Single and Double Nucleophilic Addition to Coordinated Pi-Hydrocarbons: Manganese-Mediated Functionalization of Arenes

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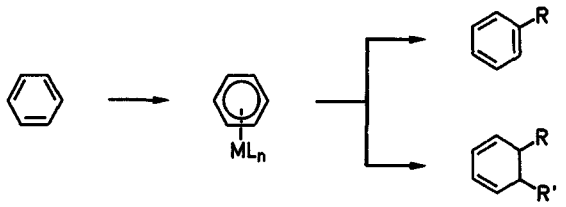
Abstract: A range of carbon-donor nucleophiles add to the arene ring in (arene)$Mn(CO)_2L^+$ cations to give neutral cyclohexadienyl complexes that liberate monofunctionalized arenes upon oxidative removal of the metal. Treatment of the cyclohexadienyl complexes with the nitrosonium salt $NOPF_6$ affords cationic metal nitrosyl complexes that are attacked by a second nucleophile to give *cis*- and *trans*-difunctionalized 1,3-cyclohexadienes. When the metal center is chiral, this procedure provides a route to enantiomerically pure cyclohexadienes.

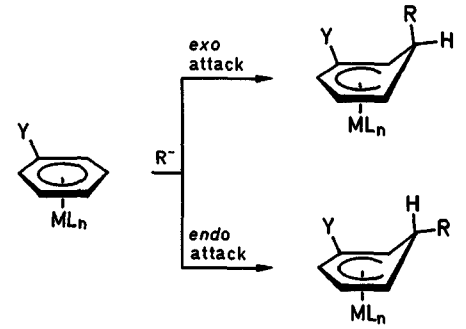
1. Introduction

Electron-rich π-hydrocarbons frequently serve as good ligands for transition metals and by so doing acquire *electrophilic* character. The extent of the electrophilic activation induced by metal coordination depends, of course, on the metal, auxiliary ligands, charge, etc. Scheme 1 illustrates the general idea with an arene as the π-hydrocarbon. For synthetic utility, it is desirable that the arene bind to the metal under mild conditions and then react cleanly with a variety of nucleophilic reagents to give mono- or, perhaps, difunctionalized products. Finally, it must be possible to remove the metal moiety and isolate the product(s).



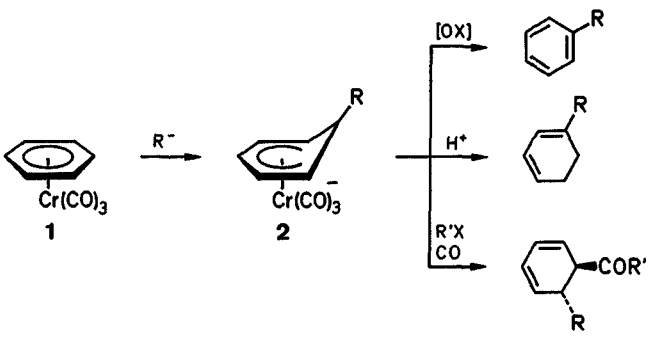
Scheme 1

The electrophilic activation of π-hydrocarbons by metal coordination has evolved into a fundamental reaction in organometallic chemistry, and a variety of useful synthetic (stoichiometric and catalytic) transformations are known.[1-3] Perhaps the best known are the many such reactions promoted by palladium(II).[1,4] In addition to imparting the necessary electronic activation to the π-hydrocarbon, the metal often directs the nucleophilic addition in a regioselective and stereoselective manner. As shown in Scheme 2, stereochemical asymmetry is imposed upon the otherwise symmetric arene by the attachment of a metal fragment to the "endo" face. This asymmetry occurs in all π-olefin and π-polyene complexes and, in the absence of reaction intermediates, leads to stereospecific "*exo*" attack at the ligand. In the less common case when the *endo* product is formed, it is likely that there is an initial interaction of the nucleophile at the metal or an auxiliary ligand, followed by migration to the ring (*vide infra*).



