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Carboxamido Carbonyl Complexes of Manganese(I)

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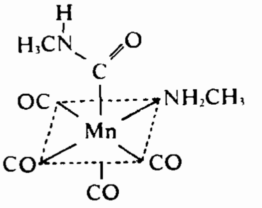
$Mn(CO)_5Br$ reacts with primary aliphatic amines, RNH_2, to form carboxamido complexes, $Mn(CO)_4(CONHR)(NH_2R)$: $Mn(CO)_5Br + 3RNH_2 \rightarrow Mn(CO)_4(CONHR)(NH_2R) + RNH_3^+Br^-$. Their reaction with HCl removes the –NHR group from the carboxamido group according to the equation: $Mn(CO)_4(CONHR)(NH_2R) + 2HCl \rightarrow [Mn(CO)_5(NH_2R)]^+Cl^- + RNH_3^+Cl^-$. The $[Mn(CO)_5(NH_2R)]^+$ ions react instantaneously with amine, RNH_2, to regenerate the carboxamido complex, $Mn(CO)_4(CONHR)(NH_2R)$. Infrared, nmr, and mass spectra of the new compounds are discussed.

Introduction

Phosphines, phosphites, arsines, pyridines and anilines are known to react with $Mn(CO)_5X$, where X is a halogen, to form the mono- and disubstituted derivatives, $Mn(CO)_4(L)X$ and $Mn(CO)_3(L)_2X$.[1,2,3] Even aliphatic amines have been found to yield $Mn(CO)_3(L)_2X$ under fairly rigorous conditions.[4,5] In a preliminary communication,[6] we reported that the initial product in the reaction of $Mn(CO)_5Br$ with primary aliphatic amines was not the CO-substituted compound but instead a substance having the composition $Mn(CO)_5(NHR)(NH_2R)$. On the basis of its infrared spectrum, it was suggested that all seven groups were directly bonded to the metal. Since that time, an x-ray crystallographic study of one of the two crystal modifications was carried out in these laboratories,[7] and the compound was shown to be six coordinated (structure A).



In this paper the details of the preparation and characterization of these complexes will be discussed along with their reactions with HCl to form the $[Mn(CO)_5(NH_2R)]^+$ cations.

Experimental Section

Preparation of $Mn(CO)_4(NH_2R)(CONHR)$. 0.4 g $Mn(CO)_5Br$ was partially dissolved in 150 ml pentane (or ethyl ether). After adding a tenfold excess of the liquid primary amine, RNH_2, the mixture was stirred until all of the $Mn(CO)_5Br$ dissolved. If the amine was a gas, it was slowly bubbled into the $Mn(CO)_5Br$ mixture. Immediately a voluminous white precipitate ($RNH_3^+Br^-$) formed which was filtered off, and the filtrate was evaporated to a pale yellow solid under a water-aspirator vacuum. The solid, $Mn(CO)_4(CONHR)(NH_2R)$, was sufficiently pure for synthetic applications, but for analysis it was washed twice with 1 or 2 ml of pentane and dried under vacuum. Yields ranged from 50 to 70%.

Anal. Calcd. for $Mn(CO)_4(CONHCH_3)(NH_2CH_3)$: C, 32.8; H, 3.54; N, 10.9; mol. wt., 256. Found: C, 32.76, 32.75; H, 3.72, 3.79; N, 11.1; mol. wt., 260 (cryoscopically in benzene). Rather than melting, it slowly decomposed near 75°. The C–O stretching absorptions occur at 2077 (w), 1986 (vs), and 1939 (s) cm^{-1} in pentane.

Mass spectrum[8] of $Mn(CO)_4(CONHCH_3)(NH_2CH_3)$: Relative intensities are given for ions which have m/e values greater than 130. $Mn(CO)_5(NHCH_3)(NH_2CH_3)^+$, parent, 3.6; $Mn(CO)_4(NHCH_3)(NH_2CH_3)^+$, 100; $Mn(CO)_5NH_2CH_3^+$, 12; $Mn(CO)_5(NHCH_3)^+$, 3.4; $Mn(CO)_3(NHCH_3)(NH_2CH_3)^+$, 8.9; $Mn(CO)_4(NH_2CH_3)^+$, 7.0; $Mn(CO)_4(NHCH_3)^+$, 4.6; $Mn(CO)_2(NHCH_3)(NH_2CH_3)^+$, 45; $Mn(CO)_3(NH_2CH_3)^+$, 7.0; $Mn(CO)_3(NHCH_3)^+$, 17.5; $Mn(CO)(NHCH_3)(NH_2CH_3)^+$, 49; $Mn(CO)_2(NH_2CH_3)^+$, 12; $Mn(CO)_2(NHCH_3)^+$, 28.

