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SYNTHESIS AND REACTIONS OF CARBAMOYL CARBONYL COMPLEXES OF RHENIUM(I)

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SUMMARY

$Re(CO)_5Br$ reacts with primary and secondary aliphatic amines, NHRR′, to form the carbamoyl complex, *cis*-$Re(CO)_4(NHRR')(CONRR')$. Anhydrous HCl removes −NRR′ from the carbamoyl group to yield the cation, $[Re(CO)_5(NHRR')]^+$. This cation reacts with NHRR′ to regenerate the carbamoyl complex. With hydrazine, $[Re(CO)_5(NH_2CH_3)]^+$ initially yields the carbazoyl compound, *cis*-$Re(CO)_4(NH_2CH_3)(CONHNH_2)$, which loses NH_3 to give the isocyanate complex *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$ as the final product. Reactions with some methyl-substituted hydrazines proceed in the same manner. The isocyanate complex may also be prepared by reaction of the cation with azide ion, N_3^-. With I^-, the cation yields $Re(CO)_5I$. IR and PMR spectra of the new compounds and mechanisms of their reactions are discussed.

INTRODUCTION

In recent years several transition metal complexes containing the carbamoyl ligand, −C(O)NRR′, have been prepared. Among them are $Mn(CO)_4(NH_2R)(CONHR)$[1], $(\pi\text{-}C_5H_5)Fe(CO)_2(CONRR')$[2,3], *cis*-$Re(CO)_4(NH_2R)(CONHR)$[4], and some less stable carbamoyl complexes derived from $Fe(CO)_5$[5]. An X-ray structural study[6] of *cis*-$Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ has established the basic geometry of the carbamoyl ligand.

It has also been noted that the carbamoyl ligand reacts with gaseous HCl to yield a terminal carbonyl ligand. For example[1]:

$$cis\text{-}Mn(CO)_4(NH_2CH_3)(CONHCH_3)+2\,HCl \rightarrow [Mn(CO)_5(NH_2CH_3)]^+Cl^- + CH_3NH_3^+Cl^-$$

Similarly $(\pi\text{-}C_5H_5)Fe(CO)_2(CONHR)$[3] has been converted to $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ and *cis*-$Re(CO)_4(NH_3)(CONH_2)$[4] to $[Re(CO)_5(NH_3)]^+$. It has been demonstrated[1,3] that the $[Mn(CO)_5(NH_2R)]^+$ and $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ cations react with amine to regenerate the carbamoyl derivatives, $Mn(CO)_4(NH_2R)(CONHR)$ and $(\pi\text{-}C_5H_5)Fe(CO)_2(CONHR)$. Very recently, we found[7] that $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ also reacts with hydrazine and the azide ion to form the isocyanate complex $(\pi\text{-}C_5H_5)Fe(CO)_2(NCO)$ according to the following eqns.:

$$[(\pi\text{-}C_5H_5)Fe(CO)_3]^+ + 2\,NH_2NH_2 \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(NCO) + NH_3 + NH_2NH_3^+$$
$$[(\pi\text{-}C_5H_5)Fe(CO)_3]^+ + N_3^- \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(NCO) + N_2$$

The purposes of the research reported in the present paper were to determine whether rhenium complexes analogous to those of manganese[1] could be prepared and to examine the reactions of $[Re(CO)_5(NH_2CH_3)]^+$ with hydrazines, N_3^-, NCO^-, NCS^-, CN^-, and I^-.

EXPERIMENTAL

The $Re_2(CO)_{10}$ (Pressure Chemical Co. and Strem Chemicals, Inc.) and the hydrazines, N_2H_4-anhydrous, 97%, CH_3NHNH_2 and $(CH_3)_2NNH_2$ were used as obtained from commercial sources. Tetrahydrofuran (THF) was dried over $LiAlH_4$ or CaH_2. All other solvents and materials were reagent grade.

IR spectra were recorded on a Beckman IR-8 spectrophotometer using a polystyrene standard. Mass spectra were obtained on an Atlas CH-4 mass spectrometer. Proton NMR were recorded on a Varian A-60 or a Varian HA-100 spectrometer with tetramethylsilane as the internal standard. Resonance peaks are recorded in δ units (tetramethylsilane: $\delta = 0.0$). Melting points are uncorrected. All of the reactions described were run in a nitrogen atmosphere as a routine precautionary measure.

Preparation of $Re(CO)_5Br$

The following procedure was briefly mentioned in a previous article[8]. An excess of bromine (5 ml) was added to a stirred solution of 5 g of $Re_2(CO)_{10}$ in 250 ml of cyclohexane. When an IR spectrum of the solution indicated that the reaction was complete, the solvent was decanted and the product dried under high vacuum. Its purity was sufficient for use in further syntheses, but it could be further purified by sublimation at 75° (1 mm).

