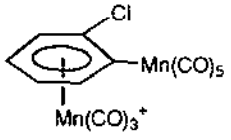
One inherent limitation of the manganese system is the apparent inaccessibility of $[(\pi\text{-dichlorobenzene})Mn(CO)_3]^+$. Attempted synthesis of the *ortho* isomer from $[Mn(CO)_5Br]$ under Lewis acidic conditions produced the unexpected substitution product **8** [15,76].



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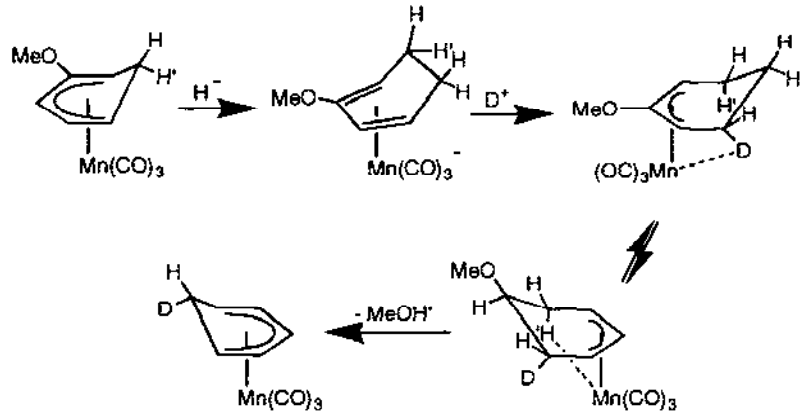
Neutral $[(\eta^5\text{-cyclohexadienyl})Mn(CO)_3]$ complexes bearing alkoxy, halide, amino, or thio substituents at unsaturated ring carbons were created with hydride donor reagents and then protonated as shown in Scheme 6 [77]. Hydride addition



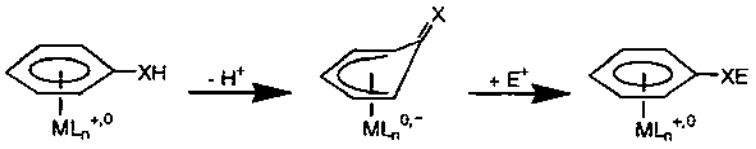
Scheme 6.

invariably occurred *para* to the methoxy group. *Endo* protonation (via the metal) produced an agostic intermediate, which readily underwent metal migration before eliminating CH_3OH. Taken together, the sequence in Scheme 6 represents a *para-tele* substitution of H^- for MeO^-. Other ring substituents also resulted in remote hydride substitution.

2.3. Ligand deprotonation reactions

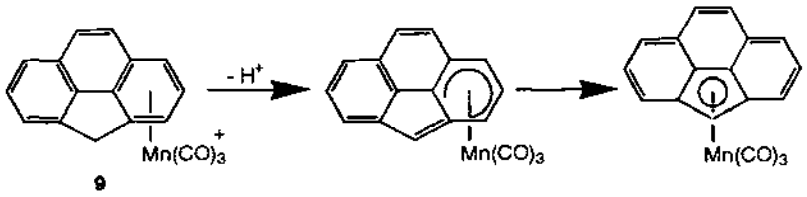
Benzylic hydrogens of cyclic π-polyene ligands (especially those coordinated to carbonyl-bearing and/or cationic metal fragments) are moderately acidic. This phenomenon results from the combination of electron-withdrawing effects upon the acid and resonance stabilization of the conjugate base. Of course, similar effects are encountered with simple electron-withdrawing substituents, such as the nitro group. As a result, studies have been conducted comparing the kinetic and thermodynamic acidities of Ph_2CH_2, Ph_3CH, and Ph_2CHCN with phenyls bearing nitro substituents or coordinated to the electrophilic metal centers: $[FeCp]^+$ and $[Cr(CO)_3]$ [78–80]. ($[Mn(CO)_3]^+$ has not been included in these studies. However, since this fragment offers the greatest nucleophilic substitution rate enhancement [1], it probably heads the list of benzylic hydrogen acidity enhancement as well.) Kinetic acidity of benzylic protons appears to be greatly enhanced by organometallic substituents: $p\text{-}NO_2 < [Cr(CO)_3] < [FeCp]^+$. However, the metal complexes are also reprotonated more rapidly. Thermodynamic acidity (pK_a) follows a somewhat different trend: $[Cr(CO)_3] < [FeCp]^+ \sim p\text{-}NO_2$. Moreover, in contrast to the effects of multiple *p*-nitrophenyl groups, the effect of two organometallic groups upon acidity is only slightly additive. This is probably a steric phenomenon.

Deprotonation α to π-coordinated arenes has been demonstrated for the metal fragments and substituents indicated in Scheme 7. The manganese [72,81,82] and iron [83,84] fragments produce stable heteroatom benzyl complexes, which have long been recognized. The anionic $[(\eta^5\text{-}C_6H_5{=}O)Cr(CO)_3]^-$ is now known as well [85]. The η^6-hydroquinone and -catechol complexes of $[Mn(CO)_3]^+$ have been prepared and deprotonated to produce η^5-semiquinone species [86]. Scheme 7 indicates that the various heteroatom cyclohexadienyl complexes react readily at the X atom with common electrophiles, including alkyl halides, acyl halides, sulfonyl halides, CS_2, alkylsilyl chlorides, and halogens. Hence, overall electrophilic substitution reactions can be carried out at these positions. The products possess renewed electrophilicity and hence are subject to nucleophilic addition [82].



$ML_n = [Cr(CO)_3], [Mn(CO)_3]^+, [FeCp]^+$; X = CH_2, NH, O, S

Scheme 7.



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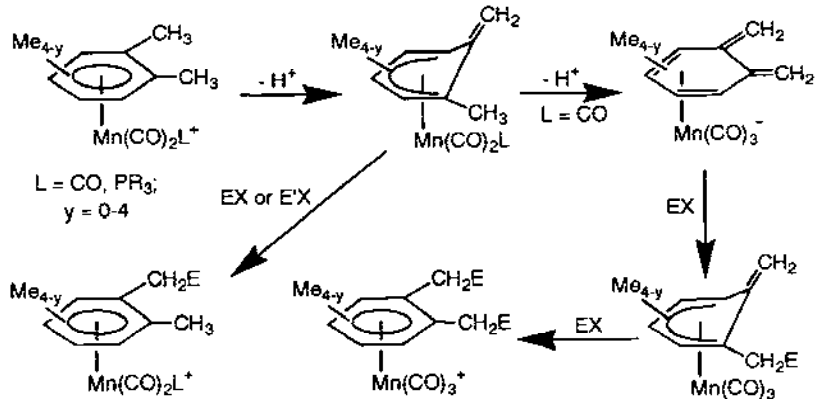
Scheme 8.

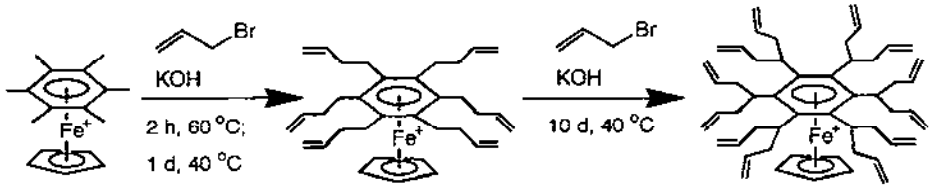
As shown in Scheme 7, benzylic carbons in π-arene complexes are also deprotonated easily. This deprotonation is especially facile for benzylic hydrogens of η^6-indene, -fluorene, and complex **9** (Scheme 8) [87]. The metal fragment undergoes a thermal ring shift reaction. Eyman's [88,89] and Gladfelter's [90] groups have produced a series of unstabilized benzyl and *o*-xylylene products through deprotonation of methylaromatic complexes of $[Mn(CO)_2L]^-$, as indicated in Scheme 9. The benzyl products react with organic electrophiles (EX), such as those listed above. Such species are particularly nucleophilic when a phosphine ligand is present on the metal. These complexes have been shown to react with organometallic electrophiles ($E'X = [Mn(CO)_5Br]$ and $[CpFe(CO)_2I]$) and to abstract halogen atoms from chloroform and carbon tetrahalides.

o-Xylylene complexes of ruthenium are also produced through double deprotonation. Base treatment of $[(\eta^6\text{-}C_6Me_6)_2Ru]^{2+}$ yields $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_6Me_4(CH_2)_2)]$ in which the metal atom is *endo*, i.e. coordinated to the cyclohexadiene portion of the hydrocarbon [91,92]. In contrast, Bennett reports that the deprotonation of $[(\eta^6\text{-}C_6Me_{6-x}H_x)RuL_2Y]^+$ ($x = 0$–4; L = phosphines, phosphites; Y = ONO_2, O_2CCF_3) producing $[(\eta^4\text{-}C_6Me_{4-x}H_x(CH_2)_2)RuL_3]$ usually results in the metal being situated in the *exo* position [8].

Astruc has reported a variety of synthetically-intriguing transformations associated with the deprotonation of $[(\eta^6\text{-}C_6Me_{6-x}H_x)FeCp]^+$ ($x = 0$–4) [6,93–95]. He has shown that one-pot deprotonation/alkylation of all methyl groups can



Scheme 9.

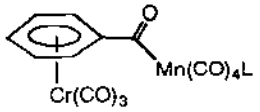


Scheme 10.

achieved. Successful alkylating agents have included alkyl, allyl, and benzyl halides. Multiple functionalizations at each methyl can often be achieved, for example as shown in Scheme 10. Similar alkylation reactions have been carried out upon the methyls in $[Cp^*CoCp]^+$ [96].