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(1) W. Hieber and W. Schropp Jr., *Z. Naturforsch.*, *14b*, 460 (1959).
(2) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).
(3) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).
(4) T. H. Coffield and N. Hebert, U.S. Pat. No. 2,902,489, Sept. 1, 1959.
(5) R. J. Angelici, *J. Inorg. Nucl. Chem.*, *28*, 2627 (1966).
(6) R. J. Angelici, *Chem. Comm.*, 524 (1965).
(7) D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, *1*, 393 (1967).
(8) Using Atlas CH4 mass spectrometer at 70 ev electron energies.

Anal. Calcd. for $Mn(CO)_4(CONHC_2H_5)(NH_2C_2H_5)$: C, 38.0; H, 4.59; N, 9.86; mol. wt., 284. Found: C, 37.7; H, 4.50; N, 9.82; mol. wt., 274 (cryoscopically in benzene). It decomposes at about 105° and has absorptions in the infrared at 2076 (w), 1985 (vs), and 1938 (s) cm^{-1} in pentane solution.

Anal. Calcd. for $Mn(CO)_4[CONHCH(CH_3)_2]$-$[NH_2CH(CH_3)_2]$: C, 42.3; H, 5.49; N, 8.97; mol. wt., 312. Found: C, 42.4; H, 5.82; N, 8.71, 8.99; mol. wt., 293 (cryoscopically in benzene). It decomposes with melting near 70° and has C–O stretching absorptions at 2075 (w), 1985 (vs) and 1938 (s) cm^{-1} in pentane.

Other primary aliphatic amines such as n-$C_4H_9NH_2$, t-$C_4H_9NH_2$ and $C_6H_{11}NH_2$ also react to give analogous $Mn(CO)_4(NH_2R)(CONHR)$ complexes which were identified only from their infrared spectra in solution. The stability of these compounds in solution decreases as the size of the R group increases. Where $R = CH_3$, little decomposition is noted in 30 min., but the corresponding propyl complex shows considerable decomposition at room temperature. Products of the decomposition of the methyl derivative at 40-50° were determined by infrared to be N-methylformamide and $Mn_2(CO)_{10}$. In the solid state, they show no decomposition over a period of 3 months when stored in the dark under vacuum. They are hygroscopic and become liquid in minutes on humid days. Upon melting, considerable decomposition to $Mn_2(CO)_{10}$ and other unidentified metal carbonyl compounds occurs.

$Mn(CO)_5Br$ also reacts with ethylenediamine to give a pale yellow solid having an infrared spectrum nearly identical to the above compounds. It is, however, far more senitive to moisture and air and is only very slightly soluble in most polar organic solvents suggesting a polymeric structure. Since the solid begins to decompose at 40°, analyses only roughly supported a composition of $Mn(CO)_4(CONHCH_2CH_2NH_2)$.

Preparation of $[Mn(CO)_5(NH_2R)]^+$. To 0.2 g $Mn(CO)_4(NH_2R)(CONHR)$ dissolved in 5 ml. benzene was added 35 ml. pentane. Gaseous HCl was bubbled into the cloudy solution for about 10 min., and the mixture was then allowed to stand at room temperature for 1½ hours. The solvent was poured off, and the residue evaporated to dryness under a water aspirator vacuum. After adding about 5 ml. H_2O to the solid, the solution was filtered, and about 0.130 g NH_4PF_6 was added to precipitate the product. The mixture was evaporated to about 3 ml. under vacuum and the solid removed by centrifugation. After drying under high vacuum, the solid was dissolved in about 1 ml. acetone and a small amount of insoluble material was removed by centrifugation. To the solution was added 10 ml. of ether dropwise. The resulting pale yellow precipitate was washed twice with 8 ml. portions of ether and dried under vacuum.

