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Kinetic and Equilibrium Studies of Carbamoyl Complex Formation from Manganese and Rhenium Carbonyls

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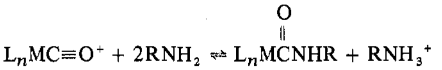
Cationic metal carbonyl complexes of manganese and rhenium react with primary aliphatic amines according to the equation *trans*-$M(CO)_4L_2^+ + 2RNH_2 \rightleftharpoons$ *trans*-$M(CO)_3L_2CONHR + RNH_3^+$ (for M = Mn, L = $P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$, or $P(C_6H_5)(CH_3)_2$; for M = Re, L = $P(C_6H_5)_3$). Kinetic studies show that the reactions follow the rate law rate = $k_3[M(CO)_4L_2^+][RNH_2]^2$, which is interpreted in terms of a mechanism involving base-catalyzed amine attack at a carbonyl carbon atom. In general, the reactions of $M(CO)_4[P(C_6H_5)_3]_2^+$ with a given amine are faster for the complex of Re than of Mn. For the $Mn(CO)_4L_2^+$ complexes, the rates decrease with L in the order $P(C_6H_5)_2(CH_3) > P(C_6H_5)(CH_3)_2 > P(C_6H_5)_3$. This order appears to be determined by both steric (*e.g.*, slow rate for L = $P(C_6H_5)_3$) and electronic factors (*e.g.*, electron-releasing CH_3 groups in L reduce amine attack). For these complexes the rates decrease with increasing bulk of the amine R group: *n*-butyl > cyclohexyl > isopropyl > *sec*-butyl. Equilibrium constants for the reactions of $Mn(CO)_4L_2^+$ in general decrease with increasing size of L ($P(C_6H_5)(CH_3)_2 > P(C_6H_5)_2(CH_3) > P(C_6H_5)_3$) and increasing size of the amine.

Introduction

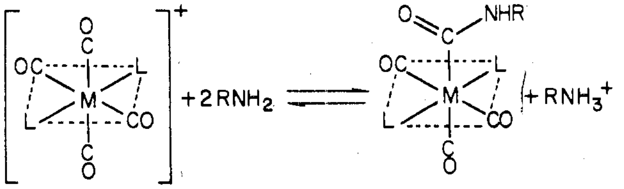
A variety[2,3] of primarily cationic metal carbonyl complexes reacts with primary and secondary alkylamines to give carbamoyl compounds according to the equation



$$L_nMC{\equiv}O^+ + 2RNH_2 \rightleftharpoons L_nM\overset{O}{\overset{\|}{C}}NHR + RNH_3^+ \qquad (1)$$

Due to the extremely rapid rate of most of these reactions, kinetic studies have not been carried out on them up to this time.

In the present paper, however, we wish to report results of rate studies on the reaction


(2)

(for M = Mn, L = $P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$, or $P(C_6H_5)(CH_3)_2$; for M = Re, L = $P(C_6H_5)_3$) which proceeds at measurable rates at 25.5°. In addition, equilibrium constants for the reaction have been determined as a function of the metal, the phosphine (L), and the amine.

Experimental Section

Starting Materials and Solvents. The complexes $Mn(CO)_5Cl$,[4] $Re(CO)_5Cl$,[5] $Mn(CO)_4[P(C_6H_5)_3]_2AlCl_4$,[6] and $Re(CO)_4[P(C_6H_5)_3]_2AlCl_4$[6] were prepared according to literature procedures. The ligands $P(C_6H_5)_2(CH_3)$ and $P(C_6H_5)(CH_3)_2$ were purchased from Pressure Chemical Co. and used without further purification. Dichloromethane used in the kinetic and equilibrium studies was refluxed over P_4O_{10} and distilled. Tetrahydrofuran (THF) was dried over $LiAlH_4$ and distilled; methanol was refluxed over Mg metal and distilled. Other solvents were reagent grade. Infrared spectra were recorded on a Perkin-Elmer Model 237-B and were calibrated against gaseous CO.

***trans*-$Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2Cl$.** To 40 ml of dry, CO-saturated THF was added 2.14 g (9.3 mmol) of $Mn(CO)_5Cl$ and about 4 ml (~45 mmol) of $P(C_6H_5)_2(CH_3)$. After the solution was refluxed for 12 hr, it was cooled and reduced to about 2 ml under a water-aspirator vacuum. Addition of pentane (100 ml) and cooling at 0° for 1 hr gave yellow crystals of the product which were recrystallized from CH_2Cl_2–pentane; yield 4.84 g (91%). The complex was identified by comparison of its infrared spectrum (Table I) with those of *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2Cl$[4] and *trans*-$Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2Cl$.[7]

The complex, *trans*-$Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2Cl$, was prepared by the ultraviolet irradiation method described in the literature.[7]