Preparation of cis-$Re(CO)_4(NH_2R)(CONHR)$

Two tenths of a gram (0.49 mmole) of $Re(CO)_5Br$ was partially dissolved in 250 ml of diethyl ether. In the case of CH_3NH_2, the gas was slowly bubbled into the refluxing mixture until its IR spectrum indicated that the reaction was complete (approximately 3 h). The CH_3NH_2 must not be bubbled through the solution too long due to the formation of other products. For isopropylamine, a tenfold excess of the amine was added, and the mixture was stirred at room temperature for 7 h. The voluminous white precipitate ($RNH_3^+Br^-$) which formed during the reaction was filtered off, and the filtrate was evaporated to a white solid under a water aspirator vacuum. If an oil was left, it could usually be precipitated with the addition of pentane (85% yield for the methyl product). The $Re(CO)_4(CONHR)(NH_2R)$ compounds were sufficiently pure for synthetic applications, but for analysis they were washed twice with 5 ml portions of pentane, dried under high vacuum, and sublimed at 60° (0.5 mm). Sublimation of the isopropyl complex is not practical for amounts larger than a few milligrams. The melting point ranges were 111.3–112.3° for the methylamine product and 88.0–89.5° for the isopropylamine product. {Found: C, 21.60; H, 2.34; N, 7.49. $Re(CO)_4(NH_2CH_3)(CONHCH_3)$ calcd.: C, 21.70; H, 2.34; N, 7.32%. Found: C, 29.35; H, 3.63; N, 6.47. $Re(CO_4)[NH_2CH(CH_3)_2][CONHCH(CH_3)_2]$ calcd.: C, 29.79; H, 3.86; N, 6.32%.}

Other primary aliphatic amines such as n-$C_4H_9NH_2$ and $C_6H_{11}NH_2$ also react to give analogous $Re(CO)_4(NH_2R)(CONHR)$ complexes which were only identified by their IR spectra in solution. The stability of these compounds in solution decreases as the size of the R group increases. The carbamoyl complexes of rhenium, both in the solid state and in solution, are more stable than those of manganese[1], and like the manganese compounds, the rhenium complexes are more stable in the solid state than in solution.

Preparation of $Re(CO)_4(NHR_2)(CONR_2)$

The procedure was similar to the one used above with the primary amines. The dimethyl amine and pyrrolidine (NHC_4H_8) products were isolated as white and light yellow solids, respectively, but the piperidine (NHC_5H_{10}) complex remained an oil. Purification of the first two was not successful as indicated by poor analyses and melting point ranges of 7°. Identification of the secondary amine products was based on the similarity of their IR spectra to those for the primary amine products. The secondary amine products are much less stable than those of the primary amines.

Preparation of $[Re(CO)_5(NH_2R)]PF_6$

To 0.2 g of $Re(CO)_4(NH_2R)(CONHR)$ dissolved in 8 ml of benzene was added 30 ml of pentane. Gaseous HCl was slowly bubbled into the solution for about 10 min and the mixture was then allowed to stand at room temperature for $1\frac{1}{2}$ h. The solvent was poured off and the residue evaporated to dryness under high vacuum. After adding 5 ml of water to the solid, the solution was filtered and 0.1 g of NH_4PF_6 was added to precipitate the product. The mixture was evaporated to 3 ml under vacuum and the remaining solution was decanted. After drying under high vacuum, the solid was dissolved in approximately 2 ml of THF, the solution filtered, and the volume reduced. To the solution were added dropwise 10 ml of diethyl ether. The resulting white precipitate (60% yield) was washed twice with 5 ml portions of ether and dried under high vacuum. It could be recrystallized from THF by dropwise addition of ether. {Found: C, 14.55; H, 1.25; N, 3.09. $[Re(CO)_5(NH_2CH_3)]PF_6$ calcd.: C, 14.35; H, 1.00; N, 2.79%. Found: C, 18.44; H, 1.78; N, 2.79. $[Re(CO)_5NH_2CH(CH_3)_2]PF_6$ calcd.: C, 18.12; H, 1.71; N, 2.64%.}

The $[Re(CO)_5(NH_2R)]PF_6$ complexes are very soluble in acetone, slightly soluble in CH_2Cl_2 and insoluble in $CHCl_3$ and hydrocarbon solvents. They slowly decompose in air but are stable for months under vacuum.

Preparation of cis-$Re(CO)_4(NH_2CH_3)(NCO)$

Method 1. *Reaction of $NH_2N(CH_3)_2$ with $[Re(CO)_5(NH_2CH_3)]PF_6$*. To 40 ml of CH_2Cl_2 at room temperature were added with stirring 0.34 g (0.68 mmole) of $[Re(CO)_5(NH_2CH_3)]PF_6$ and 0.085 g (1.4 mmoles) of $H_2NN(CH_3)_2$. After 30 min the solvent was removed using a water aspirator vacuum, and the residue was dissolved in $CHCl_3$. After filtering the solution and reducing its volume to 5 ml, 10 ml of hexane was added to give a white precipitate. The product *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$ (22% yield) was recrystallized by precipitation from a diethyl ether solution with hexane followed by drying under high vacuum. [Found: C, 19.46; H, 1.54;

N, 7.90. $Re(CO)_4(NH_2CH_3)(NCO)$ calcd.: C, 19.41; H, 1.35; N, 7.53%].