Anal. Calcd. for $[Mn(CO)_5NH_2CH_3]PF_6$: C, 19.4; H, 1.35; N, 3.78. Found: C, 19.5; H, 2.00; N, 4.40. The molar conductivity in water (94.0 $ohms^{-1}$ $cm.^{-1}$) compares well with values for known two-ion conductors.[9] To improve the solubility of the cation in organic solvents, it was converted to the $B(C_6H_5)_4^-$ salt. The addition of a saturated aqueous solution of $NaB(C_6H_5)_4$ to a saturated aqueous solution of $[Mn(CO)_5NH_2CH_3]$-PF_6 yielded a white precipitate of $[Mn(CO)_5NH_2CH_3]$-$B(C_6H_5)_4$ which was centrifuged off, washed with water and dried under high vacuum. Its infrared spectrum taken in CH_2Cl_2 is given in Table I.

Anal. Calcd. for $[Mn(CO)_5(NH_2C_2H_5)]PF_6$: C, 21.8; H, 1.82; N, 3.64. Found: C, 21.5; H, 2.06; N, 3.42.

The $[Mn(CO)_5(NH_2R)]PF_5$ complexes are very soluble in acetone, slightly soluble in CH_2Cl_2 and water, and insoluble in $CHCl_3$ and hydrocarbon solvents. In the solid state in air they show significant decomposition within a week but are stable for several weeks under vacuum.

Results and Discussion

The reaction of $Mn(CO)_5Br$ with primary aliphatic amines, RNH_2, yields $Mn(CO)_5(NHR)(NH_2R)$ according to equation (1).

$$Mn(CO)_5Br + 3RNH_2 \rightarrow Mn(CO)_5(NHR)(NH_2R) + RNH_3^+Br^- \quad (1)$$

That this is the composition of the product is established from elemental analyses and cryoscopically determined molecular weight values. Additional evidence from the mass spectrum of $Mn(CO)_5(NHCH_3)(NH_2CH_3)$ shows a distinct parent ion along with fragments corresponding to the loss of CO, $NHCH_3$ and NH_2CH_3. While all primary aliphatic amines which have been studied give analogous derivatives, secondary aliphatic amines such as $(CH_3)_2NH$ and $(C_2H_5)_2NH$ do not. With NH_3, the reaction produces $[Mn(CO)_4(NH_3)_2]Br$, as reported previously.[1]

In one crystalline modification, $Mn(CO)_5(NHCH_3)$-(NH_2CH_3) has been shown[7] to have structure (A). The solid state infrared spectra (in KBr or Nujol) of the compound contain at least five C–O stretching absorptions (Figure 1 and Table I). Although the C_s local symmetry of structure (A) requires only four C–O stretching modes, the presence of two crystalline forms in the solid state accounts for the larger number of observed absorptions in the spectrum. It was initially suspected that the excessive number of C–O stretching absorptions, as compared to the solution spectrum (Figure 1 and Table I), resulted from decomposition in the KBr pellet. This is not true, however, since the compound can be extracted from the pellet with $CHCl_3$ to give a spectrum which is identical to the solution spectrum of $Mn(CO)_5(NHCH_3)(NH_2CH_3)$. The C–O stretching frequency of the carboxamido group of structure (A) might either be the weak absorption at 1610 cm^{-1} or that of medium intensity at 1540 cm^{-1} or that of medium intensity at 1540 cm^{-1}. Both of these are relatively close to the reported 1640 cm^{-1} absorption of a carboxamido complex of iron pentacarbonyl[10] and compare with 1534 cm^{-1} for the carboxamido group in $C_5H_5Fe(CO)_2(CON(C_2H_5)_2)$.[11] More recently[12] we have found that $C_5H_5Fe(CO)_2(CONHC_2H_5)$ exhibits its absorption at 1622 cm^{-1} in methylcyclohexane solvent.

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[9] M. Sneed and J Maynard, "General Inorganic Chemistry", D. Van Nostrand Company, New York, p. 813 (1942).

[10] W. F. Edgell and B. J. Bulkin, *J. Am. Chem. Soc.*, *88*, 4839 (1966).

[11] R. B. King, *J. Am. Chem. Soc.*, *85*, 1918 (1963).

[12] L. Busetto and R. J. Angelici, to be published.