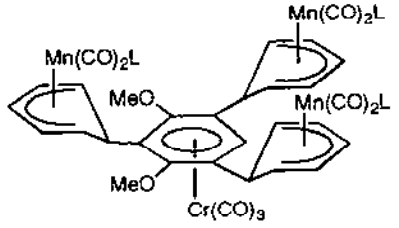
[(π-Arene)$Cr(CO)_3$] complexes have been deprotonated and alkylated at benzylic positions to synthetic advantage: this topic has been reviewed extensively [13,97]. Deprotonation of [(η^6-$C_6H_5CH_2OH$)$Cr(CO)_3$] by alkyllithium at the alcohol is accompanied by directed nucleophilic addition at an *ortho* position [98]. Unique to [(π-arene)$Cr(CO)_3$] among electrophilic arene complexes is the facile deprotonation and lithiation of the ring. This reaction and the subsequent addition of electrophiles to the lithio complexes are also widely utilized in synthesis and have been reviewed [12]. Electrophilic attack on lithioaromatic chromium complexes, when followed by nucleophilic addition, constitutes a strategy for double functionalization of coordinated arenes.

Recently, [(η^6-lithioarene)$Cr(CO)_3$] species have been utilized in the synthesis of polymetallic products. Organometallic electrophiles which have been reacted with these chromium compounds (with the displacement of halide) include: $[Cp_2TiCl_2]$, $[Au(PPh_3)_3Cl]$, and $[Mn(CO)_5Br]$ [99–101]. In the latter case, reaction in the presence of added $P(OMe)_3$ or chelating diphosphine produced migratory insertion products, such as **10**.



10, L = $P(OMe)_3$

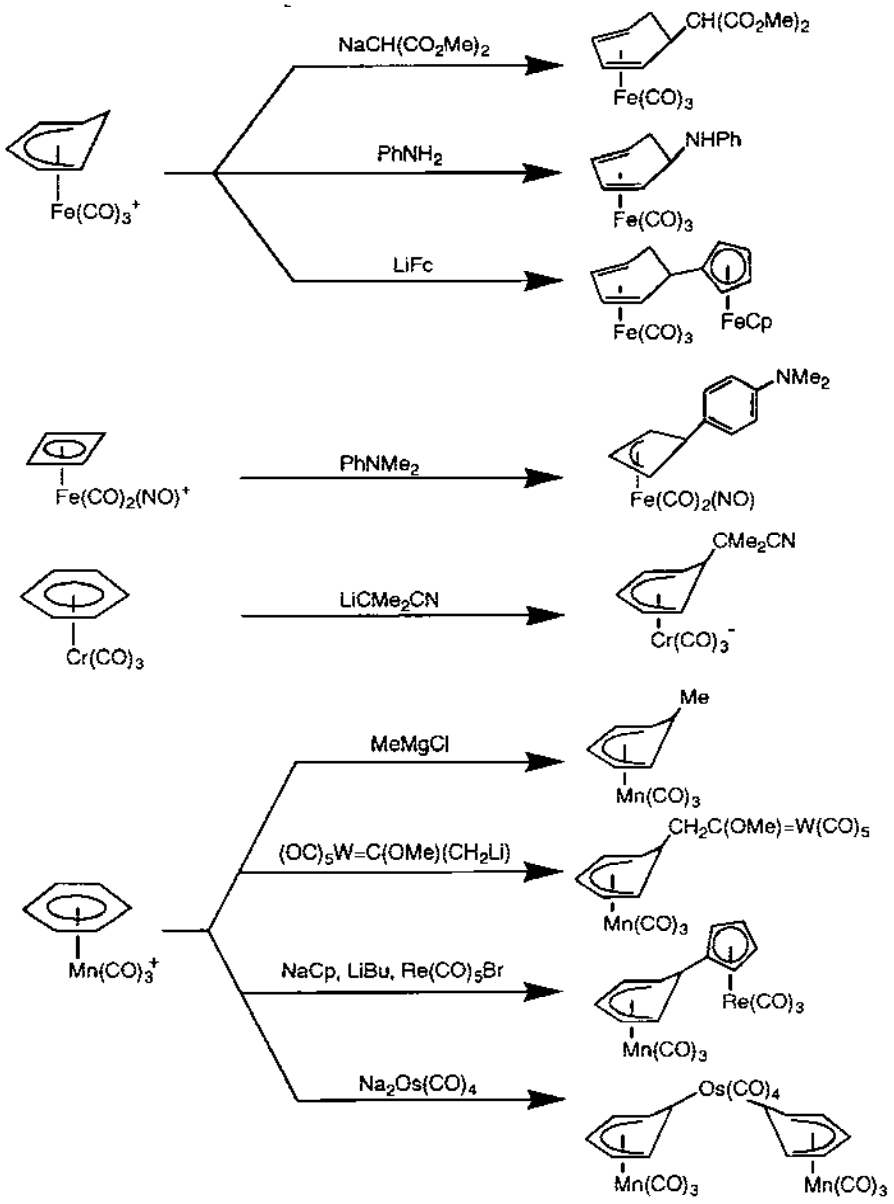
Reiterative lithiation, followed by treatment with [(η^6-benzene)$Mn(CO)_2P(OEt)_3$]$^+$, produced the interesting tetrametallic product **11** [102].



11, L = $P(OEt)_3$

2.4. Single nucleophilic addition reactions

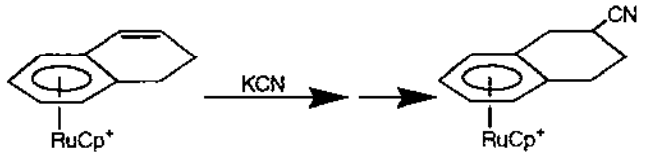
The most fundamental and important reaction of the electrophilic complexes shown in Scheme 1 is the addition of nucleophiles to the coordinated cyclic π-hydrocarbon ligand. A vast array of nucleophiles has been utilized in this



Scheme 11.

reaction, which, in spite of being termed an addition, is in reality a displacement reaction involving formation of a C–X bond with concomitant cleavage of a M–C bond. X is the nucleophile donor atom and can be C, N, P, O, S, H, or even a metal. A few reactions are collected in Scheme 11, which serve to illustrate the great diversity of nucleophiles that can be added to coordinated π-hydrocarbons. Many more examples are provided in general reviews [9–11] and in the following (selected) specific articles: $[(\eta^5$-cyclohexadienyl)$Fe(CO)_3]^+$ [10,103–107], $[(\eta^5$-cyclohexadienyl)$Mn(CO)_2NO]^+$ [2,108–110], $[(\eta^6$-arene)$Cr(CO)_3]$ [11,111–114], $[(\eta^6$-arene)$Mn(CO)_3]^+$ [2,102,110,115–122], $[(\eta^6$-arene)$MCp]^+$ (M = Fe, Ru) [11,123,124], $[(\eta^6$-arene$)_2M]^{2+}$ (M = Fe, Ru, Os) [6,125–129], $[(\eta^6$-cycloheptatriene)$Mn(CO)_3]^+$ [130,131], $[(\eta^7$-tropylium)$Cr(CO)_3]^+$ [132–136], and $[(\eta^4$-cyclobutadiene)$Fe(CO)_2NO]^+$ [137,138].

Nucleophilic addition can also occur at the exocyclic double bond in styrene and dihydronaphthalene type complexes, as illustrated by Eqs 2 and 3 [139–142].



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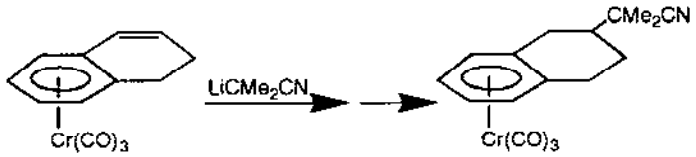
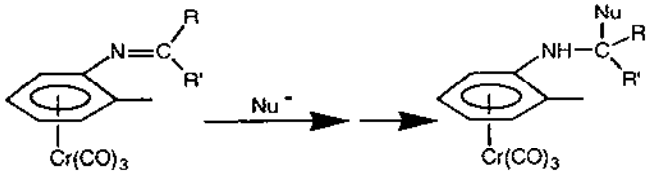


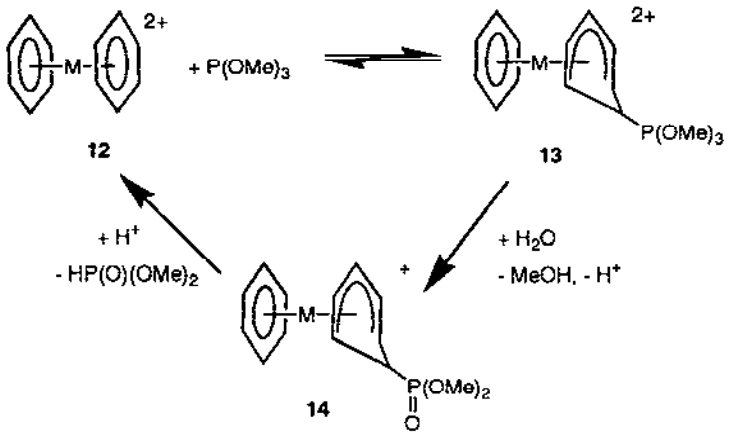
(3)

In an analogous manner, nucleophilic addition of $NaBH_4$ and LiMe to the imine in Eq. 4 has been shown to occur with substantial diastereoselectivity [143].