[*trans*-$M(CO)_4L_2]PF_6$. To a solution of 4.84 g (8.45 mmol) of *trans*-$Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2Cl$ in 200 ml of benzene was added 2.24 g of anhydrous $AlCl_3$. Carbon monoxide was bubbled into the deep red solution until it became light yellow (~10 min) and an oil separated. Under water-aspirator vacuum the mixture was reduced to an oil which was dissolved in 40 ml of $CHCl_3$. After filtration through Celite filter aid, the solution was treated with heptane to give a white precipitate of $Mn(CO)_4[P(C_6H_5)_2(CH_3)]_2AlCl_4$. Because the compound absorbs moisture readily, it was filtered under a nitrogen atmosphere. The solid was then dissolved in dry CH_3OH, and a filtered solution of NH_4PF_6 (~25 mmol) in methanol was added to cause immediate precipitation of white $Mn(CO)_4[P(C_6H_5)_2(CH_3)]_2PF_6$, which is not moisture sensitive. The product was recrystallized from CH_2Cl_2–diethyl ether–methanol and dried under high vacuum; yield 3.55 g (60%). It was identified by comparison of its infrared spectrum (Table I) with that of $Mn(CO)_4[P(C_6H_5)_3]_2AlCl_4$;[6] the presence of PF_6^- was indicated by a strong P–F stretching absorption at 850 cm^{-1}.

The preparations of *trans*-$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6$ (62% yield), *trans*-$Mn(CO)_4[P(C_6H_5)_3]_2PF_6$ (64% yield), and *trans*-$Re(CO)_4[P(C_6H_5)_3]_2PF_6$ (78% yield) were carried out similarly. Their infrared spectra are given in Table I.

***trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$.** The complex, *trans*-$Mn(CO)_4[P(C_6H_5)_3]_2PF_6$ (1.0 g), was dissolved in a minimum amount (5 ml) of CH_2Cl_2, and CH_3NH_2 was bubbled into the solution for about 15 min causing the precipitation of the bright yellow product. The solution was filtered immediately, and the solid was washed by vigorously stirring it in water for 1 hr to remove the $CH_3NH_3^+PF_6^-$ salt. It was then dried under high vacuum and recrystallized from $CHCl_3$–ether to give 0.48 g (55%) of the pure yellow product.

Anal. Calcd for $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$: C, 68.2; H, 4.71; N, 1.94. Found: C, 68.8; H, 4.98; N, 1.88.

The analogous *n*-butyl derivative was prepared *via* the reaction of 1.0 g of $Mn(CO)_4[P(C_6H_5)_3]_2PF_6$ in a minimum amount of CH_2Cl_2 with *n*-$C_4H_9NH_2$ (~10 ml) added over a 5-min period. The yellow precipitate was washed and purified as given for the methyl derivative to yield 0.69 g (75%) of the product.

Anal. Calcd for $Mn(CO)_3[P(C_6H_5)_3]_2CONHC_4H_9$: C, 69.2; H, 5.23; N, 1.83. Found: C, 68.5; H, 4.94; N, 2.25.

The analogous complexes $Mn(CO)_3[P(C_6H_5)_3]_2CONC_6H_{11}$, $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2$, and $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)(C_2H_5)$ were prepared in the same manner and characterized by their infrared (Table I) and nmr (Table II) spectra.

***trans*-$Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$.** Into a solution of 1.0 g of $Re(CO)_4[P(C_6H_5)_3]_2PF_6$ dissolved in CH_2Cl_2 (5 ml) was bubbled CH_3NH_2. After 10 min, the white precipitate containing the product

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Table I. Infrared Spectra of Compounds

Compd	ν(CO),[a] cm^{-1}
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2Cl}$	2037 w, 1952 s, 1917 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2Cl}$	2034 w, 1955 s, 1908 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2Cl}$	2033 w, 1951 s, 1904 m[b]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2Cl}$	2034 w, 1952 s, 1905 m[b]
$\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2PF_6}$	2092 vw, 2046 w, 2001 vs[c]
$\mathrm{Mn(CO)_4[P(C_6H_5)_2(CH_3)]_2PF_6}$	2092 vw, 2044 w, 2001 vs[c]
$\mathrm{Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6}$	2091 vs, 2043 w, 2001 vs[c]
$\mathrm{Re(CO)_4[P(C_6H_5)_3]_2PF_6}$	2109 vw, 2033 w, 2004 vs[c]
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3}$	2028 w, 1934 s, 1908m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2}$	2017 w, 1931 s, 1910 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3\text{-}CH_3}$	2023 w, 1933 s, 1907 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}}$	2020 w, 1932 s, 1909 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)\text{-}(C_2H_5)}$	2022 w, 1932 s, 1908 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2CONHCH_3}$	2018 w, 1933 s, 1907 m[d]
$\mathrm{Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2CONHCH_3}$	2017 w, 1931 s, 1907 m[d]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3}$	2048 w, 1947 s, 1918 m[b]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2}$	2052 w, 1952 s, 1910 m[b]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3\text{-}CH_3}$	2043 w, 1940 s, 1913 m[b]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}}$	2046 w, 1941 s, 1915 m[b]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)\text{-}(C_2H_5)}$	2043 w, 1941 s, 1913 m[b]
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3}$	2028 w, 1943 s, 1907 m[b]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3}$	2025 w, 1949 s, 1904 m[b]

[a] Key: w, weak; m, medium; s, strong; v, very. [b] $\mathrm{CHCl_3}$ solvent. [c] $\mathrm{CH_2Cl_2}$ solvent. [d] Hexane solvent.