Scheme 2

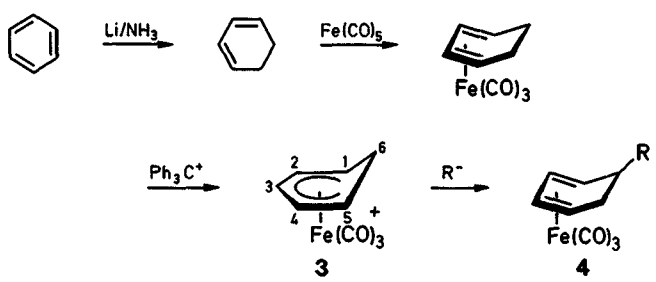
The arene system that has received the most attention,[5,6] (arene)$Cr(CO)_3$, is outlined in Scheme 3. Nucleophilic addition to **1** is limited by the weak electrophilicity of the arene ring. Only strong ester-, nitrile-, and sulfur-stabilized lithium carbanions and certain unstabilized lithium carbanions successfully add; most ketone enolates, Grignards, and copper reagents are unreactive. Rearomatization accompanies oxidative cyclohexadienyl ring removal by iodine, but the use of strong acid instead generates monofunctionalized cyclohexadienes. The latter is equivalent to the "double addition" of R^- and H^- to the arene. Treatment of **2** with an electrophilic reagent and a ligand (CO) to induce migration gives *trans*-difunctionalized 1,3-cyclohexadienes.[6] Classes of η^6-arene complexes that bear a



Scheme 3

positive charge are subject to nucleophilic attack by a wider range of reagents than found with **1**. These include (arene)$FeCp^+$,[7] (arene)Fe^{2+},[8] (arene)(arene')Ru^{2+},[9] and (arene)$Mn(CO)_3^+$.[10-13] Most arene complexes are prepared under harsh conditions (high temperature and/or strong Lewis acid). An important requirement for general synthetic utility is the availability of a mild preparative procedure (*vide infra*).

Akin to the arene complexes is the much studied[14] cyclohexadienyl–iron system illustrated in Scheme **4**. The virtue of this route to 1,3-cyclohexadienes is the wide range of nucleophiles that convert **3** to **4**. There are some limitations, however. The appropriate diene is not always available, and it is usually difficult to prepare **3** with a substituent on C-6, meaning that, in effect, only monofunctionalization is generally feasible. An important feature of the chemistry in Scheme **4** is the ability of a substituent (e.g., OMe) at C-2 to direct a nucleophile to C-5. In a similar vein, the replacement of a CO ligand in **3** with a chiral phosphine or the use of a chiral nucleophile gives rise to significant diastereoselectivity because of the stereocenter created at the diene ring; this is equivalent to preferred nucleophilic addition at C-1 (or C-5).[15]

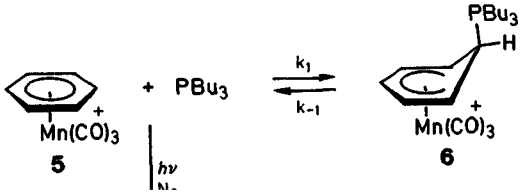


Scheme 4

We have studied a variety of metal–ligand systems, with most of our recent work focused on manganese complexes containing triene and dienyl-type ligands. The emphasis has been on the synthetic and mechanistic aspects of both single and double nucleophilic addition to the coordinated π-hydrocarbon. As will be shown, coordination by manganese can lead to a variety of useful, and in some cases surprising, transformations.

As expected, the addition of two nucleophiles to a coordinated π-hydrocarbon is generally found to be more difficult than the addition of one. Nevertheless, such "double-addition" reactions are synthetically important and are being actively investigated by a number of research groups. As Scheme **1** shows, double addition to aromatic molecules leads to difunctionalized 1,3-cyclohexadienes, molecules rarely accessible by standard methods. There are a few published examples of double nucleophilic addition to metal–arene complexes, but in each case the reaction is severely limited as to the range of nucleophiles (often only hydride works).[16-19] In certain cases it is possible[20] to synthesize difunctioned 1,3-cyclohexadienes via the intermediacy of analogues of **3**, but these reactions are not mediated route to *cis*- and *trans*-disubstituted 1,3-cyclohexadienes via the sequence: nucleophilic addition, reactivation, and a second nucleophilic addition. The regiochemistry and stereochemistry associated with this procedure are in some instances quite novel and especially interesting in a mechanistic sense.

