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Carbamoyl and Alkoxycarbonyl Complexes of Manganese and Rhenium

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Carbamoyl complexes of the formula $Re(CO)_5CONRR'$ (where R and R′ are H or alkyl groups) have been prepared by four general methods: I, reaction of $Re(CO)_6^+$ with primary and secondary alkylamines; II, reaction of $Re(CO)_6^+$ with amide ($R'RN^-$) ions; III, reaction of $Re(CO)_5^-$ with alkyl isocyanates (RNCO) and $(C_2H_5)_3NH^+$; IV, aminolysis of $Re(CO)_5CO_2CH_3$ with primary and secondary amines. The extent to which the last reaction occurs decreases with increased bulkiness of the amine: $NH_2CH_3 \gg NH_2CH_2CH_3 \gg NH(CH_3)_2 > NH_2(CH_2)_3CH_3 > NH_2CH(CH_3)_2 \gg NH_2C(CH_3)_3$. The analogous reactions of $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and $Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ with RNH_2 yield the carbamoyl complexes $M(CO)_3[P(C_6H_5)_3]_2C(O)NHR$. All three carbamoyl complexes have been reconverted to the original methoxycarbonyl derivatives by reaction with CH_3OH. The alkoxycarbonyl complexes also react with hydrazine and methyl-substituted hydrazines to give the isocyanato complexes $Re(CO)_5(NCO)$, *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$, and *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2(NCO)$ along with methanol and either ammonia or the methyl-substituted amine. These isocyanato complexes have also been prepared by the reaction of cationic metal carbonyl complexes with azide ion and hydrazines.

Introduction

In recent years, carbamoyl (*e.g.*, $L_nM\text{-}CONHCH_3$) and alkoxycarbonyl (*e.g.*, $L_nM\text{-}CO_2CH_3$) complexes of a variety of transition metals, M, have been prepared.[2] Yet relatively little is known about their reactions. In contrast, their organic analogs, carboxylic amides and esters, have been studied in great detail.[3] Among the most common reactions of esters are those with amines to yield amides

$$R'\text{-}CO_2CH_3 + NH_2R \rightleftharpoons R'\text{-}CONHR + CH_3OH \quad (1)$$

and with hydrazines to give hydrazides

$$R'\text{-}CO_2CH_3 + NH_2NH(CH_3) \rightarrow R'\text{-}CONHNH(CH_3) + CH_3OH \quad (2)$$

The purpose of the present investigation was to compare and contrast the reactivity of transition metal alkoxycarbonyl complexes with their organic analogs in these reactions. During the investigations new synthetic routes to carbamoyl complexes were devised and a variety of new complexes were prepared.

Experimental Section

General Procedure. All reagents were obtained from commercial sources and used without further purification. Solvents were all reagent grade and used without further purification except for tetrahydrofuran (THF) which was dried over $LiAlH_4$ and CH_3OH which was dried and distilled over magnesium metal. Infrared spectra were recorded on either a Beckman IR-12 or a Perkin-Elmer 237-B infrared spectrophotometer with scale expansion recorder and calibrated with gaseous CO. Proton nmr spectra were recorded on a Varian A-60 or Perkin-Elmer Hitachi R-20B spectrometer. The mass spectrum was obtained on an AEI MS-902 high-resolution spectrometer; chemical analyses were performed by Chemalytics, Inc., Tempe, Ariz.

The cation $Re(CO)_6^+$ was prepared according to a literature procedure[4] and precipitated from water as $[Re(CO)_6]PF_6$ with NH_4PF_6. The alkoxycarbonyl complexes $Re(CO)_5CO_2CH_3$,[5] *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$,[6] and *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$[6] were all prepared according to literature procedures.

Preparation of $Re(CO)_5CONHCH_3$. Method I. Reaction of $Re(CO)_6^+$ with CH_3NH_2. On a vacuum line 0.82 mmol of CH_3NH_2 was distilled into an nmr tube containing 0.208 g (0.41 mmol) of $[Re(CO)_6]PF_6$ and 0.7 ml of $CDCl_3$ at −196°. The tube was sealed and its room-temperature proton nmr spectrum was recorded as soon as the solvent and amine had thawed (~15 min). The tube was then broken open and the solution was filtered under nitrogen to remove the voluminous white precipitate $[CH_3NH_3]PF_6$. The resulting solution was evaporated to dryness and the residue sublimed at 60° (0.5 mm); yield 0.055 g (35%), mp 129–130°. The complex decomposes after a few hours of exposure to air.

Anal. Calcd for $Re(CO)_5CONHCH_3$: C, 21.88; H, 1.04; N, 3.65. Found: C, 21.64; H, 1.14; N, 3.51.

Its mass spectrum shows the following ion fragments (and their relative intensities) with *m/e* values greater than 186: $Re(CO)_6NHCH_3^+$, 45; $Re(CO)_5NHCH_3^+$, 100; $Re(CO)_4NHCH_3^+$, 98; $Re(CO)_4NCH_3^+$, 98; $Re(CO)_3NHCH_3^+$, 53; $Re(CO)_3NCH_3^+$, 98; $Re(CO)_2NHCH_3^+$, 82; $Re(CO)_2NCH_3^+$, 99; $Re(CO)NHCH_3^+$, 99; $Re(CO)NCH_3^+$, 98; $Re(CO)^+$, 99; ReC^+, 61; Re^+, 100.

