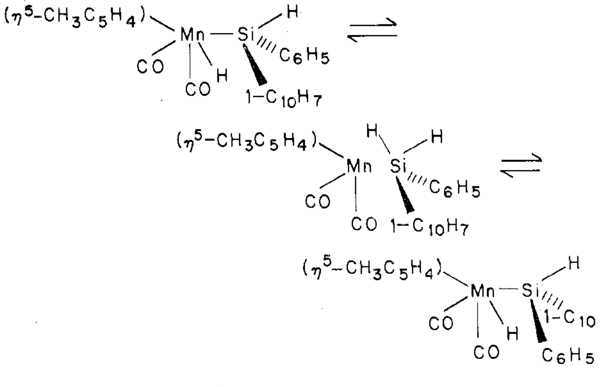
$LiAlH_4$ on the salts. This shows that reactions at silicon do not need the tautomeric equilibrium which, in the case of the anions, is obviously nonexistent.

The racemization observed for the reduction of hydrido(1-naphthylphenylmenthoxysilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese may be explained by the equilibrium with the deinserted form:



The comparison of the reactivities of the functional and nonfunctional silylmanganese hydrides toward nucleophiles is interesting. Both types of compounds undergo deinsertion with phosphines, and no carbonyl replacement is possible.

Functional silylmanganese hydrides easily gave the corresponding anions when treated with NaH, $LiAlH_4$, or organolithiums. Nonfunctional hydrides underwent H^+ abstraction with difficulty by means of NaH, whereas $LiAlH_4$ gave nucleophilic displacement of the manganese moiety at silicon and organolithiums led to deinsertion of silane.[1]

In none of the cases is attack by organolithiums at a carbonyl ligand observed. This type of reaction was found in other complexes with transition-metal–group 4B metal bonds.[11-13]

Lack of success in reacting triphenylphosphine with these salts in order to replace a carbonyl is not very surprising. Indeed, the increased electron density naturally increases the tendency of the metal atom to donate electrons back to carbon monoxide, and this donation makes the carbon monoxide ligands in metal carbonyl anions inert to substitution.[14]

The reactions reported here show the importance of the Si–H interaction in silylmanganese hydrides and the drastic changes of reactivity due to the functions at silicon. Nevertheless, we have described the possibility of substitution without cleavage of the Mn–Si bond.

Registry No. **1**, 68833-26-1; **2**, 68833-27-2; **3**, 68833-28-3; **4**, 68833-29-4; **5**·PPN, 68833-31-8; **6**·PPN, 68833-33-0; **7**·$(C_2H_5)_4N$, 68833-34-1; **8**·PPN, 68833-36-3; **9**·PPN, 68833-38-5; **9**·$(C_2H_5)_4N$, 68833-39-6; **10**·$(C_2H_5)_4N$, 68833-41-0; **11**·PPN, 68833-43-2; **11**·$(C_2H_5)_4N$, 68833-44-3; **12**·$(C_2H_5)_4N$, 68844-76-8; (η^5-$CH_3C_5H_4$)$Mn(CO)_3$, 12108-13-3; (η^5-$CH_3C_5H_4$)$(CO)_2Mn(H)Si(C_6H_5)_3$, 68833-45-4; (1-$C_{10}H_7$)$(C_6H_5)SiH_2$, 21701-61-1; (1-$C_{10}H_7$)$(C_6H_5)Si(H)OCH_3$, 41114-86-7; (1-$C_{10}H_7$)$(C_6H_5)Si(OCH_3)_2$, 36147-17-8; (1-$C_{10}H_7$)$(C_6H_5)Si(F)OCH_3$, 68813-34-3; 1-naphthylphenylmenthoxysilane, 33632-85-8; H_2O, 7732-18-5; CH_3OH, 67-56-1.

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Reactivity of Tricarbonyl(arene)manganese(I) and -rhenium(I) Cations. Nucleophilic Addition of Tributylphosphine to the Arene and Nucleophilic Displacement of the Arene by Acetonitrile

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The complexes $[(arene)M(CO)_3]^+$, M = Mn or Re, readily react with tri-*n*-butylphosphine to yield the corresponding cyclohexadienylphosphonium ring adducts $[(arene\cdot PBu_3)M(CO)_3]^+$:

$$[(arene)M(CO)_3]^+ + PBu_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(arene\cdot PBu_3)M(CO)_3]^+$$

The equilibrium constant for the addition reaction (k_1/k_{-1}) is slightly greater for M = Re. The kinetics with M = Mn were studied in detail and activation parameters obtained for k_1 and k_{-1}. Limited kinetic data for M = Re suggest a similar rate. The manganese adducts in the absence of oxygen are photochemically converted to $[(arene)Mn(CO)_2PBu_3]^+$, while the rhenium analogues fail to undergo this reaction. The $[(arene)M(CO)_3]^+$ complexes react with CH_3CN by an associative mechanism to yield $[(CH_3CN)_3M(CO)_3]^+$ and activation parameters for both metals were obtained. In contrast to addition at the arene ring, the ring displacement with CH_3CN is about 2×10^4 times faster for rhenium.

Introduction

The reactivity of π-organic molecules such as olefins and arenes is often drastically altered upon coordination to a transition metal. In particular, cyclic π-hydrocarbons when coordinated to neutral or cationic organometallic fragments frequently undergo facile nucleophilic addition reactions. Such reactions are of considerable interest since they provide simple and sometimes unique routes to new organic molecules.[1-4]

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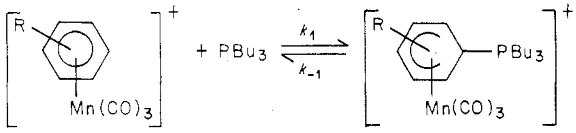
The addition of tertiary phosphines to coordinated cyclic π-hydrocarbons to yield phosphonium adducts has attracted recent attention.[5-11] Quantitative kinetic studies of this reaction have been reported[12-15] for the cationic systems $[(C_6H_7)Fe(CO)_3]^+$, $[(C_4H_4)Fe(CO)_2NO]^+$, $[(C_7H_8)Mn(CO)_3]^+$, and $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, or W). Such work provides information concerning the mechanism of nucleophilic addition to coordinated rings and allows the formulation of a reactivity order toward nucleophilic attack. In this paper, we report the results of a kinetic study of nucleophilic attack on the complexes $[(arene)M(CO)_3]^+$, M = Mn or Re.