(4)

Phosphorus donor nucleophiles have been extensively employed in nucleophilic addition reactions, in part because the reactions are generally clean and amenable to kinetic study (see Section 2.4.1). One especially interesting example is the addition of trialkyl phosphites, such as $P(OMe)_3$, to $[(C_6H_6)_2M]^{2+}$ (**12**; M = Fe, Ru). It was found [144] that the addition of a 100-fold excess of $P(OMe)_3$ to a slurry of **12** in slightly wet MeCN produced a homogeneous solution from which the starting complex **12** reprecipitated after several minutes, while all of the phosphite was converted to dimethyl phosphite, $HP(O)(OMe)_2$. In other words, complex **12** is a homogeneous catalyst for the conversion of $P(OMe)_3$ to $HP(O)(OMe)_2$. The proposed chemistry involved is illustrated in Scheme 12. The cyclohexadienyl phosphonium adduct (**13**) in this mechanism was detected and

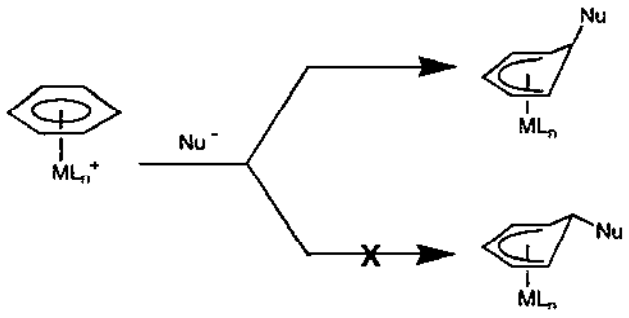


Scheme 12.

characterized. The phosphorus atom in **13** is activated to nucleophilic attack by water to afford the dimethyl phosphonate adduct **14**. The H^+ liberated in this step cleaves the phosphonate group to regenerate **12**, which then repeats the cycle until all of the $P(OMe)_3$ is consumed, after which it reprecipitates.

2.4.1. Relative rates of addition

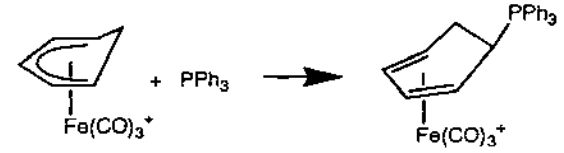
Although nucleophiles can react with electrophilic π-hydrocarbon complexes by a variety of pathways (see Section 2.1), simple addition to the hydrocarbon is the most synthetically useful reaction. There now exists sufficient mechanistic and kinetic data such that meaningful insights into the factors controlling nucleophilic addition to coordinated π-hydrocarbons are possible. At a rather basic level, it is important to note that addition reactions, as typified by Scheme 13, almost always form products with the nucleophile situated in an *exo*, and not an *endo*, position. This fact suggests strongly that addition is a direct process that is not normally preceded by initial attack at the metal or another ligand (L).



Scheme 13.

The important mechanistic questions concern how the reactivity depends on the metal, the π-hydrocarbon, the nonreacting ligands, and the nucleophile. It may be anticipated that the susceptibility of an organometallic electrophile to nucleophilic attack would be reflected in some of the former's extrakinetic properties. Thus, a correlation has been noted [145] between the rate of tertiary phosphine addition and reduction potentials for a series of planar cyclic π-hydrocarbon complexes. Bush and Angelici [146] defined a parameter, k^*_{CO}, that reflects the relative reactivity, in either a thermodynamic or kinetic sense, of benzene complexes $[(\pi\text{-}C_6H_6)ML_n]^{m+}$. The parameter k^*_{CO} is the average C–O stretching force constant for the hypothetical complex in which CO replaces the benzene, i.e. $[(OC)_3ML_n]^{m+}$, and shows in a semi-quantitative manner what would be expected qualitatively—the higher ν_{CO} stretching frequency, the more electrophilic the complex.

The kinetics of nucleophilic addition to a large number of coordinated π-hydrocarbon systems have been studied. The most informative results were obtained with P-donor nucleophiles (PR_3, $P(OR)_3$) and simple N-donor nucleophiles (RNH_2, $PhNH_2$, pyridines, imidazoles) [1]. The π-hydrocarbon ligands in these investigations included dienes, dienyls, trienes and trienyls and the organometallic fragments included the following metals: Cr, Mo, W, Mn, Re, Ru, Os and Co. Two typical reactions are given in Eqs 5 and 6.



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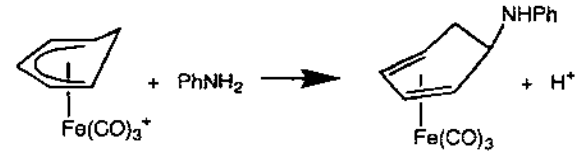
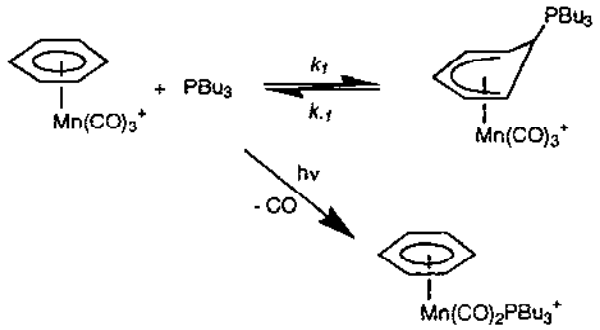


(6)

Most of these reactions are rapid, with a time scale measured in seconds or less. One of the first studied in detail was PBu_3 addition to $[(\pi\text{-arene})Mn(CO)_3]^+$, as outlined in Scheme 14. It was found [147] that PBu_3 adds rapidly and reversibly to the arene ring, with the indicated irreversible CO substitution [148] occurring by a much slower photochemical pathway. The rate law given in Eq. (7) was obtained for the addition step, from which the equilibrium constant can be calculated as $K_{eq} = k_1/k_{-1}$.

$$\text{Rate} = k_1[\text{complex}][PBu_3] + k_{-1}[\text{complex}] \tag{7}$$

Consideration of the rate constants for P- and N-donor nucleophiles in more than one hundred reactions led to the conclusion that relative nucleophilic reactivities are independent of the organometallic electrophile. This was found to be true even though the reactivities cover seven powers of ten. A convenient way to express this important result is via the linear free energy relationship given in Eq. (8).



Scheme 14.

$$\log(k_1/k_0) = N_M \tag{8}$$

In this equation, k_1 is the second order rate constant for addition of an arbitrary nucleophile, while k_0 refers to a reference nucleophile (chosen to be $P(OBu)_3$). In this manner, each nucleophile is assigned a number for the parameter N_M, which is electrophile-independent (Table 1). Because Eq. (8) contains only a single parameter, it follows that the reactivity of any new electrophile with P- and N-donors can be completely predicted by measuring the reaction rate with only one nucleophile. An important corollary to this is that relative electrophilic reactivities are nucleophile-independent. This in turn means that it is possible to quantify the relative ability of transition metal fragments to activate π-hydrocarbons, without regard for the particular hydrocarbon involved. This activation power is reflected in so-called electrophilic transferability parameters (T_E), some of which are listed in Table 2. These parameters show at a glance which fragments are good activators and which are not. For example, an arene attached to $[Mn(CO)_3]^+$ will be about 10^4 times more electrophilic than when attached to $[FeCp]^+$. Similarly, a dienyl ring (η^5-C_6H_7 or η^5-C_7H_9) is more reactive by a factor of about 90 when coordinated to $[Fe(CO)_3]^+$ compared with $[Mn(CO)(NO)PPh_3]^+$.

Table 1
Relative nucleophilic reactivities (N_M) for P- and N-donor addition to coordinated π-hydrocarbons.

Nucleophile	N_M[a]	Nucleophile	N_M[a]
$P(2\text{-}MeOC_6H_4)_3$	3.9	Pyridine	2.0
PBu_3	3.8	$C_6H_5NH_2$	1.9
$P(4\text{-}MeOC_6H_4)_3$	3.0	2-Methylpyridine	1.4
$4\text{-}MeOC_6H_4NH_2$	2.6	$P(4\text{-}ClC_6H_4)_3$	1.0
$4\text{-}MeC_6H_4NH_2$	2.4	$P(CH_2CH_2CN)_3$	0.1
Imidazole	2.1	$P(OBu)_3$	0.0
PPh_3	2.1	$P(OPh)_3$	−3.3

[a] See Eq. (8) for definition of N_M. Data refer to 20°C in acetone or nitromethane as solvent.

Table 2
The relative ability (T_E) of transition metal fragments to activate triene and dienyl rings

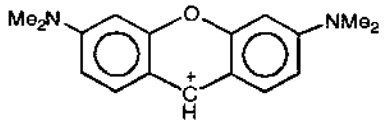
Fragment	T_E (trienes)	Fragment	T_E (dienyls)
$[Fe(C_6H_6)]^{2+}$	200 000 000	$[Fe(CO)_3]+$	1800
$[Ru(C_6H_6)]^{2+}$	6 000 000	$[Mn(CO)_2NO]^+$	1800
$[Os(C_6H_6)]^{2+}$	1 500 000	$[Fe(CO)_2PPh_3]^+$	28
$[Mn(CO)_3]^+$	11 000	$[Mn(CO)(NO)PPh_3]^+$	20
$[Re(CO)_3]^+$	10 000	$[CoCp]^+$	(1)
$[Mn(CO)_2PPh_3]^+$	160		
$[FeCp]^+$	(1)		
$[Cr(CO)]_3$	Very small		

Further examination of Table 2 reveals some interesting trends. As expected, replacement of CO by PPh_3 in $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ complexes lowers the electrophilicity (by a factor of about 70). A detailed study of $P(OBu)_3$ addition to $[(\eta^4\text{-}C_4H_4)Fe(CO)(NO)L]^+$ showed that the rate of addition decreased in the order $L = CO > P(CH_2CH_2CN)_3 > P(4\text{-}ClC_6H_4)_3 > P(4\text{-}FC_6H_4)_3 > AsPh_3 \approx PPh_3 > P(4\text{-}MeC_6H_4)_3 > P(4\text{-}MeOC_6H_4)_3$ with an overall reactivity range of 100 [138]. The dependence of the electrophilicity on the metal in the iron triad follows the order $Fe \gg Ru, Os$, and is explicible in terms of the documented [149] π-backbonding ability order $Fe(II) \ll Ru(II), Os(II)$. In the chromium and manganese triads there is probably little variation in π-backbonding ability with the metal, and this is reflected in similar T_E values for organometallic fragments within these respective triads. In contrast to these ring addition processes, reactions involving associative attack at the metal with ring displacement display very different metal dependencies: $Mo > W \gg Cr$ [150], $Re(I) > Mn(I)$ [147], and $Ru \gg Fe$ [151,152]. These differences provide further support for the assumption of a direct bimolecular mechanism for nucleophilic additions to coordinated rings.