Method II. Reaction of $Re(CO)_6^+$ with $LiNHCH_3$. To dry $LiNHCH_3$[7] (2 mmol) under nitrogen at 0° was added dropwise an N_2-saturated suspension of 1.0 g (2 mmol) of $[Re(CO)_6]PF_6$ in THF. After stirring for 1 hr at room temperature, the solvent was removed under reduced pressure and the residue sublimed at 60° (0.5 mm) overnight; yield 0.12 g (15%). The complex was characterized by its infrared and nmr spectra (see Tables I and II) and melting point.

Method III. Reaction of $NaRe(CO)_5$ with CH_3NCO and $[(C_2H_5)_3NH]Cl$. The anionic complex $Re(CO)_5^-$ was prepared by stirring a mixture of 1.14 g (1.75 mmol) of $Re_2(CO)_{10}$ dissolved in 20 ml of THF with 23 g of 1.4% sodium amalgam overnight under nitrogen.[5] The THF solution was withdrawn from the mercury by means of a hypodermic needle and added to a THF solution containing 3.5 mmol each of CH_3NCO and $[(C_2H_5)_3NH]Cl$. The mixture was stirred for 1 hr and filtered under nitrogen and the solvent was removed by water aspirator vacuum. The remaining residue was sublimed at 60° (0.5 mm) to give $Re(CO)_5CONHCH_3$ plus a small amount of unknown impurity as observed in the nmr spectrum. The impurity was removed by recrystallization from $CHCl_3$–pentane under a nitrogen atmosphere; yield 0.257 g (19%).

Method IV. Reaction of $Re(CO)_5CO_2CH_3$ with CH_3NH_2. On a vacuum line, 0.59 mmol of CH_3NH_2 was distilled into an nmr tube containing 0.227 g (0.59 mmol) of $Re(CO)_5CO_2CH_3$ and 0.7 ml of $CDCl_3$ at −196°. The tube was sealed and allowed to thaw out at which time the nmr spectrum was recorded. The tube was then broken open, the solution evaporated to dryness, and the residue sublimed at 60° (0.5 mm) to give 0.141 g (53%) of $Re(CO)_5CONHCH_3$.

Reaction of $Re(CO)_5CONHCH_3$ with CH_3OH. A mixture of 0.13 g (0.338 mmol) of $Re(CO)_5CONHCH_3$ and 50 ml of dry, N_2-saturated methanol plus a catalytic amount of $NaOCH_3$ (0.141 mmol) was stirred at room temperature for 1 hr. The methanol was removed under high vacuum and the resulting residue sublimed at 60° (0.5 mm). The white crystalline product, $Re(CO)_5CO_2CH_3$, was characterized by its infrared and nmr spectra, and its melting point;[5] yield 0.060 g (46%).

Reaction of *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ with CH_3NH_2. Again under vacuum conditions 0.127 mmol of CH_3NH_2 was distilled into an nmr tube containing 0.108 g (0.127 mmol) of *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and 0.7 ml of $CDCl_3$ at −196°. The proton nmr spectrum was recorded as soon as possible after mixing; it

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Table I. Infrared Spectra of $Re(CO)_5CONRR'$ Compounds

Compound	Solvent	ν(C–O),[f] cm^{-1}
$Re(CO)_5(CO_2CH_3)$[a]	CCl_4	2142 w, 2034 s, 2004 m
$Re(CO)_5(CONHCH_3)$[b]	$CHCl_3$	2068 w, 2022 s, 1998 m, sh
$Re(CO)_5(CONHCH_3)$[b]	CCl_4[c]	2055 w, 2013 s, 1990 m
$Re(CO)_5[CONHCH(CH_3)_2]$	$CHCl_3$	2045 w, 2020 s, 1995 m, sh
$Re(CO)_5(CONHC_2H_5)$	$CHCl_3$	2075 w, 2012 s, 1988 m, sh
$Re(CO)_5$(CONH-*n*-C_4H_9)	$CHCl_3$	2046 w, 2022 s, 1995 m, sh
$Re(CO)_5(CONHC_6H_{11})$	$CHCl_3$	2048 w, 2017 s, 1990 m, sh
$Re(CO)_5$(CONH-*sec*-C_4H_9)	$CHCl_3$	2071 w, 2026 s, 2001 m, sh
$Re(CO)_5[CONHC(CH_3)_3]$	$CHCl_3$	2071 w, 2008 s, 1985 m, sh
$Re(CO)_5[CON(CH_3)_2]$	CCl_4	2080 w, 2028 s, 2002 m
$Re(CO)_5[CON(C_2H_5)_2]$	$CHCl_3$	2088 w, 2013 s, 1985 m
$Re(CO)_5(CONC_4H_8)$	$CHCl_3$	2085 w, 2016 s, 1990 m, sh
$Re(CO)_5(CONC_5H_{10})$	$CHCl_3$	2083 w, 2016 s, 1990 m, sh
$Re(CO)_5(NH_2CH_3)^+$[d]	CH_2Cl_2	2167 vw, 2107 w, 2052 s, 2023 m
$Re(CO)_5(NCO)$[e]	CCl_4	2159 w, 2048 vs, 2020 w, 1995 s

[a] Reference 5. [b] See Discussion for the possible ν(C–O) for the $CONHCH_3$ group. [c] Decomposes slowly in CCl_4 to $Re(CO)_5Cl$. [d] Reference 12. [e] Reference 10. [f] Key: w, weak; m, medium; s, strong; v, very; sh, shoulder.

