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Solvent Assistance in Reactions Involving Carbon Monoxide Insertion into Manganese–Carbon Bonds

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Infrared spectroscopy in the carbonyl stretching region and ^{1}H NMR spectroscopy indicate that solvent (S)-coordinated acyl complexes [$(CO)_4(S)MnCOR$] form in the reactions of manganese carbonyl alkyls [$(CO)_5MnR$] with polar solvents. The extent of reaction is ethyl ≫ methyl > 2,3,4,5,6-pentamethylbenzyl > 2,4,6-trimethylbenzyl ≫ 4-methylbenzyl ~ phenyl and DMSO > DMF > pyridine > acetonitrile. The solvent-coordinated acyl complexes slowly decompose to yield, first, [$(CO)_5Mn(COR)$] and then [$(CO)_5Mn$]$^-$. Further evidence for solvent involvement in ligand-induced CO insertion reactions has been obtained from kinetic analysis of the reaction of [$(CO)_5MnCH_2C_6H_4CH_3$-4] with PPh_3 in toluene solutions containing known amounts of polar solvents or solid promoters, such as $OPPh_3$ and dibenzyl sulfoxide.

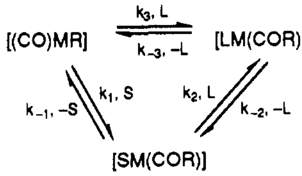
Introduction

The influence of solvent on the insertion of carbon monoxide into transition-metal–carbon σ bonds has been probed kinetically,[1-9] spectroscopically,[6,10,11] and theoretically[12,13] and variously evaluated. Solvent (S)-coordinated metal–acyl complexes have been suggested as intermediates in the reaction. In this paper, the spectroscopic identification of manganese complexes [$(CO)_4(S)MnCOR$] is reported.

Interpretation of solvent effects is complicated by the fact that the insertion reaction, which can be induced by CO, tertiary phosphines, and other nucleophiles, is two-stage (the k_1, k_2 path in Scheme I) in polar solvents.[1]

In the first, k_1, step in the solvent-dependent route, a solvent molecule (S) acts as the inducing nucleophile and a solvent-coordinated acyl complex is formed. The second, k_2, step involves the displacement of solvent by the nucleophile, L. In a number of investigations, the rate constant, k_1, has been found to increase with increasing polarity of the solvent; this stage has been described as being solvent-assisted[1,2] (or solvent catalyzed[14]). The direct influence of solvent on k_1 has also been demonstrated in the reaction of [$(\eta^5\text{-Cp})(CO)_3MoCH_3$] with $PMePh_2$ in a series of α-substituted tetrahydrofurans; the observed reactivity order in THF > 2-MeTHF ≫ 2,5-Me_2THF, a series of solvents with comparable dielectric constant but significantly different donor ability arising from the steric effect of the α-substituent(s), suggested that direct attack of the donor solvent at the metal center is occurring as the migration of the alkyl group to a carbonyl carbon atom is taking place.[3] The dependence of the rate constant, k_1, on the solvent is modest compared with the effect of different nucleophilic reagents on the rates of bimolecular displacement reactions,[1] and the extent of solvent involvement in the stabilization of the transition state of the reaction is, presumably, small. Theoretical analyses[12,13] have led to opposite conclusions as to whether such stabilization exists.

Scheme I



In addition, a solvent-independent pathway (k_3), involving the direct reaction between a metal alkyl and the inducing nucleophile, has been observed in nonpolar solvents.[1,3,9]

Although the direct observation of solvent-coordinated acyl complexes does not necessarily provide evidence for their discrete involvement in the k_1 reaction step, there has been some interest in the characterization of such species. Iron alkyls [$(\eta^5\text{-Cp})(CO)_2FeR$], R = C_2H_5, CH_2Cy, Np, etc., react with DMSO to yield [$(\eta^5\text{-Cp})(CO)(DMSO)FeCOR$],[6,10] [(diars)$Fe(CO)_2L(Me)$] reacts with acetonitrile to form [(diars)$Fe(CO)(CH_3CN)L(COMe)$],[5] and [$(CO)_5ReEt$] reacts with acetonitrile to form [$(CO)_4(CH_3CN)ReCOEt$].[11] The existence of the compounds [$(\eta\text{-Cp})(S)(CO)FeCOMe$]$^{0,+}$ has been inferred from electrochemical studies.[15]

The ease of reaction of the ethylrhenium complex with acetonitrile was surprising to us in view of the reluctance of [$(CO)_5ReR$] to undergo CO insertion[16] and has prompted the present study of solution species of the manganese alkyls [$(CO)_5MnR$] (R = CH_3, C_2H_5, C_6H_5, and substituted benzyl) in a variety of polar solvents.