The reactivity of $[(arene)Mn(CO)_3]^+$ cations (I) toward nucleophiles has been the subject of several studies. Addition to the arene ring occurs with hydride,[16] phenide,[17] cyanide,[18] and some other nucleophiles.[19] On the other hand, acetonitrile displaces the arene ring,[19] while amines attack coordinated CO to yield carboxamido complexes.[20] Pauson and Segal[21] recently reported substitution of halide and methoxide groups in $[(C_6H_5X)Mn(CO)_3]^+$ (X^- = OCH_3^-, halide) by various nucleophiles.

We recently have shown[8] that tri-*n*-butylphosphine, PBu_3, reacts with I to form phosphonium ring adducts according to reaction 1. Reaction 1 is readily reversible and the equilibrium



(1)

mixture reacts to yield $[(arene)Mn(CO)_2PBu_3]^+$ when exposed to light in the absence of oxygen. In air, however, the equilibrium mixture is stable in solution. Previous workers[19] reported the CO-substituted product but failed to detect the initial ring addition. We report herein a detailed kinetic study of reaction 1, including activation parameters for both forward and reverse steps.

In contrast to the $[(arene)Mn(CO)_3]^+$ cations, very little appears in the literature concerning the rhenium analogues. In 1963 Winkhaus and Singer[22] published a brief note reporting the synthesis of $[(C_6Me_6)Re(CO_3)]ClO_4$ and the hydride addition complex $[(C_6Me_6H)Re(CO_3)]$. The synthesis followed closely that of Wilkinson et al.[16] for the manganese derivatives. No yield was reported for the perchlorate salt, but Angelici[20] repeated the synthesis in 1972 and claimed a 19% yield. Winkhaus and Singer[22] state that arenes other than C_6Me_6 can be used but the yields are lower. However, no details of the preparations with other arenes were given and no chemical or physical properties mentioned. In 1965 Nyholm et al.[23] reported that an attempt to prepare $[(mesitylene)Re(CO)_3]ClO_4$ according to the recipe of Wilkinson et al.[16] for the manganese analogue yielded no product. We report here an improved method for the synthesis of $[(arene)Re(CO)_3]PF_6$ complexes, obtaining yields of 25 and 49% for arene = toluene and *p*-xylene, respectively. The low yield and lack of reproducibility previously reported are shown to arise from the reaction of the rhenium salts with water during final workup. Preliminary kinetic data are also reported for the addition of tri-*n*-butylphosphine to $[(toluene)Re(CO)_3]PF_6$.

Walker and Mawby[19] reported that acetonitrile attacks $[(arene)Mn(CO)_3]^+$ to yield $[(CH_3CN)_3Mn(CO)_3]^+$ and measured some rates in neat acetonitrile. We show herein that the rhenium analogues undergo the same reaction but at a rate more than 10^4 times faster. The rate law for both metals was determined and activation parameters were obtained. Previous kinetic studies of monomeric manganese(I) and rhenium(I) complexes have shown the manganese complexes to be more reactive.[24]

Table I. IR Spectra of Rhenium Compounds

compound	solvent	ν(C–O)/cm^{-1}
$[(benzene)Re(CO)_3]PF_6$	CH_3NO_2	2081, 2012
$[(benzene \cdot PBu_3)Re(CO)_3]PF_6$	CH_3NO_2	2033, 1950, 1940
$[(toluene)Re(CO)_3]PF_6$	CH_3NO_2	2079, 2008
	acetone	2077, 2005
$[(toluene \cdot PBu_3)Re(CO)_3]PF_6$	CH_3NO_2	2031, 1947, 1937
	acetone	2031, 1947, 1937
$[(toluene \cdot H)Re(CO)_3]$	hexane	2028, 1948, 1935
$[(toluene \cdot CN)Re(CO)_3]$	acetone	2030, 1938
$[(p\text{-xylene})Re(CO)_3]PF_6$	CH_3NO_2	2072, 2001
	acetone	2071, 2000
$[(p\text{-xylene} \cdot PBu_3)Re(CO)_3]PF_6$	acetone	2029, 1944, 1935
$[(p\text{-xylene} \cdot H)Re(CO)_3]$	hexane	2023, 1940, 1931
$[(p\text{-xylene} \cdot CN)Re(CO)_3]$	acetone	2024, 1934
$[(CH_3CN)_3Re(CO)_3]PF_6$	CH_3CN	2055, 1952
$[(acetone)_3Re(CO)_3]PF_6$	acetone	2042, 1925

Experimental Section

All solvents were distilled and dried prior to use. Infrared spectra were recorded on a Perkin-Elmer Model 257, NMR spectra on a Perkin-Elmer R32, and field desorption (FD) mass spectra on a Varian MAT CH-5 instrument.

$[(arene)Mn(CO)_3]PF_6$ (or BF_4). These compounds were prepared as described in the literature.[16,21]

$[(arene \cdot PBu_3)Mn(CO)_3]PF_6$ (or BF_4). Tri-*n*-butylphosphine was added to an acetone or nitromethane solution of $[(arene)Mn(CO)_3]^+$ in air and the product (or an equilibrium mixture) formed rapidly in situ. Attempts to precipitate the product with ether or hexane yielded only starting material (see Results and Discussion).

$[(arene)Mn(CO)_2PBu_3]PF_6$ (or BF_4). A solution of PBu_3 and $[(arene)Mn(CO)_3]^+$ in acetone or acetonitrile, but not nitromethane, generated the product in situ within 15 min when exposed to daylight in the absence of oxygen.

$[Re(CO)_5Br]$. This compound was prepared by combining $Re_2(CO)_{10}$ and Br_2 in carbon tetrachloride or cyclohexane as described by Kaesz et al.[25]

$[(toluene)Re(CO)_3]PF_3$. To toluene (ca. 50 mL) was added 0.8 g of $Re(CO)_5Br$ and 1.4 g of $AlCl_3$. The mixture was refluxed under nitrogen for 4 h by which time a thick orange-brown tar had formed. The mixture was cooled in an ice bath and the solvent decanted from the solidified tar. To the residue 20 mL of an ice-water slush was added and the flask shaken vigorously for 1 min or less to dissolve the tar. The flask was kept in an ice bath during this process to prevent heating due to hydrolysis of excess $AlCl_3$. The aqueous solution was washed quickly with cold ether and filtered. An aqueous solution containing excess NH_4PF_6 was added immediately. The resultant white precipitate was filtered and washed with cold water, methanol, and ether. The product was purified by dissolving in 1–2 mL of acetone and *immediately* reprecipitating by the addition of ether; yield 0.25 g (25%). Anal. Calcd for $[(toluene)Re(CO)_3]PF_6$: C, 23.7; H, 1.59. Found: C, 23.5; H, 1.6.