When we started research in the organometallic field in 1975, much of the chemisty described above was not yet known. In fact, the decision to explore this area arose in a completely fortuitous manner. One of us (D.S.) was teaching an undergraduate course in inorganic chemistry, and a student selected for a required oral presentation a paper by Walker and Mawby.[11] This paper described the reaction of (arene)$Mn(CO)_3^+$ with a range of nucleophiles and showed that attack can occur at the ring, at a CO, or at the metal with loss of CO or the arene. D.S. was planning to spend most of the 1975/76 academic year working with L. Kane-Maguire in Cardiff, and thought it would be useful to try to sort out the mechanistic reasons for the multiple pathways of nucleophilic attack on (arene)$Mn(CO)_3^+$. Kane-Maguire was interested in chemistry analogous to that shown in Scheme **4**, and so our respective interests nicely coincided. The research in Cardiff began with a kinetic investigation of the reaction of (arene)$Mn(CO)_3^+$ with tributylphosphine (PBu_3), which Walker and Mawby reported[11] as leading to (arene)$Mn(CO)_2PBu_3^+$. In retrospect, it was fortunate that the first experiments were performed on a rainy Saturday. The weather forced cancellation of other planned activities, and the day of the week meant that most of the laboratories and instrument rooms were locked. With facilities thus limited, it was decided to run a few quick and preliminary IR spectra and wait until Monday for the serious quantitative work. To our surprise, the IR spectrum of an acetone solution of (benzene)$Mn(CO)_3^+$ and PBu_3 prepared under air did not have ν_{CO} bands even close to the reported ones. Furthermore, the spectrum did not change over an hour or so. Since the first rule for a kineticist is "Know thy reactants and thy products",[21] on the following sunny Monday we prepared the solutions again, this time with more care and under nitrogen. The IR spectrum now matched Walker and Mawby's results perfectly. However, repeating this experiment led to variable results – sometimes the published ν_{CO} bands appearing, sometimes the "new" ones, and sometimes both. It soon became apparent that a photochemical reaction was occurring that was quenched by oxygen. The chemistry was sorted out and is shown in Scheme **5**. PBu_3 does replace a CO ligand in **5**, but there exists a much faster (and reversible) ring addition leading to **6**. At the time, we were surprised that *neutral* tertiary phosphines could add to coordinated arenes, and this reaction served to spark our group's interest in the general mechanistic aspects of electrophile–nucleophile combinations. This in turn led to a



six- or seven-year period of kinetic studies with an assortment of organometallic and organic electrophiles, culminating in general conclusions that pointed the way to a variety of synthetic applications (*vide infra*).

2. Mechanism of Nucleophilic Addition

Whatever the class of reaction may be, the elucidation of any existing general reactivity patterns is required for the rational (and cost-effective) prediction and development of synthetic applications. Aside from this self-evident fact, understanding how reactions occur is what chemistry is about. Regarding the general class of electrophilic π-hydrocarbon complexes, MO theory has been applied[22] with some success to the question of the preferred site of nucleophilic attack. With a moderate level of confidence one can predict which site (terminal or internal carbon in the π-system) or which π-hydrocarbon (if there is more than one) will be attacked.

Using *P*- and *N*-donor nucleophiles, the kinetics of nucleophilic addition to a large number of coordinated π-hydrocarbon systems has been studied.[12,23-27] The π-hydrocarbon ligands in these investigations included simple olefins, dienes, dienyls, trienes, and trienyls. The organometallic fragments responsible for the activation included the following metals: Cr, Mo, W, Mn, Re, Fe, Ru, Os, and Co. The reactions span a time frame from milliseconds to hours, with most being on the fast side of the scale. For example, the transformation **5** $\rightleftarrows$ **6** is established in much less than one second under typical conditions. A consideration of the combined results led to a number of useful conclusions. Foremost was the observation that relative nucleophilic reactivity, although covering seven powers of ten, did not depend on the electrophile chosen. This means that a new electrophilic system can be completely defined with respect to reactivity (with *P*- and *N*-donors) by measuring the rate with only one nucleophile. (The important question of relative reactivity with *C*-donors has yet to be addressed experimentally.) This result implies a linear free energy relationship containing a single nucleophile-dependent (but electrophile-independent) parameter, which we label N_M. Such a unified relationship is surprising, since nucleophile 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[28] has reported that *N*- and *O*-donor nucleophilic additions to free carbocations follow a similar single-parameter reactivity law. By measuring the rates of *P*- and *N*-donors with uncomplexed carbocations, we[26] showed that relative nucleophilicities are the same whether or not the hydrocarbon is coordinated. Hence, the indicated single-parameter relationship is a very general and important one that applies to a wide range of chemical reactions.

