and for comparison the symmetric deformation of CH_3^+, where the $1a_2''$ electron has been removed, has been identified at 1380 cm^{-1}.[30] The shift of this mode to lower energies with Ca and Sr agrees as well, as these metals are less electronegative than Mg, so that there will be less electron density on the metal center and more on the terminal halogen and methyl group, leading to a shift to lower energy. A similar trend was observed for the methyl alkali halide species, using Li, Na, and K.

Conclusions

The codeposition of magnesium atoms with methyl halides in argon matrices does lead to a reaction product in which the carbon-halogen bond is ruptured. The spectra in each case was dominated by the symmetric deformation mode of the CH_3 unit in the reaction product, although the remaining vibrations of the CH_3 unit were also detected. However, since neither a C-Mg stretch nor a Mg-X stretch was observed, no definitive conclusions concerning the exact structure of the product can be made.

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Kinetics and Mechanisms of Substitution Reactions on Decacarbonylmanganeserhenium

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Abstract: The kinetics of substitution reactions on decacarbonylmanganeserhenium, $MnRe(CO)_{10}$, are reported for the entering ligands $P(C_6H_5)_3$, $P(C_4H_9)_3$, and $P(OC_6H_5)_3$. Synthesis of all products and careful infrared analysis have allowed complete product assignment. For all three ligands the rhenium-substituted product, $(CO)_5MnRe(CO)_4L$, predominates, although formation of the bis-substituted product, $L(CO)_4MnRe(CO)_4L$, can be quite significant depending on the reaction conditions. A very small amount of the manganese isomer, $L(CO)_4MnRe(CO)_5$, was formed early in the reaction. In no case were the homodimetallic species ($Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$) or substituted derivatives of the diatomics observed. The manganese isomer fails to rearrange to the rhenium isomer under the conditions of the kinetics reaction. The rate constants and activation parameters are nearly identical for the three ligands. These data strongly suggest that CO dissociation is the rate-determining step and are inconsistent with cleavage of the manganese-rhenium bond. Our proposed mechanism involves CO dissociation from the manganese center and an intermediate/transition state with carbon monoxide bridging the manganese and rhenium.

Introduction

Despite a very large number of reports on structures and reactivity of metal-metal bonded complexes, there have been relatively few studies of the kinetics of reactions of compounds containing metal-metal bonds.[1-11] Whether the metal-metal bond remains intact during reactions remains in question.[1,3,8] The substitution reactions of the dinuclear metal carbonyls, $M_2(CO)_{10}$, M = Mn, Tc, and Re, have been the most thoroughly explored mechanistically of the metal-metal bonded complexes.[12-21] Wawersik and Basolo reported kinetics studies of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9L$ with L′ (L,L′ = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(C_4H_9)_3$, and $As(C_6H_5)_3$) and interpreted the rate data as being consistent with a CO dissociative process.[12]

$$Mn_2(CO)_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn_2(CO)_9 + CO$$

$$Mn_2(CO)_9 + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Mn_2(CO)_9L$$

The similarity in rates and activation parameters for the dif-

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ferent ligands provided strong evidence for this mechanism. In a series of studies of the thermal decomposition and substitution of $P(C_6H_5)_3$ for CO on $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $MnRe(CO)_{10}$, Poe and co-workers suggested homolytic cleavage of the metal-metal bond as a primary step in the mechanism of reaction.[13-21]

$$M_2(CO)_{10} \rightleftarrows 2\,M(CO)_5$$

$$M(CO)_5 + L \rightleftarrows M(CO)_4L + CO$$

$$M(CO)_5 + M(CO)_4L \rightleftarrows M_2(CO)_9L$$

Other reactions are also possible, but this sequence would explain the first substitution reaction. Dissociation of CO was ruled out because of the nature of the rate law and because the O_2 decomposition and ligand substitution reactions have very similar activation parameters. The reaction between the 17-electron radical, $M(CO)_5$, and $P(C_6H_5)_3$ would have to occur by an associative process to fit the rate law.[12-14] The $MnRe(CO)_{10}$ complex is especially interesting in its reaction with $P(C_6H_5)_3$. Poe and co-workers reported that only the rhenium monosubstituted product, $(CO)_5MnRe(CO)_4[P(C_6H_5)_3]$, was observed and that no homodimetallic species ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, or substituted derivatives) were formed as would be expected with formation of $Mn(CO)_5$ and $Re(CO)_5$.[16] It was argued that this demonstrated a marked extra stability for heterodimetallic species.