$[(p\text{-xylene})Re(CO)_3]PF_6$. This compound was prepared in a similar manner to the toluene analogue. A mixture of *p*-xylene and cyclohexane boiling at ca. 110 °C was the solvent and heating time was 4 h; yield 49%. Anal. Calcd for $[(p\text{-xylene})Re(CO)_3]PF_6$: C, 25.4; H, 1.93. Found: C, 25.0; H, 1.8.

$[(benzene)Re(CO)_3]PF_6$. To benzene (ca. 50 mL) was added 0.7 g of $[Re(CO)_5Br]$ and 1.3 g of $AlCl_3$. The mixture was refluxed under nitrogen for 20 h. The same procedure as above was followed. A yield of only 20 mg was obtained and most of the $Re(CO)_5Br$ was recovered unreacted. Undoubtedly a higher reaction temperature would improve the yield.

$[(arene \cdot H)Re(CO)_3]$. Excess $NaBH_4$ and 30 mg of $[(arene)Re(CO)_3]PF_6$ were added to 10 mL of hexane and the mixture was stirred vigorously under nitrogen in the dark for 1 h. The product dissolves in the solvent as it is formed (the reactants are insoluble in hexane) and was characterized via its IR spectrum (Table I). The manganese analogues were prepared similarly.

$[(arene \cdot CN)Re(CO)_3]$. Excess KCN was added to an acetone solution of $[(arene)Re(CO)_3]PF_6$. The cyanocyclohexadienyl product was formed after a few minutes of vigorous shaking and characterized via its IR spectrum (Table I). The manganese analogues were prepared similarly.

Kinetic Studies. A thermostated stopped-flow apparatus, previously described,[26] was used to measure the rate of addition of PBu_3 to the $[(arene)M(CO)_3]^+$ (M = Mn or Re) cations. A pseudo-first-order excess of PBu_3 was always used and the wavelength was 350–360 nm. The rate of nucleophilic attack of CH_3CN on $[(arene)M(CO)_3]^+$ to displace the arene was measured in CH_3CN–CH_3NO_2 mixtures, with $[CH_3CN]$ ranging from 0 to 19 M (neat). These latter reactions were carried out in the dark, under nitrogen, and monitored by periodically withdrawing a sample via syringe and recording the IR spectrum. All kinetic data were analyzed by making the standard $\ln (A - A_\infty)$ vs. time plots. Good first-order plots were generally obtained for the entire reaction in each case. The disappearance of reactant bands and appearance of product bands occurred at the same rate.

Equilibrium Constants. The equilibrium constants for reaction 2

$$[(\text{arene})\text{M(CO)}_3]^+ + \text{PBu}_3 \overset{K}{\rightleftharpoons} [(\text{arene}\cdot\text{PBu}_3)\text{M(CO)}_3]^+ \quad (2)$$

were measured at 25 °C by recording the IR spectra of mixtures of PBu_3 and $[(arene)M(CO)_3]^+$. Solutions were equilibrated in a constant-temperature bath and an aliquot was removed and its IR spectrum recorded immediately. Experiments suggested that heating of the solutions by the IR beam was not substantial within the scanning time. However, to allow valid comparisons to be made between manganese and rhenium and between the different arenes, all the equilibrium constants were measured at least four times under identical conditions; e.g., each solution was in the IR beam for the same period of time.

Results and Discussion

Synthesis of $[(arene)M(CO)_3]PF_6$. The $[(arene)M(CO)_3]^+$ complexes (M = Mn or Re) are prepared by similar methods. Modifications outlined in the present work greatly increase the yields and reproducibility for the rhenium compounds. The crucial step in the synthesis is the extraction of the crude product $[(arene)Re(CO)_3]AlCl_3Br$ from the reaction mixture into water, followed by washing with ether and precipitation with NH_4PF_6. Experiments showed that the $[(arene)Re(CO)_3]^+$ species are very reactive toward water and hence the time in the aqueous phase must be minimal. For example, the yield of $[(toluene)Re(CO)_3]^+$ increased from a few percent to 25% when the water extraction treatment was reduced from 10 to ca. 2 min. The yield of $[(p\text{-xylene})Re(CO)_3]PF_6$ reached a respectable 49%. The reaction of these cations with water, most likely producing $[(H_2O)_3Re(CO)_3]^+$ accounts for the difficulty encountered by others[20,22,23] attempting their preparation.

The manganese salts are stable for days at room temperature in solvents such as acetone, nitromethane, etc. However, acetonitrile very slowly (days) displaces arene[19] yielding $[(CH_3CN)_3Mn(CO)_3]^+$. The rhenium analogues also react with acetonitrile, producing the known[27] $[(CH_3CN)_3Re(CO)_3]^+$, but the reaction time is a matter of minutes instead of days. Acetone also attacks $[(arene)Re(CO)_3]^+$ rapidly to displace arene whereas ring displacement by nitromethane solvent requires several hours.

The formulation of the $[(toluene)Re(CO)_3]PF_6$ complex was proven beyond doubt by obtaining its field desorption (FD) mass spectrum. The only significant mass peaks were 361, 362, 363, and 364, which are assigned to M and M + 1 ions for the two rhenium isotopes of $[(toluene)Re(CO)_3]^+$. In agreement with earlier studies on the FD mass spectra of organometallic carbonyl complexes, fragment ions due to carbonyl loss were not obtained.

The ^1H NMR spectrum of $[(toluene)Mn(CO)_3]BF_4$ in nitromethane consists of two multiplets centered at τ 3.30 and 3.55 (relative areas 2:3) and the methyl resonance at τ 7.48. Following the work of Pauson and Segal,[21] we assign the two multiplets as $H^{3,5}$ and $H^{2,6,4}$, respectively. The spectrum of $[(toluene)Re(CO)_3]PF_6$ in nitromethane is very similar, the multiplets being centered at τ 3.09 and 3.37 (area ratio 2:3) and the methyl resonance at τ 7.26. The downfield shift of the NMR spectrum for rhenium compared to manganese is similar to that reported[28] for the complexes $[CpM(CO)_3]$ and $[CpM(CO)_2(NO)]$ (M = Mn or Re).