Table II. Proton Nmr Spectra[a,b] of $Re(CO)_5CONRR'$ in $CDCl_3$

R	R′	NH	α-CH	β-CH
CH_3	H	4.55 b	7.30 d (5.4)[c]	
$CH(CH_3)_2$	H	4.90 b	5.85 m	8.89 d (6.0)[d]
C_2H_5	H	4.90 b	6.80 m	8.87 t (6.9)[d]
$C(CH_3)_3$	H	5.04 b		8.74 s
CH_3	CH_3		7.08, 7.18	
$Re(CO)_5CO_2CH_3$			6.54 s	
CH_3OH			6.64 s	

[a] Chemical shifts in τ units; tetramethylsilane is at τ 10.00. [b] Abbreviations: b, broad; s, singlet; d, doublet, t, triplet; m, multiplet. [c] Number in parentheses is *J*(HNCH) in hertz. [d] Number in parentheses is *J*(HCCH) in hertz.

showed resonances of CH_3OH, unreacted $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and CH_3NH_2, and the carbamoyl complex *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$. The spectrum did not change over a 12-hr period. With 2 mol or more of amine per mole of complex, the reaction went to completion. The nmr tube was then broken open, the solution evaporated to dryness, and the residue extracted with a minimum amount of $CHCl_3$ (~5 ml). Addition of pentane to the filtered $CHCl_3$ solution yielded the white product; yield 0.096 g (89%). The *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ was identified from a comparison of its infrared and nmr spectra with those of the same complex made from the reaction of $Re(CO)_4[P(C_6H_5)_3]_2^+$ and CH_3NH_2.[9]

Similar carbamoyl products were isolated from the reactions of *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ with isopropyl-, cyclohexyl-, *sec*-butyl-, and *n*-butylamines.

Reaction of *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ with CH_3NH_2. The reaction was carried out in a sealed nmr tube using 0.127 g (0.174 mmol) of $Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and 0.348 mmol of CH_3NH_2 in 0.7 ml of $CDCl_3$. The proton nmr spectrum recorded as soon as possible after mixing showed no signals due to the alkoxycarbonyl group but only those of CH_3OH, excess CH_3NH_2, and the carbamoyl moiety, $CONHCH_3$. Within 30 min at room temperature the yellow solution began to turn green, and bands in the nmr spectrum began broadening until no peaks were distinguishable. This is probably due to oxidation, perhaps by the solvent, of the complex to give paramagnetic Mn(II). A small amount of the bright yellow carbamoyl product (~10% yield) was isolated and identified by comparison of its spectral features with those of the same complex made from the reaction of $Mn(CO)_4[P(C_6H_5)_3]_2^+$ and CH_3NH_2.[9]

Reaction of *trans*-$M(CO)_3[P(C_6H_5)_3]_2CONHR$ (M = Mn or Re) with CH_3OH. To an nmr tube containing 0.114 g (1.8 mmol) of $Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ dissolved in 0.7 ml of $CDCl_3$ was added 1.8 mmol of CH_3OH. The room-temperature proton nmr spectrum was recorded periodically over a 30-min period until the integrated ratio of methyl protons at 2.58 ppm, corresponding to those in the methoxycarbonyl group ($-CO_2CH_3$), to phenyl protons was about 1:10 indicating reaction completion. The tube was then broken open, the solvent removed, and the residue extracted with 30 ml of $CHCl_3$. The $CHCl_3$ solution was filtered and reduced to a volume of about 2 ml, and hexane was added to cause precipitation of the white product, *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$; yield 0.084 g (76%).

The same procedures were followed for the reactions of *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CONHC_6H_{11}$ and *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ with excess methanol. The manganese derivative was not isolated as oxidation of the complex took place, but the continual growth of a single band at 2.61 ppm strongly suggests that *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ was produced.

Reaction of $Re(CO)_5CO_2CH_3$ with Hydrazines. On a vacuum line, 1.04 mmol of NH_2NHCH_3 was distilled into an nmr tube containing 0.20 g (0.52 mmol) of $Re(CO)_5CO_2CH_3$ and 0.7 ml of $CDCl_3$ at −196°. The tube was sealed and the room-temperature nmr spectrum recorded. The tube was broken open and the solvent distilled into a reaction flask containing CH_3NCO dissolved in $CHCl_3$. The solution was evaporated to dryness and the residue sublimed at 75° (0.5 mm) to yield the white urea $(CH_3NH)_2CO$ (76%). It was identified by absorptions in its infrared spectrum at approximately 3480, 3400, 1680, 1555, and 1430 cm^{-1} ($CHCl_3$ solvent) and in the nmr spectrum at τ 7.25, J_{HCNH} = 5 Hz, and τ 4.45 (broad) in a 3:1 integrated ratio; its melting point was 106°.

Methanol was identified from the original reaction mixture by gas chromatography. The residue remaining in the nmr tube was extracted with 25 ml of $CHCl_3$. The solvent was reduced under vacuum to about 2 ml. Hexane was added causing a white crystalline precipitate to form. This precipitate was shown to be $Re(CO)_5(NCO)$ as established by comparing its infrared spectrum with that of the known $Re(CO)_5(NCO)$;[10] yield 0.063 g (33%).