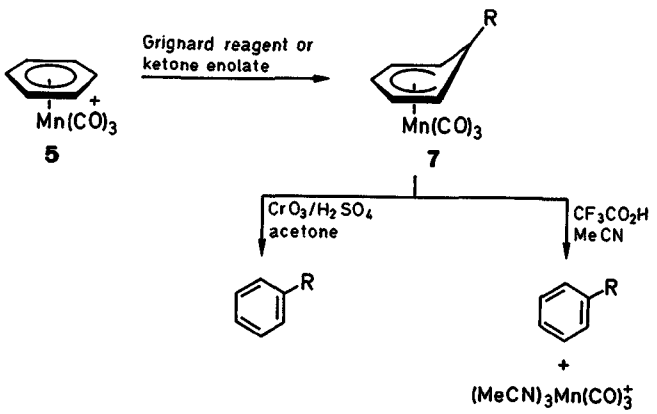
The above results lead to an important corollary: relative electrophilic reactivities are nucleophile-independent. This in turn means that it is possible to quantify the relative ability of transition metal fragments to activate π-hydrocarbons, without regard for the particular hydrocarbon chosen. This activation power is reflected by what we term electrophilic transferability parameters (T_E's), some of which are given in Table I. It is likely that the reaction thermodynamics follow a pattern qualitatively similar to the reactivities. As would be expected, the T_E's are very charge dependent. They show, for example, that an arene attached to $Ru(C_6H_6)^{2+}$ will be ca. 6×10^6 times more electrophilic than when attached to $FeCp^+$. Another important aspect of our mechanistic work concerns the dependence of electrophilic activation on the metal. The result is that the chromium triad, as well as manganese, rhenium, show little metal dependence, while for the iron triad the order is Fe > > Ru > Os.[23,24]

Table I. The Relative Ability (T_E) of Transition Metal Fragments to Activate Triene and Dienyl Rings

fragment	T_E(trienes)	fragment	T_E(dienyls)
$Fe(C_6H_6)^{2+}$	200000000	$Fe(CO)_3^+$	1800
$Ru(C_6H_6)^{2+}$	6000000	$Mn(CO)_2NO^+$	1800
$MN(CO)_3^+$	11000	$Fe(CO)_2PPh_3^+$	28
$Mn(CO)_2PPh_3^+$	160	$Mn(CO)(NO)PPh_3^+$	20
$FeCp^+$	(1)	$CoCp^+$	(1)
$Cr(CO)_3$	very small		

3. Single Nucleophilic Addition

Fairly early on we decided to determine the usefulness of $(arene)Mn(CO)_3^+$ complexes for arene functionalization. We found that the attachment of the arene to the $Mn(CO)_3^+$ moiety can be done under conditions mild enough to preclude any reaction or isomerization of arene-ring substituents.[29] Next, the range of successful carbon nucleophiles had to be established and a method found for cleanly removing the manganese fragment from the product. It was known from previous work[10,11] that the organolithium reagents LiPh and LiMe, and stabilized enolates such as $NaCH(CO_2Et)_2$, add to the ring in $(arene)Mn(CO)_3^+$. We found[13,30] that Grignard reagents and ketone enolates add cleanly and in high yield to give thermally stable cyclohexadienyl complexes according to Scheme 6. Furthermore, the metal in **7** is easily and rapidly removed by oxidation with a stoichiometric amount of Jones reagent (CrO_3/H_2SO_4/acetone) to afford high yields of the functionalized arene. This procedure is sufficiently mild that oxidation or rearrangement of carbon–carbon double bonds in the R group in **7** is not expected.[31] Alternatively, the functionalized arene product can be obtained by treating **7** with acid in acetonitrile. With this procedure the manganese ends up as $(MeCN)_3Mn(CO)_3^+$, which can be isolated and recycled to **5**.

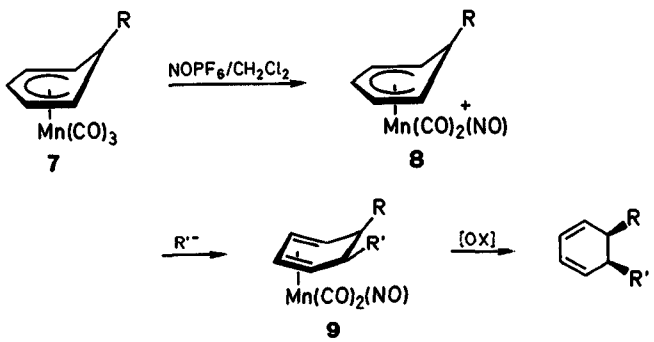


Scheme 6

Based on these studies, we concluded that the manganese-mediated monofunctionalization of arenes is a very attractive procedure. The ease of synthesis of (arene)$Mn(CO)_3^+$, the range of carbon-donor nucleophiles that react in high yield, the absence of any observed products of single-electron transfer, and the ready removal of the metal all suggest that the manganese system is as good or better than any alternative. Another feature of Scheme **6** that has important synthetic implications concerns the regiochemistry of nucleophilic attack when the benzene ring in **5** is replaced by a substituted aromatic. It was found that a methoxy substituent, as in anisole, directs a nucleophile regiospecifically to the *meta* position. Directing effects are present with other substituents (e.g., Cl, Me), but the regioselectivity is less marked and is dependent on the nucleophile (probably for steric reasons). Nucleophilic additions to (arene)$Mn(CO)_3^+$ are very easily and conveniently monitored by following the IR ν_{CO} bands, which shift to much lower frequencies during the reaction. Some of the attractive features of the manganese complexes, especially the high level of activation without interference by undesirable redox chemistry, may also be available with (arene)(arene')Ru^{2+} complexes, but this has yet to be fully demonstrated.[9]