Table II. IR Spectra of Magnanese Compounds[a]

compounds	ν(C-O)/cm^{-1}
$[(benzene)Mn(CO)_3]BF_4$	2080, 2026
$[(benzene\cdot PBu_3)Mn(CO)_3]BF_4$	2028, 1950
$[(benzene)Mn(CO)_2PBu_3]BF_4$	1997, 1950
$[(toluene)Mn(CO)_3]BF_4$	2079, 2021
$[(toluene\cdot PBu_3)Mn(CO)_3]BF_4$	2025, 1948
$[(toluene)Mn(CO)_2PBu_3]BF_4$	1991, 1946
$[(toluene\cdot H)Mn(CO)_3]$	2020, 1949, 1939[b]
$[(toluene\cdot CN)Mn(CO)_3]$	2023, 1943
$[(p\text{-xylene})Mn(CO)_3]PF_6$	2076, 2019
$[(p\text{-xylene}\cdot PBu_3)Mn(CO)_3]PF_6$	2021, 1944
$[(p\text{-xylene})Mn(CO)_2PBu_3]PF_6$	1989, 1943
$[(p\text{-xylene}\cdot H)Mn(CO)_3]$	2018, 1941, 1936[b]
$[(p\text{-xylene}\cdot CN)Mn(CO)_3]$	2020, 1941
$[(mesitylene)Mn(CO)_3]BF_4$	2072, 2015
$[(mesitylene)Mn(CO)_2PBu_3]BF_4$	1985, 1939
$[(chlorobenzene)Mn(CO)_3]PF_6$	2087, 2031
$[(chlorobenzene\cdot PBu_3)Mn(CO)_3]PF_6$	2035, 1961
$[(p\text{-methylchlorobenzene})Mn(CO)_3]PF_6$	2082, 2029
$[(p\text{-methylchlorobenzene}\cdot PBu_3)Mn(CO)_3]PF_6$	2031, 1958
$[(anisole)Mn(CO)_3]PF_6$	2077, 2019
$[(anisole\cdot PBu_3)Mn(CO)_3]PF_6$	2027, 1942
$[(anisole)Mn(CO)_2PBu_3]PF_6$	1991, 1942
$[(CH_3CN)_3Mn(CO)_3]BF_4$	2068, 1978[c]

[a] Solvent acetone except where marked. [b] Solvent hexane. [c] Solvent acetonitrile.

The ^1H NMR spectrum of $[(toluene)Re(CO)_3]PF_6$ in acetone-d_6 taken within a few minutes of dissolution shows the two expected multiplets centered at τ 2.79 and 3.08; with the methyl band at τ 7.19. As the spectrum is rescanned, free toluene appears and the bands due to coordinated toluene weaken. After 1 h only free toluene remains, confirming that acetone displaces the arene in $[(arene)Re(CO)_3]^+$.

The $[(arene)Re(CO)_3]^+$ salts readily add hydride and cyanide ions to the arene ring to produce neutral $[(arene\cdot X)Re(CO)_3]$ in analogy with the known manganese derivatives. With substituted arenes, the hydride, cyanide, or tri-*n*-butylphosphine adducts could exist in a number of isomeric forms. Pauson[29] has found that directive effects for ortho, meta and para positions in $[(arene)Mn(CO)_3]^+$ complexes, though present, are relatively weak. The site of addition has not been determined in the present study.

Table I lists IR frequencies in the carbonyl region for the $[(arene)Re(CO)_3]^+$ salts and for tri-*n*-butylphosphine, hydride, and cyanide addition products. IR data for the analogous manganese complexes are summarized in Table II.

Addition of PBu_3 to $[(arene)M(CO)_3]^+$. Recent studies have established that tertiary phosphines can react with π-hydrocarbon metal complexes in a variety of fashions: (i) addition at the organic ring to yield phosphonium complexes;[5-10] (ii) displacement of a carbonyl ligand,[30,31] or (iii) displacement of the π-hydrocarbon ligand.[19,31-33] The present study shows that, contrary to previous belief,[19] reaction of PBu_3 with $[(arene)Mn(CO)_3]^+$ leads to ring addition giving the new phosphonium adducts $[(arene\cdot PBu_3)Mn(CO)_3]^+$ and that a similar process occurs with the rhenium analogues, reaction 2.

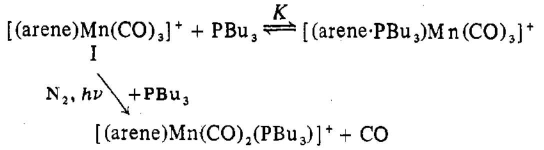
The static equilibrium constants for reaction 2, were determined as described in the Experimental Section and are summarized in Table III. The addition of PBu_3 was readily reversible as shown by IR dilution experiments. Addition of ether to an acetone solution of $[(arene)M(CO)_3]^+$ containing sufficient excess PBu_3 to generate the phosphonium ring adduct caused the quantitative precipitation of $[(arene)M(CO)_3]PF_6$. This also clearly demonstrates the reversibility of reaction 2.

Table III. Equilibrium Constants[a] for Addition of PBu_3 to $[(arene)M(CO)_3]^+$

compound	solvent	K/M^{-1}
$[(benzene)Mn(CO)_3]^+$	acetone	260
$[(benzene)Re(CO)_3]^+$	CH_3NO_2	>500
$[(toluene)Mn(CO)_3]^+$	acetone	60
$[(toluene)Mn(CO)_3]^+$	CH_3NO_2	90
$[(toluene)Re(CO)_3]^+$	acetone	260
$[(toluene)Re(CO)_3]^+$	CH_3NO_2	320
$[(p\text{-xylene})Mn(CO)_3]^+$	acetone	4
$[(p\text{-xylene})Re(CO)_3]^+$	acetone	7
$[(mesitylene)Mn(CO)_3]^+$	acetone	<1

[a] Temperature 25 °C.

Scheme I



The equilibrium constants for this reversible addition show the rhenium complexes to be slightly more electrophilic in a thermodynamic sense (Table III). As expected, increasing methyl substitution decreases the electrophilicity of the coordinated arene, K decreasing in the order chlorobenzene > benzene > toluene > p-xylene > mesitylene. Our best judgment is that anisole lies near toluene in adduct stability. The very large equilibrium constant for the chlorobenzene complex (M = Mn) correlates with simple inductive ideas, while the very small K for arene = mesitylene may arise from a combination of electronic and steric factors.