The solvent effect on the *overall* rate constant observed in polar solvents has also been studied for the reaction of [$(\eta^5\text{-Cp})(CO)_2FeCH_2Cy$] with PPh_3.[6] The overall rate constant for the k_1,k_2 path can be expressed,[1] on the basis of the application of the steady-state approximation to the concentration of the solvent-coordinated intermediate, by eq 1. No specific overall rate enhancement in DMSO and

$$k_{\text{overall}} = k_1k_2[\mathrm{L}]/(k_{-1} + k_2[\mathrm{L}]) \qquad (1)$$

no correlation with solvent donicity was observed. This could reasonably imply that the k_2 step is retarded by a strongly bound solvent molecule. The experiments raised the question of whether the reaction with tertiary phos-

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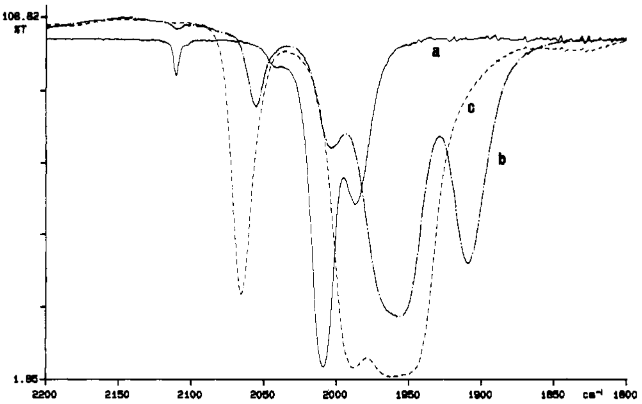

Figure 1. Infrared spectra in the carbonyl stretching region of $[(CO)_5MnCH_3]$ (a) in toluene, (b) in DMSO, and (c) in DMSO after the addition of PPh_3.

phines proceeded after prior dissociation of a solvent molecule from the intermediate. The separate measurement of k_2, over a variety of solvents, has not yet been achieved in any system, and precise analysis of solvent trends is not possible. Electrochemical results for $[(\eta^5\text{-}Cp)(S)(CO)FeCOMe]^{0,+}$ suggest that, in the iron(II) state, the substitution of solvent by another nucleophile involves a preequilibrium dissociative process but is associative for iron(III).[15] Evidence for a dissociative mechanism has been presented in a kinetic study of the reaction, which is promoted by PPh_3O or polar solvents, between $[(CO)_5MnCH_2C_6H_4OMe\text{-}p]$, *cis*-$[HMn(CO)_4(PMe_2Ph)]$, and CO, which yields *p*-$MeOC_6H_4CH_2CHO$ and *axial*-$[Mn_2(CO)_9(PMe_2Ph)]$,[14] and in the reaction of $[(CO)_5ReEt]$ with $[(CO)_5ReH]$ in acetonitrile.[17]

Experimental Section

The complexes $[(CO)_5MnR]$, R = CH_3,[18] C_2H_5,[19] C_6H_5,[20] $CH_2C_6H_{5-n}X_n$,[7,8] were prepared by standard methods and purified by chromatography, recrystallization (hexane), or sublimation (except for the thermally unstable $[(CO)_5MnC_2H_5]$). Infrared spectra were recorded on a Perkin-Elmer Model 1640 FTIR spectrometer, and ^1H NMR spectra, on Jeol PS 100 and GX 400 spectrometers. Solution spectroscopic studies were carried out at room temperature under nitrogen. The kinetic measurement of k_1, for the reactions of $[(CO)_5MnC_6H_5]$ and $[(CO)_5MnCH_3]$ with PPh_3 in acetonitrile at 30 °C, was carried out as described previously.[7,8] An estimate of k_1' $(=k_1/[S])$, at 30 °C, for the reaction of 0.2 M $[(CO)_5MnCH_2C_6H_4CH_3\text{-}4]$ with 0.5 M PPh_3, in toluene with added polar solvents or promoters (S), was obtained from the gradient of the linear plot of the pseudo-first-order rate constant (which approximates to k_1) against concentration of the added polar solvent or promoter.