Table II. Proton Nmr Spectra[a] of $\mathrm{M(CO)_3[P(C_6H_5)_3]_2CON\bar{H}R}$ in $\mathrm{CDCl_3}$ Solvent

Compd	NH	α-CH	β-CH
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2\text{-}CONHCH_3}$	5.15 b	8.01 d (4.2)[b]	
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2\text{-}CONHCH_3}$	5.60 b	8.08 d (4.2)[b]	
$\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2\text{-}CONHCH(CH_3)_2}$	5.25 b	*c*	9.43 d (6.0)[d]
$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2\text{-}CONHCH(CH_3)_2}$	5.55 b	*c*	9.47 d (6.0)[d]

[a] Chemical shifts in τ units; tetramethylsilane at τ 10.00. Abbreviations: b, broad; d, doublet. [b] Number in parentheses is J(HNCH) in Hz. [c] Not observed. [d] Number in parentheses is J(HCCH) in Hz.

was filtered and washed with water. After drying under high vacuum, it was recrystallized from $\mathrm{CH_2Cl_2}$-pentane; yield 0.36 g (41%).

Anal. Calcd for $\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3}$: C, 57.8; H, 3.99; N, 1.64. Found: C, 57.2; H, 4.25; N, 1.49.

The same procedure was used to prepare *trans*-$\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2}$. Isopropylamine (25 ml) was added over a period of 5 min with stirring to a solution of 1.0 g of $\mathrm{Re(CO)_4[P(C_6H_5)_3]_2PF_6}$ in 5 ml of $\mathrm{CH_2Cl_2}$. The resulting white precipitate was washed and recrystallized as described for the methyl analog; yield 0.59 g (65%).

Anal. Calcd for $\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2}$: C, 58.6; H, 4.31; N, 1.59. Found: C, 58.4; H, 4.22; N, 1.26.

The related complexes, $\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3CH_3}$, $\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}}$, and $\mathrm{Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)(C_2H_5)}$ were prepared in a similar manner and characterized by their infrared spectra (Table I).

Attempted Syntheses. Carbamoyl complexes could not be isolated from the reactions of $\mathrm{Mn(CO)_4[P(C_6H_5)_2(CH_3)]_2PF_6}$ or $\mathrm{Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6}$ with $\mathrm{CH_3NH_2}$, $\mathrm{CH_3(CH_2)_3NH_2}$, $\mathrm{C_6H_{11}NH_2}$ $\mathrm{(CH_3)_2CHNH_2}$, or $\mathrm{(C_2H_5)(CH_3)CHNH_2}$, although infrared spectra (Table I) of the reaction solutions clearly indicated that a reaction had occurred, and the product was the expected *trans*-$\mathrm{Mn(CO)_3L_2CONHR}$ derivative. Unlike the reactions of $\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2PF_6}$, no precipitation of the carbamoyl product occurred. Evaporation of the solutions to dryness caused the reactions rapidly to reverse themselves to leave only the starting complexes $\mathrm{[Mn(CO)_4L_2]PF_6}$. Likewise, addition of a nonpolar solvent such as pentane or ether precipitated only $\mathrm{[Mn(CO)_4L_2]PF_6}$. This reversibility and the resulting difficulty in isolating carbamoyl complexes is very similar to that encountered in the reactions of $\mathrm{(arene)Mn(CO)_3^+}$ complexes with amines.[3] The isolation of the $\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONHR}$ complexes is apparently possible only because of the lower solubility of these derivatives.

Reactions of $\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2PF_6}$ and $\mathrm{Re(CO)_4[P(C_6H_5)_3]_2PF_6}$ with secondary amines are not understood at the present time. For example, the reaction of $\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2PF_6}$ with excess $\mathrm{(CH_3)_2NH}$ at room temperature in $\mathrm{CH_2Cl_2}$ solvent gives a 75% yield of $\mathrm{HMn(CO)_3[P(C_6H_5)_3]_2}$,[8] yet no oxidation product such as the urea $\mathrm{(CH_3)_2NC(O)N(CH_3)_2}$ has been identified. Although $\mathrm{Re(CO)_4[P(C_6H_5)_3]_2PF_6}$ reacts with $\mathrm{(CH_3)_2NH}$ and other secondary amines, no products have been established.