Similarly, the reaction of $Re(CO)_5CO_2CH_3$ with $NH_2N(CH_3)_2$ gave the products $Re(CO)_5(NCO)$, $NH(CH_3)_2$, and CH_3OH. With N_2H_4 the identified products were $Re(CO)_5(NCO)$ and CH_3OH although NH_3 was also believed to be produced.

Reactions of *trans*-$Mn(CO)_4L_2^+$ (L = $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$, or $P(C_6H_5)(CH_3)_2$) with N_3^- and Hydrazines. To a solution of 0.24 g (0.29 mmol) of $Mn(CO)_4[P(C_6H_5)_3]_2PF_6$[9] in 25 ml of acetone was added a solution of 0.035 g (0.55 mmol) of NaN_3 dissolved in 5 ml of water. After 3 min of stirring the solution turned cloudy and a bright yellow solid precipitated. This was filtered, dried under high vacuum, and recrystallized from benzene–hexane to yield $Mn(CO)_3[P(C_6H_5)_3]_2(NCO)$; yield 0.113 g (61%); mp 95–96°.

Anal. Calcd for $Mn(CO)_3[P(C_6H_5)_3]_2(NCO)$: C, 68.54; H, 4.75; N, 2.48. Found: C, 68.66; H, 4.70; N, 2.51.

Ir spectrum ($CHCl_3$ solvent): ν(CO) at 2020 (w), 1959 (s), 1928 (m) cm^{-1}; ν(NCO) at 2242 (m) cm^{-1}.

The reactions of *trans*-$Mn(CO)_4[P(C_6H_5)_2CH_3]_2PF_6$ and $Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6$[9] with NaN_3 were carried out in an identical manner. The products *trans*-$Mn(CO)_3[P(C_6H_5)_2CH_3]_2(NCO)$ [44% yield; ir spectrum in $CHCl_3$ solvent: ν(CO) at 2020 (w), 1960 (s), 1925 (m) cm^{-1}; ν(NCO) at 2250 (m) cm^{-1}; mp 145°] and *trans*-$Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2(NCO)$ [40% yield; ir spectrum in $CHCl_3$ solvent: ν(CO) at 2020 (w), 1959 (s), 1923 (m) cm^{-1}; ν(NCO) at 2250 (m) cm^{-1}] were characterized by their very similar infrared spectra.

A typical reaction with a hydrazine follows. A solution of 0.246 g (0.294 mmol) of $Mn(CO)_4[P(C_6H_5)_3]_2PF_6$ and 0.353 mmol of anhydrous hydrazine in 15 ml of $CHCl_3$ was stirred under an N_2 atmosphere for 15 min. The solvent was removed under vacuum and the residue was dissolved in 10 ml of benzene. After concentration to 2 ml, heptane was added to precipitate *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2(NCO)$ in 35% yield. Its infrared spectrum was identical with that of the same compound prepared from the NaN_3 reaction. The reaction with NH_2NHCH_3 gave a 26% yield and with $NH_2N(CH_3)_2$ an 18% yield.

The reactions of *trans*-$Mn(CO)_4[P(C_6H_5)_2CH_3]_2PF_6$ with hydrazines gave *trans*-$Mn(CO)_3[P(C_6H_5)_2CH_3]_2(NCO)$ in the following yields: 25% (NH_2NH_2) and 15% ($NH_2N(CH_3)_2$). The hydrazine reactions of *trans*-$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6$ gave *trans*-$Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2(NCO)$ in the following yields: 19% (NH_2NH_2) and 12% (NH_2NHCH_3 and $NH_2N(CH_3)_2$).

Reactions of *trans*-$Re(CO)_4L_2^+$ with N_3^- and Hydrazines. To a solution of 0.20 g (0.21 mmol) of $Re(CO)_4[P(C_6H_5)_3]_2PF_6$[9] in 35 ml of acetone was added with stirring 0.027 g (0.41 mmol) of NaN_3 dissolved in 5 ml of water. Within several minutes the solution became cloudy and a white precipitate formed which was removed by filtration. It was dried under high vacuum and recrystallized from

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benzene-hexane to yield white crystalline *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$; yield 0.129 g (73%); mp 163-165°.

Anal. Calcd for $Re(CO)_3[P(C_6H_5)_3]_2(NCO)$: C, 56.40; H, 3.59; N, 1.67. Found: C, 56.15; H, 3.67; N, 1.82.

Ir spectrum ($CHCl_3$ solvent): $\nu(CO)$ at 2055 (w), 1960 (s), 1918 (m) cm^{-1}; $\nu(NCO)$ at 2252 (m) cm^{-1}.

A typical preparation of *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$ using hydrazines follows. To a suspension of 0.139 g (0.144 mmol) of $Re(CO)_4[P(C_6H_5)_3]_2PF_6$ in 50 ml of THF under nitrogen was added 0.172 mmol of NH_2NH_2. After stirring for 1 hr, the solution was evaporated to dryness under vacuum. The residue was dissolved in a minimum of benzene, and the solution was filtered. The white product, *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$, 82% yield, precipitated upon addition of hexane. It was identified by its ir spectrum. The same procedure was followed with the other hydrazines giving 54% (with NH_2NHCH_3) and 43% (with $NH_2N(CH_3)_2$) yields.