In the past few years studies by Wrighton and co-workers[22,23] and Brown and Byers[24-26] have provided new information on the 17-electron species $Mn(CO)_5$ and $Re(CO)_5$. Photolysis of $MnRe(CO)_{10}$ led to $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in a 1:1 ratio and photolysis of monosubstituted complexes such as $Mn_2(CO)_9P(C_6H_5)_3$ led to $Mn_2(CO)_{10}$ and $Mn_2(CO)_8(P(C_6H_5)_3)_2$.[23] Thus recombination of the mononuclear intermediates (which could be different than thermally generated intermediates) generated by photolysis occurs in a statistical fashion. Substitution reactions on $Re(CO)_5$ were reported to occur by a CO dissociative process; for the ligands $P(C_4H_9)_3$ and $P(C_6H_5)_3$ no dependence on the concentration was observed. The bis-substituted product, $Re(CO)_3L_2$, was observed for $P(C_4H_9)_3$ but not for $P(C_6H_5)_3$.[24-26] The 17-electron species in these studies show basic differences to those required to explain the thermal reactions as postulated by Poe.[13-21]

We have investigated the thermal ligand substitution reactions of $MnRe(CO)_{10}$ with different ligands in an attempt to answer these questions. We have chosen this complex because of the many possible products ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $MnRe(CO)_9L$, etc.) which could clarify the mechanism and because this complex can provide unique information about the stability of ligand binding to different metal centers. The ligands used in the substitution reaction, $P(C_6H_5)_3$, $P(C_4H_9)_3$, and $P(OC_6H_5)_3$, were chosen to span a range of σ-donor and π-acceptor capabilities.

Experimental Section

Preparations. Manganese and rhenium carbonyls (Strem Chemical Inc.) were used as received. Triphenylphosphine and triphenylphosphite (Aldrich Chemical Co.) were used as received; tri-*n*-butylphosphine was vacuum distilled over sodium before use. All solvents were dried before use and all work was performed under an argon atmosphere.

Decacarbonylmanganeserhenium, $MnRe(CO)_{10}$. This compound was prepared as previously described.[27] Microanalysis (Anal. Calcd: Mn, 10.54; Re, 35.73; C, 23.04. Found: Mn, 10.64; Re, 35.56; C, 23.03) and the infrared spectrum in hexane as shown in Table I confirmed the product as $MnRe(CO)_{10}$.

Triphenylphosphinenonacarbonylmanganeserhenium, $[P(C_6H_5)_3](CO)_4MnRe(CO)_5$. This complex was prepared by reacting equimolar amounts of $Mn(CO)_4[P(C_6H_5)_3]Cl$[28] and $NaRe(CO)_5$[29] for 22 h at room temperature in THF. After evaporation of the solvent, toluene was added to the residue and the solution was filtered. The orange filtrate was reduced in volume to a few milliliters and passed down a silica gel column, using toluene as the elutant. The desired product came off the column in the second band. Further purification was achieved by placing this fraction on an alumina column and eluting pure product with a 2:1 hexane-toluene mixture. Recrystallization from hexane yielded orange-yellow crystals. The infrared spectrum reported in Table I is in agreement with that previously assigned.[33]

Table I. Infrared Spectra of the Substituted Derivatives of $MnRe(CO)_{10}$

compd	IR spectrum
$MnRe(CO)_{10}$	2055 (m), 2017 (s), 1978 (s)
$[P(C_6H_5)_3](CO)_4MnRe(CO)_5$	2006 (s), 1970 (m), 1928 (m)
$[P(OC_6H_5)_3](CO)_4MnRe(CO)_5$	2009 (s), 1977 (m), 1950 (m)
$[P(C_4H_9)_3](CO)_4MnRe(CO)_5$	2005 (s) 1972 (m), 1925 (m)
$(CO)_5MnRe(CO)_4[P(OC_6H_5)_3]$	2041 (m), 1999 (s), 1974 (m)
$(CO)_5MnRe(CO)_4[P(C_4H_9)_3]$	2032 (m), 1990 (s), 1973 (m)
$MnRe(CO)_8[P(C_4H_9)_3]_2$	1952 (s)
$MnRe(CO)_8[P(OC_6H_5)_3]_2$	1986 (s)

Triphenyl Phosphitenonacarbonylmanganeserhenium, $[P(OC_6H_5)_3](CO)_4MnRe(CO)_5$. This compound was prepared by a procedure similar to that used for the triphenylphosphine derivative.[30] In this case, the toluene-soluble fraction of the reaction product was passed down an alumina column, using toluene as the elutant. The second band off this column contained the desired product. Further purification was achieved by placing this fraction on a silica gel column and eluting the product with a 4:1 hexane-toluene mixture. Recrystallization from hexane yielded orange crystals. The infrared spectrum is shown in Table I.

Tri-*n*-butylphosphinenonacarbonylmanganeserhenium, $[P(n\text{-}C_4H_9)_3](CO)_4MnRe(CO)_5$. This complex was prepared by a method similar to the triphenyl phosphite derivative, with a reaction time of 36 h. As with the triphenylphosphine derivative, the toluene-soluble part of the reaction mixture was placed on a silica gel column. Using 2:1 hexane-toluene as the eluting solvent, the desired product was contained in the first column fraction. Purification was achieved by passing this fraction down a Florisil column, using hexane as the elutant. The first band contained the product. Recrystallization from ethanol yielded yellow crystals. The infrared spectrum is reported in Table I.