All of the carbamoyl complexes react with trichloroacetic acid in $\mathrm{CH_2Cl_2}$ according to the equation

$$\mathrm{M(CO)_3L_2CONHR + 2CCl_3CO_2H \rightarrow M(CO)_4L_2^+ + RNH_3^+ + 2CCl_3CO_2^-}$$

Determination of Rates. Reaction rates were determined by monitoring the decrease of the very strong low-frequency carbonyl stretching absorption of the $\mathrm{M(CO)_4L_2^+}$ complexes at about 2000 cm^{-1}. In a typical experiment, 91 mg of $\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2PF_6}$ was dissolved in 10 ml of $\mathrm{CH_2Cl_2}$ in an aluminum foil wrapped vessel equipped with a rubber septum. After thermostating the vessel at 25.5 ± 0.05° for about 20 min, the amine which also had been thermostated was pipetted into the vessel. The system was purged with nitrogen.

Samples were withdrawn from the reaction solution with a syringe, preceded by the injection of a small volume of nitrogen to compensate for the solution removed; the absorbances of the samples were immediately measured on a Beckman IR-8 infrared spectrophotometer. Pseudo-first-order reaction conditions were maintained by using amine concentrations which were 10 times greater than that of the carbonyl complex. Pseudo-first-order rate constants, k_{obsd}, were determined from initial slopes of $\ln (A_t - A_\infty)$ *vs.* t plots where A_t is the absorbance at time t and A_∞ is the background absorbance determined with solvent in both sample and reference cells (A_∞ was nearly 0.0). These rate constants were reproducible to within 10% or better (Table III), except for the reactions with *n*-butylamine which proceeded at a much faster rate than the other amines; k_{obsd} values in this case were difficult to measure and were reproducible within only 30%. There was no reaction between $\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2^+}$ and the bulky *tert*-butylamine.

Equilibrium Constant Determinations. Equilibrium measurements were made on samples used in the determinations of the rates. These systems had essentially come to equilibrium within 1 hr and did not change appreciably over a 6-hr period. The equilibrium absorbance readings were generally taken about 2 hr after initial mixing of reactants. Equilibrium constants, K, were calculated from

$$K = \mathrm{[M(CO)_3L_2CONHR][RNH_3^+]/[M(CO)_4L_2^+][RNH_2]^2} \quad (3)$$

The equilibrium concentration of $\mathrm{M(CO)_4L_2^+}$ was determined from its absorbance at approximately 2000 cm^{-1} using the absorbance of a solution containing a known concentration of the complex as a standard. From this quantity and the other known starting concentrations, equilibrium concentrations of the other species in eq 3 were calculated. Since the concentrations of $\mathrm{RNH_2}$ were so much larger than that of $\mathrm{M(CO)_4L_2^+}$, the equilibrium concentrations of $\mathrm{RNH_2}$ were taken to be the same as the $\mathrm{RNH_2}$ concentration originally added. Values of K for a given reaction were reproducible within 10% (Table III).

To demonstrate that the reactions were truly reversible, the equilibrium in one case was approached from the other side. Thus $\mathrm{CH_3NH_3^+Cl^-}$ was added to a $\mathrm{CH_2Cl_2}$ solution of pure $\mathrm{Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3}$. Each addition of $\mathrm{CH_3NH_3^+Cl^-}$ shifted the equilibrium further to the cationic complex, $\mathrm{Mn(CO)_4[P(C_6H_5)_3]_2^+}$, as evidenced by the growth of its 2001-cm^{-1} absorption.

Results

The reactions studied are represented in eq 2. The reacting cations, $\mathrm{M(CO)_4L_2^+}$, had previously[9] been assigned a trans geometry on the basis of ir evidence. Likewise, the phosphine L groups are trans to each other in the carbamoyl products, $\mathrm{M(CO)_3L_2CONHR}$; this assignment is made on the basis of the characteristic[10] weak, strong, medium pattern of

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Table III. Rate and Equilibrium Constants for Reaction 2 at 25.5° in CH_2Cl_2 Solvent