Results and Discussion

The reactions of the manganese alkyl and aryl compounds with DMSO, DMF, acetonitrile, tetrahydrofuran, pyridine, and 2-ethoxyethyl ether were investigated by infrared spectroscopy in the carbonyl stretching region and by ^1H NMR spectroscopy. Further information on the reaction course was obtained by adding an excess of PPh_3 to the solution, which gave the known derivatives *cis*- and *trans*-$[(CO)_4(PPh_3)MnCOR]$.[21]

Carbonyl stretching absorptions associated with $[(CO)_5MnCH_3]$ in toluene were observed at 2110 w, 2041 w, 2012 s, 2004 s, and 1986 cm^{-1} m (Figure 1a). The weak absorption at 2041 cm^{-1} probably corresponds to one of the absorptions of $Mn_2(CO)_{10}$ present as an trace impurity. Very rapid reaction (time of mixing) occurred when $[(CO)_5MnCH_3]$ was dissolved in DMSO, as shown by new peaks at 2056 w, 1957 s, and 1910 cm^{-1} m (Figure 1b). A small absorption associated with unreacted $[(CO)_5MnCH_3]$ was observed at 2110 cm^{-1}. The absorptions associated with the reaction with DMSO are assigned to *cis*-$[(CO)_4(DMSO)MnCOCH_3]$; they correspond broadly with those of *cis*-$[(CO)_4(PPh_3)MnCOCH_3]$[21] (2067 m, 1988 s, 1961 vs, 1605 cm^{-1} w) but are significantly to lower energy (as are the carbonyl stretching absorptions of *cis*-$[(CO)_4(CH_3CN)ReCOC_2H_5]$ compared with *cis*-$[(CO)_4(PPh_3)ReCOC_2H_5]$[11]). The observation of an absorption at 1594 cm^{-1}, in the acyl stretching region, further supports the characterization. A broad absorption around 1664 cm^{-1}, associated with traces of water in the solvent, was also present. When excess PPh_3 was added, the peaks associated with the solvent-coordinated species and the starting material rapidly disappeared and *cis*-$[(CO)_4(PPh_3)MnCOCH_3]$ was formed (Figure 1c). Over several hours, slow isomerization to the trans complex (associated with additional peaks at 2056 cm^{-1} and a stronger and sharper acyl stretch at 1612 cm^{-1}) took place.

Solutions of $[(CO)_5MnCH_3]$ in DMSO slowly decomposed. Growing absorptions at 2116 w and 2004 cm^{-1} s (see Figure 1b) correspond with those produced in the direct reaction of CO with $[(CO)_5MnCH_3]$ in DMSO and with those of an authentic sample of $[(CO)_5MnCOCH_3]$. The absorptions persisted even after addition of PPh_3 to the reaction mixture. $[(CO)_5MnCOCH_3]$ is known to react relatively slowly with PPh_3.[21] On longer standing (around 24 h), further reaction occurred and absorptions associated with $[Mn(CO)_5]^-$ (1896 s, 1862 cm^{-1} m)[22] were observed. The decomposition process at 50 °C was rapid; after 8 h, only the characteristic peaks of $[Mn(CO)_5]^-$ were present.

The mechanism of the decomposition reaction is unclear. We believe that decomposition may be promoted by traces of water, indicated by an absorption at 1664 cm^{-1}, in the solvent. Indeed, as decomposition proceeds, the intensity of this absorption decreases. Carbon monoxide, which is required for the formation of $[(CO)_5MnCOCH_3]$, could be produced by solvent-induced disproportionation processes. For example, $Mn_2(CO)_{10}$ is known to react with DMSO to form $[Mn(DMSO)_6][Mn(CO)_5]_2$.[23]

The ^1H NMR spectrum for the $[(CO)_5MnCH_3]$/DMSO reaction provides further evidence for the formation of the solvent-coordinated acyl species and the decomposition process. The experiment was complicated by the limited solubility of $[(CO)_5MnCH_3]$ in DMSO, by the proximity of the $CD_3S(O)CD_2H$ resonance to the resonances of the products, and by line broadening (presumably arising from paramagnetic Mn^{2+} produced in the decomposition process). Broadening particularly affected the methyl resonances of the acyl complex and the water impurity resonance in the solvent.