Method 2. Reaction of NH_2NHCH_3 with $[Re(CO)_5(NH_2CH_3)]PF_6$. The procedure for this reaction was identical to that in Method 1 except for the use of the different methyl substituted hydrazine. The yield of *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$, identified by its IR spectrum (Table 1), was 27%.

Method 3. Reaction of NH_2NH_2 with $[Re(CO)_5(NH_2CH_3)]PF_6$. This procedure was also analogous to Method 1 with the exceptions that the time was 70 min and the solvent used to precipitate the product, *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$, was pentane.

Method 4. Reaction of NaN_3 with $[Re(CO)_5(NH_2CH_3)]PF_6$. A solution of 0.026 g (0.40 mmole) of NaN_3 in 5 ml of water was added with stirring to a solution of 0.20 g (0.40 mmole) of $[Re(CO)_5(NH_2CH_3)]PF_6$ in 40 ml of acetone. After stirring for 20 min at room temperature, during which time a colorless gas was evolved, the acetone was removed under a water aspirator vacuum, and 10 ml of water was added to the water solution. The desired product was extracted from the mixture with 20 ml of $CHCl_3$. Evaporation of the solution to 5 ml followed by dropwise addition of 10 ml of pentane gave a 21% yield of *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$, identified by its IR spectrum.

Reaction of KI with $[Re(CO)_5(NH_2CH_3)]PF_6$

A solution of 0.10 g (0.60 mmole) of KI in 5 ml of water was added with stirring to a solution of 0.30 g (0.60 mmole) of $[Re(CO)_5(NH_2CH_3)]PF_6$ in 40 ml of acetone. The solution was refluxed for $3\frac{1}{2}$ h. After evaporation to dryness under a high vacuum, $CHCl_3$ was added, the mixture filtered, and its volume reduced to a few milliliters. Upon addition of pentane, an off-white solid precipitated. This was sublimed at 75° (1 mm) giving colorless crystals of $Re(CO)_5I$ (30%), which was identified by its IR spectrum (Table 1).

Attempted Reactions of KNCO, KNCS, and KCN with $[Re(CO)_5(NH_2CH_3)]PF_6$

The reactions of KNCO, KNCS, and KCN with $[Re(CO)_5(NH_2CH_3)]PF_6$ were also tried in a manner similar to that of KI. No reaction occurred with KNCS. For the other two salts, impure products were isolated, but characterization was not successful.

Attempted Reactions of $[Mn(CO)_5(NH_2CH_3)]PF_6$

The reactions of $[Mn(CO)_5(NH_2CH_3)]PF_6$[1] with NaN_3, the hydrazines, KNCS, KNCO, KCN, and KI were tried. IR spectral results showed that the products in many cases were different from those with the rhenium cation. However, the manganese products were much less stable and no products could be isolated and characterized.

DISCUSSION

cis-$Re(CO)_4(NHRR')(CONRR')$ complexes

Primary and secondary aliphatic amines react with $Re(CO)_5Br$ according to eqn. (1):

$$Re(CO)_5Br + 3\,RR'NH \rightarrow cis\text{-}Re(CO)_4(NHRR')(CONRR') + RR'NH_2^+Br^- \qquad (1)$$

The $Re(CO)_4(NHRR')(CONRR')$ products from the reaction with CH_3NH_2 and

$(CH_3)_2CHNH_2$ have been isolated and purified. Their compositions have been established by elemental analysis and their mass spectra which show distinct parent ion peaks. While pure products were not isolated from the reactions of n-butylamine, cyclohexylamine, dimethylamine, pyrrolidine and piperidine, the similarities of their IR spectra (Table 1) to those of the well-characterized methylamine and isopropylamine complexes in the C–O stretching region strongly suggests that these products also have compositions of the type given in eqn. (1).