NH_2R	$[NH_2R]$, M	k_{obsd}, sec^{-1}	k_3, M^{-2} sec^{-1}	K, M^{-1}
$Mn(CO)_4[P(C_6H_5)_3]_2{}^+PF_6{}^-$, 0.0108 M				
$NH_2CH(CH_3)(C_2H_5)$	3.28	3.08×10^{-4}	2.86×10^{-5}	1.29×10^{-3}
	4.65	6.15×10^{-4}	2.84	1.18
	4.95	7.33×10^{-4}	2.90	1.40
	5.95	1.0×10^{-3}	2.82	1.23
	6.77	1.36×10^{-3}	2.96	1.33
$NH_2C_6H_{11}$	0.795	1.73×10^{-4}	2.74×10^{-4}	1.31×10^{-2}
	1.15	3.26×10^{-4}	2.45	1.58
	1.74	7.20×10^{-4}	2.37	1.42
	2.02	1.05×10^{-3}	2.56	1.40
$NH_2CH(CH_3)_2$	1.06	2.0×10^{-4}	1.78×10^{-4}	1.85×10^{-2}
	1.52	3.34×10^{-4}	1.45	1.09
	1.95	5.05×10^{-4}	1.33	1.65
	2.33	7.4×10^{-4}	1.36	1.96
	2.70	1.1×10^{-3}	1.49	1.52
$NH_2(CH_2)_3CH_3$	0.77			1.64×10^{-2}
	1.11			1.81
	1.59			1.82
	1.88			1.91
	2.40			1.71
$Mn(CO)_4[P(C_6H_5)_2CH_3]_2{}^+PF_6{}^-$, 0.0117 M				
$NH_2CH(CH_3)(C_2H_5)$	0.99	3.82×10^{-4}	3.90×10^{-4}	1.70×10^{-2}
	1.65	1.06×10^{-3}	3.88	1.59
	1.98	1.38×10^{-3}	3.52	1.82
	2.28	1.67×10^{-3}	3.20	1.65
	2.56	2.47×10^{-3}	3.77	1.59
$NH_2C_6H_{11}$	0.795	4.90×10^{-4}	7.75×10^{-4}	1.49×10^{-2}
	1.15	7.80×10^{-4}	5.85	1.68
	1.45	1.39×10^{-3}	6.60	2.24
	1.74	2.0×10^{-3}	6.62	1.60
$NH_2CH(CH_3)_2$	1.06	6.05×10^{-4}	5.40×10^{-4}	3.92×10^{-2}
	1.52	1.43×10^{-3}	6.16	3.98
	1.95	2.02×10^{-3}	5.34	3.42
	2.33	3.20×10^{-3}	5.87	4.16
$NH_2(CH_2)_3CH_3$	0.592			3.95×10^{-2}
	1.11			3.96
	1.59			3.36
	2.02			3.76
	2.70			3.38
$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2{}^+PF_6{}^-$, 0.0121 M				
$NH_2CH(CH_3)(C_2H_5)$	1.29	4.65×10^{-4}	2.80×10^{-4}	1.12×10^{-1}
	1.65	6.05×10^{-4}	2.20	1.21
	2.28	1.06×10^{-3}	2.03	1.02
	2.56	1.61×10^{-3}	2.46	1.27
$NH_2C_6H_{11}$	0.795	3.12×10^{-4}	4.95×10^{-4}	1.86×10^{-1}
	1.15	6.75×10^{-4}	5.11	1.45
	1.58	1.37×10^{-3}	5.5	2.4
	2.02	2.1×10^{-3}	5.2	1.48
$NH_2CH(CH_3)_2$	1.06	3.70×10^{-4}	3.28×10^{-4}	1.31×10^{-1}
	1.52	8.32×10^{-4}	3.60	1.26
	1.95	1.27×10^{-3}	3.42	1.04
	2.33	1.71×10^{-3}	3.14	1.16
$NH_2(CH_2)_3CH_3$	0.592			2.49×10^{-2}
	0.946			2.28
	1.28			2.42
	1.88			2.02
	2.60			2.37
$Re(CO)_4[P(C_6H_5)_3]_2{}^+PF_6{}^-$, 0.00392 M				
$NH_2CH(CH_3)(C_2H_5)$	0.90	8.04×10^{-4}	9.9×10^{-4}	3.75×10^{-3}
	1.29	1.55×10^{-3}	9.27	3.92
	1.65	3.12×10^{-3}	11.4	3.68
	1.98	4.05×10^{-3}	10.3	4.1
$NH_2C_6H_{11}$	0.415	7.95×10^{-4}	4.62×10^{-3}	1.54×10^{-2}
	0.795	2.62×10^{-3}	4.15	1.43
	0.970	3.82×10^{-3}	4.06	1.27
$NH_2CH(CH_3)_2$	0.395	7.20×10^{-4}	4.61×10^{-3}	3.25×10^{-2}
	0.449	8.78×10^{-4}	4.35	3.29
	0.556	1.41×10^{-3}	4.56	3.28
	0.815	2.99×10^{-3}	4.49	3.12
$NH_2(CH_2)_3CH_3$	0.592			3.24×10^{-2}
	0.946			3.47
	1.28			3.49
	1.88			3.37

intensities for the three C-O stretching absorptions in their infrared spectra (Table I). In addition to the terminal $\nu(CO)$ absorptions, their spectra contained a broad, medium-intensity band at about 1535 cm^{-1} which is probably associated with both the carbamoyl $\nu(C=O)$ stretching and NH bending modes.