The spectrum, recorded after 15 min of reaction at 23 °C, showed resonances (relative intensities in parentheses) at δ 2.58 (7), assigned to $[(CO)_5MnCOCH_3]$; δ 2.57 (59), assigned to the DMSO-coordinated acyl, $[(CO)_4(DMSO)MnCOCH_3]$; δ −0.08 (10) assigned to its decarbonylated analogue, $[(CO)_4(DMSO)MnCH_3]$; and δ −0.20 (100), assigned as unreacted $[(CO)_5MnCH_3]$. The decarbonylated solvent-coordinated complex was not detectable in the

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infrared spectrum. After 3 h, the relative intensities (21:55:18:100) indicated the greater extent of the decomposition reaction and the decarbonylation to $[(CO)_4(DMSO)MnCH_3]$. The relative intensities yield an equilibrium constant of 0.59 at 22 °C for the alkyl $\rightleftharpoons$ solvent-coordinated acyl conversion.

After the addition of PPh_3, the peak at δ 2.58 (relative intensity 13) was unchanged, which is consistent with its assignment as $[(CO)_5MnCOCH_3]$. New peaks at δ 2.60 (6) and 2.27 (100) and a doublet centered at δ −0.60 (13) appeared. After 2.5 h, the relative intensities of the four resonances were 66:23:100:20. On the basis of the known course of the reaction and chemical shifts reported previously,[21,24] the major peak at δ 2.27 is assigned as *cis*-$[(CO)_4(PPh_3)MnCOCH_3]$. This slowly converts to *trans*-$[(CO)_4(PPh_3)MnCOCH_3]$ at δ 2.60. The doublet at δ −0.60 is assigned to *cis*-$[(CO)_4(PPh_3)MnCH_3]$.[24]

The same general behavior was observed in 75:25 v/v DMSO-d_6/benzene-d_6 solution, which was used initially in an attempt to overcome difficulties arising from the low solubility of $[(CO)_5MnCH_3]$ in DMSO; the formation of the solvent-coordinated acyl was significantly less favored, with an equilibrium constant of around 0.25 at 22 °C. When the relative solvent composition is less than 50:50 v/v, the extent of reaction is slight. Infrared measurements on the mixed-solvent systems mirrored these observations.

Reaction with solvent with $[(CO)_5MnCH_3]$ was also observed, by the infrared method, for pyridine > dimethylformamide ≫ acetonitrile. The reaction with pyridine proceeded to a slightly lesser extent than in DMSO. Peaks additional to those of $[(CO)_5MnCH_3]$ were observed at 2065 w, 1970 s, and 1934 cm^{-1} m. Further peaks at 1995 and 1887 cm^{-1} slowly developed. After 3 days, these were the only carbonyl absorptions. The decomposition pathway is thus different from that in DMSO, but the final product is unknown. Previous workers have experienced difficulties with product characterization in this reaction.[24]

In dimethylformamide, the formation of the solvent-coordinated acyl compound was indicated by broad absorptions at 2053 m, 1965 s, and 1910 cm^{-1} m. Decomposition, monitored by the growth of the high-frequency stretch around 2115 cm^{-1}, occurred slowly.

The slight reaction of $[(CO)_5MnCH_3]$ with acetonitrile was detectable through an additional peak at 2077 cm^{-1} and a broad shoulder at around 1960 cm^{-1}. A weak acyl stretch at around 1616 cm^{-1} was also observed. When PPh_3 was added, the 2077 cm^{-1} peak moved to 2068 cm^{-1}, the shoulder around 1960 cm^{-1} became more pronounced, and the acyl peak moved to 1601 cm^{-1}. The speed of this reaction (monitored by the 2077 → 2068 cm^{-1} conversion), which is followed by the slower ongoing reaction of $[(CO)_5MnCH_3]$ with PPh_3, is also an indication that the reactive solvent-coordinated species $[(CO)_4(CH_3CN)MnCOCH_3]$ has been formed in small amounts. Definitive analysis of the acyl region for $[(CO)_5MnCH_3]$ in acetonitrile was not feasible because of the absorption around 1636 cm^{-1} associated with water impurity. Insufficient reaction between $[(CO)_5MnCH_3]$ and acetonitrile occurred to allow detection of the product by ^1H NMR spectroscopy.

Over long periods, solutions of $[(CO)_5MnCH_3]$ in acetonitrile slowly decompose to give brown (possibly colloidal MnO_2) solutions. The infrared spectrum suggests, through the appearance of an additional peak at 2118 cm^{-1}, that CO evolution has occurred, with the formation of $[(CO)_5MnCOCH_3]$. The same peak grew in the direct reaction of CO with $[(CO)_5MnCH_3]$ in acetonitrile.