Upon exposure of an equilibrium mixture of $[(arene)Mn(CO)_3]^+$ and $[(arene{\cdot}PBu_3)Mn(CO)_3]^+$ in acetone or acetonitrile to daylight in the absence of oxygen, the solution turns deep yellow within 15 min and CO is evolved to produce the $[(arene)Mn(CO)_2PBu_3]^+$ cation originally reported by Walker and Mawby.[19] This photochemical reaction is easily quenched by oxygen. In air, or in the absence of light, CO displacement does not occur. It also does not occur in nitromethane, probably due to strong solvent absorption below ca. 375 nm. The complex $[(mesitylene)Mn(CO)_3]^+$ did not form a PBu_3 adduct because K (Table III) is too small, but photochemical conversion to displace CO by PBu_3 is facile. On the other hand, the adduct with $[(chlorobenzene)Mn(CO)_3]^+$ has a K too large to measure by our techniques, but it does not undergo the photochemical reaction, and prolonged exposure to light eventually causes general decomposition.

Strong support for the above conclusions comes from ^1H NMR data for the $[(benzene)Mn(CO)_3]^+$ species. The spectrum in acetone-d_6 consists of a single resonance at τ 3.10. Addition of excess PBu_3 (air, dark) produces $[(benzene{\cdot}PBu_3)Mn(CO)_3]^+$: τ 3.7, 4.5, 5.6, 6.6; relative areas 1:2:1:2. This latter spectrum agrees well with that reported[19] for the related $[(benzene{\cdot}CN)Mn(CO)_3]$ [τ 4.0 (H^4), 4.9 ($H^{3,5}$), 6.4 (H^1), 7.2 ($H^{2,6}$)], after the influence of the positive charge in the phosphonium complex is considered. Removal of oxygen and exposure to light cause the ^1H NMR spectrum to change after several minutes to the single resonance at τ 3.58 reported by Walker and Mawby[19] for $[(benzene)Mn(CO)_2(PBu_3)]^+$.

Interestingly, the rhenium salts do not undergo photochemical replacement of CO with PBu_3, even in acetonitrile as solvent and upon exposure to a UV lamp for a few minutes.

Since the phosphine is probably bonded to the ring in the exo position,[18,19] it seems unlikely that the phosphonium adduct is converted directly into $[(arene)Mn(CO)_2(PBu_3)]^+$. The probable direct precursor is I as shown in Scheme I. Scheme I is consistent with the observation that $[(mesitylene)Mn(CO)_3]^+$ readily undergoes the photochemical reaction while $[(chlorobenzene)Mn(CO)_3]^+$ does not.

Table IV. Rate Constants[a] for Addition of PBu_3 to $[(arene)Mn(CO)_3]^+$

arene	$T/°C$	$[PBu_3]/M$	k_{obsd}/s^{-1}
benzene	0	0.0028	0.99
		0.0063	2.15
		0.0094	2.92
		0.0143	4.51
		0.0244	7.28
	10	0.0011	1.11
		0.0019	1.47
		0.0043	2.65
		0.0089	4.75
		0.0150	8.0
	20	0.0030	4.17
		0.0066	7.00
		0.0101	9.37
		0.0116	10.8
		0.0186	16.2
	26	0.0015 (5)	5.17
		0.0029 (5)	7.40
		0.0050	8.00
		0.0090	12.4
		0.0150	19.9
	33	0.0012	9.00
		0.0020 (5)	10.3
		0.0042 (5)	14.0
		0.0065	16.0
		0.0126	24.0
toluene	0	0.0019	0.54
		0.0038	0.86
		0.0067 (5)	1.21
		0.0095	1.45
		0.0150	2.30
p-xylene	0	0.0150	9.10
		0.0300	9.80
		0.0450	11.8
		0.0600	12.0
		0.0800	16.0
anisole	0	0.0050	0.54
		0.0079	0.67
		0.0125	1.20
		0.0250	2.10
		0.0390	3.30
chlorobenzene	0	0.0030	10.3
		0.0050	16.3
		0.0070	23.1
		0.0110	35.0
p-methylchlorobenzene	0	0.0030	9.6
		0.0070	21.0

[a] Solvent is acetone; total complex concentration was (1–5) × 10^{-4} M.

Table V. Rate Law for Addition of PBu_3 to $[(arene)Mn(CO)_3]^+$

arene	$T/°C$	k_{obsd}/s^{-1}
benzene	0	– + 295 $[PBu_3]$
	10	0.55 + 480 $[PBu_3]$
	20	1.8 + 770 $[PBu_3]$
	26	3.6 + 1035 $[PBu_3]$
	33	7.7 + 1420 $[PBu_3]$
toluene	0	0.35 + 122 $[PBu_3]$
p-xylene	0	7.2 + 98 $[PBu_3]$
anisole	0	(0.2) + 80 $[PBu_3]$
chlorobenzene	0	– + 3200 $[PBu_3]$
p-methylchlorobenzene	0	– + 3000 $[PBu_3]$

Also consistent with Scheme I is the observation that reaction of $[(C_6H_6)Mn(CO)_3]^+$ with triphenylphosphine or triethyl phosphite gave no IR spectral evidence for ring adduct formation, presumably due to a low K value; yet both nucleophiles readily replace CO when exposed to light in the absence of oxygen.

The kinetics of reaction 2 (M = Mn) were followed in acetone as solvent using a thermostated stopped-flow appa-

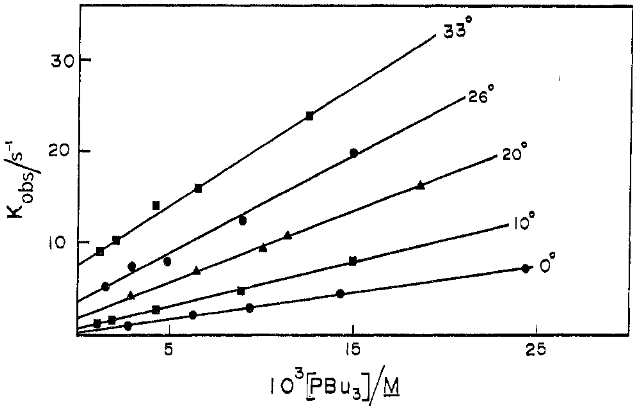


Figure 1. Rate data for the reaction $[(\text{benzene})\text{Mn(CO)}_3]^+ + \text{PBu}_3 \rightarrow [(\text{benzene}\cdot\text{PBu}_3)\text{Mn(CO)}_3]^+$. Solvent is acetone.

ratus. The results are given in Tables IV and V and plots of k_{obsd} vs. $[\text{PBu}_3]$ for $[(\text{benzene})\text{Mn(CO)}_3]^+$ appear in Figure 1. The observed rate law is what one expects from reaction 2, i.e.

$$k_{\text{obsd}} = k_1[\text{PBu}_3] + k_{-1} \qquad (3)$$

It can be seen that the equilibrium constants calculated from the kinetic data ($K = k_1/k_{-1}$) are in agreement with the static measurements (Table III). For arene = benzene, Arrhenius plots were made for k_1 and k_{-1} and the results (least squares) are as follows: k_1, $\Delta H^\ddagger = 7.3 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -20.3 \pm 0.2$ eu/mol; k_{-1}, $\Delta H^\ddagger = 19.0 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = +7.7 \pm 0.1$ eu/mol. These results combine to yield for K: $\Delta H^\circ = -11.9$ kcal/mol and $\Delta S^\circ = -28.5$ eu/mol. A direct least-squares analysis of $K = k_1/k_{-1}$ produces $\Delta H^\circ = -11.6 \pm 0.1$ kcal/mol and $\Delta S^\circ = -27.6 \pm 0.1$ eu/mol.