The reaction of *trans*-$Re(CO)_4[P(C_6H_5)_3]_2PF_6$ with NCO^- also yields *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$, as follows. To 0.30 g (0.35 mmol) of $Re(CO)_4[P(C_6H_5)_3]_2PF_6$ in 50 ml of acetone was added 0.10 g (1.23 mmol) of KNCO. After stirring for 6 hr at room temperature the solvent was removed under vacuum and the residue was dissolved in benzene. After filtering and reducing the volume to 5 ml, the product was precipitated (21% yield) with 20 ml of hexane.

Reaction of *trans*-$M(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ (M = Mn or Re) with Hydrazines. The reactions of NH_2NH_2, NH_2NHCH_3, and $NH_2N(CH_3)_2$ with $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and $Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ were all carried out under identical conditions. As an example, only the reaction of $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ with NH_2NHCH_3 will be given. Under vacuum in an nmr tube were mixed 0.107 g (0.125 mmol) of $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and 0.250 mmol of NH_2NHCH_3 in $CDCl_3$. The proton nmr spectrum was recorded, the tube broken open, and the solvent distilled into a flask containing CH_3NCO. Sublimation gave a 55% yield of the urea $(CH_3NH)_2CO$. The urea and methanol were identified by methods described in the $Re(CO)_5CO_2CH_3$ reaction.

The remaining residue was dissolved in a minimum amount of benzene (10 ml); the solution was filtered and evaporated to a few milliliters. Addition of pentane yielded a white precipitate of the complex *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$; yield 0.03 g (29%). The lower yield (12%) of *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2(NCO)$ is presumably due to oxidation of the complex as evidenced by the rapid solution color change from yellow to green. These isocyanate complexes were identified by comparing their infrared spectra with those of the complexes prepared from $Re(CO)_4[P(C_6H_5)_3]_2^+$ and $Mn(CO)_4[P(C_6H_5)_3]_2^+$. Dimethylamine from the reactions involving $NH_2N(CH_3)_2$ was identified by gas chromatography as was CH_3OH.

Results and Discussion

Synthetic Routes to $Re(CO)_5CONRR'$ Complexes. Four general types of reactions have been used to prepare these derivatives.

Method I. This approach involves the well-established reaction of cationic metal carbonyl complexes with primary and secondary amines at room temperature in an organic solvent[11]

$$Re(CO)_6^+ + 2HNRR' \rightarrow Re(CO)_5CONRR' + H_2NRR'^+ \quad (3)$$

where R and R′ are H or alkyl groups. The monomethylamine complex, $Re(CO)_5CONHCH_3$, has been isolated and characterized. While pure products were not isolated from the reactions of *n*-butylamine, isopropylamine, cyclohexylamine, *sec*-butylamine, ethylamine, *tert*-butylamine, dimethylamine, pyrrolidine, and piperidine, the similarity of the infrared spectra of their reaction solutions (Table I) to that of $Re(CO)_5CONHCH_3$ strongly suggests that these products also have compositions of the type given in eq 3.

In addition to the terminal C-O stretching absorptions, an absorption corresponding to the C-O stretching mode of the -CONRR′ groups would be expected. In $Re(CO)_5CO_2CH_3$ and $Re(CO)_5CON(CH_3)_2$, this absorption appeared with moderate intensity at 1639 and 1625 cm^{-1}, respectively. A broad band about 1570 cm^{-1} in $Re(CO)_5CONHCH_3$ is probably associated with both the N-H bending as well as the C-O stretching mode.

As has previously been reported,[10] with more than 2 mol of amine per mole of $Re(CO)_6^+$, the reaction rapidly proceeds to give the known[12] *cis*-$Re(CO)_4(NHRR')(CONRR')$ derivatives which were identified from their infrared spectra. This reaction presumably proceeds *via* initial formation of $Re(CO)_5CONRR'$ followed by CO replacement by additional amine. This is supported by the rapid reaction of $Re(CO)_5CONRR'$ with excess amine to give $Re(CO)_4(NHRR')(CONRR')$.

The reaction mixture of $Re(CO)_5CONHCH_3$ with equimolar $NH_2CH(CH_3)_2$ in $CDCl_3$ gave an nmr spectrum which indicated the formation of only *cis*-$Re(CO)_4[NH_2CH(CH_3)_2]CONHCH_3$. This result shows that the CH_3NH group does not interchange with $NH_2CH(CH_3)_2$ during the CO replacement reaction.

Method II. This method probably involves nucleophilic attack of the amide ion ($R'RN^-$) on the carbonyl carbon atom of $Re(CO)_6^+$

$$Re(CO)_6^+ + LiNRR' \rightarrow Re(CO)_5CONRR' + LiPF_6 \quad (4)$$

where R = H or CH_3 and R′ = CH_3. Although $Re(CO)_5CONHCH_3$ was isolated, the instability of $Re(CO)_5[CON(CH_3)_2]$ only permitted its characterization by ir and nmr spectroscopy (Tables I and II). Amide ions had previously been reported to react with $Ni(CO)_4$,[13] $Fe(CO)_5$,[14] and $Cr(CO)_6$[15] to give very unstable anionic complexes containing the $M-CONR_2$ group.