The higher reactivity of ethyl– over methyl–metal bonds toward CO insertion,[10] coupled with the known reactivity of $[(CO)_5ReCH_2CH_3]$ with acetonitrile,[11] then led us to investigate the reactivity of $[(CO)_5MnC_2H_5]$ with acetonitrile. As expected, the reaction was very much more complete but was complicated by the thermal instability of the starting material. The presence of $[(CO)_4(CH_3CN)MnCOC_2H_5]$ was suggested by peaks at 2075 m (sharp), 1943 s, and 1615 cm^{-1} w. Even after short reaction times, the characteristic peaks of the decomposition product, $[(CO)_5MnCOC_2H_5]$, at 2116, 2006, and 1636 cm^{-1} were pronounced. The absorptions associated with the solvent-coordinated acyl immediately disappeared after the addition of PPh_3, but those of the decomposition product remained. The further reaction to give $[(CO)_4(PPh_3)MnCOC_2H_5]$ was indicated by the disappearance of the 2075- and 1943-cm^{-1} absorptions and the appearance of peaks at 2067 and 1964 cm^{-1}.

We also investigated solutions of $[(CO)_5MnCH_3]$ in THF and in 2-ethoxyethyl ether. Infrared spectroscopy of the carbonyl stretching region gave no indication of reaction. Although a previous report[4] has claimed the formation of a solvent-coordinated acyl in 2-ethoxyethyl ether, we believe that the observation of an infrared band at 1650 cm^{-1} is probably the result of water impurity in the solvent.

Infrared spectroscopy of several substituted benzylmanganese carbonyl complexes $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in DMSO gave evidence for the formation of solvent-coordinated acyl compounds. The extent of reaction was 2,3,4,5,6-Me_5 > 2,4,6-Me_3 ≫ 4-Me, which reflects the trend in k_1 values, which we have reported previously for the PPh_3-induced reaction in acetonitrile at 30 °C.[7,8] For the pentamethylbenzyl system, the reaction with DMSO proceeded only slightly less than with $[(CO)_5MnCH_3]$.

The general features of the infrared spectra, for example for the 2,4,6-trimethylbenzyl compound, are analogous to those for $[(CO)_5MnCH_3]$. In addition to the peaks of starting material (2103 m, 2040 w, 2014 s, 2007 s, 1987 m, 1974 cm^{-1} w in hexane), absorptions, assigned to the solvent-coordinated acyl, were present at 2052 w, 1956 s, 1912 m, and 1600 cm^{-1} w, br. After the addition of PPh_3, these and the absorptions of starting material disappeared to give the characteristic absorptions[25] of *cis*-$[(CO)_4(PPh_3)MnCOCH_2C_6H_2Me_3\text{-}2,4,6]$ at 2059, 1985, and 1960 cm^{-1} (and, on standing, the trans isomer, characterized by its 2045-cm^{-1} absorption). The decomposition reaction was slower than for $[(CO)_5MnCH_3]$, but after 21 h, solutions of $[(CO)_5MnCH_2C_6H_2Me_3\text{-}2,4,6]$ in DMSO showed absorptions characteristic of $[(CO)_5MnCOCH_2C_6H_2Me_3\text{-}2,4,6]$, at 2112 and 2008 cm^{-1}, and of $[Mn(CO)_5]^-$, at 1899 and 1864 cm^{-1}.

The extent of reaction of the benzylmanganese compounds with acetonitrile similarly was less than that for $[(CO)_5MnCH_3]$. The same general features were obvious with additional absorptions at 2074, 1988, and 1945 cm^{-1}. These disappeared on the addition of PPh_3 (giving peaks at 2062, 1989, and 1966 cm^{-1} for the cis-substituted acyl and, more slowly, a peak at 2054 cm^{-1} for the trans isomer).

The (pentamethylbenzyl)manganese compound was insufficiently soluble in DMSO for ^1H NMR studies. However supporting NMR evidence for the infrared characterization was obtained by using the less reactive $[(CO)_5MnCH_2C_6H_2Me_3\text{-}2,4,6]$/DMSO system.