Separation of the k_{obsd} values for addition of PBu_3 to $[(\text{arene})\text{Mn(CO)}_3]^+$ into k_1 and k_{-1} terms was possible in most instances (eq 3, Table V). The forward k_1 values are seen to decrease in the order chlorobenzene ≥ *p*-methylchlorobenzene > benzene > toluene > *p*-xylene > anisole (40:37:3.7:1.5:1.2:1). Except for anisole, this is also the order of decreasing phosphonium adduct stability (K). Thus, both the reactivity and stability orders seem to follow simple inductive ideas. It should be noted that PBu_3 addition to $[(\text{toluene})\text{Mn(CO)}_3]^+$ and $[(p\text{-xylene})\text{Mn(CO)}_3]^+$ occurs at nearly the same rate; yet K is about 15 times greater for the toluene complex. As Table V shows, this difference in K is largely due to differences in k_{-1}.

An attempt was made to study the rate of reaction 2 with rhenium as the metal. A study in acetone was impossible owing to rapid decomposition of $[(\text{arene})\text{Re(CO)}_3]^+$ by solvent. The complex $[(\text{toluene})\text{Re(CO)}_3]^+$ is fairly stable in nitromethane, but solvent absorption limits the choice of wavelength to ≥375 nm. Unfortunately there is very little absorbance change during the reaction at this wavelength, and reliable results could not be obtained. However, preliminary rate data suggest that $[(\text{toluene})\text{Re(CO)}_3]^+$ reacts with PBu_3 ca. 3–5 times more rapidly than does $[(\text{toluene})\text{Mn(CO)}_3]^+$ under similar conditions.

There have been two recent reports[34,35] that in some cases nucleophiles attack the metal prior to ring addition. For our reactions, we found neither spectroscopic nor kinetic evidence for any intermediates in reaction 2, and we conclude that the most likely mechanism is simply direct bimolecular attack on the arene ring. The activation parameters are clearly consistent with this suggestion. If prior attack occurs at the metal, one might expect that the observed rate constant (k_1) for reaction 2 would differ by more than it does as the metal is changed from Mn to Re. As discussed below, arene ring displacement by CH_3CN, which invokes attack at the metal, is faster for rhenium by a factor of 2×10^4. In this context, it is pertinent to note that the rate of PBu_3 addition to the ring in $[(\text{tropylium})\text{M(CO)}_3]^+$ (M = Cr, Mo, or W) also does not depend strongly on the metal[13] whereas displacement of the tropylium ring by CH_3CN is strongly metal dependent.[36]

Table VI. Rate Data for Arene Displacement from $[(\text{toluene})\text{M(CO)}_3]^+$

M	T/°C	CH_3CN/M[a]	$10^4k_{\text{obsd}}/\text{s}^{-1}$
Re[b]	15	4.0	1.3
Re	15	19	4.2
Re	20	4.0	2.1
Re	20	19	8.3
Re	25	0.0	0.5
Re	25	1.0	1.2 (5)
Re	25	2.0	2.0
Re	25	3.0	2.7 (5)
Re	25	4.0	3.6
Re	25	19	13.3
Re	35	4.0	9.2
Mn[c]	60	19	0.042
Mn	72.2	0	0.008
Mn	72.2	3	0.040
Mn	72.2	6	0.070
Mn	72.2	19	0.165
Mn[d]	100	19	2.17

[a] Solvent is CH_3NO_2. [b] Anion is PF_6^- for rhenium salts. [c] Anion is BF_4^- for manganese salts. [d] From ref 19.

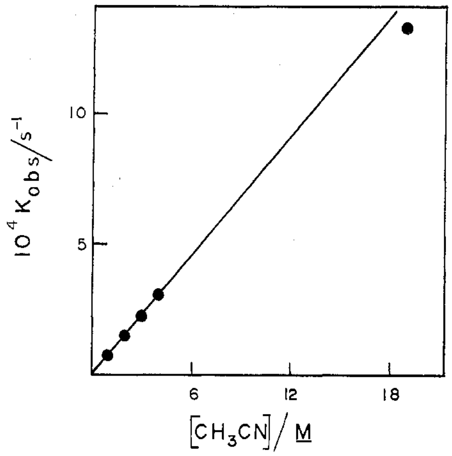


Figure 2. Rate data at 25 °C for the reaction $[(\text{toluene})\text{Re(CO)}_3]^+ + \text{CH}_3\text{CN} \rightarrow [(\text{CH}_3\text{CN})_3\text{Re(CO)}_3]^+ + \text{toluene}$. Solvent is $\text{CH}_3\text{CN}-\text{CH}_3\text{NO}_2$ mixture.

Kinetic studies of the nucleophilic addition of tertiary phosphines to coordinated cyclic π-hydrocarbons have been reported,[12-15,37] and the following approximate reactivity order can now be stated: $[(\text{C}_7\text{H}_8)\text{Mn(CO)}_3]^+$ (12000) > $[(\text{C}_4\text{H}_4)\text{Fe(CO)}_2\text{NO}]^+$ (1200) > $[(\text{C}_6\text{H}_7)\text{Fe(CO)}_3]^+$ (160) > $[(\text{C}_7\text{H}_7)\text{M(CO)}_3]^+$ (M = Cr, Mo, or W) (40) ≈ $[(\text{C}_6\text{H}_6\text{OMe})\text{Fe(CO)}_3]^+$ (40) > $[(\text{C}_6\text{H}_6)\text{Mn(CO)}_3]^+$ (1). All of these complexes have relatively small values of $\Delta H^\ddagger$ and large negative values of $\Delta S^\ddagger$ for the tertiary phosphine addition step, suggesting a common mechanism. It is interesting to note that the resonance energy of the arene ring in $[(\text{C}_6\text{H}_6)\text{Mn(CO)}_3]^+$ makes this complex less electrophilic than the cycloheptatriene ring in $[(\text{C}_7\text{H}_8)\text{Mn(CO)}_3]^+$ by a factor of about 10^4.