Electrophilic reactivity depends, of course, on the nature of the π-hydrocarbon. Most systematic work has centered on trienes and dienyls. With trienes, it was found that coordinated cycloheptatriene is much more reactive than benzene, e.g. $[(\eta^6\text{-}C_7H_8)Mn(CO)_3]^+ > [(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+$ by a factor of at least 10^4. This order no doubt reflects the loss of resonance energy accompanying addition to arene complexes. Conversely, with dienyls it was found that coordinated cycloheptadienyl rings are less reactive than cyclohexadienyl rings, e.g. $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+ < [(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ by a factor of 70. In this case, the lower reactivity of the cycloheptadienyl rings is readily explained as a result of the steric disposition of the methylene hydrogens, which eclipse the carbon atoms to which the nucleophile adds [153]. This steric interference is much reduced with the cyclohexadienyl ring.

It is surprising that the simple single parameter LFER expression given in Eq. (8) holds, since nucleophilic additions are in reality S_N2 reactions involving M–C bond cleavage, with the leaving group remaining attached to the periphery of the molecule. Ritchie [154] has reported that the same equation holds for N- and

O-donor nucleophilic additions to free carbocations. By measuring the rates of addition of P- and N-donors to carbocations **15** and **16**, we have shown [155] that a relationship analogous to Eq. (8) holds for these reactions as well.



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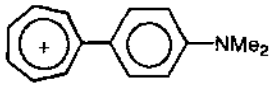


16

More significantly, the relative reactivities (N_M) of the P- and N-donors towards **15** and **16** are the same as those obtained with organometallic electrophiles. This is rather surprising and suggests that the transition state for most of the organometallic reactions is an early one, so that cleavage of the M–C bond does not play a major energetic role. This important point follows in part from the observation that the activation energies for the organometallic reactions are generally small (e.g. 25 kJ mol^{-1}), yet involve M–C bond cleavage. The conclusion is that relative nucleophilicities for addition to a π-hydrocarbon are the same whether or not the hydrocarbon is coordinated to a metal. Apparently, the LFER in Eq. (8) is a very general one that applies to a wide range of electrophile–nucleophile combination reactions.

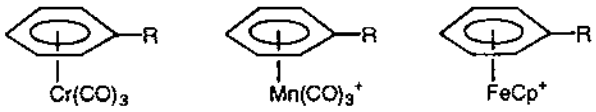
It has been established that P- and N-donor additions to sterically uncongested π-hydrocarbon complexes occur with relative nucleophilic (electrophilic) reactivities that are electrophile (nucleophile) independent—regardless of the nature of the metal, nonreacting ligands, or the π-hydrocarbon. An important question is whether or not this is also true with carbon nucleophiles. Rate studies have been made with a variety of aromatic nucleophiles, e.g. furan, pyrrole, indole, thiophene, *N*,*N*-dimethylaniline, methoxybenzenes, and it is clear that Eq. (8) is not obeyed [1]. All of these reactions occur with C–C bond formation and are a rather exotic type of electrophilic aromatic substitution, with the organometallic complex serving as the electrophile (see Scheme 11 for an example with $[(\eta^4\text{-}C_4H_4)Fe(CO)_2NO]^+$). An analysis of the rate laws, activation parameters, and other kinetic data suggests that aromatic nucleophiles react by first forming a π-complex with the organometallic substrate, followed by rate-determining C–C bond formation and subsequent rapid proton loss. Thus, the reactivities reflect the strength of the precursor π-complex as well as the rate of formation of the σ C–C bond. It is believed that this accounts for observed substantial dependence of the relative nucleophilicities (N_M) on the nature of the electrophile with aromatic nucleophiles.

It was predicted [1] that simple (nonaromatic) C-donors would react in accordance with Eq. (8). Recently, Mayr has studied the reactions of a series of $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ cations with simple H- and vinyl C-donors that are unlikely

to form precursor π-complexes [156,157]. The conclusion was reached that these nucleophiles indeed obey Eq. (8). Thus, it appears that the discussion given above concerning P- and N-donor addition to free and complexed hydrocarbons also applies to simple C-donors.

2.4.2. Regiochemical and stereochemical aspects

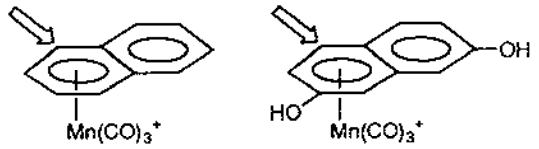
With complexed arenes, the effect of substituents on the regioselectivity of nucleophilic attack has been studied for a variety of systems [11,136]. The directing influence of the R group in simple monosubstituted complexes **17–19** is only modest for R = alkyl, aryl, or chloride.



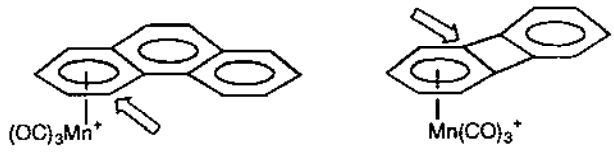
17 **18** **19**

However, for R = OMe or NMe_2, nucleophilic addition generally occurs at a *meta* site with high regioselectivity, a fact of considerable synthetic significance. The observed regioselectivities have been variously interpreted in terms of charge distribution in the arene ligand, frontier orbital interaction between the complex lowest unoccupied molecular orbital (LUMO) and the nucleophile highest occupied molecular orbital (HOMO), and conformational preferences of the $[Cr(CO)_3]$ moiety in the case of **17** [11,114,158,159].

Hydride and carbanion addition to simple fused ring hydrocarbons coordinated to $[Mn(CO)_3]^+$ occurs predominantly at the sites indicated by the arrows in structures **20–23** [121,160].



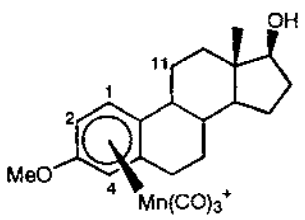
20 **21**



22 **23**

The biphenylene complex (**23**) is unusual in that addition takes place exclusively at a substituted (bridgehead) carbon. This site preference, as well as the observed exceptionally high electrophilicity of the bridgehead carbons, was suggested to be due to steric and electronic constraints inherent in the cyclobutadiene ring, which are relaxed upon nucleophilic addition.

Coordination of $[Mn(CO)_3]^+$ to the aromatic steroid 3,17-dimethoxyestradiol occurs with nearly equal facility to the β (up) and α (down) faces to afford diastereomers **24** and **25**, respectively [122,161].



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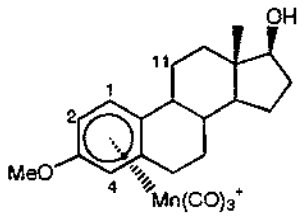
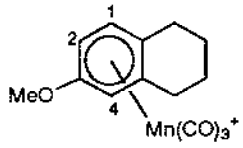


25

The β-isomer is attacked by nucleophiles only at the electronically favored C-1 *meta* position. With the α-analogue **25**, both electronic and steric factors play a role, with the result that attack can occur at C-1, C-2 and/or C-4. The distribution among these sites is highly nucleophile dependent. Thus, $NaBH_4$ and $LiCH_2C(O)CMe_3$ give only C-1 addition, MeMgCl and LiMe add to all three positions nearly equally, and PhMgBr attacks at C-2 and C-4, but not C-1. That steric interactions are important in determining the regioselectivity with **25** is evident from the fact that addition to the electronically-similar tetralin complex **26** is stereospecific at the C-1 *meta* position.



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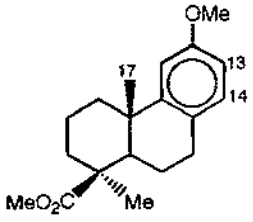
A series of X-ray structural analyses established that the relevant interaction is between an incoming nucleophile situated at C-1 and the CH_2 group at C-11. This interaction is much greater when the nucleophile is β (metal α), and constitutes a kinetic barrier that results in competitive addition to several sites. With **24**, however, X-ray data show this barrier to be much smaller.

The regioselectivity of carbanion addition to the arene in derivatives of methylated podocarpic acid (**27**) coordinated to $[Cr(CO)_3]$ [162] and $[Mn(CO)_3]^-$ [119] also differ for the α (down) and β (up) isomers.

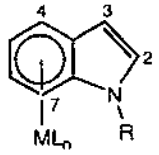


27

In this case it is the α isomer that suffers *meta* (C-14) addition. The β isomer is attacked at both *meta* and *ortho* (C-13) sites, with the latter predominating. A series of X-ray structures show clearly that the C-17 methyl constrains the conformation of the $[M(CO)_3]$ moiety (when the metal is β) such that it is energetically unfavorable for a M–C–O link to eclipse C-14 in the *meta* addition product. It is

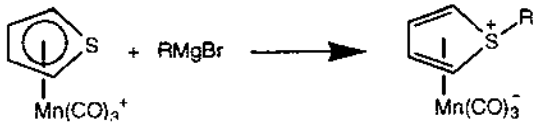
known [114,159] that in unconstrained complexes eclipsing of this sort is the preferred conformation and the consequence in this case is that addition to C-13 predominates.

The transition metal fragments $[Cr(CO)_3]$ and $[Mn(CO)_3]^+$ coordinate to the carbocyclic ring in indoles to produce **28**.