Triphenyl Phosphitenonacarbonylmanganeserhenium, $(CO)_5MnRe(CO)_4[P(OC_6H_5)_3]$. This compound was prepared by reacting equimolar amounts of $NaMn(CO)_5$[29] and $Re(CO)_4[P(OC_6H_5)_3]Br$[30] in THF at room temperature for 70 h. After evaporation of the solvent, toluene was added to the residue and the solution filtered. The filtrate was passed down a silica gel column with hexane as the eluting solvent. The product came off the column as the second fraction, eluting with a 3:1 hexane-toluene mixture. The infrared spectrum is reported in Table I.

Tri-*n*-butylphosphinenonacarbonylmanganeserhenium, $(CO)_5MnRe(CO)_4[P(C_4H_9)_3]$. This compound was prepared by a method similar to that of the triphenyl phosphite derivative, except with a reaction time of 50 h. The toluene-soluble portion of the reaction mixture was placed on a silica gel column with a 4:1 hexane-toluene mixture as the elutant. The third band off of this column, eluting with 3:1 toluene-THF, contained the crude product. Further purification was achieved by passing this fragment down a Florisil column using toluene as the solvent. The product came off as the second band, eluting with THF. The infrared spectrum is listed in Table I.

Bis(tri-*n*-butylphosphine)octacarbonylmanganeserhenium, $[P(C_4H_9)_3](CO)_4MnRe(CO)_4[P(C_4H_9)_3]$. This compound was prepared by reacting equimolar amounts of $NaMn(CO)_4[P(C_4H_9)_3]$[31] and $Re(CO)_4[P(C_4H_9)_3]Br$ in THF for 60 h. After evaporation of the solvent, toluene was added to the residue and the solution was filtered. The red filtrate was reduced in volume and placed on an alumina column, using a 1:1 hexane-toluene eluting mixture. The third band off this column contained the desired product. Purification was achieved by dissolving this fraction in hexane and passing it down an alumina column. Eluting with hexane yields pure product. Recrystallization from hexane yielded orange crystals. The infrared spectrum in hexane is listed in Table I.

Bis(triphenyl Phosphite)octacarbonylmanganeserhenium, $[P(OC_6H_5)_3](CO)_4MnRe(CO)_4[P(OC_6H_5)_3]$. Reaction of 2 equiv of

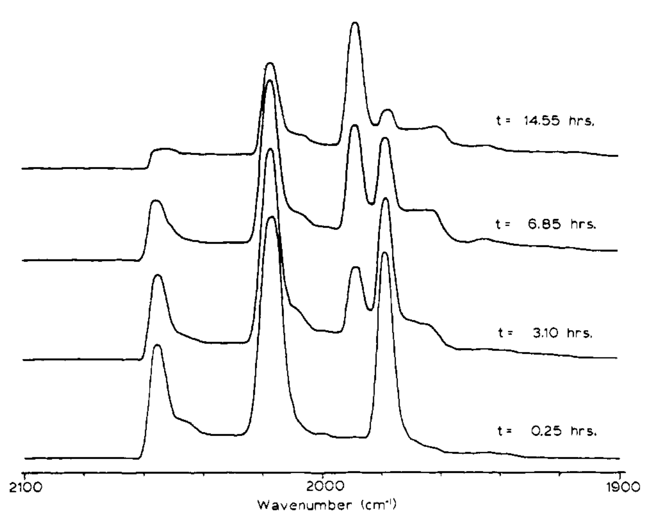

Figure 1. Infrared spectra during the substitution of $P(C_6H_5)_3$ for CO on $MnRe(CO)_{10}$ at 120 °C in decane.

Table II. Rate Constants[a] for the Reaction $MnRe(CO)_{10}$ + L under Argon Atmosphere

ligand	temp, °C	$10^6 k_{obsd}$, s^{-1}
$P(C_6H_5)_3$	130	117 ± 3
		46.7 ± 0.6[b]
		130 ± 2[c]
	120	31.6 ± 0.7
		13.2 ± 0.5[b]
	110.5	9.43 ± 0.13
		3.14 ± 0.04[b]
$P(OC_6H_5)_3$	129.5	88.3 ± 0.6
	120	24.6 ± 0.1
	110	6.85 ± 0.10
$P(n\text{-}C_4H_9)_3$	130	108 ± 2
	120	34.1 ± 0.8
	110	8.78 ± 0.11

Error limits are quoted as: [a] 95% confidence interval. [b] Initial rate under 2 atm CO. [c] $[P(C_6H_5)_3] = 4.8 \times 10^{-2}$ M.

$P(OC_6H_5)_3$ with 1 equiv of $MnRe(CO)_{10}$ under octane reflux for 3 days led to the bis-substituted complex. The octane was removed in vacuo and the sample purified by elution down an alumina column with hexane-toluene mixtures. Crystallization was effected from hexane yielding colorless crystals. The infrared spectrum is reported in Table I.