Data available for the addition of aromatic and heterocyclic nucleophiles to coordinated cyclic π-hydrocarbons[38] suggest that there is not a single quantitative order of electrophilicities. The order is nucleophile dependent in such a way that does not reflect the reactivity-selectivity principle. This will be discussed in a future communication.

Kinetics of Arene Displacement. Reaction 4 was studied in $\text{CH}_3\text{CN}-\text{CH}_3\text{NO}_2$ mixtures. Table VI gives the results. In

$$[(\text{toluene})M(CO)_3]^+ + 3CH_3CN \rightarrow [(CH_3CN)_3M(CO)_3]^+ + \text{toluene} \quad (4)$$

all cases, IR spectra showed the reactions to be very clean, with no observable side-products. The solvent nitromethane reacted slowly with the toluene complex and after correcting for this Figure 2 is obtained for M = Re, which shows that reaction 4 is first order in CH_3CN. The data point for neat acetonitrile also gives an approximate fit to this plot, a result probably due at least partially to the similar dielectric constants of nitromethane and acetonitrile. The data for manganese show (after correcting for the CH_3NO_2 reaction) that the rate doubles as $[CH_3CN]$ changes from 3 to 6 M, and hence the reaction is also first order in CH_3CN.

Activation parameters for reaction 4 were obtained for M = Mn from an Arrhenius plot of the data in neat CH_3CN. Rate constants were divided by 19 to correct to second-order values. A least-squares fit of the three points, one of which is from the work of Walker and Mawby,[19] gave $\Delta H^{\ddagger} = 24.0 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -17.6 \pm 0.5$ eu/mol. The rhenium activation parameters were obtained from the four rates available for $[CH_3CN] = 4$ M. The rate constants obtained for rhenium in neat CH_3CN were considered less reliable since their rapidity restricted the number of aliquots that could be measured in each run. An Arrhenius plot of the solvent-corrected second-order rate constants yielded $\Delta H^{\ddagger} = 16.6 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -21.5 \pm 0.3$ eu/mol. The errors reflect the quality of the least-squares fit and from an experimental viewpoint are unrealistically low.

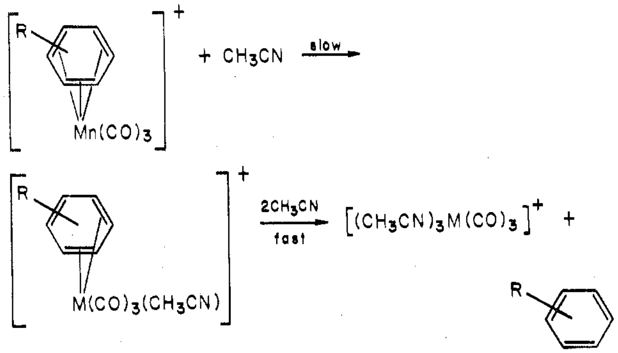
In sharp contrast to the similar rates of PBu_3 addition to the arene ring in $[(\text{arene})M(CO)_3]^+$ (M = Mn and Re), attack at the metal by acetonitrile leading to arene displacement is much more rapid at rhenium. A second-order rate constant of 3.2×10^{-9} M^{-1} s^{-1} is calculated for reaction 4 at 25 °C for M = Mn. For rhenium, the rate constant at 25 °C is 7.5×10^{-5} M^{-1} s^{-1}. Thus, displacement of toluene by acetonitrile in $[(\text{toluene})M(CO)_3]^+$ is faster for rhenium by a factor of 23 000 to 1. Expressed another way, the half-life for reaction 4 in neat CH_3CN at 25 °C is about 9 min for rhenium, and 130 days for manganese!

There are several published reports[24] of CO substitution in the monomeric manganese and rhenium complexes, $[M(CO)_5X]$ (X = Cl, Br, or I). These reactions follow a dissociative mechanism and rhenium is *less* reactive than manganese by ca. 1:60. The reason for the qualitative change in reactivity in the present arene systems is that the mechanism is associative. Because of its size, rhenium should be much more susceptible to S_N2 attack than manganese. An associative mechanism is favored because the toluene can act as an electron sink and accept electron density provided by the nucleophile. An intermediate having more than 18 electrons need never be formed. This, of course, cannot occur with $[M(CO)_5X]$, and so these complexes react dissociatively and the stronger Re–CO bond makes rhenium less reactive. The mechanism of arene displacement can be pictured as shown in Scheme II. This mechanism is similar to that proposed[39] for arene displacement from $[(\text{arene})M(CO)_3]$ (M = Cr, Mo, or W) complexes, where a second-order rate law also holds. A similar mechanism holds for reaction 5, M = Cr, Mo, or W.[36]

$$[(C_7H_7)M(CO)_3]^+ + 3CH_3CN \rightarrow [(CH_3CN)_3M(CO)_3] + C_7H_7^+ \quad (5)$$

This last mentioned reaction is of particular interest because the rate order is Mo > W ≫ Cr whereas, as mentioned above, the rate of addition of nucleophiles to the tropylium ring depends little on the metal. The rate order of the S_N1 reaction of $[M(CO)_6]$ with nucleophiles is Cr > W.[40] Hence, it seems that the relative rates of manganese and rhenium for addition to coordinated arenes and attack at the metal with displacement of arene is qualitatively similar to the analogous reactions of the $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, or W) systems.

Scheme II



That the larger size of rhenium compared to manganese can have important kinetic implications when nucleophilic attack occurs in the vicinity of the metal was shown by Angelici and Brink,[41] who reported a kinetic study of nucleophilic attack of primary amines on coordinated CO to yield carboxamido complexes, eq 6 (M = Mn or Re; L = a phosphine). They found that Re > Mn in rate by as much as 30:1 when the amine R group is bulky, but the rates became equal for a sterically uncrowded amine (n-$BuNH_2$).

$$[L_2M(CO)_4]^+ + 2RNH_2 \rightleftharpoons L_2M(CO)_3C(=O)NHR + RNH_3^+ \quad (6)$$

Finally, the activation parameters for reaction 4 show that $\Delta S^{\ddagger}$ is very negative as expected for an S_N2 mechanism and that the large rate differences between manganese and rhenium stem almost entirely from $\Delta H^{\ddagger}$. That $\Delta H^{\ddagger}$ is larger by about 7 kcal for manganese does not necessarily imply a stronger metal–arene bond, since $\Delta H^{\ddagger}$ also includes the influence of bond formation to CH_3CN and these two effects oppose each other.