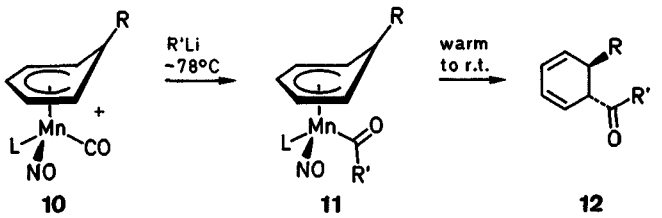
4. Double Nucleophilic Addition

As noted above, the double addition of two nucleophiles to an arene to form difunctionalized cyclohexadienes as in Scheme **1** has been a desirable but rather elusive goal. However, considerable progress has been made with manganese as the mediator, as is now described. Having performed the chemistry in Scheme **6**, we next sought a way to add a second nucleophile. The problem was that complex **7** and its analogues, in contrast to **5**, are at best very weakly electrophilic – less so than (arene)$Cr(CO)_3$. It was obvious that a way had to be found to "reactivate" **7** so that the second nucleophile could be added. We thought that electrochemical activation might do the job, but preliminary experiments along this line were not fruitful. Based on discussions with N.G. Connelly,[32,33] reactivation of **7** was achieved by reaction with $NOPF_6$. The idea was to replace a CO ligand with NO^+, thereby obtained a cationic, and hence electrophilic, complex. With many organometallic complexes, NO^+ functions as an 1-electron oxidant rather than giving a metal nitrosyl. Our initial experiments with **7** in acetonitrile and in toluene/methanol,[32] the solvents most commonly used for reactions with $NOPF_6$, were unsuccessful. It was soon discovered, however, that **7** and $NOPF_6$ react smoothly in dry dichloromethane to give the desired metal nitrosyl. The chemistry involved is shown in Scheme **7**. It was found that **7** and its analogues containing substituents on the carbons in the π-system react rapidly with $NOPF_6$ to afford good yields of **8**; the only exception occurs when R = H, in which case $NOPF_6$ leads (predominantly) to the formal abstraction of the *exo*-hydride from **7** to give **5**.



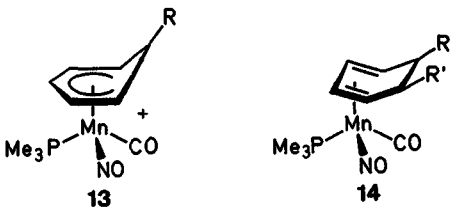
Scheme 7

The new complexes **8** are in fact more electrophilic than **5** and react readily with *P*-, *N*-, and *H*-donor nucleophiles to yield cyclohexadiene complexes **9**.[34] A number of the complexes **8** and **9**, have been characterized by X-ray diffraction.[35-37] Unfortunately, many useful carbon donors, such as Grignard reagents, react with **8** by what appears to be single-electron transfer to give none of the desired diene **9**. The hard carbon donors LiR (R = Me, Ph), however, react with **10** (L = CO) at −78°C by attacking a CO ligand (Scheme **8**). The same reaction occurs with **10** (L = PMe_3).



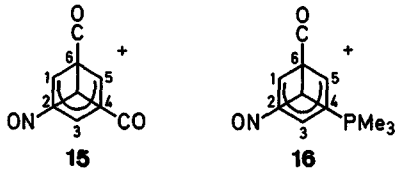
Scheme 8

Interestingly, acyl and benzoyl complexes **11**, when warmed to room temperature in dichloromethane, spontaneously liberate the *trans*-difunctionalized 1,3-cyclohexadiene **12**, implying that the -C(O)R' ligand in **11** migrates to the ring. We reasoned that the disappointing tendency of **8** to react with many carbon donors (other than LiMe and LiPh) by single-electron transfer could be circumvented by replacing a CO ligand in **8** with PMe_3. This would render the complex more difficult to reduce. It would also lower the activation towards nucleophilic addition, but we thought probably not enough to constitute a problem. Indeed, complex **13** was found to react with a variety of stabilized enolates to give the desired *cis*-difunctionalized 1,3-cyclohexadiene complex **14** in good yield. Extension to a wider range of carbon donors is currently being pursued.