Proton nmr spectra (Table II) of the $M(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ complexes exhibit a broad resonance at τ 5.15 (Mn) or τ 5.60 (Re) which we assign to the NH proton; in addition a methyl doublet (due to coupling with the NH proton) occurs at higher field. It is interesting to compare the τ values of the methyl doublet in $Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ (τ 8.08) with those of $Re(CO)_5CONHCH_3$[11] (τ 7.30) and *cis*-$Re(CO)_4(NH_2CH_3)CONHCH_3$[5] ($\tau$ 7.17). The unusually high-field position of the CH_3 group in $Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ is presumably due to shielding by the phenyl groups in the phosphine ligands as has also been found in palladium and platinum carbamoyl complexes.[12] A similar trend is observed for $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ (τ 8.01) and *cis*-$Mn(CO)_4(NH_2CH_3)CONHCH_3$ (τ 7.08).[13]

All kinetic and equilibrium studies were carried out at 25.5° in CH_2Cl_2 solvent. The pseudo-first-order rate constants, k_{obsd} (Table III), indicate that all of the reactions obey the rate law

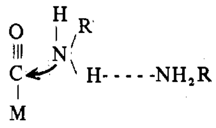
$$\text{rate} = k_3[M(CO)_4L_2{}^+][RNH_2]^2 \qquad (4)$$

where $k_{obsd} = k_3[RNH_2]^2$. Values of k_3 for the different reactions are summarized in Table IV.

Equilibrium constants, K, determined at various concentrations of reactants are given in Table III. Average values are summarized in Table IV.

Discussion

Kinetic Studies. Although there are several mechanisms that might be considered to account for the second-order dependence of reaction 2 on the amine concentration (eq 4), the most probable might be a base-catalyzed nucleophilic attack of the amine at the carbonyl carbon atom



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By this pathway, both the carbamoyl complex and alkylammonium salt would be formed in a concerted process. This mechanism is similar to that proposed for the second-order amine dependence in the reactions of organic esters with amines to form amides.[14] It is also related to the mechanism suggested for the reactions of (methoxycarbene)pentacarbonylchromium complexes with amines to give the corresponding aminocarbene complexes.[15] Kinetic studies of carbanion[16] and azide[17] attack at carbonyl groups have been reported previously.

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Table IV. Summary of Average Rate and Equilibrium Constants for Reaction 2 at 25.5° in CH_2Cl_2 Solvent

Complex	NH_2R	k_3, M^{-2} sec^{-1}	K, M^{-1}
$Mn(CO)_4[P(C_6H_5)_3]_2^+$	$NH_2CH(CH_3)(C_2H_5)$	2.88×10^{-5}	1.29×10^{-3}
$Mn(CO)_4[P(C_6H_5)_2CH_3]_2^+$		3.65×10^{-4}	1.67×10^{-2}
$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2^+$		2.37×10^{-4}	1.16×10^{-1}
$Re(CO)_4[P(C_6H_5)_3]_2^+$		1.02×10^{-3}	3.86×10^{-3}
$Mn(CO)_4[P(C_6H_5)_3]_2^+$	$NH_2C_6H_{11}$	2.53×10^{-4}	1.43×10^{-2}
$Mn(CO)_4[P(C_6H_5)_2CH_3]_2^+$		6.71×10^{-4}	1.75×10^{-2}
$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2^+$		5.19×10^{-4}	1.80×10^{-1}
$Re(CO)_4[P(C_6H_5)_3]_2^+$		4.28×10^{-3}	1.41×10^{-2}
$Mn(CO)_4[P(C_6H_5)_3]_2^+$	$NH_2CH(CH_3)_2$	1.49×10^{-4}	1.61×10^{-2}
$Mn(CO)_4[P(C_6H_5)_2CH_3]_2^+$		5.69×10^{-4}	3.87×10^{-2}
$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2^+$		3.36×10^{-4}	1.19×10^{-1}
$Re(CO)_4[P(C_6H_5)_3]_2^+$		4.50×10^{-3}	3.24×10^{-2}
$Mn(CO)_4[P(C_6H_5)_3]_2^+$	$NH_2(CH_2)_3CH_3$	$\sim 8.8 \times 10^{-3}$	1.78×10^{-2}
$Mn(CO)_4[P(C_6H_5)_2CH_3]_2^+$		$\sim 6.0 \times 10^{-3}$	3.68×10^{-2}
$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2^+$		$\sim 5.5 \times 10^{-3}$	2.32×10^{-2}
$Re(CO)_4[P(C_6H_5)_3]_2^+$		$\sim 5.5 \times 10^{-3}$	3.39×10^{-2}

The rate of reaction 2 has been studied as a function of the metal atom (Mn or Re), the nature of the phosphine (L) in the complex, and the nature of the attacking primary amine.

With the exception of *n*-butylamine, the amines react with $Re(CO)_4[P(C_6H_5)_3]_2^+$ approximately 17-30 times faster than with the manganese analog, $Mn(CO)_4[P(C_6H_5)_3]_2^+$. This is perhaps due to the decreased crowding near the larger Re atom making the carbonyl group more accessible to attack. Although the rate constants for the *n*-butylamine reactions are significantly less accurate because of their higher rates, the Mn and Re complexes appear to react at roughly the same rate. That this is the case with the least sterically bulky amine suggests that crowding around the metal atom is not as important when the attacking amine is relatively small.