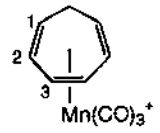
28

This preferentially activates the carbocyclic ring over the pyrrole ring, and nucleophiles have been found to add C-4 and C-7 in a ratio that depends on the nucleophile and on the nature of any substituents at C-3 and N [163–165]. Similarly, complexes of benzofuran [163,165], dibenzofuran [166], benzothiophene [167,168], and dibenzothiophene [166] undergo nucleophilic attack predominantly at C-4 and C-7. Thiophene complexes of $[Mn(CO)_3]^+$ add the nucleophiles CN^-, H^- and PBu_3 at a carbon adjacent to the sulfur atom [169], but Grignard reagents and cuprates add to the sulfur to give zwitterionic complexes according to Eq. 9 [170,171].



(9)

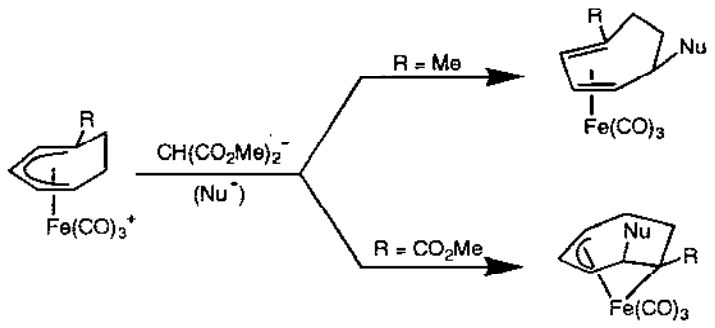
As noted above, coordinated cycloheptatriene is much more electrophilic than is coordinated benzene, and a wide range of nucleophiles add to the terminus of the π-system in C_7H_8 complexes such as $[(\eta^6\text{-}C_7H_8)Mn(CO)_3]^+$ (**29**), $[(\eta^6\text{-}C_7H_8)FeCp]^-$, and $[(\eta^6\text{-}C_7H_8)Ru(\eta^5\text{-}C_7H_9)]^+$ [130,131,136,172–174].



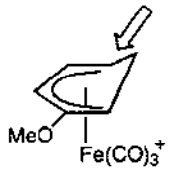
29

That nucleophiles attack at C-1 in these complexes, as opposed to an internal position (C-2, C-3) is in agreement with the rules of Davies et al. [175]. Note, however, that nucleophilic addition to internal sites is known in some other types of π-complexes (vide infra).

The most extensively studied electrophilic dienyl system is based on $[(\eta^5\text{-}cyclohexadienyl)Fe(CO)_3]^+$. Nucleophiles generally add to the terminus of the π-system, with substituent effects as indicated for the commonly employed 2-OMe complex **30** [10,176,177].



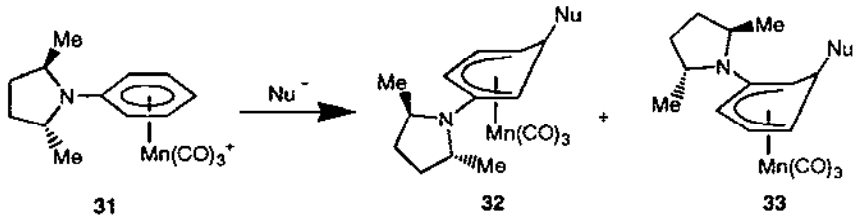
Scheme 15.



30

Analogous results were obtained for $[(\eta^5\text{-cyclohexadienyl})Mn(CO)_2NO]^+$ [108]. The situation with $[(\eta^5\text{-cycloheptadienyl})Fe(CO)_3]^+$ complexes differs markedly in that the regioselectivity of addition is strongly dependent on the nature of any substituents as well as that of the nucleophile, with soft nucleophiles favoring the terminal dienyl carbon and hard ones favoring internal attack to afford σ,π-allyl products [178,179]. An example of the effect of substituents is given in Scheme 15.

The addition of the chiral enolate of *N*-acyloxazolidinone and a chiral glycine enolate equivalent to $[(\pi\text{-arene})Mn(CO)_3]^+$ complexes occurs with high diastereoselectivity and has been used to prepare enantiomerically enriched 2-arylpropionic acids and α-arylglycine derivatives [73,75,180]. In one case, the chiral cyclohexadienyl manganese intermediate was subsequently converted to (+)-juvabione via a chiral cyclohexadiene [181]. The synthesis of coordinated chiral disubstituted cyclohexadienes has been demonstrated by sequential addition of a nucleophile to $[(\pi\text{-arene})Mn(CO)_2PMe_3]^+$, followed by treatment with NO^+ to afford $[(\eta^5\text{-cyclohexadienyl})Mn(CO)(NO)PMe_3]^+$, and finally addition of a second nucleophile to give the diene (see Section 2.5) [2]. The attachment of a dimethylpyrrolidinyl



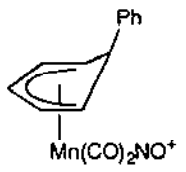
31 **32** **33**

Scheme 16.

substituent to $[(\pi\text{-benzene})Mn(CO)_3]^+$ to afford **31** enables asymmetric nucleophilic additions as outlined in Scheme 16 [182,183]. With PhMgBr, the diastereomeric excess of **32** over **33** is greater than 80%. While strong hydride donors also favor **32**, it was found that relatively weak hydride donors such as $NaBH_4$ lead to a reversal in selectivity, so that **33** is favored over **32** by as much as 4:1. The explanation for this interesting effect is that the extent of bond formation in the transition state is weak for the strong donors, but much more substantial for weaker donors, with the result that the former reflect the kinetic preferences and the latter reflect the product stabilities [183].

As illustrated in Scheme 13, nucleophilic addition to coordinated cyclic π-hydrocarbons almost always occurs at an *exo* face to give the *exo* product stereospecifically. With hydride donors, there are reports that *endo* addition may sometimes occur, at least to some extent. For example, Eyman et al. [184] reported that hydride donors add to $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]^+$ to give both *exo* and *endo* cyclohexadienyl products, with the *endo* pathway favored by protic solvents and bulkier hydride sources. Low temperature NMR experiments indicated the presence of a formyl species as an intermediate, from which the *endo* product is formed via migration of H^- to the *endo* side of the ring. It was suggested that larger hydride donors have a propensity to attack at a more sterically accessible carbonyl. The greater amount of *endo* attack in protic solvents was explained as due to hydrogen bonding from the solvent to the hydride donor, thereby increasing the latter's steric bulk.

Stereospecific *endo* addition of hydride (deuteride) to a coordinated cyclic π-hydrocarbon was first reported for $NaBD_4$ addition to **34** to give **35** [185].



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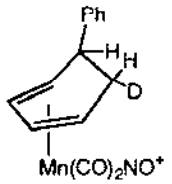
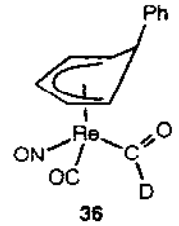


35

Subsequent work showed that hydride adds stereospecifically endo to $[(\eta^5\text{-cyclohexadienyl})Mn(CO)(NO)L]^+$ complexes regardless of the hydride source, any substituents on the dienyl ring, and the nature of ligand L. Similarly, when the metal is rhenium or the ring is cycloheptadienyl, the addition is still *endo* [173,186]. Low temperature IR and NMR experiments showed [186] that $[(\eta^5\text{-cyclohexadienyl})Re(CO)(NO)L]^+$ reacts rapidly with hydride (deuteride) to give a formyl species **36** that converts to the cyclohexadiene complex.



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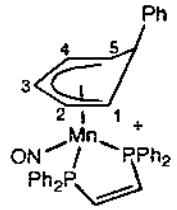
When no CO ligands are present, as in **37**,



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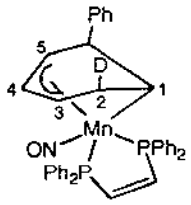
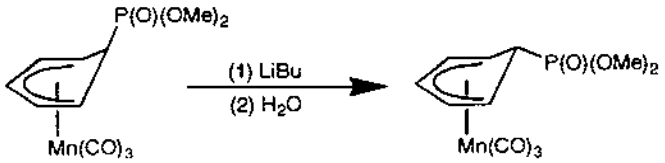
deuteride addition occurs by *exo* attack at C-2 to afford the σ,π-allyl complex **38**.



38

From these results, it was concluded that the presence of a CO ligand is a necessary but not sufficient condition to guarantee an *endo* product. (It is not sufficient because many electrophilic carbonyl-containing complexes add hydride *exo*.) It is possible that the *endo* stereochemistry involves conversion of the formyl to a metal carbonyl hydride, followed by hydride migration to the ring. The presence of a nitrosyl ligand offers the advantage of allowing the formation of a M(CO)(H) species while maintaining an 18-electron count via bending of the NO ligand.

Chung et al. [187] reported an interesting case of *exo* to *endo* conversion involving the phosphonate complex shown in Eq. 10.



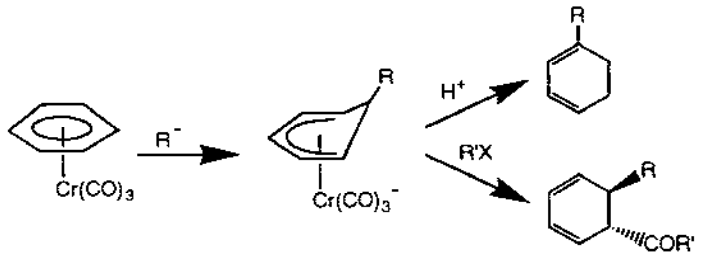
(10)

Deprotonation of the saturated carbon with LiBu, followed by protonation with water, generated the *endo* isomer in 65% yield.

2.5. Double addition reactions

Since cyclohexadienyl complexes usually rearomatize upon decomplexation, in order to transform aromatics to substituted 1,3-cyclohexadienes, it is necessary to carry out two addition reactions. These additions can follow either of two general pathways: consecutive addition of two nucleophiles to sufficiently electrophilic complexes or addition of an electrophile and a nucleophile.