Method III. The $Re(CO)_5CONHR$ complexes can also be prepared from the reaction of $Re(CO)_5^-$ with an alkyl isocyanate and $[(C_2H_5)_3NH]Cl$

$$Re(CO)_5^- + RN{=}C{=}O + (C_2H_5)_3NH^+ \rightarrow Re(CO)_5CONHR + (C_2H_5)_3N \quad (5)$$

where R = CH_3, C_2H_5, C_6H_{11}, and $C(CH_3)_3$. Again only the $Re(CO)_5CONHCH_3$ complex was isolated but the oils obtained with C_2H_5NCO, $C_6H_{11}NCO$, and $(CH_3)_3CNCO$ had ir and nmr spectra (Tables I and II) which were identical with those of the same compounds prepared by the other methods.

The reaction (eq 5) presumably involves initial attack of $Re(CO)_5^-$ on the isocyanate C atom to give $Re(CO)_5C(O)NR^-$ which abstracts H^+ from the ammonium salt to yield $Re(CO)_5CONHR$. Analogous reactions have previously been found to occur with $(C_5H_5)W(CO)_3^-$[16] and $(C_5H_5)Fe(CO)_2^-$.[17] The tungsten complex reaction is reversible; thus $(C_5H_5)W(CO)_3CONHCH_3$ reacts with excess $(C_2H_5)_3N$ to give $(C_5H_5)W(CO)_3^-$ and CH_3NCO. In contrast, $Re(CO)_5CONHCH_3$ does not react with $(C_2H_5)_3N$, and like that for $(C_5H_5)Fe(CO)_2CONHCH_3$ the equilibrium associated with reaction 5 apparently lies far to the right. The much higher nucleophilicities[18] (and presumably basicities)[19] of $(C_5H_5)Fe(CO)_2^-$ and $Re(CO)_5^-$ as compared to that of $(C_5H_5)W(CO)_3^-$ are consistent with this result.

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Method IV. Like organic esters, $Re(CO)_5CO_2CH_3$ reacts with amines to produce carbamoyl derivatives and CH_3OH

$$Re(CO)_5CO_2CH_3 + NHRR' \rightleftharpoons Re(CO)_5CONRR' + CH_3OH \qquad (6)$$

The aminolysis of $Re(CO)_5CO_2CH_3$, however, proceeds several orders of magnitude faster than such organic esters as methyl acetate.[20] With primary and secondary amines reaction 6 occurred instantly at room temperature, and even at −10° it was complete within 15 min. Again only $Re(CO)_5CONHCH_3$ was isolated from the reaction, but spectra (Tables I and II) of the reaction mixtures with other amines clearly indicated that these reactions also proceeded according to eq 6.

The extent to which reaction 6 proceeded depended greatly on the nature of the amine. These equilibria were studied by proton nmr spectrometry in $CDCl_3$ solution containing equimolar $Re(CO)_5CO_2CH_3$ and amine (7.45 *M*). The nmr tubes containing the reaction mixtures were thermostated at 34° for 0.5 hr before the spectra were recorded. The ratios of peak integrals did not change over a 12-period. Duplicate runs were within 8% or better of each other. Integrated ratios of the methyl groups of CH_3OH (τ 6.64) and $Re(CO)_5CO_2CH_3$ (τ 6.54) were used to calculate the equilibrium constants, *K*

$$K = \frac{[Re(CO)_5CONRR'][CH_3OH]}{[Re(CO)_5CO_2CH_3][NHRR']}$$

given in Table III. It should be noted, however, that these values were obtained from data at only one set of concentration conditions.

In general the values of *K* for primary amines decrease with increasing bulkiness of the alkyl group, *e.g.*, $NH_2CH_3 \gg NH_2CH_2CH_3 \gg NH_2CH(CH_3)_2 \gg NH_2C(CH_3)_3$. The secondary amines are less reactive than their primary amine counterparts. There is no correlation between the basicities (pK_a) of the amines and their equilibrium constants in this reaction.

Like that of $Re(CO)_6^+$, the reaction of $Re(CO)_5CO_2CH_3$ with a large excess of amine proceeds to give the known *cis*-$Re(CO)_4(NHRR')(CONRR')$.[12] The excess of amine needed is dependent upon the amine used. With CH_3NH_2, a 2:1 mole ratio of amine to complex is sufficient to give this complex whereas a 10:1 ratio is required for *tert*-butylamine. The product of this latter reaction was identified only from its infrared spectrum.

Proton nmr spectra of the $Re(CO)_5CONRR'$ derivatives at ambient temperature are given in Table II. Of particular interest are the two singlet resonances of the CH_3 groups in $Re(CO)_5CON(CH_3)_2$. This suggests that there is restricted rotation around the $C-N(CH_3)_2$ bond as has been found in other $-CON(CH_3)_2$ complexes.[21]

Like other carbamoyl complexes,[2] $Re(CO)_5CONHCH_3$ reacts rapidly with trichloroacetic acid in $CHCl_3$ to give $Re(CO)_6^+$

$$Re(CO)_5CONHCH_3 + Cl_3CCO_2H \rightarrow Re(CO)_6^+ + CH_3NH_3^+ + 2Cl_3CCO_2^- \qquad (7)$$