With the exception of *n*-butylamine, the rates decrease with the phosphine (L) in the $Mn(CO)_4L_2^+$ complexes as follows: $P(C_6H_5)_2(CH_3) > P(C_6H_5)(CH_3)_2 > P(C_6H_5)_3$. There are two factors which almost certainly enter into determining this order. First is the steric factor which would suggest that the $P(C_6H_5)_3$ complex would react more slowly than the methylphosphines,[18] and a second is an opposing trend, the electronic effect of replacing a phenyl group by a more electron-releasing methyl group. This latter factor has been shown markedly to affect the tendency (equilibrium constant)[3] of carbonyl ligands to react with amines. Thus it would be expected that the more electron-releasing methylphosphines would increase the electron density at the carbonyl carbon making it less susceptible to amine attack, thereby decreasing the rate of reaction. The observed order apparently is determined by both factors; the $P(C_6H_5)_2(CH_3) > P(C_6H_5)(CH_3)_2$ trend follows the electronic argument, and the unusually slow rate for the $P(C_6H_5)_3$ complex is apparently caused by the bulkiness of this ligand. Indeed the slowest rate of all those studied is that observed for $Mn(CO)_4[P(C_6H_5)_3]_2^+$ with the bulkiest amine, *sec*-butylamine.

With the least bulky ligand, *n*-butylamine, steric considerations appear to be much less important since the order of reactivity is that predicted on the basis of electronic arguments only: $P(C_6H_5)_3 > P(C_6H_5)_2(CH_3) > P(C_6H_5(CH_3)_2$. It should be added, however, that within the relatively large experimental error, the rate constants for these complexes could be considered the same.

The rates of reaction of the manganese complexes decrease with the nature of the amine in the following order: *n*-butylamine > cyclohexylamine > isopropylamine > *sec*-butylamine. This order is characteristic of the increasing bulkiness of the attacking amine (and/or assisting amine) and has been observed in the reaction of organic esters with amines to give amides.[19] The lack of reaction between $Mn(CO)_4[P(C_6H_5)_3]_2^+$ and *tert*-butylamine is consistent with the trend but also could be due to an equilibrium effect. Where the amine structures are very similar as in cyclohexylamine and isopropylamine, the rates are also very much the same. For $Re(CO)_4[P(C_6H_5)_3]_2^+$ the trend is essentially the same except the rates for cyclohexylamine and isopropylamine are the same within experimental error.

The importance of steric effects in these reactions suggests that steric crowding around the metal atom is the reason that the reactions of these complexes are slow enough to study. The more reactive carbonyl complexes[3] are less crowded.

Equilibrium Studies. Equilibrium constants, *K* (eq 3), for reaction 2 are summarized in Table IV. The K values for the reactions of $Mn(CO)_4[P(C_6H_5)_3]_2^+$ and $Re(CO)_4[P(C_6H_5)_3]_2^+$ with a given amine are generally slightly smaller for Mn than Re. The differences, however, are small—significantly smaller than the effect of the metal on the rates of these reactions.

With the amines *sec*-butyl, isopropyl, and cyclohexyl, the values of *K* decrease with the phosphine (L) in the $Mn(CO)_4L_2^+$ complexes in the order $P(C_6H_5)(CH_3)_2 > P(C_6H_5)_2(CH_3) > P(C_6H_5)_3$. This is also the order of increasing bulkiness of the phosphine[18] which apparently decreases the extent to which amines add to form the carbamoyl complexes. It should be noted that this trend is different from that observed for the kinetics of this series of compounds where both electronic and steric factors were required to explain the results. The overriding importance of steric effects on the equilibrium constants may be associated with the large steric repulsions between the amine R group and the remainder of the complex in the carbamoyl product. In contrast, the effect of steric factors on the rate constants would be associated with repulsions in the activated complex (1) where the amine is not completely bound to the complex and the R group is therefore not as close to the other ligands.

With *n*-butylamine the order is somewhat different: $P(C_6H_5)_2(CH_3) > P(C_6H_5)(CH_3)_2 > P(C_6H_5)_3$. It is not clear what factors cause this order, but it should be noted that the differences in *K*'s for the phosphines in this series

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are significantly smaller than observed with the other more bulky amines where steric factors were of predominant importance.