Relative to the ^1H NMR spectrum of $[(CO)_5MnCH_2C_6H_2Me_3\text{-}2,4,6]$ in CS_2, the spectrum in

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DMSO showed a $COCH_2$ resonance at δ 4.33. The CH_3 region of the spectrum had resonances at δ 2.13 and 2.24 (in relative intensity 1:2), which are assigned to the unreacted benzyl compound, and resonances at δ 2.06 and 2.17 (relative intensity 2:1) assigned to $[(CO)_4(DMSO)MnCOCH_2C_6H_2Me_3\text{-}2,4,6]$. The equilibrium constant at 22 °C is 0.50. A single aromatic ^1H resonance at δ 6.73 was observed.

After the addition of excess PPh_3, the peaks associated with the starting material and the solvent-coordinated acyl disappeared. The CH_3 resonances were observed at δ 1.95 and 2.13, a $COCH_2$ resonance was observed at δ 4.29, and an aromatic resonance was observed at δ 6.69. The relative intensities of the four peaks were, appropriately, 6:3:2:2. The solution species is characterized as *cis*-$[(CO)_4(PPh_3)MnCOCH_2C_6H_2Me_3\text{-}2,4,6]$. Over time, partial isomerization to the trans complex (δ 2.08, 2.17, 4.36, 6.72; relative intensity 6:3:2:2) occurred. The trans:cis ratio after 18 h at 25 °C is 1.3. This acyl complex, unlike the majority of (benzylacyl)manganese compounds, does not decarbonylate readily at room temperature in solution.[8]

The infrared spectrum of the phenylmanganese complex, $[(CO)_5MnC_6H_5]$, indicated that slight reaction had occurred with DMSO. Absorbances, additional to those observed for this compound in hexane (2115 m, 2046 w, 2021 vs, 1998 s, 1984 cm^{-1} w), appeared in the characteristic regions associated with DMSO-coordinated acyl species (2055, 1960, 1902 cm^{-1}). The solvent-coordinated acyl peaks quickly disappeared on the addition of PPh_3. There was no apparent reaction with acetonitrile.

The low reactivity of the phenylmanganese compound is consistent with the relative k_1 values for the PPh_3-induced insertion of CO in acetonitrile ($[(CO)_5MnC_6H_5]$, $k_1 = 1.0 \times 10^{-3}$ s^{-1}; $[(CO)_5MnCH_3]$, $k_1 = 4.7 \times 10^{-3}$ s^{-1} at 30 °C). On the basis of our previous studies of the reactions of $[(\eta^5\text{-}Cp)(CO)_2FeR]$ with DMSO,[10] the rate constant k_1 and the equilibrium constant should trend similarly. The lower reactivity of the phenyl compound is also consistent with the equilibrium constants, 66 and 366 L mol^{-1}, respectively, measured, at 30 °C, for the direct reactions of CO with $[(CO)_5MnC_6H_5]$ and $[(CO)_5MnCH_3]$ in 2-ethoxyethyl ether,[26] although these values reflect the overall effect of both the k_1 and k_2 steps. The phenylmanganese complex also gave a lower rate constant, k_1, in the reaction with CO in 2-ethoxyethyl ether.[27] A higher relative reactivity for a phenyl- over a methylmetal derivative has however been observed for the CO insertion process in the $[(\eta^5\text{-}C_5Me_5)(CO)IRhR]/PPh_3$ reaction in a variety of solvents.[28]

Triphenylphosphine oxide, $OPPh_3$, has been found to act as a promoter of the reaction between $[(CO)_5MnCH_2C_6H_4OMe\text{-}p]$, *cis*-$[HMn(CO)_4(PMe_2Ph)]$, and CO, which yields *p*-$MeOC_6H_4CH_2CHO$ and *axial*-$[Mn_2(CO)_9(PMe_2Ph)]$ via the catalyzed formation of acyl intermediates.[14] Similar behavior was observed for $OPBu_3$, acetonitrile, and tetrahydrofuran. The result encouraged us to search spectroscopically for complexes of $OPPh_3$ in the direct reaction with $[(CO)_5MnCH_3]$ in a nonreactive solvent, toluene. No evidence for a solvent-coordinated species was obtained, but the experiment was limited by the low solubility of $OPPh_3$.