Unlike the very reactive anionic carbamoyl compounds[13-15] such as $Cr(CO)_5CONR_2^-$ which reacts with $[(C_2H_5)_3O]BF_4$ to give $Cr(CO)_5C(OC_2H_5)NR_2$, $Re(CO)_5CONHCH_3$ reacts with $(C_2H_5)_3O^+$ in CH_2Cl_2 to give $Re(CO)_6^+$ and presumably $NH(CH_3)(C_2H_5)$. The analogous reaction of *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ with $(C_2H_5)_3O^+$ yields $Re(CO)_5(NH_2CH_3)^+$.[12]

Table III. Equilibrium Constants for Reaction 6 in $CDCl_3$ at 34°

Amine	*K*	pK_a
Methylamine	1.54×10^4	10.64
Ethylamine	1.51×10^2	10.67
Dimethylamine	1.91	10.7
Pyrrolidine	1.54	11.27
n-Butylamine	1.21	10.61
Cyclohexylamine	1.0	10.7
sec-Butylamine	1.0	10.56
Isopropylamine	1.0	10.63
Piperidine	0.21	11.12
tert-Butylamine	0.043	10.45

Attempts to replace one or more CO groups in $Re(CO)_5CONHCH_3$ and $Re(CO)_5CO_2CH_3$ with $P(C_6H_5)_3$ were unsuccessful. With excess $P(C_6H_5)_3$ in benzene at room temperature neither complex showed any reaction over a 6-hr period. On refluxing the solutions, $Re(CO)_5CONHCH_3$ decomposed whereas $Re(CO)_5CO_2CH_3$ simply remained unreacted.

Reactions of *trans*-$M(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ (M = Mn or Re) with Amines. The reactions of *trans*-$M(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ ($P(C_6H_5)_3$ groups are trans to each other) with the primary amines NH_2CH_3, $NH_2CH(CH_3)_2$, $NH_2C_6H_{11}$, *n*-$C_4H_9NH_2$, and *sec*-$C_4H_9NH_2$ proceed as (M = Mn or Re)

$$trans\text{-}M(CO)_3[P(C_6H_5)_3]_2CO_2CH_3 + NH_2R \rightleftharpoons trans\text{-}M(CO)_3[P(C_6H_5)_3]_2CONHR + CH_3OH \qquad (8)$$

For M = Re, the reaction is complete in approximately 10 min at 15°; thus it is slower than the analogous reactions of $Re(CO)_5CO_2CH_3$. Equilibrium constants were not obtained for reaction 8 as the methyl group of the methoxycarbonyl moiety ($-CO_2CH_3$) has a resonance at the same position as the nitrogen hydrogen of the free amine making integrated ratios somewhat ambiguous. Qualitatively, however, in a $CDCl_3$ solution of equimolar amine and complex, the reactions of $Re(CO)_5CO_2CH_3$ with primary amines proceeded further toward the products than did those of *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$. This is presumably due to the smaller size of the CO group as compared to $P(C_6H_5)_3$ and also because CO is a better electron-withdrawing group than $P(C_6H_5)_3$ which favors addition of a nucleophile to either the carbon of the $-CO_2CH_3$ or the CO group. As pointed out by Brunner,[22] the most probable site of attack is a CO ligand rather than CO_2CH_3.

In contrast to the reactions of $Re(CO)_5CO_2CH_3$ which with a large excess of amine produce *cis*-$Re(CO)_4(NHRR')(CONRR')$ complexes, both $Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ and $Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ do not undergo at room temperature further substitution of a CO or $P(C_6H_5)_3$ ligand.

Also unlike $Re(CO)_5CO_2CH_3$, these two complexes do not react with secondary amines to yield the corresponding carbamoyl complexes. At room temperature no reaction is observed. This unreactivity is probably related to the reactions of secondary amines with $Re(CO)_4[P(C_6H_5)_3]_2^+$ and $Mn(CO)_4[P(C_6H_5)_3]_2^+$ which are not straightforward and do not yield the carbamoyl complexes as do the reactions of primary amines with these cations.[9]

Interconversion of Carbamoyl and Alkoxycarbonyl Ligands. Equations 6 and 8 depict the aminolysis of the metal alkoxycarbonyl complexes. The reverse of these reactions may also be carried out under mild conditions.

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The reactions of *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ and *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$ with a 10-fold molar excess of CH_3OH in $CDCl_3$ solvent take place at room temperature within approximately 45 min. Under the same conditions, there is essentially no reaction between $Re(CO)_5CONHCH_3$ and CH_3OH. Addition of a catalytic amount of CH_3O^- allowed this reaction to proceed to $Re(CO)_5CO_2CH_3$ within 1 hr. These reactions are much faster than is observed for the alcoholysis of organic amides.

Reactions of *trans*-$M(CO)_4L_2^+$ Complexes with N_3^- and Hydrazines. Like the reaction of $Re(CO)_6^+$ with N_3^- to give $Re(CO)_5(NCO)$,[10] the *trans*-bisphosphine cationic complexes of Mn and Re react readily with azide ion to convert one of the CO groups into an NCO group, *i.e.*

$$trans\text{-}M(CO)_4L_2^+ + N_3^- \rightarrow trans\text{-}M(CO)_3L_2(NCO) + N_2 \tag{9}$$

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 = $P(C_6H_5)_3$. The mechanism[23] of this reaction presumably involves initial N_3^- attack at a carbonyl carbon atom to give $M-C(O)N_3$, which rearranges with loss of N_2 to give M-NCO. The phosphine ligands are trans to each other in the reaction products.