Double addition to [(η^6-arene)Cr(CO)$_3$] can be pursued through either of the pathways shown in Scheme 17. Protonation of substituted [(η^5-cyclohexadi-

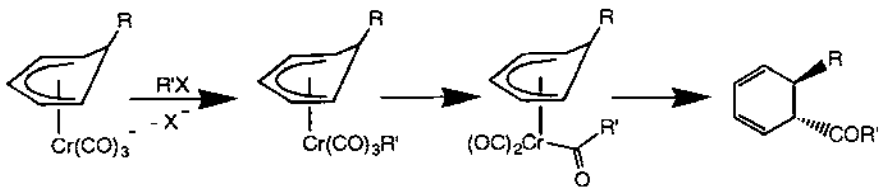


Scheme 17.

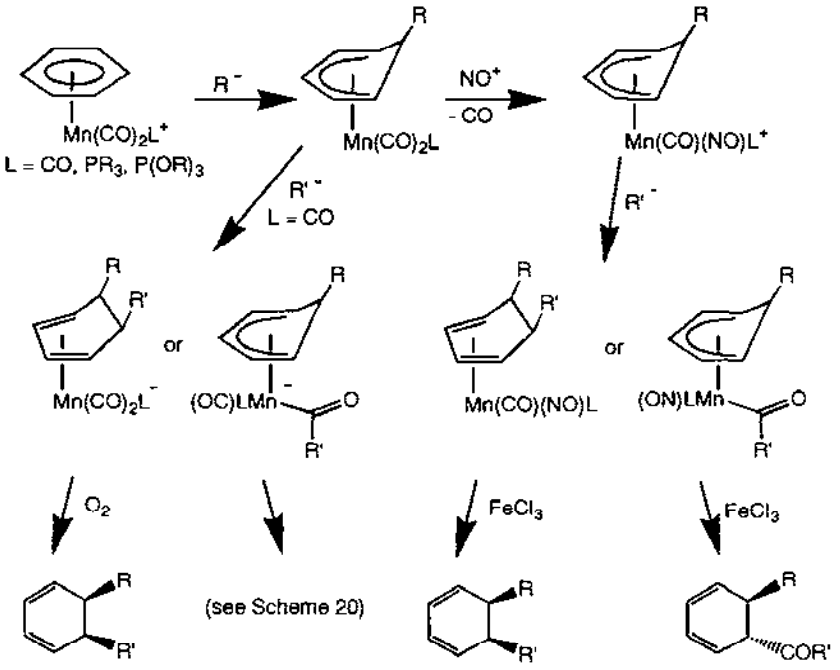
enyl)$Cr(CO)_3]^-$ typically affords 1-substituted 1,3-cyclohexadienes [3,61,111]. The presence of a methoxy group results in cyclohexenones [188]. When LiR (R = CMe_2CN) was reacted with [(η^6-*p*-fluorotoluene)$Cr(CO)_3$], both nucleophilic substitution and addition occurred. Upon protonation, a 1-methyl-1,3-cyclohexadiene product bearing R groups at the 1 and 5 positions was obtained [189]. Kündig's group has shown that the anionic chromium dienyl products of nucleophilic addition can be quenched with alkyl halide electrophiles to produce *trans*-disubstituted acyl cyclohexadienones according to the mechanism shown in Scheme 18 [3,112,113,190–192]. Initial addition of the electrophile to chromium was confirmed by an X-ray structure of an [(η^5-cyclohexadienyl)$Cr(CO)_3SnPh_3$] product resulting from addition of Ph_3SnCl.

Double nucleophilic addition reaction pathways for the [(η^6-arene)$Mn(CO)_3]^+$ system are shown in Scheme 19. The direct addition of a second nucleophile to [(η^5-cyclohexadienyl)$Mn(CO)_3$] has been demonstrated by two groups, with differing outcomes. In either case, strong nucleophiles are needed to react with this neutral complex. McDaniel has shown that phenyl-, sulfide-, cyano-, and ester enolate-stabilized carbanions directly add to the dienyl ring with *ortho* regiochemistry and *exo* stereochemistry [193]. Oxidative demetallation of the anionic products results in good yields of *cis*-disubstituted 1,3-cyclohexadienes. In contrast to this, Sheridan has found that alkyl- and aryllithiums attack a carbonyl ligand of [(η^5-cyclohexadienyl)$Mn(CO)_3$] and [(η^5-cycloheptadienyl)$Mn(CO)_3$] [194–196]. The resulting acyl anions can be protonated at the *endo* position to produce agostic complexes via the mechanism shown in Scheme 20. Further deprotonation and alkylation of these complexes has also been demonstrated, as indicated.

A more general strategy for the second nucleophilic addition in the manganese system involves electrophilic reactivation via substitution of a CO ligand with NO^+



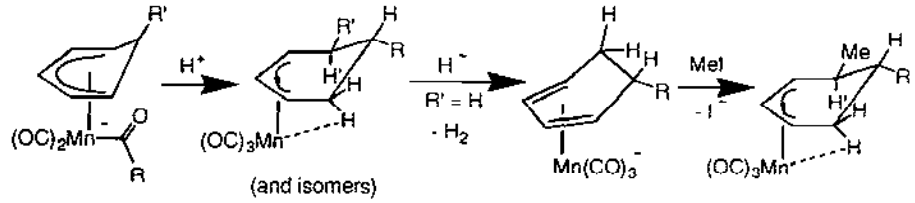
Scheme 18.



Scheme 19.

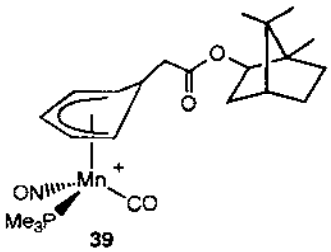
[2,108,185]. We have shown that soft carbanions, such as enolates, directly attack the dienyl ring (*ortho* and *exo*), producing stable, neutral η^4-diene complexes (Scheme 19) [2,197]. Hard carbanions, such as aryllithiums, attack the metal, leading to carbonyl insertion and acyl migration (similar to that shown in Scheme 10). This results in *trans*-acyl diene product formation. Similarly, addition of hydride results in the formation of a metal formyl group, which gives way to *endo* hydride migration (see Section 2.4.2) [186]. Preparation of 1,3-cyclohexadiene complexes of $[Re(CO)_3(NO)]$ via double addition is also possible [198]. However, the preparation of $[(\pi\text{-arene})Re(CO)_3]^+$ is largely restricted to highly methylated arenes.

Double nucleophilic addition to manganese-arene complexes has significant synthetic potential. For example, when a methoxy group is present on the diene portion of the disubstituted η^4-cyclohexa-1,3-diene metal complexes, the latter are



Scheme 20.

converted to disubstituted cyclohexanones upon oxidative demetallation [197]. This finding has been exploited in a formal synthesis of juvabione [181]. When L = a phosphine or phosphite in Scheme 19, NO^+ substitution produces a chiral center at manganese. Addition of a second nucleophile then results in a pair of diastereomers. Diastereoselectivities are modest, but the isomers have been separated and a pair of X-ray structures have been reported [109]. The addition of a chiral nucleophile (the enolate of (−)-bornyl acetate) to $[(\eta^6\text{-}C_6H_6)Mn(CO)_2PMe_3]^+$, followed by NO^+ ligand substitution, produced a single diastereomeric product, **39** [2,109].



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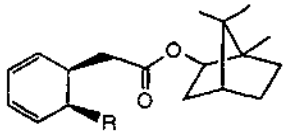
The reaction of **39** with a nucleophile, followed by demetallation, can potentially be used to synthesize enantiomerically pure dienes, **40**.



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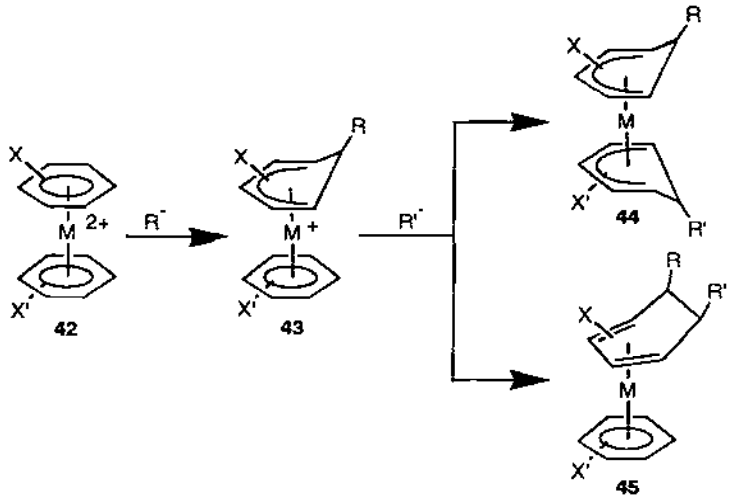
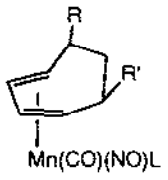


Scheme 21.

Disubstituted 1,3-cycloheptadiene complexes (**41**) can be produced by nucleophilic addition to *exo*-substituted [(η^5-cycloheptadienyl)Mn(CO)(NO)L] [173].