Further evidence for $OPPh_3$ as a reaction promoter of the k_1 reaction step has, however, been obtained from rate measurements at 30 °C for the reaction of $[(CO)_5MnCH_2C_6H_4Me\text{-}4]$ with PPh_3 in toluene solutions that contained known amounts of more polar solvents or solid promoters. Although both the overall reaction via a solvent-coordinated intermediate (k_1,k_2 path) and the direct reaction of phosphine with the metal alkyl (k_3 path) are possible under these conditions (see Scheme I), the latter route is unimportant because of the relatively low concentration and low nucleophilicity of PPh_3. The concentration of PPh_3 (0.5 M in each experiment) is high enough effectively to achieve saturation kinetics in the k_1,k_2 path, and k_{obs} reduces to k_1. (There is a small increase in k_1 with increasing concentration of PPh_3; e.g. for the reaction involving 0.14 M DMSO in toluene, $10^5k_1 = 6.73$ s^{-1} for $[PPh_3] = 0.25$ M, 6.90 s^{-1} for 0.50 M, 7.08 s^{-1} for 0.75 M, and 7.17 s^{-1} for 1.00 M.)

Table I. Rate Constants, k_1 (s^{-1}), for the Reaction of $[(CO)_5MnCH_2C_6H_4CH_3\text{-}4]$ with PPh_3 at 30 °C in Toluene Containing Added Polar Solvent or Promoter

$[OPPh_3]$, M	10^5k_1	[DMSO], M	10^5k_1	[DMF], M	10^5k_1
0.05	3.83	0.07	3.88	0.13	3.36
0.10	6.02	0.14	6.90	0.26	6.12
0.20	14.0	0.28	21.8	0.65	18.1
0.30	21.2	0.71	39.7	1.29	37.8
		1.41	93.1	2.58	80.1

[py], M	10^5k_1	$[CH_3CN]$, M	10^5k_1	[THF], M	10^5k_1
1.24	3.78	0.96	3.07	1.23	0.22
1.98	6.77	1.91	5.09	2.46	0.35
2.48	8.62	2.87	7.48	12.3	1.68
4.96	17.1	4.60	11.3		
		7.66	19.1		

Table II. Rate Constants, k_1', for the Reaction of $[(CO)_5MnCH_2C_6H_4CH_3\text{-}4]$ with PPh_3 at 30 °C in Toluene Containing Added Polar Solvent or Promoter (S)

S	$10^4k_1'$/L mol^{-1} s^{-1}	S	$10^4k_1'$/L mol^{-1} s^{-1}
$OPPh_3$	7.1	CH_3CN	0.25
DMSO	6.4	2-ethoxyethyl ether	0.22
dibenzyl sulfoxide	3.2	THF	0.14
DMF	3.0	toluene	0.008
py	0.34		

In this experiment, the observed rate constant, k_1, is effectively a second-order rate constant, equal to k_1'[S], where [S] is the concentration of the added polar solvent or promoter. For each solvent or promoter with the exception of dibenzyl sulfoxide and 2-ethoxyethyl ether, k_1 has been measured at a number of concentrations (Table I), and k_1' was obtained from the gradient of the linear k_1 versus [S] plot. The results, which are shown in Table II, generally reinforce earlier results[1] on solvent effects (DMF > MeOH > $MeNO_2$ > 2-methoxyethyl ether > THF > 2-ethoxyethyl ether ≫ mesitylene) on the k_1 step. As expected, the $OPPh_3$ and the sulfoxides exhibit very high reactivity, but the relatively small rate constant for pyridine is surprising.

Within experimental error, the linear plots of k_1 versus concentration of solvent pass through the origin. This is consistent with the kinetic analysis based on the reaction scheme outlined, which implies that the intermediate is coordinatively saturated and that the k_2 process is associative. A dissociative route, based on the analysis of Halpern and co-workers[14] for the reaction of $[(CO)_5MnCH_2C_6H_4OMe\text{-}p]$ with *cis*-$[HMn(CO)_4(PMe_2Ph)]$, which assumes that the steady-state approximation applies to both the solvent-coordinated acyl complex and a coordinatively unsaturated acyl intermediate formed after the loss of a solvent molecule, requires that a plot of $1/k_1$ versus $1/[S]$ should have nonzero intercepts

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that would be inversely proportional to the concentration of the phosphine. However, as pointed out by Halpern and co-workers, the intercepts could be too small to be observed in the case of species, such as PPh_3, which are highly reactive toward the trapping of the intermediate. Our experiments thus may not distinguish between the two mechanisms. Our study[29] of the variation of k_2 with tertiary phosphine in the reaction of the phosphine with $[(\eta^5\text{-Cp})(CO)_2FeCH_2Cy]$ in DMSO, and of the variation of k_2/k_{-1} in the reaction of tertiary phosphine with $[(\eta^5\text{-Cp})(CO)_3MoCH_2Ph]$ in acetonitrile, showed a strongly decreasing k_2 with increasing cone angle of the phosphine but no correlation with the electronic parameter. We believe that significant steric discrimination would be unlikely if the intermediate were coordinatively unsaturated.