Kinetic Studies. The triphenylphosphine (Aldrich Chemical Co.) was used as received. Triphenyl phosphite and tri-*n*-butylphosphine were purified by vacuum distillation over sodium and stored under argon. Decane, used as solvent for all kinetics studies, was purified by mixing with sulfuric acid, washing with water, passing down an alumina column, and storing over sodium.

The reactions were accomplished in foil-wrapped vessels in darkened hoods and followed by IR, using a Perkin-Elmer 521 grating infrared spectrophotometer and 1.0-mm NaCl cells. A Haake FS constant-temperature circulator was used to maintain the reactions at the desired temperature, to within ±0.1 °C.

The kinetics were followed by monitoring the decrease in absorbance at 2055 cm^{-1}, due to $MnRe(CO)_{10}$, for a minimum of 3 half-lives. Spectra obtained during the substitution of $MnRe(CO)_{10}$ with $P(C_6H_5)_3$ and $P(C_4H_9)_3$ are shown in Figures 1 and 2, respectively. A plot of ln A_t vs. time yielded the rate constants quoted herein.

Unless otherwise noted, the initial concentration of $MnRe(CO)_{10}$ used was $7.6 \pm 0.2 \times 10^{-4}$ M and the entering ligand concentration was $9.6 \pm 0.2 \times 10^{-3}$ M.

Results

Reaction of $MnRe(CO)_{10}$ with $P(C_6H_5)_3$ under Argon. These reactions followed first-order kinetics for a minimum of 3 half-lives. The rate constants at the various temperatures studied are given in Table II and the activation parameters are reported in Table III. During the reaction, IR bands grew in at 2095 (w), 2005 (w), 1988 (s), 1961 (m), and 1945 cm^{-1} (m) as shown in Figure 1. The absorbances at 2095, 1988, and 1945 cm^{-1} can be assigned to $(CO)_5MnRe(CO)_4[P(C_6H_5)_3]$ as shown in Table I. The band at 2005 cm^{-1} is assigned to $[P(C_6H_5)_3](CO)_4MnRe(CO)_5$, and the 1961-$cm^{-1}$ absorbance to $[P(C_6H_5)_3](CO)_4MnRe(CO)_4[P(C_6H_5)_3]$. Both monosubstituted complexes appear very early in the reaction, while the bis-substituted compound appears later.

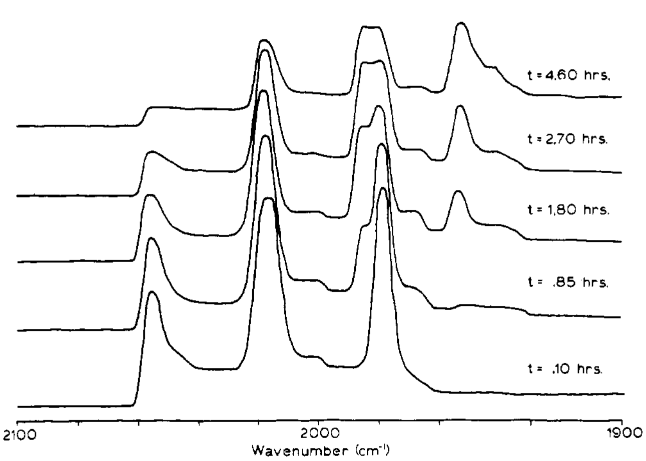

Figure 2. Infrared spectra during the substitution of $P(C_4H_9)_3$ for CO on $MnRe(CO)_{10}$ at 130 °C in decane.

Table III. Activation Parameters[a] for $MnRe(CO)_{10}$ + L

ligand	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
$P(C_6H_5)_3$	38.9 ± 1.6	19.3 ± 4.1
$P(OC_6H_5)_3$	39.5 ± 2.1	20.4 ± 5.4
$P(C_4H_9)_3$	37.6 ± 0.3	16.0 ± 0.6
$P(C_6H_5)_3$[b]	38.9	18.5

[a] 95% confidence interval. [b] Poe's values (ref 15).

The mono-Re-substituted complex is the major reaction product. Small amounts of the mono-Mn-substituted isomer, about 5% as abundant as Re isomer, are formed in the reaction. At the end of the reaction, when the absorbance at 2055 cm^{-1} ($MnRe(CO)_{10}$) is negligible, the bis-substituted complex is about 30% as abundant as the Re isomer.

At higher concentrations of $P(C_6H_5)_3$, the final concentration of bis-substituted compound is equal to that of the Re isomer. The relative abundance of the Mn isomer, with respect to the Re one, was not affected.

Reaction of $MnRe(CO)_{10}$ with $P(C_6H_5)_3$ under CO. These reactions obeyed first-order kinetics for about the first 1.5 half-lives. At that point, the reactions deviated from first order, slowing considerably. The initial reaction rates are given in Table II.