These complexes also react with hydrazine and its methyl-substituted derivatives, NH_2NHCH_3 and $NH_2N(CH_3)_2$, to give the same isocyanato complexes, *i.e.*

$$trans\text{-}M(CO)_4L_2^+ + NH_2NRR' \rightarrow trans\text{-}M(CO)_3L_2(NCO) + RR'NH_2^+ \tag{10}$$

where R and R' are H or CH_3. This reaction presumably[24] proceeds *via* initial hydrazine attack at a carbonyl carbon atom to give a carbazoyl intermediate, $M-C(O)NHNRR'$, which rearranges with loss of $NHRR'$ to M-NCO.

Reactions of Methoxycarbonyl Complexes with Hydrazines. Hydrazine and its methyl-substituted derivatives, NH_2NHCH_3 and $NH_2N(CH_3)_2$, react with $Re(CO)_5CO_2CH_3$, *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, and *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$ according to

$$M(CO)_3L_2CO_2CH_3 + NH_2NRR' \rightarrow M(CO)_3L_2(NCO) + CH_3OH + NHRR' \tag{11}$$

where for M = Re, L = CO or $P(C_6H_5)_3$; for M = Mn, L = $P(C_6H_5)_3$. Although no mechanistic studies have been carried out on this reaction, the similarity of this reaction to that of organic esters (eq 2) and the known occurrence of carbazoyl complexes as intermediates in reactions of cationic metal carbonyl complexes with hydrazines[2] suggest the initial formation of a carbazoyl intermediate (eq 12), which

$$M\text{-}CO_2CH_3 + NH_2NRR' \rightarrow M\text{-}CONHNRR' + CH_3OH \tag{12}$$

rearranges with loss of $NHRR'$ to give the isocyanate product. There was no spectral evidence for a carbazoyl intermediate, but this was presumably due to its rapid decay to the final products. The relatively low yields of the products are probably due to the use of small quantities of reactants rather than the formation of side products. There was no ir or nmr evidence for other products in the reaction solutions.

Registry No. $MeNH_2$, 74-89-5; *i*-$PrNH_2$, 75-31-0; $EtNH_2$, 75-04-7; $BuNH_2$, 109-73-9; $C_6H_{11}NH_2$, 108-91-8; *s*-$BuNH_2$, 13952-84-6; *t*-$BuNH_2$, 75-64-9; Me_2NH, 124-40-3; Et_2NH, 109-89-7; $(CH_2)_4NH$, 123-75-1; $(CH_2)_5NH$, 110-89-4; $LiNHCH_3$, 37123-26-5; CH_3NCO, 624-83-9; EtNCO, 109-90-0; $C_6H_{11}NCO$, 3173-53-3; *t*-BuNCO, 1609-86-5; MeOH, 67-56-1; NaN_3, 26628-22-8; NH_2NH_2, 25415-88-7; NH_2NHCH_3, 60-34-4; $NH_2N(CH_3)_2$, 57-14-7; KNCO, 590-28-3; $[Re(CO)_6]PF_6$, 38656-75-6; $NaRe(CO)_5$, 33634-75-2; $Re(CO)_5CO_2CH_3$, 29832-17-5; *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, 38619-40-8; *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CO_2CH_3$, 38619-41-9; *trans*-$Mn(CO)_4[P(C_6H_5)_3]_2PF_6$, 38426-96-9; *trans*-$Mn(CO)_4[P(C_6H_5)_2CH_3]_2PF_6$, 38496-52-5; *trans*-$Mn(CO)_4[P(C_6H_5)(CH_3)_2]_2PF_6$, 38496-53-6; *trans*-$Re(CO)_4[P(C_6H_5)_3]_2PF_6$, 38496-54-7; $Re(CO)_5(CONHCH_3)$, 38619-38-4; $Re(CO)_5[CONHCH(CH_3)_2]$, 38619-37-3; $Re(CO)_5(CONHC_2H_5)$, 38619-36-2; $Re(CO)_5(CONHBu)$, 38619-35-1; $Re(CO)_5(CONHC_6H_{11})$, 38619-34-0; $Re(CO)_5(CONHBu\text{-}s)$, 38619-33-9; $Re(CO)_5(CONHBu\text{-}t)$, 38619-32-8; $Re(CO)_5[CON(CH_3)_2]$, 38619-31-7; $Re(CO)_5[CON(C_2H_5)_2]$, 38619-30-6; $Re(CO)_5(CONC_4H_8)$, 38619-29-3; $Re(CO)_5(CONC_5H_{10})$, 38619-28-2; *trans*-$Re(CO)_3[P(C_6H_5)_3]_2CONHCH_3$, 38619-42-0; *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2CONHCH_3$, 38466-94-3; $Re(CO)_5(NCO)$, 31340-77-9; *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2(NCO)$, 38673-70-0; *trans*-$Mn(CO)_3[P(C_6H_5)_2CH_3]_2(NCO)$, 38673-71-1; *trans*-$Mn(CO)_3[P(C_6H_5)(CH_3)_2]_2(NCO)$, 33988-80-6; *trans*-$Re(CO)_3[P(C_6H_5)_3]_2(NCO)$, 33990-58-8; $[(C_2H_5)_3NH]Cl$, 554-68-7.

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