Conclusions

Solvent-coordinated acyl complexes have been identified in the direct reactions of manganese alkyl complexes $[(CO)_5MnR]$ with polar solvents. Kinetic analysis of the reactions of $[(CO)_5MnCH_2C_6H_4Me\text{-}4]$ with PPh_3 in toluene, containing polar solvents or reaction promoters, is unable to distinguish whether the solvent-coordinated acyl complexes react directly with PPh_3 or whether prior dissociation of solvent takes place.

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Reactions of the Low-Valent Rhenium Oxo Anions $NaRe(O)(RC{\equiv}CR)_2$ with Alkyl and Aryl Halides; Evidence for both S_N2 and Radical Mechanisms[1]

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The low-valent monooxo compounds $NaRe(O)(RC{\equiv}CR)_2$ [R = Me (**1a**), Et (**1b**), Ph (**1c**)] are strong bases and potent reducing agents, highly unusual reactivity for terminal oxo compounds. They are all protonated by H_2O in CD_3CN, **1a** and **1b** even by stoichiometric acetone in this solvent, to form the Re(III) oxo hydride complexes $Re(O)H(RC{\equiv}CR)_2$. Compounds **1** react as nucleophiles with the Me^+ sources MeI, MeOTs, and $Me_3O^+BF_4^-$ and with the acyl sources acetic anhydride and acetyl chloride, forming $Re(O)Me(RC{\equiv}CR)_2$ and $Re(O)[C(O)Me](RC{\equiv}CR)_2$, respectively. While there is no evidence for radical intermediates with these reagents, reactions with primary to tertiary alkyl halides occur at least in part by an electron-transfer pathway. Primary and secondary alkyl halides react to form mixtures of Re(III) alkyls, $Re(O)R'(RC{\equiv}CR)_2$, and Re(II) dimers, $Re_2(O)_2(RC{\equiv}CR)_4$ (**2**). ^tBuI and **1** produce solely **2** and the organic radical disproportionation products isobutane and isobutylene. The intermediacy of organic radicals is confirmed by significant cyclization of the hexenyl radical clock in the reaction of 6-iodo-1-hexene with **1a**. Aryl halides are also reactive with **1a** and **1b** to produce, in roughly equal yields, novel $Re(O)Ph(RC{\equiv}CR)_2$ compounds and **2** in C_6D_6 solvent. In CH_3CN, however, trapping of aryl radicals by the solvent occurs to produce $Re(O)CH_2CN(RC{\equiv}CR)_2$ compounds and arene (together with **2**). These reactions appear to occur via initial electron transfer from rhenium to the organic halide. Compounds **1** are tightly ion paired and show reactivity that is dependent on the solvent and on the presence or absence of 15-crown-5. The diphenylacetylene derivative **1c** is significantly less reactive than the dialkylacetylene complexes **1a** and **1b** because of the influence of the better π acceptor $PhC{\equiv}CPh$ on the HOMO in **1**.

Transition metal–terminal oxo complexes are typically high-valent species and are widely used as reagents and catalysts in oxidation reactions.[4,5] We have recently isolated novel rhenium–oxo–bis(acetylene) anions, $NaRe(O)(RC{\equiv}CR)_2$ [R = Me (**1a**), R = Et (**1b**), R = Ph (**1c**)],[6] that are formally Re(I) and typically act as reductants.

Scheme I

Halogen Atom Abstraction

$$RX + M^n \longrightarrow R^\bullet + XM^{n+1}$$

Electron Transfer

$$RX + M^n \longrightarrow RX^{\bullet -} + M^{n+1}$$

Nucleophilic Attack

$$RX + M^n \longrightarrow RM^{n+2} + X^- \text{ or } RM^{n+2}X$$

This report describes the reactions of compounds **1** with alkyl and aryl halides, in order to better understand the unusual reactivity of these remarkable species.

Reactions of alkyl halides with transition-metal compounds have been extensively studied for their role in a variety of processes such as the synthesis of transition-metal alkyls,[7] the coupling reactions assisted by transition

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