Complex **13** possesses a chiral metal center and this gives rise to the possibility of asymmetric induction when a nucleophile adds. A view of **8** and **13** from normal to the dienyl plane is given in **15** and **16**. The rotational conformations shown were established by X-ray structural studies. In **15**, C-1 and C-5 (also C-2, C-4) are equivalent due to rapid rotation[38] about the metal–ring axis, which interconverts the structure shown with its mirrow image. The ^{1}H-NMR spectrum shown in Figure 1 A indicates the equivalence of C-

1 and C-5. With **16**, however, enantiomeric interconversion cannot be accomplished by rotation, and this means that C-1 and C-5 have different chemical environments. The much lower field ^{1}H-NMR resonance of H-1 compared to H-5, shown in Figure 1B, suggests that C-1 is more electrophilic than C-5 and hence should be the preferred site of nucleophilic attack in **16**.



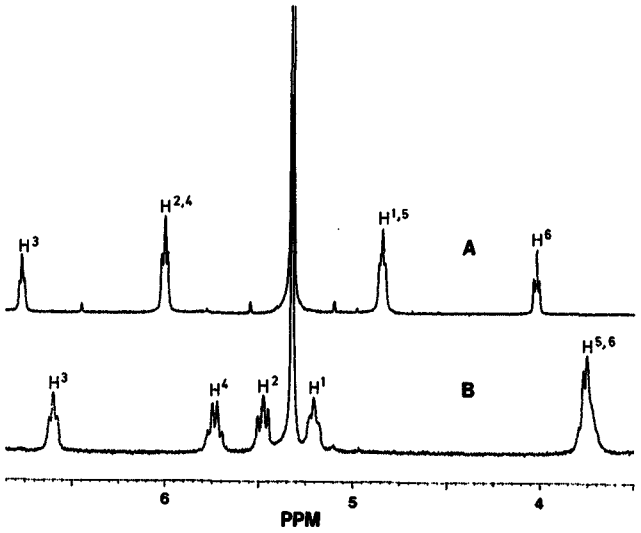
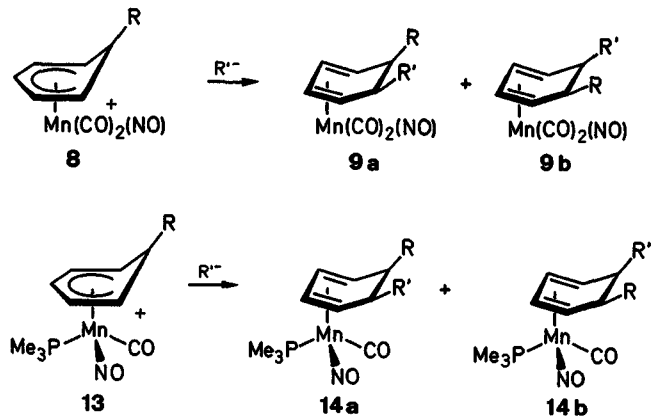
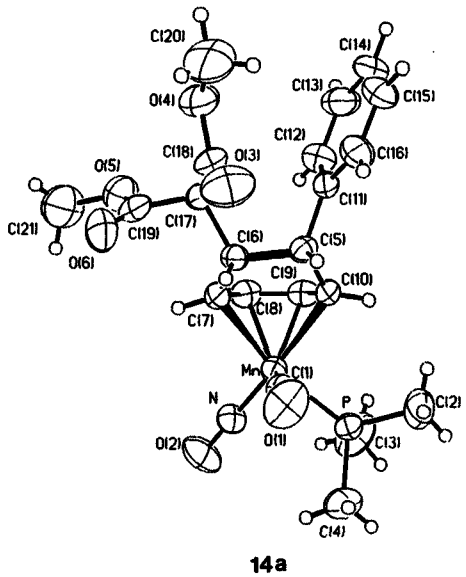


Figure 1. A portion of the room temperature ^{1}H-NMR spectrum of (A) **15** and (B) **16**. The R group was phenyl in both cases and the solvent was CD_2Cl_2.