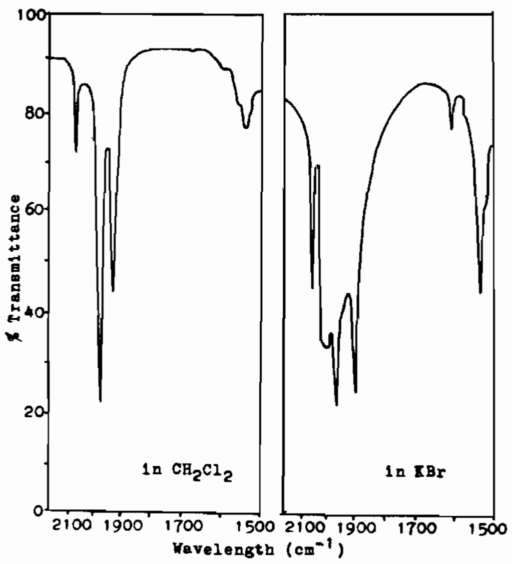

Figure 1. Infrared spectra of Mn(CO)$_4$(CONHCH$_3$)(NH$_2$CH$_3$) in CH$_2$Cl$_2$ solution (left) and in KBr pellet (right).

Table I. Infrared Stretching Frequencies (cm^{-1})

Compound	Solvent	>N–H	–NH$_2$	–C≡O	>C=O
Mn(CO)$_4$(CONHCH$_3$)(NH$_2$CH$_3$)	CHCl$_3$	3463 (w)	3333 (w)	2075 (w) 1983 (s) 1930 (m)	1605 (vw, sh)
	CH$_2$Cl$_2$	3476 (w)	3300 (w)	2077 (w) 1980 (s) 1938 (m)	1596 (vw, sh) 1545 (w)
	KBr pellet	3479 (w)	3264 (w)	2071 (m) 1995 (s, br) 1964 (s) 1893 (s)	1610 (w) 1540 (m)
	Nujol mull	3473 (w)	3260 (w)	2074 (m) 2009 (s) 1984 (s, br) 1962 (s) 1906 (s)	1609 (w) 1540 (m)
[Mn(CO)$_5$(NH$_2$CH$_3$)]$^+$B(C$_6$H$_5$)$_4^-$	CH$_2$Cl$_2$	---	3239 (vw, sh) 3219 (w)	2141 (w) 2055 (vs) 2032 (s)	---
[Mn(CO)$_5$P(C$_6$H$_5$)$_3$]$^+$FeCl$_4^-$ [a]	THF	---	---	2138 (m) 2086 (w) 2046 (vs)	---
Mn(CO)$_5$Cl [b]	CCl$_4$	---	---	2138 (w) 2054 (vs) 1999 (s)	
NH$_2$CH$_3$	CH$_2$Cl$_2$	---	3400 (s)	---	---
$\underset{\overset{\|}{\mathrm{O}}}{\mathrm{HC}}\mathrm{NHCH_3}$	CH$_2$Cl$_2$	3462 (m)	---	---	1696 (s)

[a] T. Kruck and M. Noack, *Chem. Ber.*, 96. 3028 (1963). [b] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, *1*, 933 (1962).

The infrared spectrum of Mn(CO)$_5$(NHCH$_3$)(NH$_2$CH$_3$) in solution significantly differs from that in the solid state. Firstly, there are only 3 terminal C–O stretching frequencies, and secondly, the carboxamido C–O stretching absorption is either very weak or altogether absent. While the compound does not have the expected 4 terminal C–O stretching absorptions required for structure (A), Mn(CO)$_5$(NHC$_2$H$_5$)(NH$_2$C$_2$H$_5$) in CHCl$_3$ solvent shows a distinct shoulder on the most intense absorption at 1980 cm^{-1}. This shoulder could not be detected in any other solvents or with any of the other compounds. This observation does suggest, however, that the most intense band in the solution spectrum results from two accidentally degenerate modes. The spectrum would then be consistent with the C$_s$ symmetry of structure (A).

The two possible absorptions (1610 or 1540 cm.$^{-1}$) which might be assigned to the carboxamido-C–O stretching mode are much weaker in intensity in the solution spectrum (Figure 1). Their assignment to the C–O mode is highly tenuous. The molecule either no longer possesses a carboxamido group (and is perhaps a seven-coordinated complex) or the intensity of this carbonyl absorption has a much lower extinction coefficient in solution than in the solid state, as has been noted for CH$_3$CORe(CO)$_5$.[13] For the sake of simplicity, we will assume that these complexes have structure (A), Mn(CO)$_4$(CONHR)(NH$_2$R), in solution also. The N–H stretching frequency of the carboxamido group supports this structure since it occurs at virtually the same position as the N–H stretch in N-methyl formamide (Table I). The N–H frequency of the NH$_2$CH$_3$ group in the complex is lower than that in the free amine as is usually observed for such compounds.[14] That this frequency is lower in the KBr pellet and Nujol mull spectra than in solution is consistent with the proposed intermolecular hydrogen bonding in the solid.[7]

The proton nuclear magnetic resonance spectra are summarized in Table II. For the methyl derivative,

(13) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, *94*, 862 (1961).