TABLE 1

INFRARED SPECTRA OF PRODUCTS

Compound	Solvent	Terminal C–O region (cm^{-1})			
$Re(CO)_5I$[a]	CCl_4	2145 w	2042 s	2013 w	1987 m
cis-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$	KBr[b]	2092 m	1990 s	1965 s	1919 s
	CCl_4	2083 w	1984 s		1934 m
cis-$Re(CO)_4[NH_2CH(CH_3)_2][CONHCH(CH_3)_2]$	KBr[b]	2096 m	2008 s	1969 s	1931 s
	CCl_4	2088 w	1976 s		1934 m
cis-$Re(CO)_4(NH_2\text{-n-}C_4H_9)(CONH\text{-n-}C_4H_9)$	$CHCl_3$	2088 m	1980 s		1931 m
cis-$Re(CO)_4(NH_2C_6H_{11})(CONHC_6H_{11})$	$CHCl_3$	2083 m	1984 s		1927 m
cis-$Re(CO)_4[NH(CH_3)_2][CON(CH_3)_2]$	CCl_4	2083 m	1984 s	1969 s	1934 s
cis-$Re(CO)_4(NHC_5H_{10})(CONC_5H_{10})$	CCl_4	2088 m	1984 s	1969 s	1931 s
cis-$Re(CO)_4(NHC_4H_8)(CONC_4H_8)$	CCl_4	2088 m	1984 s	1976 s	1931 s
$[Re(CO)_5(NH_2CH_3)]PF_6$	CH_2Cl_2	2167 vw	2107 w	2052 s	2023 m
$[Re(CO)_5NH_2CH(CH_3)_2]PF_6$	CH_2Cl_2	2169 vw	2105 w	2059 s	2055 s, 2022 m
$Re(CO)_4(NH_2CH_3)(NCO)$[c]	$CHCl_3$	2114 m	2008 s	2000 s	1949 s

[a] See ref. 8. [b] See Discussion for possible carbamoyl C–O assignment. [c] Asymmetric N=C=O stretching frequency at 2247 m cm^{-1}.

Previously it was reported[1] that $Mn(CO)_5Br$ reacted with primary and secondary aliphatic amines analogously to that given for $Re(CO)_5Br$ in eqn. (1). The structure of *cis*-$Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ has been established by an X-ray study[6]. The similarity of the IR spectra of *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ (2083 w, 1984 s, 1934 m, in CCl_4) and *cis*-$Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ (2075 w, 1983 s, 1930 m, in $CHCl_3$)[1] in the terminal C–O stretching region suggests that the structure of the Re complex (Fig. 1) is similar to that already known for the manganese derivative.

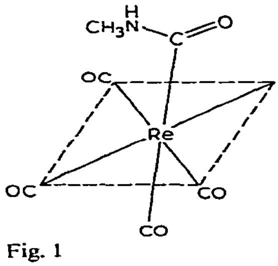

Fig. 1

Behrens and coworkers[4] had previously suggested this structure for *cis*-$Re(CO)_4(NH_3)(CONH_2)$ and *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ which were prepared from $Re(CO)_5Cl$ and NH_3 or CH_3NH_2.

The solid state (KBr pellet) IR spectrum (Table 1)[4] of *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ contains four terminal C–O stretching frequencies; this is the number which is required by the C_s local symmetry of the above structure. In solution the carbamoyl complexes resulting from reaction of $Re(CO)_5Br$ with secondary amines also exhibit four terminal absorptions whereas the complexes of primary amines only show 3 absorptions. The very strong intensity of the middle absorption band in the primary amine products suggests that this absorption is actually a composite of two accidentally degenerate modes. Thus these complexes probably also have four IR active C–O stretching absorptions, which is consistent with the C_s structure shown in Fig. 1.

In addition to the terminal C–O stretching absorptions, one would expect to observe an absorption corresponding to the C–O stretching mode in the –CONHR group. In $(\pi\text{-}C_5H_5)Fe(CO)_2(CONHCH_3)$[3], this absorption appeared with moderate intensity at 1625 cm^{-1}. The compound, *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ in a KBr pellet has absorptions at 1610 m, 1512 m, and 1486 m cm^{-1} which could possibly originate in the carbamoyl C–O stretching mode. Behrens and co-workers[4], who also prepared this compound, assigned the 1610 cm^{-1} absorption to an $-NH_2$ bending mode and the 1512 and 1486 cm^{-1} absorptions to a coupling of the C=O and $C{=}N\!<$ stretching modes in the carbamoyl group. We prepared the deuterated compound *cis*-$Re(CO)_4(ND_2CH_3)(CONDCH_3)$ from $Re(CO)_5Br$ and CH_3ND_2[9] and found that the band at 1610 cm^{-1} must indeed be associated with an N–H bending mode because this absorption is absent in the deuterated complex.

Since $(\pi\text{-}C_5H_5)Fe(CO)_2(CONHCH_3)$[3] exhibits only one band in this region which can be attributed to the carbamoyl group, it seems unlikely that bands corresponding to coupled $\nu(C{=}O)$ and $\nu(C{=}N)$ modes would be observed in the present complex. Probably the 1512 or the 1486 cm^{-1} absorption corresponds to the C–O stretching mode in *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$. It should be emphasized that the bands at 1610, 1512 and 1486 cm^{-1} are much less intense relative to the terminal C–O absorptions when the spectra are recorded in solution than they are in KBr pellets. This was also observed for the manganese analog[1], *cis*-$Mn(CO)_4(NH_2CH_3)(CONHCH_3)$; in that case it was also not possible to make a definite assignment to the C–O stretching mode in the carbamoyl group.