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Registry No. $[(\text{benzene})Re(CO)_3]PF_6$, 68927-90-2; $[(\text{benzene}\cdot PBu_3)Re(CO)_3]PF_6$, 68927-92-4; $[(\text{toluene})Re(CO)_3]PF_6$, 68927-93-5; $[(p\text{-xylene})Re(CO)_3]PF_6$, 68927-95-7; $[(CH_3CN)_3Re(CO)_3]PF_6$, 66610-18-2; $[(\text{acetone})_3Re(CO)_3]PF_6$, 68927-97-9; $[(\text{benzene})Mn(CO)_3]BF_4$, 41646-79-1; $[(\text{benzene}\cdot PBu_3)Mn(CO)_3]BF_4$, 59537-71-2; $[(\text{benzene})Mn(CO)_2PBu_3]BF_4$, 68927-98-0; $[(\text{toluene})Mn(CO)_3]BF_4$, 49564-37-6; $[(\text{toluene})Mn(CO)_2PBu_3]BF_4$, 68928-00-7; $[(p\text{-xylene})Mn(CO)_3]PF_6$, 38834-28-5; $[(p\text{-xylene})Mn(CO)_2PBu_3]PF_6$, 68928-02-9; $[(\text{mesitylene})Mn(CO)_3]BF_4$, 41656-03-5; $[(\text{mesitylene})Mn(CO)_2PBu_3]BF_4$, 68928-03-0; $[(\text{chlorobenzene})Mn(CO)_3]PF_6$, 57812-91-6; $[(p\text{-methylchlorobenzene})Mn(CO)_3]PF_6$, 57813-15-7; $[(\text{anisole})Mn(CO)_3]PF_6$, 57812-97-2; $[(\text{anisole})Mn(CO)_2PBu_3]PF_6$, 68928-05-2; $[(CH_3CN)_3Mn(CO)_3]BF_4$, 68928-06-3; PBu_3, 998-40-3; $NaBH_4$, 16940-66-2; KCN, 151-50-8; $Re(CO)_5Br$, 14220-21-4; $Re_2(CO)_{10}$, 14285-68-8; Br_2, 7726-95-6.

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Sorbitol and Related Polyol Complexes of Manganese(II), -(III), and -(IV): Redox and Oxygenation Equilibria

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Sorbitol, a straight-chain hexitol, complexes and stabilizes the +2, +3, and +4 oxidation states of manganese in aqueous alkaline solution in a manner analogous to that observed with D-gluconate and D-glucarate. The redox and coordination chemistry for the manganese–sorbitol complexes, as well as their reactions with molecular oxygen and hydrogen peroxide, have been studied by spectrophotometric, electrochemical, and magnetic measurements. The kinetics of their reactions with molecular oxygen have been studied by means of an oxygen membrane electrode. Molecular oxygen oxidizes the Mn(II) and Mn(III) complexes to the Mn(III) and Mn(IV) complexes, respectively, and is reduced to the peroxide anion in each case. Equilibrium constants and rate constants have been evaluated. Reaction mechanisms are proposed which are now thought to be general for the redox and oxygenation behavior of polyhydroxy complexes of manganese in aqueous alkaline solution.

Manganese is an essential component of several biological oxidation–reduction systems, including photosystem II in green plant photosynthesis[1–4] and mitochondrial superoxide dismutase.[5] The +2, +3, and +4 oxidation states of manganese are believed to be involved in these processes,[6–9] but this has not yet been established.

Several polarographic studies by Doležal[10–15] have shown that polyhydroxy ligands will effectively stabilize the +3 and +4 oxidation states of manganese in aqueous, alkaline solution. These studies indicate that sorbitol, a straight-chain hexitol, has the highest stability constant, 1.94×10^{16} M^{-1}.[15]

Recent studies[16] also have shown that the addition of sorbitol enhances the catalytic activity[17] of manganese for the oxygen–alkali pulping process in the manufacture of paper. This may be due to an effective increase in the solubilization and activation of molecular oxygen by the manganese–sorbitol complexes. The presence of sorbitol significantly increases the stability and solubility of the +3 and +4 oxidation states.

Recent studies in this laboratory have established that salts of D-gluconate and D-glucarate will also effectively stabilize the +2, +3, and +4 oxidation states of manganese in aqueous alkaline solution.[18,19] The manganese(II) gluconate complex reacts rapidly in a bimolecular process ($k_{obsd} = 2.8 \times 10^4$ M^{-1} s^{-1}) with molecular oxygen to produce the Mn(III) complex and peroxide ion and reacts in a slower reaction ($k_{obsd} = 3.9 \times 10^1$ M^{-1} s^{-1}) to produce the Mn(IV) complex and peroxide ion.[20,21] The Mn(II) complex also is oxidized by peroxide in a much slower reaction ($k_{obsd} = 6 \times 10^{-1}$ M^{-1} s^{-1}) to give the Mn(III) complex. The manganese(III)–gluconate system apparently can form both binuclear and mononuclear complexes; the relative amount depends on the ligand and hydroxide ion concentrations.[18,19]

This paper summarizes the results of a corresponding study for the sorbitol complexes of manganese(IV), -(III), and -(II) and establishes a general scheme for the redox behavior of polyhydroxy complexes of manganese and their reactivity with molecular oxygen and hydrogen peroxide. It also includes a more detailed spectroscopic and electrochemical study of the manganese–polyol complexes.

Experimental Section

Equipment. Polarography and cyclic voltammetry were performed with a three-electrode potentiostat based on the use of solid-state amplifiers.[22] Both the dropping-mercury electrode and the conventional polarographic cell, with built-in calomel reference electrode, have been described previously.[23] For cyclic voltammetry a Beckman hanging-drop mercury electrode was used with the standard three-electrode cell. A Princeton Applied Research Model 173 potentiostat, with a Model 179 digital coulometer and mercury-pool working electrode, was used for controlled-potential coulometry.

The spectrophotometric measurements were performed with a Cary Model 17 recording spectrophotometer. Circular dichroic spectra were recorded by use of a Cary Model 60 spectrometer with a Cary Model 6002 CD accessory. Quartz cells were used for all measurements.

The magnetic susceptibilities were determined by the modified[24] NMR method that was developed by Evans.[25] The paramagnetic shift

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