(14) G. W. Watt, B. B. Hutchinson, and D. S. Klett, *J. Am. Chem. Soc.*, *89*, 2007 (1967).

Table II. Proton NMR Spectra[a] of $Mn(CO)_4(CONHR)(NH_2R)$ in $CDCl_3$ Solvent

R	NHR			NH_2R		
	HN–	α–CH	β–CH	H_2N–	α–CH	β–CH
$-CH_3$	5.78 (br)	2.92 (4.3) [b]		3.11 (br)	2.50 (5.7) [b]	
$-CH_2CH_3$	5.70 (br)	3.47 (7.1)	1.22 (7.1)	2.83 (br)	3.38 (7.1)	1.18 (7.1)
$-CH(CH_3)_2$	5.54 (br)	4.38 (~6.1)	1.23 (6.1)	3.05 (br)	2.83 (~6.8)	1.17 (6.8)

[a] Chemical shifts in ppm downfield from tetramethylsilane. Numbers in parentheses are J_{HCCH}, except those labelled b. The abbreviation br means broad. [b] Number in parentheses is J_{HNCH}.

$Mn(CO)_4(CONHCH_3)(NH_2CH_3)$, the methyl protons of the carboxamido group are split into a doublet by the single proton on the nitrogen, and the methyl on the amine is split into a triplet by the two protons on the amine nitrogen. The splittings in the methyl compound and the intensity data allowed us to make assignments by analogy to the other derivatives. It is interesting that the methyl protons in the $-CONHCH_3$ group of $Mn(CO)_4(CONHCH_3)(NH_2CH_3)$ and in $HCONHCH_3$ have similar chemical shifts—2.92 and 2.79 ppm, respectively. The corresponding coupling constants, J_{HNCH}, are 4.3 and 5.0 cps, respectively. Another interesting comparison is that of uncoordinated $(CH_3)_2CHNH_2$ with the amine in $Mn(CO)_4(CONHCH(CH_3)_2)(NH_2CH(CH_3)_2)$. The free amine has chemical shifts of 1.14 (NH_2), 3.09 (α–CH), and 1.04 ppm (β–CH_3). The $-NH_2$ protons shift about 2 ppm downfield upon coordination while the α–CH protons move upfield slightly.

The most intense peak in the mass spectrum of $Mn(CO)_4(CONHCH_3)(NH_2CH_3)$ corresponds to the parent ion minus one CO group. Since it is well known[15] that acylmanganese carbonyls such as $CH_3COMn(CO)_5$ readily lose CO to give the σ-bonded alkyl compounds, *e.g.* $CH_3Mn(CO)_5$, we assume that a similar process readily occurs to yield a high concentration of $Mn(CO)_4(NHCH_3)(NH_2CH_3)^+$ in the mass spectrum. The mass spectrum is dominated by fragments resulting from the loss of CO; amine groups appear to be lost much less readily.

$Mn(CO)_4(CONHR)(NH_2R)$ reacts with HCl in a non-polar solvent to yield the cationic complex, $[Mn(CO)_5(NH_2R)]^+$, according to equation (2).

$$Mn(CO)_4(CONHR)(NH_2R)+2HCl \longrightarrow [Mn(CO)_5(NH_2R)]^+Cl^- + RNH_3^+Cl^- \qquad (2)$$

This cation has been precipitated as the hexafluorophosphate salt which was identified by elemental analysis and molar conductance. The infrared spectra of these complexes in the C–O stretching region are very similar to that of $Mn(CO)_5Cl$ and $[Mn(CO)_5P(C_6H_5)_3]^+$ (Table I). The two highest frequencies of $[Mn(CO)_5NH_2CH_3]^+$ and $Mn(CO)_5Cl$ which primarily correspond to the symmetric and antisymmetric stretching modes of the four equivalent CO groups (A_1+E) are essentially the same. The stretching frequency of the CO *trans* to NH_2CH_3 or Cl^- is noticeably lower in $Mn(CO)_5Cl$ While $[Mn(CO)_5NH_2CH_3]^+$ exhibits only its three infrared allowed absorptions, the intensities of the absorptions of $[Mn(CO)_5P(C_6H_5)_3]^+$ suggest that the 2086 (w) peak is the forbidden B_1 mode and the very strong band at 2046 cm^{-1} is actually a composite of the E and A_1 mode of the CO group *trans* to $P(C_6H_5)_3$. Similar behavior has been observed for the analogous $W(CO)_5NH_2R$ and $W(CO)_5P(C_6H_5)_3$ complexes.[16]