Proton NMR spectral results on the *cis*-$Re(CO)_4(NH_2R)(CONHR)$ products are given in Table 2. For *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$, assignments to the –NH and $-NH_2$ protons were based on integrations. The methyl protons in the

TABLE 2

PROTON NMR SPECTRA[a] OF *cis*-$Re(CO)_4(NH_2R)(CONHR')$ IN $CDCl_3$ SOLVENT

R,R'	NHR'			NH_2R		
	HN	α-CH	β-CH	H_2N	α-CH	β-CH
$R{=}R'{=}CH_3$	5.54 (br)	2.83 (5.1)[b]		4.19 (br)	2.85 (6.4)[b]	
$R{=}R'{=}CH(CH_3)_2$	5.35 (br)	4.26 (6.5)	1.14 (6.5)	4.20 (br)	2.95 (6.5)	1.26 (6.5)
$R{=}CH_3$[c] $R'{=}CH(CH_3)_2$	5.59 (8)	~4.10	1.13 (6.5)	~3.90 (br)	2.81 (6.4)	

[a] Chemical shifts in ppm downfield from tetramethylsilane. Numbers in parentheses are J(H–C–C–H) (Hz), except those labelled [b]. The abbreviation (br) means broad. [b] Number in parentheses is J(H–N–C–H) (Hz). [c] Peaks at 6.42, 3.45, and 1.30 were attributed to $(CH_3)_2CHNH_3^+Br^-$. An NMR spectrum of pure $(CH_3)_2CHNH_3^+Br^-$ gave peaks at 6.07, 3.45 and 1.32 ppm.

NH_2CH_3 ligand (Fig. 1) were split into a triplet and those in the $-CONHCH_3$ group gave a doublet. Since these two splitting patterns badly overlapped, spin decoupling experiments involving the irradiation of the $-NH_2$ and $-NH$ protons were performed. These experiments allowed the methyl groups to be assigned without difficulty as given in Table 2.

For *cis*-$Re(CO)_4[NH_2CH(CH_3)_2][CONHCH(CH_3)_2]$, the $-NH$ and NH_2 protons were again assigned on the basis of integrated intensities. The $-CH$ protons of the ligand amine and the carbamoyl group were assigned to the septuplets at δ 2.95 and 4.26, respectively. Each line of the septuplet at δ 4.26 is split into a doublet, presumably by coupling to the $-NH$ proton in the carbamoyl group. Each line of the septuplet at δ 2.95 is split into a triplet; this is presumably caused by coupling to the $-NH_2$ protons. Spin decoupling experiments were again used to assign the CH_3 protons. These experiments indicated that CH_3 groups at δ 1.14 were bonded to the carbamoyl $-CH$ carbon and those at δ 1.26 were bonded to the amine $-CH$ carbon. The final assignments are given in Table 2.

Previously[1] we suggested a mechanism for the reaction of $Mn(CO)_5Br$ with amines to form *cis*-$Mn(CO)_4(NH_2R)(CONHR)$. We believe the same two steps (eqns. (2) and (3)] to be involved in the analogous $Re(CO)_5Br$ reactions:

$$Re(CO)_5Br + RNH_2 \rightarrow [Re(CO)_5(NH_2R)]^+Br^- \quad (2)$$

$$[Re(CO)_5(NH_2R)]^+Br^- + 2\,RNH_2 \rightarrow Re(CO)_4(NH_2R)(CONHR) + RNH_3^+Br^- \quad (3)$$

Although there is no spectral evidence for the intermediacy of $[Re(CO)_5(NH_2R)]^+Br^-$, it is known (*vide infra*) that this cation reacts very rapidly with amines to form the carbamoyl product according to eqn. (3). Its high rate of reaction with amines suggests that it would probably not be detected in the present reaction even if it did occur as an intermediate. It should be pointed out that the above mechanism has not been established. Behrens and coworkers[4] have suggested that the first step in the reaction of $Re(CO)_5Cl$ with NH_3 to form $Re(CO)_4(NH_3)(CONH_2)$ is NH_3 attack to give $ClRe(CO)_4(CONH_3)$ followed by Cl^- displacement. Our preference for initial formation of $Re(CO)_5(NH_2R)^+$ followed by RNH_2 attack is the demonstrated ease (*vide infra*) with which amines attack cationic metal carbonyl complexes.

Kinetic studies of the reaction of $Re(CO)_5Br$ with n-$C_4H_9NH_2$ in CH_2Cl_2 solvent at 27.5° were conducted by following the rate of disappearance of the most intense C–O stretching absorption in the IR spectrum of $Re(CO)_5Br$. While a thorough investigation was not attempted, the rate of reaction was approximately 1.4 order in n-$C_4H_9NH_2$.