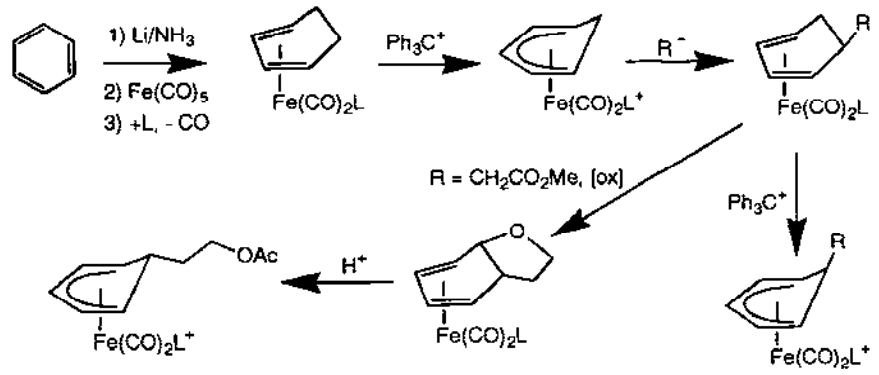


41

The direct addition of two nucleophiles is practicable with [(π-arene)$_2$M]$^{2+}$ (**42**, M = Fe, Ru), as indicated in Scheme 21. The typical outcome of double addition is the bis-cyclohexadienyl product, **44**. Attempts have been made to overcome this limitation. The iron system, in particular, suffers from several other difficulties. The Lewis acid-promoted synthesis does not readily allow for mixed arene complexes and can also result in arene rearrangements or decomposition. Moreover, the first nucleophilic addition to the bis-arene iron complex is plagued by single electron transfer problems [126–128,199]. Astruc has shown that, when the first nucleophile used is hydride, the second nucleophilic addition produces the diene complex **45** (R = H) [127]. The *exo*-hydride can be abstracted using Ph_3C^+ to regenerate **43**. Cyanide can then be added to yield **45** (R, R' ≠ H).

The ruthenium complexes **42** can be prepared with X ≠ X'. Nevertheless, although [(η^6-C_6H_6)Ru(η^6-arene)]$^{2+}$ (arene = C_6H_6, C_6Me_6, 1,3,5-$C_6H_3Me_3$, and 1,3,5-$C_6H_3^iPr_3$) are attacked by the first nucleophile at the unsubstituted ring, second addition occurs at the other ring, producing **44** [200]. When the [2.2]paracyclophane ligand is used, double addition to benzene to generate **45** is found only for R, R' = H [92,201]. Finally, it should be noted that there is one report of double addition of OMe^- or Cp^- to the benzene ring in [(η^6-C_6H_6)CoCp]$^{2+}$ to give 1,3-cyclohexadiene complexes [202].

Another nucleophilic addition route which leads to 1,3-cyclohexadiene products is shown in Scheme 22. The strategy involves the Birch reduction of benzene to



Scheme 22.

cyclohexadiene, followed by its coordination to $[Fe(CO)_3]$, hydride abstraction, and nucleophilic addition. Addition of a second nucleophile requires regeneration of a cationic cyclohexadienyl complex, usually via hydride abstraction [178,203,204]. The strategy is readily applicable to seven-membered rings as well as six-membered rings. However, it suffers from the need to start with diene substrates and the fact that hydride abstraction can fail for steric reasons. Pearson has found that oxidative ring closure, followed by protonation can also be used to regenerate the cationic dienyl complexes, as shown in Scheme 22 [205]. Acid removal of methoxide is another way to convert the diene complexes to cationic dienyls [206,207].

2.6. Ligand replacement reactions

Most complexes containing a simple monocyclic arene ligand only slowly undergo arene substitution. A typical reaction is given in Eq. (11), which is thought to follow an associative mechanism with the arene undergoing $\eta^6 \rightarrow \eta^4$ ring slippage in the rate determining step [208].

$$[(\pi\text{-arene})Cr(CO)]_3 + 3PR_3 \rightarrow [(PR_3)_3Cr(CO)_3] + \text{arene} \quad (11)$$

Changing from a monocyclic to a polycyclic arene, such as naphthalene, leads to a dramatic increase in the rate of Eq. (11). Almost certainly, the major reason for the reactivity order naphthalene $\gg$ benzene is the relative ease with which polycyclic arenes can undergo the required $\eta^6 \rightarrow \eta^4$ ring slippage. The important energy factor in this process is the loss in resonance energy (ΔRE) upon slippage. It is known [208] that ΔRE follows the order benzene (84 kJ) > naphthalene (44 kJ), from which it can be appreciated that the change in ΔRE can have an order-of-magnitude impact on relative reactivity. A similar interpretation applies to the observation that arene exchange in $[(\pi\text{-arene})Cr(CO)_3]$ is 10^3–10^4 times faster for naphthalene as compared to benzene [17]. These results have prompted the use of $[(\eta^6\text{-naphthalene})Cr(CO)_3]$ as a $[Cr(CO)_3]$ transfer reagent according to Eq. (12).

$$[(\pi\text{-naphthalene})Cr(CO)_3] + \text{arene} \rightarrow [(\pi\text{-arene})Cr(CO)_3] + \text{napthalene} \quad (12)$$

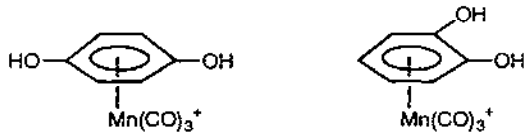
This reaction, as well as an analogous one using the pyrophoric $[(\pi$-*N*-methylpyrrole$)Cr(CO)_3]$ as the transfer reagent, appear to have significant potential in that they allow the synthesis of $[(\pi\text{-arene})Cr(CO)_3]$ complexes under much milder conditions than those ordinarily required [209].

Enhanced reactivity also has been observed with other polycyclic arene complexes. Thus, $[(\pi\text{-naphthalene})M(Cp)]^+$ (M = Fe, Ru) and $[(\pi$-naphthalene$)Ru(COD)]$ undergo rapid arene substitution [8,210]. The order of reactivity in the former case is Ru $\gg$ Fe. The complex $[(\pi\text{-naphthalene})Ir(Cp^*)]^{2+}$ rapidly loses naphthalene in DMSO, while the benzene analogue is inert [211]. In a kinetic study of the reaction in Eq. (13), it was found that rhenium is more reactive than manganese by a factor of 10^4 [147].

$$[(\eta^6\text{-toluene})M(CO)_3]^+ + 3MeCN \rightarrow [(MeCN)_3M(CO)_3]^+ + \text{toluene}$$
$$(M = Mn, Re) \quad (13)$$

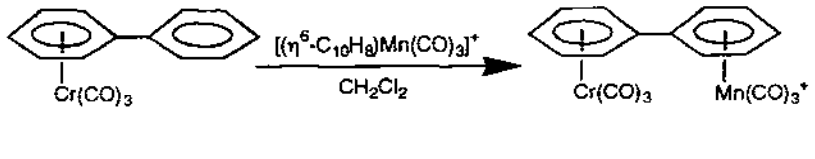
This was attributed to the larger size of rhenium, which facilitates nucleophilic attack at the metal. The much greater ease with which the arene is displaced from $[(\eta^6\text{-arene})Re(CO)_3]^+$ by donor solvents and trace nucleophilic impurities severely limits the utility of such systems for arene functionalization [198]. The half-life for $[(\eta^6\text{-toluene})Mn(CO)_3]^+$ (Eq. (13)) at room temperature is calculated to be ca. 4 years. In comparison, the half-life for the analogous reaction of $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$ with MeCN is ca. 1 min! A kinetic study of this reaction with a series of polycyclic arene complexes of $[Mn(CO)_3]^+$ gave the following results for arene displacement by 1.0 M MeCN in CH_2Cl_2 at 25°C ($t_{\frac{1}{2}}$ in min in parentheses): naphthalene (1) > acenaphthene (2) > phenanthrene (50) ≈ benzothiophene (55) > dibenzothiophene (250) ≈ dibenzofuran (260) ≫ toluene (2×10^6) [18].

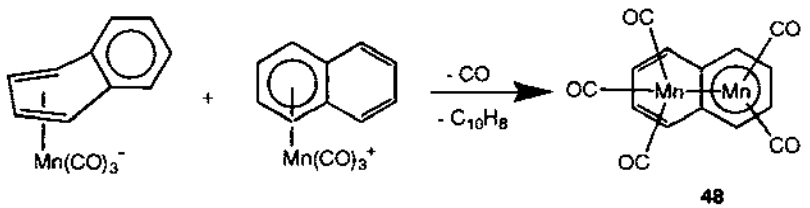
Any of the naphthalene-type complexes of manganese are effective at transferring the $[Mn(CO)_3]^+$ moiety to other arenes. For example, simply heating $[(\pi\text{-acenaphthene})Mn(CO)_3]^+$ for about 1 h in dichloromethane containing only a slight excess of any of a number of arenes leads to clean substitution and liberation of the acenaphthene [18]. The value of this reaction is that it permits the coordination of arenes that fail to react satisfactorily by other available methods due to the presence of sensitive functional groups, or for other reasons, e.g. phenylacetylenes, phenols, anilines and certain aromatic steroids. An interesting use of this methodology was the reported high-yield synthesis of hitherto unavailable π-bonded hydroquinone and catechol complexes **46** and **47** [86].



46 **47**

It has also been used to synthesize a variety of multimetallic complexes, as exemplified by Eq. 14 [212,213].





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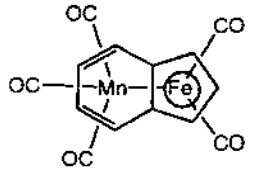
Scheme 23.

As discussed above, the utility of $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$ and related complexes as $[Mn(CO)_3]^+$ transfer reagents is dependent on facile $\eta^6 \rightarrow \eta^4$ ring slippage. In a novel application of this chemistry, the known [214] $[(\eta^4\text{-naphthalene})Mn(CO)_3]^-$ complex was used as the incoming arene to displace the naphthalene from $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+$. This resulted in the *syn*-facial bimetallic complex **48** shown in Scheme 23 [215]. The use of $[(\eta^3\text{-indenyl})Fe(CO)_3]^-$ as the incoming arene gave the *syn*-facial heterobimetallic **49** whereas $[(\eta^4\text{-naphthalene})FeCp]^-$ gave the *anti*-facial zwitterionic **50**.