The cation, $[Mn(CO)_5(NH_2R)]^+$, instantaneously reacts (equation (3))

$$[Mn(CO)_5(NH_2R)]^+Cl^- + 2RNH_2 \longrightarrow Mn(CO)_4(CONHR)(NH_2R) + RNH_3^+Cl^- \qquad (3)$$

with NH_2R in CH_2Cl_2 solvent to regenerate $Mn(CO)_4(CONHR)(NH_2R)$, which suggests that the reaction proceeds by a nucleophilic attack of NH_2R on a terminal CO carbon atom. To test this we reacted $[Mn(CO)_5NH_2CH_3]^+$ with $NH_2C_2H_5$ hoping to observe the formation of $Mn(CO)_4(CONHC_2H_5)(NH_2CH_3)$. Unfortunately the only product obtained was $Mn(CO)_4(CONHC_2H_5)(NH_2C_2H_5)$ as determined from the nmr spectrum. Since under the same conditions $Mn(CO)_4(CONHCH_3)(NH_2CH_3)$ reacts only very slowly with $C_2H_5NH_2$ to form $Mn(CO)_4(CONHC_2H_5)(NH_2C_2H_5)$, it appears that the reaction of $[Mn(CO)_5NH_2CH_3]^+$ with $C_2H_5NH_2$ first produces $[Mn(CO)_5NH_2C_2H_5]^+$ which then reacts rapidly with additional $C_2H_5NH_2$ to form $Mn(CO)_4(CONHC_2H_5)(NH_2C_2H_5)$. Hence it is not clear whether the carboxamido group formation occurs as a result of RNH_2 attack directly on a carbonyl carbon atom or from the migration of the RNH_2 group in $[Mn(CO)_5NH_2R]^+$ to a carbonyl carbon atom with simultaneous attack of RNH_2 on the Mn atom. That the presence of an RNH_2 group in the complex is not necessary for the formation of a carboxamido carbonyl compound[12] suggests that its generation is the result of a direct attack of RNH_2 on a carbonyl carbon atom. Attempted reactions of $[Mn(CO)_5NH_2CH_3]^+$ with CO and $P(C_6H_5)_3$ in CH_2Cl_2 were very slow at room temperature and gave no isolable products at higher temperatures.

The fast reaction of $[Mn(CO)_5NH_2R]^+$ with NH_2R to form $Mn(CO)_4(CONHR)(NH_2R)$ suggests that the reaction of $Mn(CO)_5Br$ with NH_2R proceeds according to the following mechanism:

$$Mn(CO)_5Br + NH_2R \longrightarrow [Mn(CO)_5NH_2R]^+Br^- \qquad (4)$$

$$[Mn(CO)_5NH_2R]^+Br^- + 2NH_2R \longrightarrow Mn(CO)_4(CONHR)(NH_2R) + RNH_3^+Br^- \qquad (5)$$

Reaction (4) apparently occurs via a nucleophilic attack

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(15) F. Calderazzo and F. A. Cotton, *Inorg Chem.*, *1*, 30 (1962).

(16) R. J. Angelici and Sr. M. D. Malone, *Inorg. Chem.*, *6*, 1731 (1967).

by NH_2R on $Mn(CO)_5Br$ since the overall reaction takes place much faster than the known S_N1 rates of dissociation of Br or CO from $Mn(CO)_5Br$.[3,17] Attempts to prepare $[Mn(CO)_5NH_2R]^+$ by using a deficiency of RNH_2 yielded only unreacted $Mn(CO)_5Br$ and $Mn(CO)_4(CONHR)(NH_2R)$, suggesting that step (5) occurs much faster than reaction (4).

Preliminary work indicates that $Re(CO)_5Br$ reacts with amines to form complexes which are analogous to those discussed in this paper.[18]

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(17) W. Hieber and K. Wollmann, *Chem. Ber.*, 94, 305 (1961).

(18) A. E. Kruse and R. J. Angelici, to be published.