$[Re(CO)_5(NH_2R)]^+$ complexes

The *cis*-$Re(CO)_4(NH_2R)(CONHR)$ complexes react rapidly with anhydrous HCl in a benzene/pentane solvent mixture to remove the $-NHR$ moiety[4] from the carbamoyl group to yield the cation $[Re(CO)_5(NH_2R)]^+$ according to eqn. (4):

$$\textit{cis}\text{-}Re(CO)_4(NH_2R)(CONHR) + 2\,HCl \rightarrow [Re(CO)_5(NH_2R)]^+Cl^- + RNH_3^+Cl^- \quad (4)$$

The cation may be precipitated from water as the hexafluorophosphate salt, $[Re(CO)_5(NH_2R)]PF_6$. The IR spectrum (Table 1) exhibits 4 bands in the C–O stretching region which may be assigned to the following modes of $[Re(CO)_5(NH_2CH_3)]^+$, which has C_{4v} local symmetry:

	$A_1{}^2$	B_1	E	$A_1{}^1$
$[Re(CO)_5(NH_2CH_3)]^+$	2167 vw	2107 w	2052 s	2023 m
$Re(CO)_5Cl^{8,10}$	2156 w		2045 s	1982 m

The IR-forbidden B_1 mode is apparently present in both the $[Re(CO)_5NH_2CH_3]^+$ and $\{Re(CO)_5[NH_2CH(CH_3)_2]\}^+$ cations; in the latter complex (Table 1) the E mode is slightly split, as has been observed previously for $Mn(CO)_5R$, $Re(CO)_5R$[11] and $W(CO)_5NH_2R$[12] compounds with bulky groups on the carbon atom β to the metal.

It would be expected that all of the C–O stretching frequencies of the cation would be higher than those of $Re(CO)_5Cl$ due to decreased back-π-bonding from Re to the CO groups. In fact, the frequencies of the modes associated with the four equivalent CO groups ($A_1{}^2$ and E) are much the same in both compounds. The $A_1{}^1$ mode of the CO *trans* to the non-carbonyl ligand is, however, significantly higher in the cation. This result suggests that the negative charge on the Cl^- ligand is more available to the CO *trans* to it than it is to the *cis* CO groups.

A comparison of the C–O stretching frequencies of the isoelectronic $\{Re(CO)_5[NH_2CH(CH_3)_2]\}^+$ and $W(CO)_5[NH_2CH(CH_3)_2]$[12] complexes indicates that all of the C–O stretching frequencies are roughly 100 cm^{-1} higher in the cation than in the neutral tungsten complex.

	$A_1{}^2$	E	$A_1{}^1$
$\{Re(CO)_5[NH_2CH(CH_3)_2]\}^+$	2169 vw	2057 s*	2022 m
$W(CO)_5[NH_2CH(CH_3)_2]$	2072 vw	1932 s	1919 m

Similar differences in C–O stretching frequencies have previously[13] been reported for $[Re(CO)_6]^+$, 2081 cm^{-1} and $W(CO)_6$, 1997 cm^{-1}.

Reactions of $[Re(CO)_5(NH_2R)]^+$

Upon bubbling gaseous CH_3NH_2 into a room-temperature CH_2Cl_2 solution of $[Re(CO)_5(NH_2CH_3)]PF_6$, formation of the carbamoyl complex, *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$, occurs immediately [eqn. (3)]. This reaction presumably takes place via a nucleophilic attack of the amine on a terminal carbonyl carbon (Re–C≡O), followed by the removal of a proton by excess amine to give the other product $CH_3NH_3^+$. It now appears that CO groups in cationic metal carbonyl complexes are very susceptible to attack by amines and other nucleophiles. Examples of this type of reaction have previously been reported for $[Mn(CO)_5(NH_2R)]^+$ (ref. 1), and $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ (refs. 3 and 7). Work in progress[14] suggests that this is a general reaction for cationic metal carbonyl complexes. The only neutral carbonyl complex which is reported[5] to undergo this reaction is $Fe(CO)_5$ yielding the very unstable $[Fe(CO)_4(CONHR)]^-$.

The mechanism of reaction (3) may be one in which the nucleophilic RNH_2 attacks a terminal carbonyl directly *or* it may involve attack of the amine at the

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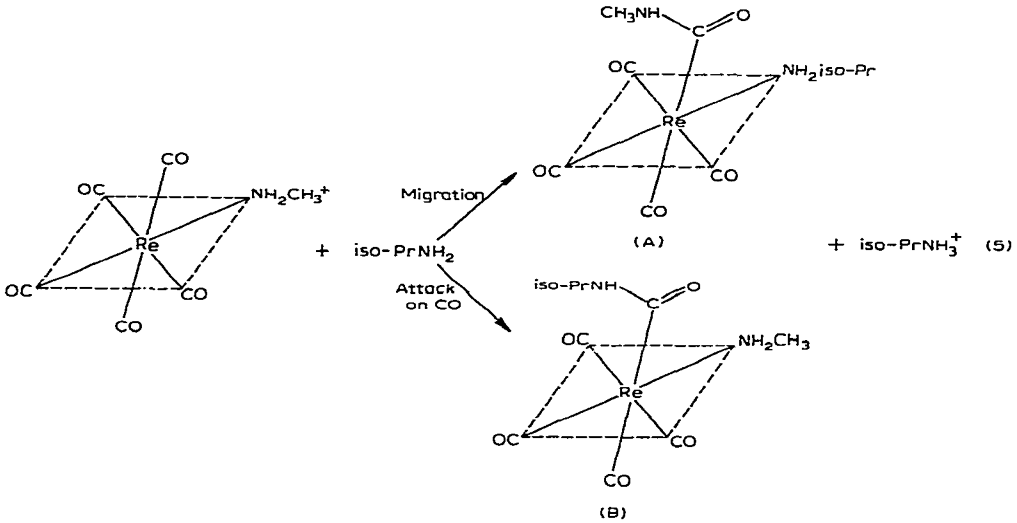
* Average of the two bands of the split E mode.