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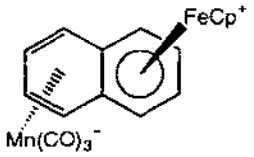
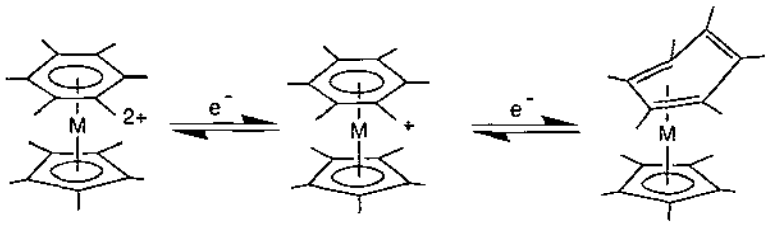


50

3. Electron transfer reactions of cyclic π-hydrocarbon complexes

As would be expected, the electrophilic π-hydrocarbon complexes that form the subject of this review are easily reduced, either chemically or electrochemically. Upon reduction, there are several common reaction pathways in addition to ligand dissociation or decomposition. In particular, the initially-formed 19-electron complex can (1) couple through the π-hydrocarbon rings, (2) accept a second electron with concomitant ring slippage, or (3) do nothing. Reductive coupling is sometimes an unwanted consequence of an attempted nucleophilic addition, especially with electron-rich carbanion and organometallic donors. Early examples of this with $[(\pi\text{-tropylium})Cr(CO)_3]^+$ and other electrophiles have been described by Pauson [136,216]. In an interesting study, Kochi showed [217] that the reaction of $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$ with $[CpMo(CO)_3]^-$ at room temperature gives the dimeric products indicative of initial electron transfer, namely, $[CpMo(CO)_3]_2$ and $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]_2$. However, reaction at $-78°C$ gives the nucleophilic addition product $[(\eta^4\text{-}C_6H_7\text{-}Mo(CO)_3Cp)Fe(CO)_3]$, which converts to the coupled dimers upon warming. The conclusion is that nucleophilic addition is favored kinetically over electron transfer, even if the latter produces the thermodynamic products.

Two-electron reduction of $[(\pi\text{-naphthalene})Cr(CO)_3]$ leads to $[(\eta^4\text{-naphthalene})Cr(CO)_3]^{2-}$, which has been characterized thoroughly [218,219]. The η^4-benzene analogue is far less stable, but has been utilized in a number of reactions with electrophiles [219–222]. Reduction of $[(\pi\text{-arene})FeCp]^+$ affords the stable 19-electron radical that has been used to promote or initiate a range of chemical reactions [6,223,224]. The complexes $[(\pi\text{-}C_6Me_6)MCp^*]^{2+}$ (M = Rh, Ir) undergo a hapticity change upon 2-electron reduction, as shown in Scheme 24. The monoreduced complexes retain the planar $\eta^6\text{-}C_6Me_6$ bonding, and are best described as 19-electron. The second (electrochemical) reduction is accompanied by η^6 to η^4 slippage of the arene, and this structural change is manifested by a slow rate of

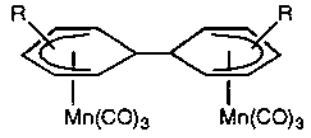


M = Rh, Ir

Scheme 24.

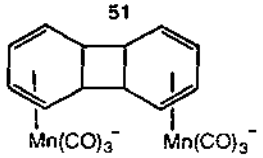
heterogeneous charge transfer [225–228]. The $[(\eta^6\text{-}C_6Me_6)CoCp^*]^{2+}$ system differs from the others in having a planar $\eta^6\text{-}C_6Me_6$ in the neutral state (20-electron) [229]. The complexes $[(\eta^6\text{-}C_6Me_6)_2M]^{2+}$ (M = Fe, Ru) behave analogously in that the neutral species is $\eta^4\text{-}C_6Me_6$ (18-electron) for M = Ru [228,230], and $\eta^6\text{-}C_6Me_6$ (20-electron) for M = Fe [6].

Depending on the exact experimental conditions, chemical reduction of $[(\eta^6\text{-monoarene})Mn(CO)_3]^+$ can give the $[(\eta^4\text{-arene})Mn(CO)_3]^-$ anion, which is attacked by electrophiles to afford neutral cyclohexadienyl species [214]. Alternatively, coupling of the neutral $[(\pi\text{-arene})Mn(CO)_3]$ radical can occur to yield bis-cyclohexadienyl complexes **51** [231–233], which, for benzene as the arene, can undergo reductive dimerization to **52** [233,234].



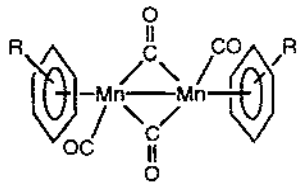
51

51

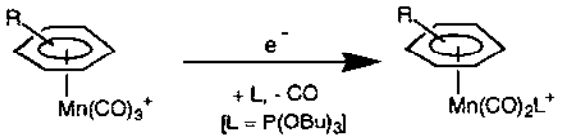


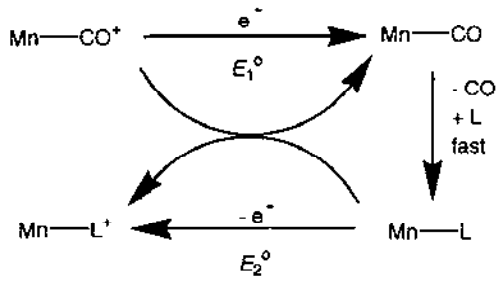
52

Another pathway is CO dissociation from $[(\pi\text{-monoarene})Mn(CO)_3]^+$, followed by coupling or subsequent reduction to $[(\pi\text{-monoarene})Mn(CO)_2]^-$; in either case the ultimate product is the dimer **53** [235].



53





Scheme 25.

Interestingly, $[(\pi\text{-mesitylene})Re(CO)_3]^+$ (**54**$^+$) behaves quite differently in comparison with its manganese analog. Electrochemical experiments show that **54**$^+$ undergoes a chemically reversible 2-electron reduction with very slow heterogeneous charge transfer [232]. The interpretation is that after a 1-electron reduction to neutral **54**, a slow and spontaneous second reduction occurs as the ring slips to η^4-bonding. In analogy to the behavior of arene complexes of manganese and rhenium, the reduction of $[(\eta^5\text{-cyclohexadienyl})M(CO)_2NO]^+$ is irreversible for M = Mn and reversible (1-electron) for M = Re, again showing that the manganese radicals are much more reactive [198].

In the presence of a nucleophile such as $P(OBu)_3$, the various reaction pathways for $[(\pi\text{-monoarene})Mn(CO)_3]^+$ after chemical or electrochemical reduction are short-circuited in favor of an electron-transfer-catalyzed (ETC) substitution to give $[(\pi\text{-monoarene})Mn(CO)_2P(OBu)_3]$ [232,236]. Thus, the application of a reducing current for a few seconds, or the addition of a few mole percent of a reducing agent leads to quantitative CO substitution. The mechanism for this ETC process is given in Scheme 25. Its success depends on the 19-electron Mn–CO being very reactive with respect to CO dissociation and on the potentials being in the order $E_1^\circ > E_2^\circ$.

In marked contrast to the behavior of $[(\pi\text{-monoarene})Mn(CO)_3]^+$, chemical or electrochemical reduction of $[(\pi\text{-naphthalene})Mn(CO)_3]^+$ occurs in a 2-electron reversible process to give the thermally-stable η^4-bonded anion [110,214]. The potential for this reduction is about 0.5 V positive of the 1-electron reduction of the monoarene complex $[(\pi\text{-tetrahydronaphthalene})Mn(CO)_3]^+$. This large difference in potential is a manifestation of the great ease with which the putative radical intermediate, $[(\pi\text{-naphthalene})Mn(CO)_3]$, can accept a second electron as the ring slips. (The potential of the second reduction is positive of the first.) In agreement with this is the observation that the presence of a nucleophile has no effect on the electrochemical reduction of $[(\pi\text{-naphthalene})Mn(CO)_3]^+$.

Oxidation of [(π-benzene)Cr(CO)$_3$] produces a 17-electron radical cation that is sufficiently stable so that CO substitution reactions can be studied [236,237]. The Mo and W analogues are far more reactive, and only with sterically-protected systems, e.g. [(π-C_6Et_6)M(CO)$_3$], are the radical cations observable. For associative CO substitution by phosphite nucleophiles, the reactivity order for [(π-arene)M(CO)$_3$]$^+$ is: Mo > W $\gg$ Cr. The much greater rate of Mo and W compared to Cr is likely due to the larger size of the former. There appears to be a fundamental difference in the way P-donors react with the chromium triad complexes [(π-arene)M(CO)$_3$] and [(π-arene)M(CO)$_3$]$^+$: the former undergo arene displacement [208], whereas the latter prefer CO substitution, Eqs. (15) and (16).

$$[(\pi\text{-arene})M(CO)_3] + 3PR_3 \rightarrow [(PR_3)_3M(CO)_3] + \text{arene} \quad (15)$$

$$[(\pi\text{-arene})M(CO)_3]^+ + 3PR_3 \rightarrow [(\pi\text{-arene})M(CO)_2PR_3]^+ + CO \quad (16)$$

Eq. (15) is thought to proceed via $\eta^6 \rightarrow \eta^4$ ring slippage when the first nucleophile binds to the metal. It is suggested that [(π-arene)M(CO)$_3$] reacts with P-donors to lose arene while [(π-arene)M(CO)$_3$]$^+$ reacts to lose CO because ring slippage need not occur with substitution reactions of 17-electron complexes since 19-electron complexes are viable intermediates. Because there is no ring slippage, the metal-arene bond is not weakened when the nucleophile attacks the radical, so CO, rather than arene, is lost.

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