During these reactions, IR absorbances grew in at 2093 (w), 2030 (w), 2006 (w), 1991 (sh), 1988 (s), 1968 (m), and 1946 cm^{-1} (m). The bands at 2030, 1991, and 1968 cm^{-1} can also be assigned to $(CO)_5MnRe(CO)_4[P(C_6H_5)_3]$. Again, both monosubstituted compounds appeared early in the reaction.

As with the reaction under argon, the mono-Re-substituted isomer was the major product with the mono-Mn-substituted product formed in small amounts. Under a CO atmosphere, however, the Mn isomer disappears toward the end of the reaction. Also, no bis-substituted product was detected.

Reaction of $MnRe(CO)_{10}$ with $P(OC_6H_5)_3$ under Argon. These reactions followed first-order kinetics for a minimum of 3 half-lives. The reaction rates at the temperatures investigated are listed in Table II and the activation parameters are given in Table III.

During the reaction, IR bands grew in at 2040 (w), 2009 (sh), 1998 (s), 1987 (s), 1973 (sh), and 1943 cm^{-1} (w). The absorbances at 2040, 1998, and 1973 cm^{-1} can be assigned to $(CO)_5MnRe(CO)_4[P(OC_6H_5)_3]$ as shown in Table I. The band at 2009 cm^{-1} is assigned to $[P(OC_6H_5)_3](CO)_4MnRe(CO)_5$, whereas the 1987-cm^{-1} absorbance is assigned to $[P(OC_6H_5)_3](CO)_4MnRe(CO)_4[P(OC_6H_5)_3]$. Both monosubstituted compounds appeared early in the reaction, while the bis-substituted complex appeared later. Further assessment was difficult because of the overlap of the absorptions.

Reaction of $MnRe(CO)_{10}$ with $P(n\text{-}C_4H_9)_3$ under Argon. These reactions obeyed first-order kinetics for at least 3 half-lives. The rate constants at the various temperatures studied are listed in Table II and the activation parameters are listed in Table III.

The manganese isomer (2005 cm^{-1}) appeared immediately; after 8 min (at 130 °C) the rhenium isomer (1987 and 1969 cm^{-1}) began to grow; after 34 min the manganese isomer had maximized and the bis-substituted complex began to grow (1952 cm^{-1}); after 2.5 h the rhenium isomer had reached the maximum concentration and the bis-substituted species continued to grow. At the end of the reaction the bis-substituted complex was the predominant species present.

Isomerization Studies on $[P(C_6H_5)_3](CO)_4MnRe(CO)_5$. An attempt to convert the mono-Mn-substituted isomer, $[P(C_6H_5)_3](CO)_4MnRe(CO)_5$, into the Re isomer failed at 115 °C in decane under argon.

$$[P(C_6H_5)_3](CO)_4MnRe(CO)_5 \underset{\text{argon}}{\overset{115\ ^{\circ}\text{C}}{\nrightarrow}} (CO)_5MnRe(CO)_4[P(C_6H_5)_3]$$

No rhenium-substituted product was observed; only a slow decomposition of the Mn isomer. The isomerization was also attempted in the presence of excess $P(C_6H_5)_3$.

$$[P(C_6H_5)_3](CO)_4MnRe(CO)_5 \underset{\substack{P(C_6H_5)_3\\ \text{argon}}}{\overset{110\ ^{\circ}\text{C}}{\nrightarrow}} (CO)_5MnRe(CO)_4[P(C_6H_5)_3]$$

Again, no mono-Re-substituted isomer was seen, although some bis-substituted complex, $[P(C_6H_5)_3](CO)_4MnRe(CO)_4[P(C_6H_5)_3]$, was observed.

Discussion

The reaction under consideration is the substitution of L for CO in $MnRe(CO)_{10}$.

$$MnRe(CO)_{10} + L \rightarrow MnRe(CO)_9L + CO$$

This substitution has been studied for L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(OC_6H_5)_3$ in decane between 110 and 140 °C. We have not investigated the ligand concentration dependence of this reaction in detail, although there is a slight dependence as shown by the increase in rate constant from 1.17×10^{-4} to 1.30×10^{-4} upon a fivefold increase in ligand ($P(C_6H_5)_3$) concentration. A slight dependence of the ligand concentration such as this has been observed in the reactions of manganese and rhenium carbonyl dimers.[12] The rate law is probably of the form

$$k_{\text{obsd}} = (k_1 + k_2[L])[MnRe(CO)_{10}]$$

which has been observed previously in transition metal carbonyl kinetics studies.[32,33] This type dependence has been ascribed to competing associative and dissociative steps,[32] metal-metal bond cleavage,[13-15] and dissociative interchange,[33] so little mechanistic information can be obtained from the ligand concentration dependence.

Table IV. Comparison of Our Ligand Dependence with Previous Studies Which Probably Involve I_d Mechanisms[a]

	k_{obsd}, s^{-1}		
L	this study[b]	$Cr(CO)_6$[c]	$Mo(CO)_5Am$[d]
$P(C_6H_5)_3$	3.2×10^{-5}	1.38×10^{-4}	2.0×10^{-5}
$P(OC_6H_5)_3$	2.5×10^{-5}	1.32×10^{-4}	1.7×10^{-5}
$P(C_4H_9)_3$	3.4×10^{-5}	1.38×10^{-4}	

[a] The values are selected at a ligand to metal carbonyl complex ratio of 10:1. [b] Temperature = 120 °C. [c] Reference 31. [d] Reference 32.