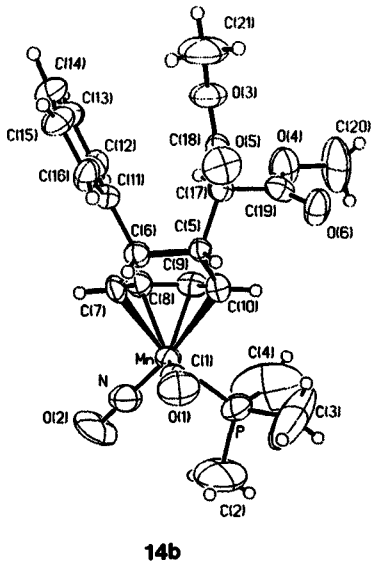
The chiral nature of the cyclohexadiene ring in **9** ($R \neq R'$) means that it is formed from **8** as non-separable enantiomers (**9a,b**), corresponding to nucleophilic attack at C-1 (50%) and C-5 (50%). However, because of the chiral metal center, **14** is formed from **13** as diastereoisomers that can be separated by chromatography. Scheme **9** illustrates the stereochemistry. The diastereoisomers are formed in unequal amounts, with **14a** preferred over **14b** by carbon donors (i.e., attack is favored at C-1 in **16**). Figure 2 shows



Scheme 9



14a

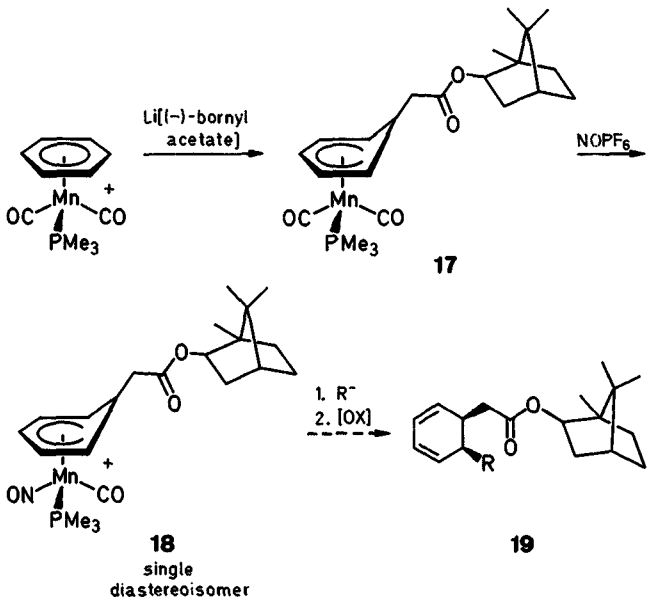


14b

Figure 2. ORTEP drawings of diastereoisomers **14a** and **14b** with R = Ph, R′ = $CH(CO_2Me)_2$.

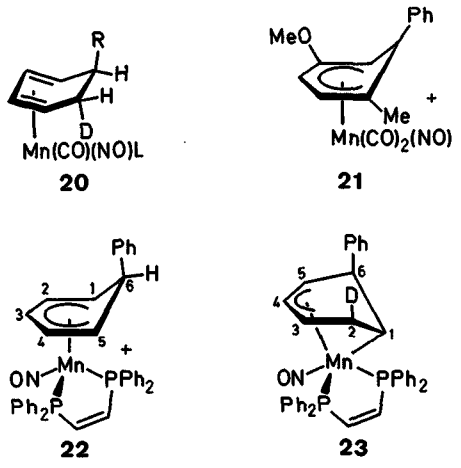
the structure[37] of a **14a,b** pair with dimethylmalonate as the nucleophile. As predicted from NMR, the major isomer (**14a**) was found to have the nucleophile situated on the side of the ring nearer the NO ligand. Interestingly, it was found that the other stereoisomer (**14b**) is favored by a ratio of up to 10:1 with hydride as the nucleophile; this may be due to the unusual mechanism of hydride addition (*vide infra*). As prepared, **13** exists as a racemic mixture and this means that each diastereoisomer **14a** and **14b** is formed as a racemic mixture of enantiomers. If **13** were resolved, each diastereoisomer would be optically pure and therefore an *optically pure* 1,3-cyclohexadiene would be generated by removal of the metal from **14a** (or **14b**). The resolution of **13** has been achieved in an indirect sense by the chemistry in Scheme **10**. The readily available enolate of (−)-bornyl acetate serves as a chiral auxiliary and the asymmetric induction anticipated during the carbonyl replacement in **17** to give **18** was found to be *stereospecific* in favor of a single diastereoisomer.[37] This means that **18** should react with

nucleophiles to produce two enantiomerically pure dienes **19**. These in turn could be converted into other optically resolved dienes by standard manipulations (reduction, transesterification) of the bornyl acetate substituent.



