cases. These observations could be taken as additional evidence that the chemistry of excited states is definitely different from that of the ground state.[14]

Although cobalt(III) photochemistry is in general rather different from that of chromium(III),[14] in a recent paper ligand-field excitation of the analogous $Co(NH_3)_5(OCOCH_3)^{2+}$ ion is reported to cause mainly NH_3 aquation (with $\phi = 0.01$).[33] It is suggested that for d–d states of cobalt(III) acidoammines NH_3 release may be a much more common process than previously thought.[14]

The present results are pertinent to the dispute as to whether or not Adamson's rules imply stereochemical consequences in the configuration of photolysis products.[14,15,34-36] The main products of acidopentaammine photoaquation, i.e., $Cr(NH_3)_4(H_2O)X^{2+}$, were reported to be the trans isomer when $X = NCS$[15,37] and the cis isomer when $X = Cl$[16,35] and Br.[18] Our results for $X = RCOO$ suggest that cis-$Cr(NH_3)_4(H_2O)$-$(OCOR)^{2+}$ is the species preferentially formed. It has been pointed out[36] that stereomobility in chromium(III) photolysis may be the rule, rather than the exception, in contrast to the retention of configuration observed for thermal aquation. The behavior of $trans$-$Cr(en)_2Cl_2^+$ provides the first clear-cut demonstration of such a stereochemical change: the photo-

reaction is one of chloride aquation (the weak-field axis is the one labilized), yet most of the photoproduct is the cis isomer.[38] A dramatic example that stereomobility may be necessary for photosubstitution to occur is offered by the photoinertness of $trans$-$Cr(cyclam)Cl_2^+$ in which stereorigidity of the octahedral framework is imposed by the cyclam ring.[39,40] In the present case, while the mode of photoreaction is correctly predicted by the rules, no information can be gained knowing only the isomer produced, the final configuration of which could depend on how collapse takes place in the structure of the thermally equilibrated (quartet) excited state produced after light absorption.[39] The stereospecificity or otherwise cannot be decided, unless the particular NH_3 ligand photoreleased can be determined. It follows that the acidopentaammine complexes are not adapted for testing any stereochemical aspects of photolysis.

Investigations in our laboratory on several more suitable systems, such as $trans$-$Cr(NH_3)_4XY$,[41] do confirm that stereomobility is always involved. The ligands preferentially aquated are, in all cases, again those predicted by the empirical rules, while the photoproducts are exclusively in the cis configuration.

(33) E. R. Kantrowitz, M. Z. Hoffmann, and J. F. Endicott, *J. Phys. Chem.*, **75**, 1914 (1971).
(34) A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).
(35) M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).
(36) A. D. Kirk, *J. Amer. Chem. Soc.*, **93**, 283 (1971).
(37) Recent work in this laboratory shows that also in this case the major part of the photoproduct is the cis isomer.

(38) A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971).
(39) C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc*, **93**, 5581 (1971).
(40) cyclam = 1,4,8,11-tetraazacyclotetradecane.
(41) P. Riccieri and E. Zinato, unpublished results.

Contribution from the Institute for Atomic Research and the Department of Chemistry,
Iowa State University, Ames, Iowa 50010

# Carboxamido Complexes of (Arene)tricarbonylmanganese(1+). A Correlation with Infrared Data[1]

By ROBERT J. ANGELICI[*2] and LAWRENCE J. BLACIK

The $(\pi$-arene)$Mn(CO)_3^+$ complexes react with primary alkylamines, (arene)$Mn(CO)_3^+ + 2RNH_2 \rightleftarrows$ (arene)$Mn(CO)_2$-$CONHR + RNH_3^+$, to give carboxamido complexes, where the arene is toluene, p-xylene, mesitylene, durene, or $C_6(CH_3)_6$. In a few cases, the carboxamido complex may be isolated, but generally the reversibility of the reaction allows the isolation of only starting (arene)$Mn(CO)_3^+$ when the solutions are evaporated to dryness. Qualitative equilibrium studies indicate the reaction proceeds further to the right when the electron density at the carbonyl carbon atom is reduced by decreasing the number of CH_3 groups in the arene. Since the electron density at a carbonyl carbon is reflected by its C–O stretching force constant, these constants have been correlated with the tendency of carbonyl groups to react with amines to form carboxamido complexes. This correlation extends to complexes of Fe, Ru, Mn, Re, Pd, Pt, Mo, and W. The (arene)-$Mn(CO)_3^+$ complexes also react with hydrazine to yield (arene)$Mn(CO)_2(NCO)$ derivatives.

Introduction

Recently we have reported the reactions of a variety of cationic metal carbonyl complexes with primary and secondary alkylamines to form carboxamido complexes.

$$L_nM\!-\!C\!\equiv\!O^+ + 2RNH_2 \longrightarrow L_nM\!-\!\overset{\overset{\displaystyle O}{\|}}{C}NHR + RNH_3^+ \quad (1)$$
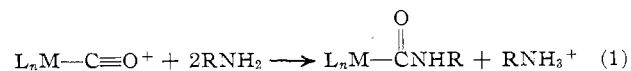
This route has been used to prepare carboxamido complexes of Fe,[3] Ru,[4] Mn,[5] Re,[6] Pd,[7] Pt,[7] Mo,[8] and W.[8]

(3) L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968).
(4) A. E. Kruse and R. J. Angelici, *J. Organometal. Chem.*, **24**, 231 (1970).
(5) R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, **2**, 3 (1968).
(6) R. J. Angelici and A. E. Kruse, *J. Organometal. Chem.*, **22**, 461 (1970).
(7) C. R. Green and R. J. Angelici, *Inorg. Chem.*, in press.
(8) W. Jetz and R. J. Angelici, *J. Amer. Chem. Soc.*, **94**, 3799 (1972).