From the large number of possible products of the substitution reaction, we have observed only three. For $P(C_6H_5)_3$, the rhenium-substituted isomer, $(CO)_5MnRe(CO)_4[P(C_6H_5)_3]$, is the major product and small amounts of the manganese isomer, $[P(C_6H_5)_3](CO)_4MnRe(CO)_5$, and the bis-substituted complex $[P(C_6H_5)_3](CO)_4MnRe(CO)_4[P(C_6H_5)_3]$ were formed. In the $P(C_4H_9)_3$ and $P(OC_6H_5)_3$ substitution reactions the major products were the rhenium isomer $(CO)_5MnRe(CO)_4[P(C_4H_9)_3]$ and $(CO)_5MnRe(CO)_4[P(OC_6H_5)_3]$, respectively, and the bis-substituted complexes, $MnRe(CO)_8[P(C_4H_9)_3]_2$ and $MnRe(CO)_8[P(OC_6H_5)_3]_2$, respectively. Small amounts of the manganese isomers were also observed for these ligands. In no case were homodimetallic species (Mn–Mn or Re–Re) observed. The manganese and rhenium isomers were synthesized to make certain of the product assignments. We found the following reaction to be applicable for all three manganese isomers:

$$Mn(CO)_4LCl + NaRe(CO)_5 \rightarrow L(CO)_4MnRe(CO)_5 + NaCl$$

Air must be carefully excluded during the preparation of these derivatives, although the products are only slightly air sensitive in the solid state. The absence of any homodimetallic species (dimanganese or dirhenium complexes) at any time during the substitution reaction suggests that the Mn–Re bond is not cleaved during the reaction. Wrighton has shown that, when the 17-electron species are generated by photolytic cleavage of the $MnRe(CO)_{10}$, both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are formed, although the photochemical and thermal intermediates could be different. The mechanism must account for the appearance of only the three products. A comparison of the growth rate for $L(CO)_4MnRe(CO)_5$ and $(CO)_5MnRe(CO)_4L$ would be very helpful but is impossible quantitatively because the strongest absorption of the manganese isomer grows in as a shoulder on the 2017-cm^{-1} band of $MnRe(CO)_{10}$. An additional complicating factor is that the manganese-substituted isomer, $L(CO)_4MnRe(CO)_5$, may react with excess ligand at a rate different than that of the rhenium isomer, $(CO)_5MnRe(CO)_4L$. Poe observed that for $P(C_6H_5)_3$ the manganese isomer reacts with $P(C_6H_5)_3$ at five times the rate of the rhenium isomer.[34] The best we can do is estimate that the rates of appearance are comparable in magnitude. The bis-substituted product grows in later in the reaction and at a somewhat reduced rate.

As shown in Table III there is very little dependence on the nature of the incoming ligand for rates or activation parameters. The ligands span a wide range of σ-donor and π-acceptor capabilities and the lack of any dependence on the nucleophilicity of the reaction coupled with a small concentration dependence suggests that the ligand is merely present to fill a coordination position and is not actively attacking the complex. As shown in Table IV the dependence (or lack thereof) on the nature of the ligand is very similar to that observed previously for $Cr(CO)_6$[32] and $Mo(CO)_5Am$.[33] The values are all reported with the ligand in a tenfold excess and suggest a common mechanism. The dissociative interchange, I_d, has been shown previously to account for this dependence.[33]

An attempt to convert the manganese isomer,

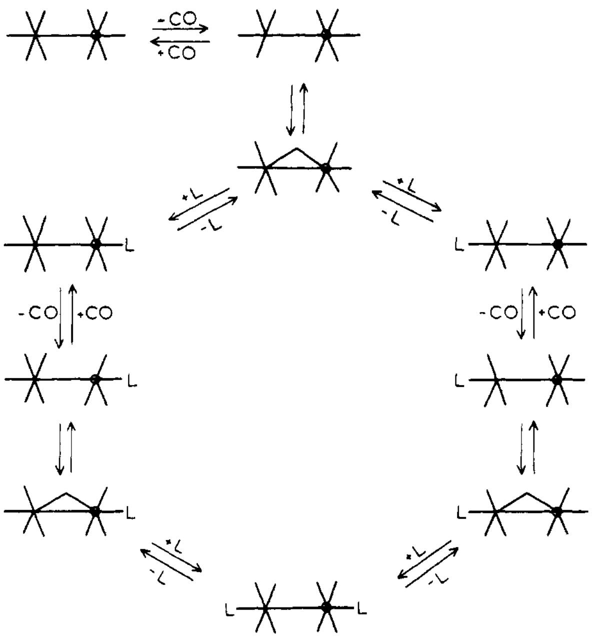

Figure 3. Suggested scheme for the substitution reactions of $MnRe(CO)_{10}$ involving CO dissociation. The open circles represent rhenium atoms.