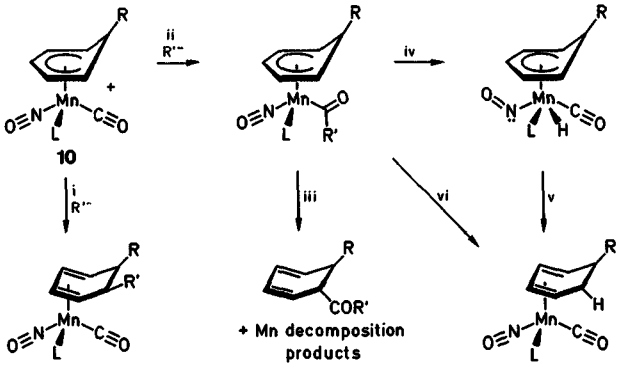
Scheme **10**

Early in our research on manganese, graduate student Y.K. Chung reported that deuteride adds to **10** in a stereospecifically *endo* manner to yield **20**. This initial result was based on ^{1}H-NMR coupling constants and seemed to be indisputable. Nevertheless, it was a most surprising result, since nucleophiles almost always add to cyclic π-hydrocarbons in an *exo* manner. Although H-donors have been used in many studies, Chung's discovery constituted the first example of stereospecific *endo* hydride (deuteride) addition to a cyclic π-hydrocarbon. Proof of the *endo* stereochemistry came from an X-ray structure[35] of the diene complex resulting from hydride addition to **21**. The hydride added to the methyl-bearing carbon, and the structure showed the methyl on this carbon to be *exo*, implying an *endo* hydride. Further work[34,39,40] showed that hydride addition occurs stereospecifically *endo* to **10** regardless of the hydride source, the nature of the R group, or the nature of ligand L. Similarly, when the metal is rhenium or the ring is cycloheptadienyl, the addition is still *endo*.



Low temperature IR and NMR experiments showed[41] that **10** (with rhenium as the metal) reacts rapidly with hydride to give a formyl species that then converts to the final product, the cyclohexadiene complex. When no CO ligands are present, as in **22**, the addition occurs by *exo* attack at the *internal* C-2 (or C-4) carbon (shown as deuteride in **23**). Complex **23** is an example of the very rare addition to an internal carbon in a cyclohexadienyl ligand. We concluded[41] that a CO ligand is a necessary but not sufficient condition for *endo* hydride addition. It is not sufficient because many other complexes, e.g., (arene)Mn(CO)$_3^+$, add hydride *exo*, yet have very electrophilic CO ligands.

The mechanism we favor for hydride addition to **10** and a summary of the reactions of **10** with other donor types is provided in Scheme **11**. *P*-, *N*-, and a variety of *C*-donors attack the ring by pathway i to give the *exo*-diene. Some hard *C*-donors attack initially at a CO, yielding M–C(O)R′ species that, upon warming, liberate the free diene possessing *trans* substituents R and C(O)R′ (step iii). Hydride also adds initially to a CO (R′ = H), with the final diene product likely arising via route vi or via iv and v. We favor pathway iv, v with hydride for several reasons: (1) the C(O)H group, unlike C(O)R′, was never observed to migrate to the ring and (2) pathway vi does not explain why other complexes such as (arene)Mn(CO)$_3^+$ do not undergo net *endo* addition. On the other hand, route iv, v explains the role of the NO ligand – to act as an electron sink as the formyl converts to the thermodynamically favored metal carbonyl hydride, from which hydride migrates to the ring to afford the *endo* product.



Scheme **11**

5. Conclusions

We have shown that the manganese-mediated monofunctionalization of arenes is a viable synthetic procedure. Similarly, double nucleophilic addition to a manganese-coordinated arene is possible, provided the complex is "reactivated" after the first addition. The difunctionalized 1,3-cyclohexadiene products can have *cis* or *trans* stereochemistry. Chiral discrimination in appropriate cases may lead to the synthesis of enantiomerically pure dienes. The general procedure of nucleophilic addition, reactivation with $NOPF_6$, and a second addition is equally successful in converting cycloheptatrienes to difunctionalized 1,3-cycloheptadienes.[40] Related research currently in progress involves the synthesis and electrophilic reactivity of (arene)Mn(CO)$_2$(alkene)$^+$ cations,[42] which offer a potential alternate route to *trans*-disubstituted 1,3-cyclohexadienes

via initial nucleophilic attack at the alkene, migration to the arene, reactivation, and a second nucleophilic addition. The feasibility of inducing nucleophilic additions via electroactivation is being studied with manganese and tungsten systems.[43]

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