rhenium atom causing the coordinated amine to migrate to a terminal CO group in the complex. A mechanism involving migration of the methyl group has been established[15] for the reaction of $Mn(CO)_5CH_3$ with $P(C_6H_5)_3$ to form $Mn(CO)_4[P(C_6H_5)_3](COCH_3)$. To determine whether a migration occurred in this case or not the reaction of $[Re(CO)_5(NH_2CH_3)]^+$ with isopropylamine (iso-$PrNH_2$) was carried out. The possible products (A or B) are given in eqn. (5). The reaction was carried out in CH_2Cl_2 solution at room temperature using 2 moles of iso-$PrNH_2$ per mole of $[Re(CO)_5(NH_2CH_3)]PF_6$. After 5 min, the solvent was evaporated. The residue, consisting of the complex and $[(CH_3)_2CHNH_3]PF_6$ was dissolved in $CDCl_3$, and the proton NMR spectrum was recorded. The relative intensities and the chemical shifts (Table 2) of the protons in the product can only be assigned by assuming that it has structure (B). This result suggests that the reaction proceeds by direct attack of iso-$PrNH_2$ on a carbonyl carbon and that CH_3NH_2 migration is *not* involved.



Another reaction of the cation involves that with hydrazines. Earlier work[7] showed that $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ reacts with hydrazine, NH_2NH_2, to form first $(\pi\text{-}C_5H_5)Fe(CO)_2(CONHNH_2)$ which loses NH_3 to finally upon rearrangement yield $(\pi\text{-}C_5H_5)Fe(CO)_2(NCO)$. We have conducted the analogous reaction with the cationic complex, $[Re(CO)_5(NH_2CH_3)]PF_6$. As determined by taking IR spectra of the CH_2Cl_2 reaction solution, an initial fast reaction [eqn. (6)] occurred which produced an intermediate having a spectrum (2096 w, 1992 s and 1942 m cm^{-1}) which is very similar to that of the carbamoyl compounds, *cis*-$Re(CO)_4(NH_2R)(CONHR)$. By analogy with the $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ reaction, we believe this intermediate to be the carbazoyl derivative, *cis*-$Re(CO)_4(NH_2CH_3)(CONHNH_2)$.

$$[Re(CO)_5(NH_2CH_3)]^+ + 2\ NH_2NH_2 \rightarrow \textit{cis}\text{-}Re(CO)_4(NH_2CH_3)(CONHNH_2) + NH_2NH_3^+ \quad (6)$$

$$\textit{cis}\text{-}Re(CO)_4(NH_2CH_3)(CONHNH_2) \rightarrow \textit{cis}\text{-}Re(CO)_4(NH_2CH_3)(NCO) + NH_3 \quad (7)$$

This intermediate more slowly went to form the isocyanate product, *cis*-$Re(CO)_4$-

$(NH_2CH_3)(NCO)$, with the loss of NH_3 [eqn. (7)]. This last reaction presumably occurs by the transfer of the $-N-H$ proton to the $-NH_2$ which then departs as NH_3 (Fig. 2). Migration of the rhenium yields the final isocyanate product.

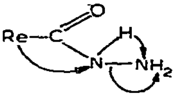


Fig. 2

The methyl-substituted hydrazines, H_2NNHCH_3 and $H_2NN(CH_3)_2$, also reacted with $[Re(CO)_5(NH_2CH_3)]^+$ according to eqns. (6) and (7). The carbazoyl intermediate was detected by IR spectroscopy in both of these reactions. The rate of reaction of the cation to form the isocyanate product increased with the hydrazine as follows: $NH_2NH_2 < NH_2NHCH_3 < NH_2N(CH_3)_2$. This is the same order of reactivity noted[7] in their reactions with $(\pi\text{-}C_5H_5)Fe(CO)_3^+$. IR spectra taken during all of these reactions indicated that the only carbonyl-containing products involved in the reactions were the carbazoyl intermediate and the final isocyanate product. The relatively low yields of the final product are probably due to our use of small quantities of reactants and inefficient work-up procedures and not due to side products in the reaction.

The *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$ exhibits an asymmetric $-N{=}C{=}O$ stretching absorption in its infrared spectrum at 2247 m cm^{-1}. The four terminal C–O stretching frequencies (Table 1) establish[16] the *cis* geometry of the complex.