$[P(C_6H_5)_3](CO)_4MnRe(CO)_5$, into the rhenium isomer failed.

$$[P(C_6H_5)_3](CO)_4MnRe(CO)_5 \cancel{\xrightarrow{115\ ^{\circ}C}} (CO)_5MnRe(CO)_4[P(C_6H_5)_3]$$

No rhenium product could be observed; only a slow decomposition of the manganese isomer was seen. Attempting the reaction in the presence of $P(C_6H_5)_3$ provided no evidence for the rhenium isomer, although formation of some bis-substituted complex was observed.

$$[P(C_6H_5)_3](CO)_4MnRe(CO)_5 \cancel{\xrightarrow[P(C_6H_5)_3]{110\ ^{\circ}C}} (CO)_5MnRe(CO)_4[P(C_6H_5)_3]$$

The failure of the manganese isomer to rearrange to the rhenium isomer is very significant mechanistically. As shown in Table II and previously noted,[16] the presence of CO inhibits the reaction. This inhibition suggests that an important step in the reaction involves reversible CO dissociation.

A number of mechanisms have been postulated for the metal carbonyl dimers.[12-21] Any type of associative process can be ruled out based on the kinetics observed and on the lack of ligand dependence on the rates or activation parameters. Homolytic fission of the manganese-rhenium bond is the initial step of the commonly accepted mechanism as shown in Scheme I.

Scheme I

$$MnRe(CO)_{10} \rightleftharpoons \cdot Mn(CO)_5 + \cdot Re(CO)_5 \quad (1)$$

$$\cdot Mn(CO)_5 + L \rightleftharpoons \cdot Mn(CO)_4L + CO \quad (2)$$

$$\cdot Re(CO)_5 + L \rightleftharpoons \cdot Re(CO)_4L + CO \quad (3)$$

$$\cdot Mn(CO)_{5-n}L_n + \cdot Mn(CO)_{5-m}L_m \rightleftharpoons Mn_2(CO)_{10-n-m}L_{n+m} \quad (4)$$

$$\cdot Re(CO)_{5-n}L_n + \cdot Re(CO)_{5-m}L_m \rightleftharpoons Re_2(CO)_{10-n-m}L_{n+m} \quad (5)$$

$$\cdot Re(CO)_4L + \cdot Mn(CO)_5 \rightleftharpoons (CO)_5MnRe(CO)_4L \quad (6)$$

$$\cdot Mn(CO)_4L + \cdot Re(CO)_5 \rightleftharpoons L(CO)_4MnRe(CO)_5 \quad (7)$$

$$\cdot Mn(CO)_4L + \cdot Re(CO)_4L \rightleftharpoons L(CO)_4MnRe(CO)_4L \quad (8)$$

To fit the observed product distributions equilibria 4, 5, and 7 would have to lie far to the left and equilibrium 6 would have to lie far to the right. Even with these equilibria it would be difficult to explain the disubstituted product growing later in the reaction because both $\cdot Mn(CO)_4L$ and $\cdot Re(CO)_4L$ should be present early in the reaction and should react together if the product $MnRe(CO)_8L_2$ is stable. To fit the rate expression reaction 3 would have to be associative but would then be expected to show a dependence on the ligand nucleophilicity. Also Brown and co-workers have shown that 17-electron species react by CO dissociation, not by associative steps.[24-26,35] The failure of the manganese isomer, $L(CO)_4MnRe(CO)_5$, to rearrange to the rhenium isomer rules out Scheme I as a possible mechanism for reaction of $MnRe(CO)_{10}$ with ligands. Reactions 7 and 6 (especially in the presence of excess L) must allow for isomerization of the manganese isomer to the rhenium isomer.

The alternate mechanism would seem to involve CO dissociation and product distribution would indicate that dissociation occurs at the rhenium center. A number of studies, however, have indicated the Re-CO bond to be considerably more stable toward dissociation than a Mn-CO bond. A CO bound to a manganese would be expected to dissociate at a rate 100 times that of a CO bound to a rhenium.[13,14,36,37] The mechanism which we propose is shown in Figure 3. The initial CO dissociation would have to proceed by a dissociative interchange, I_d, mechanism to satisfy the small concentration dependence of the substituting ligand. There is literature precedent for the I_d mechanism in metal carbonyl kinetics.[32,33] The key feature of Figure 3 is the intermediate/transition state with the CO bridging (semibridging) the two unsaturated metal centers. This allows for initial dissociation from the manganese and transfer of the unsaturation from manganese to the rhenium. If the bridging species is actually an intermediate, then the unsaturation would be shared between the manganese and rhenium centers and reaction with ligand L could lead to either the manganese or the rhenium isomer depending on stabilities of the products. The independence of the rate on the nature of the ligand would follow from the CO dissociative nature of the reaction. The formation of the bis-substituted complex would follow naturally by dissociation of CO from $MnRe(CO)_9L$.