Equilibrium constants for the reactions of a given $M(CO)_4L_2^+$ complex with different amines depend on at least two factors: the bulkiness of the amine and the basicity of the amine, since one of the products is RNH_3^+ (eq 2). In water, all of the amines have essentially the same pK_a values (10.6-10.7). If this were also true in CH_2Cl_2 solvent, steric effects should then establish the observed trend. In fact, except for $Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2^+$, all other $M(CO)_4L_2^+$ complexes follow the trend *n*-butylamine > isopropylamine > cyclohexylamine > *sec*-butylamine, expected from steric arguments. In this trend, isopropylamine is believed to be slightly less bulky than cyclohexylamine, where the 3-, 4-, and 5-CH_2 groups in the cyclohexyl ring are also repelled by the L groups. It should be added that in several instances the differences in K values for different amines are very small, and it is difficult to rationalize some cases where there are large differences. In general, however, the results are very similar to equilibrium constants for the related reaction[11]

$$Re(CO)_5CO_2CH_3 + RNH_2 \rightarrow Re(CO)_5CONHR + CH_3OH \qquad (5)$$

where the K value order was as follows: *n*-butylamine (1.2) > isopropylamine (1.0) ~ cyclohexylamine (1.0) ~ *sec*-butylamine (1.0).

Registry No. $Mn(CO)_5Cl$, 14100-30-2; $P(C_6H_5)_2(CH_3)$, 1486-28-8; CO, 630-08-0; NH_2CH_3, 74-89-5; $NH_2(CH_2)_3CH_3$, 109-73-9; $NH_2CH(CH_3)_2$, 75-31-0; $NH_2C_6H_{11}$, 108-91-8; $NH_2CH(CH_3)(C_2H_5)$, 13952-84-6; $Mn(CO)_3[P(C_6H_5)_3]_2Cl$, 29961-98-6; $Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2Cl$, 38496-58-1; $Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2Cl$, 33988-79-3; $Re(CO)_3[P(C_6H_5)_3]_2Cl$, 19394-85-5; $Mn(CO)_4[P(C_6H_5)_3]_2PF_6$, 38426-96-9; $Mn(CO)_4[P(C_6H_5)_2(CH_3)]_2PF_6$, 38496-52-5; $Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6$, 38496-53-6; $Re(CO)_4[P(C_6H_5)_3]_2PF_6$, 38496-54-7; $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$, 38466-94-3; $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2$, 38466-95-4; $Mn(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3CH_3$, 38466-96-5; $Mn(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}$, 38466-97-6; $Mn(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)(C_2H_5)$, 38466-98-7; $Mn(CO)_3[P(C_6H_5)_2(CH_3)]_2CONHCH_3$, 38466-99-8; $Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2CONHCH_3$, 38599-47-2; $Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$, 38467-00-4; $Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)_2$, 38467-01-5; $Re(CO)_3[P(C_6H_5)_3]_2CONH(CH_2)_3CH_3$, 38467-02-6; $Re(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}$, 38467-03-7; $Re(CO)_3[P(C_6H_5)_3]_2CONHCH(CH_3)(C_2H_5)$, 38467-04-8; $Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, 38496-55-8; $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, 38496-56-9.

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A Carbon-13 Nuclear Magnetic Resonance Study of Carbene-Pentacarbonyl Complexes of Chromium(0) and Tungsten(0)

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The ^{13}C nmr spectra of a variety of complexes of the type $(CO)_5MC(X)R'$ (M = Cr, W; X = NH_2, OR; R' = CH_3, Ph, and meta- and para-substituted phenyl) have been studied. The extremely low-field position of the carbene carbon resonance together with the strong interaction of this carbon atom with the X and R' groups (when R' = phenyl) suggests that this carbon atom be considered as a transition metal stabilized carbonium ion center. In tetrahydrofuran solvent, a 6-7-ppm upfield shift of the carbene carbon resonance relative to the shift found in $CHCl_3$ or CH_2Cl_2 was observed. This result is interpreted as due to Lewis acid-base complexation of the ether with the carbene carbon. Better electron-donating carbene groups cause the cis carbonyl carbon resonance to move to lower field. It is suggested that variations in the metal-to-carbonyl π bond are chiefly responsible for the observed trend.

Introduction

Stable group VIb transition metal complexes containing apparent "carbene" ligands were first reported in 1964.[2] These compounds are of considerable interest because of their synthetic possibilities and the unusual bonding that occurs between the metal atom and the carbene carbon. We have undertaken an investigation of the bonding in this type of compound by analyzing the ^{13}C nmr spectra of a variety of complexes of the general type $(CO)_5MC(X)R'$ (M = Cr, W; X = NH_2, OR; R' = CH_3, Ph, and meta- and para-substituted phenyl). During the course of our investigation a brief note appeared on this subject from another laboratory.[3] Our study is in excellent agreement with that reported by Kreiter and Formacek. We wish to report here additional results which were obtained from our more extensive investigation.

Experimental Section

Materials. Trimethyloxonium[4] and triethyloxonium[5] tetrafluoroborate were prepared by the methods of Meerwein and stored under argon in a sealed container at −20°. Butyllithium in hexane and phenyllithium in 20% ether-80% benzene were obtained from the Foote Chemical Co. Chromium and tungsten hexacarbonyls were obtained from Pressure Chemical Co. Complexes of the type $(CO)_5MC(OR)R'$ (M = Cr, W) were prepared by the method of Aumann and Fischer.[6] The modification suggested by Darensbourg and Darensbourg[7] for removing unreacted metal hexacarbonyl was

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