The cation $[Re(CO)_5(NH_2CH_3)]^+$ also reacts with sodium azide in acetone/water solution to produce *cis*-$Re(CO)_4(NH_2CH_3)(NCO)$, eqn. (7). This reaction presumably proceeds by a mechanism very similar to that suggested for the hydrazine

$$[Re(CO)_5(NH_2CH_3)]^+ + N_3^- \rightarrow cis\text{-}Re(CO)_4(NH_2CH_3)(NCO) + N_2 \qquad (7)$$

reactions. Thus attack by N_3^- would yield the unstable intermediate $Re(CO)_4(NH_2CH_3)(CON_3)$, which rearranges with loss of N_2 to give the isocyanate complex; this latter reaction is analogous to the well-known Curtius reaction of organic chemistry. Kinetic studies of the reaction of $M(CO)_6$, where M = Cr, Mo, or W, with N_3^- to form $[M(CO)_5(NCO)]^-$ and N_2 have previously[17] indicated this mechanism.

Although $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ was found[7,18] to react with NCO^-, NCS^-, CN^- and I^- to form $(\pi\text{-}C_5H_5)Fe(CO)_2(NCO)$, $(\pi\text{-}C_5H_5)Fe(CO)_2(NCS)$, $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$, respectively, only $Re(CO)_5I$ could be isolated from similar reactions of $[Re(CO)_5(NH_2CH_3)]^+$.

$$[Re(CO)_5(NH_2CH_3)]^+ + I^- \rightarrow Re(CO)_5I + CH_3NH_2 \qquad (8)$$

It was identified by its IR spectrum[8]. Reactions of the analogous[1] $[Mn(CO)_5(NH_2CH_3)]PF_6$ with the hydrazines, N_3^-, NCO^-, NCS^-, CN^-, and I^- did not yield products which we were able to purify and characterize.

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REFERENCES

1 R. J. ANGELICI AND D. L. DENTON, *Inorg. Chim. Acta*, 2 (1968) 3; R. J. ANGELICI, *Chem. Commun.*, (1965) 524.
2 R. B. KING, *J. Amer. Chem. Soc.*, 85 (1963) 1918; R. B. KING, M. B. BISNETTE AND A. FRONZAGLIA, *J. Organometal. Chem.*, 5 (1966) 341.
3 L. BUSETTO AND R. J. ANGELICI, *Inorg. Chim. Acta*, 2 (1968) 391.
4 H. BEHRENS, E. LINDNER AND P. PÄSSLER, *Z. Anorg. Allg. Chem.*, 365 (1969) 137; H. BEHRENS, E. LINDNER AND P. PÄSSLER, *Z. Anorg. Allg. Chem.*, 361 (1968) 125.
5 W. F. EDGELL, M. T. YANG, B. J. BULKIN, R. BAYER AND N. KOIZUMI, *J. Amer. Chem. Soc.*, 87 (1965) 3080; W. F. EDGELL AND B. J. BULKIN, *J. Amer. Chem. Soc.*, 88 (1966) 4839.
6 D. M. CHIPMAN AND R. A. JACOBSON, *Inorg. Chim. Acta*, 1 (1967) 393.
7 R. J. ANGELICI AND L. BUSETTO, *J. Amer. Chem. Soc.*, 91 (1969) 3197.
8 J. C. HILEMAN, D. K. HUGGINS AND H. D. KAESZ, *Inorg. Chem.*, 1 (1962) 933.
9 H. J. EMELEUS AND H. V. A. BRISCOE, *J. Chem. Soc.*, (1937) 127.
10 M. A. EL-SAYED AND H. D. KAESZ, *J. Mol. Spectrosc.*, 9 (1962) 310.
11 J. B. WILFORD AND F. G. A. STONE, *Inorg. Chem.*, 4 (1965) 389; K. NOACK, U. SCHAERER AND F. CALDERAZZO, *J. Organometal. Chem.*, 8 (1967) 517.
12 R. J. ANGELICI AND M. D. MALONE, *Inorg. Chem.*, 6 (1967) 1731.
13 W. HIEBER AND TH. KRUCK, *Z. Naturforsch., B*, 16 (1961) 709.
14 R. J. ANGELICI, A. E. KRUSE, L. BLACIK AND B. DOMBEK, to be published.
15 F. CALDERAZZO AND K. NOACK, *Coord. Chem. Rev.*, 1 (1966) 118; K. NOACK AND F. CALDERAZZO, *J. Organometal. Chem.*, 10 (1967) 101.
16 W. HIEBER, G. FAULHABER AND F. THEUBERT, *Z. Anorg. Allg. Chem.*, 314 (1962) 125.
17 H. WERNER, W. BECK AND H. ENGELMANN, *Inorg. Chim. Acta*, 3 (1969) 331; W. BECK, H. WERNER, H. ENGELMANN AND H. S. SMEDAL, *Chem. Ber.*, 101 (1968) 2143.
18 R. K. KOCHHAR AND R. PETTIT, *J. Organometal. Chem.*, 6 (1966) 272.