There is no route in Figure 3 for the conversion of the manganese isomer to the rhenium isomer; L dissociation would be required for isomerization. This is consistent with our failure to observe isomerization. As noted earlier the reaction of the substituted complexes ($L(CO)_4MnRe(CO)_5$ and $(CO)_5MnRe(CO)_4L$, L = $P(C_6H_5)_3$, $P(C_4H_9)_3$, and $P(OC_6H_5)_3$) with excess ligand may occur at different rates. This would be expected for reactions proceeding by CO dissociation. The appearance of significant amounts of the disubstituted species, $[P(OC_6H_5)_3](CO)_4MnRe(CO)_4[P(OC_6H_5)_3]$ and $[P(C_4H_9)_3](CO)_4MnRe(CO)_4[P(C_4H_9)_3]$, is readily explained by Figure 3 with L substitution for CO on the monosubstituted species. The disubstituted species should appear late in the reaction as observed. The observed CO inhibition of the substitution reaction follows naturally from the CO dissociation (I_d) in the first step of the reaction. Thus Figure 3 provides an explanation for all of the kinetic data while the other possible schemes are inconsistent with substantial parts of the observed data. This proposed mechanism is also consistent with the observation on μ-$HMo_2(CO)_{10}^-$ showing that initial substitution occurs with the dimer intact.[38-40]

A very interesting feature in the substitution reactions of metal-metal bonded carbonyl compounds is the effect of ligands on further substitutions. Reactions of substituted derivatives of dimanganese decacarbonyl show a variation with the ligands as shown in Table V.[12]

$$Mn_2(CO)_9L + L \rightarrow Mn_2(CO)_8L_2 + CO$$

Table V. Rate Constants for the Reaction $Mn_2(CO)_9L + L \rightarrow Mn_2(CO)_8L_2$ at 100 °C[a]

L	k, s^{-1}	L	k, s^{-1}
$P(C_6H_5)_3$	8.3×10^{-4}	$P(OC_6H_5)_3$	3.1×10^{-5}
$P(C_4H_9)_3$	2.4×10^{-4}	CO	1.7×10^{-5}

[a] Reference 12.

This type of effect is also seen in reactions of metal carbonyl clusters such as $Ir_4(CO)_{12}$ and $Ru_3(CO)_{12}$.[4-10] While our experiments on $MnRe(CO)_{10}$ do not show the second substitution to proceed more rapidly than the first,[41] our proposed mechanism is pertinent to these substitutions. It has been shown that the presence of a ligand can accelerate CO dissociation from positions cis to that ligand in mononuclear carbonyl complexes.[36] If the same type of effect is operable at one metal center of a dimer (or cluster), then CO dissociation would create a 16e center at the site which already was substituted. Steric interactions would prohibit further substitution at that metal, but the unsaturation could be transferred to a different metal center by bridging CO in the unsaturated intermediate. Thus, the accelerated CO dissociation on one metal can be transferred to other metal atoms. The order and magnitude of rate constants shown in Table V are very similar to those expected for cis labilization.[36,37]

There is ample literature precedence for the presence of bridging (or semibridging) carbonyls between metal centers that are electron rich and electron poor.[42-45] The complex which provides the most relevant example is $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, in which one vanadium is bound to one cyclopentadienyl and two carbonyls and the other vanadium is bound to one cyclopentadienyl and three carbonyls. Two of the three carbonyls on the one vanadium are semibridging, or equalizing the charge distribution between the vanadium centers. In our intermediate we have one 18-electron rhenium center and one 16-electron manganese center and it should not be unexpected that a bridging (or semibridging) carbonyl would stabilize the intermediate. The number of bridging carbonyls is unclear in our complex. We have represented only a single carbonyl bridge in Figure 3 as there is some precedence for singly bridging carbonyls between different metal centers.[45] The importance of bridging COs in the substitution reactions of $Ir_4(CO)_{12}$ and $P(C_6H_5)_3$ was previously shown.[5] Although $Ir_4(CO)_{12}$ contains no bridging COs, $Ir_4(CO)_{11}[P(C_6H_5)_3]$ and $Ir_4(CO)_{10}[P(C_6H_5)_3]_2$ both contain bridging carbonyls and show a marked acceleration of CO dissociation compared to the unsubstituted species, $Ir_4(CO)_{12}$.[5]

By a careful reinvestigation of the kinetics of the substitution reactions of $MnRe(CO)_{10}$ we have shown that the previously accepted mechanism involving homolytic fission of the metal-metal bond is incorrect and have suggested a new mechanism involving CO dissociation in an I_d-type mechanism which is consistent with all of the kinetics data. We suggest that this mechanism applies to the other dimeric species, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Tc_2(CO)_{10}$. The presence of a CO bridging between a formally 16-electron center and a formally 18-electron center may have wide applicability in reactions of metal-metal bonded carbonyl compounds.

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