Other ligands (L$_n$ of eq 1) in the complexes included phosphines, amines, CO, Cl, and the cyclopentadienyl group. In the present investigation, we have extended these reactions to the (arene)tricarbonylmanganese-(1+) cations.

On the other hand, the tris(alkylamine)tricarbonylmanganese(1+) ions do not react with amines to yield carboxamido complexes. These variations in reactivity of the coordinated carbonyl group have been correlated with their C–O stretching force constants for a wide range of complexes. It appears possible to predict on the basis of force constants which carbonyl groups will react according to eq 1.

Experimental Section

Materials.—The [(arene)Mn(CO)$_3$]$^+$ complexes were prepared by a method reported by Coffield, Sandel, and Closson[9] and later described in more detail by Winkhaus, Pratt, and Wilkinson.[10] A typical preparation involved refluxing a mixture of 7.3 mmol of Mn(CO)$_5$Br, 11 mmol of AlCl$_3$, and 51 mmol of the arene in 130 ml of hexane until CO evolution ceased (8–33 hr). This reaction mixture was worked up as described[10] to give yields of the products ranging from 36 to 76%. The method of Abel, Bennett, and Wilkinson[11] was used to prepare [(dien)Mn(CO)$_3$]I from [(mesitylene)Mn(CO)$_3$]I.

Winkhaus and Singer[12] briefly reported the synthesis of [C$_6$-(CH$_3$)$_6$Re(CO)$_3$]$^+$. We prepared this complex according to details kindly provided by G. Winkhaus as follows: a mixture of 0.52 g (1.4 mmol) of Re(CO)$_5$Cl,[6] 0.70 g (4.3 mmol) of hexamethylbenzene, 1.2 g (8.7 mmol) of AlCl$_3$, and 29 ml of tridecane (*n*-C$_{13}$H$_{28}$) was allowed to reflux for 9 hr at 125°. The product, [C$_6$(CH$_3$)$_6$Re(CO)$_3$]PF$_6$ (19% yield), was obtained from this mixture as described for the manganese analogs[10] and finally precipitated from water with 0.24 g (1.5 mmol) of NH$_4$PF$_6$. The complex [(NH$_3$)$_3$Re(CO)$_3$]Cl was obtained in 52% yield from Re$_2$(CO)$_{10}$, NH$_4$Cl, and NH$_3$ according to the method of Behrens and Pässler.[13]

All syntheses were carried out under a nitrogen atmosphere in dry solvents. Infrared spectra and proton nmr spectra were recorded on the Beckman IR-12 and Varian A-60 spectrometers, respectively. The mass spectra were obtained on an Atlas CH-4 spectrometer.

C$_6$(CH$_3$)$_6$Mn(CO)$_2$CONHC$_6$H$_{11}$.—The complex [C$_6$(CH$_3$)$_6$Mn-(CO)$_3$]PF$_6$ (0.55 g, 1.2 mmol) was dissolved in 3 ml (30 mmol) of cyclohexylamine. On stirring at room temperature the product precipitated. After 15 min, the yellow precipitate was filtered and dried under vacuum. It was recrystallized by dissolving it in about 450 ml of hexane. The solution was filtered and was reduced in volume under vacuum until it became cloudy. The cloudy solution was cooled to −78° to complete the precipitation of the yellow product (38% yield).

Anal. Calcd for C$_6$(CH$_3$)$_6$Mn(CO)$_2$CONHC$_6$H$_{11}$: C, 63.1; H, 7.57; N, 3.51. Found: C, 62.1; H, 7.33; N, 3.39.

A mass spectrum run at 70 eV showed the following major metal-containing ions and their intensities: C$_6$(CH$_3$)$_6$Mn(CO)$_2$-CONHC$_6$H$_{11}$$^+$, 0.8; C$_6$(CH$_3$)$_6$Mn(CO)CONHC$_6H_{11}$$^+$, 3.3; C$_6$(C-H$_3$)$_6$MnCONHC$_6H_{11}$$^+$, 11; C$_6$(CH$_3$)$_6$MnNHC$_6H_{11}$$^+$, 14; C$_6$(C-H$_3$)$_6$Mn(CO)$_3$$^+$, 23; [C$_6$(CH$_3$)$_5$(CH$_2$)]Mn(CO)$_3$$^+$, 47; C$_6$(CH$_3$)$_6$-Mn(CO)$_2$$^+$, 6; C$_6$(CH$_3$)$_6$Mn(CO)$^+$, 21; C$_6$(CH$_3$)$_6Mn^+$, 100. The loss of a CO entity from C$_6$(CH$_3$)$_6$MnCONHC$_6$H$_{11}$ to form C$_6$(C-H$_3$)$_6$MnNHC$_6$H$_{11}$ was supported by a metastable peak at *m/e* 289, *i.e.*, (315)^2/343.

C$_6$(CH$_3$)$_6$Mn(CO)$_2$CONH$_2$.—On adding 0.244 g (0.547 mmol) of [C$_6$(CH$_3$)$_6$Mn(CO)$_3$]PF$_6$ to 35 ml of liquid NH$_3$, a bright yellow precipitate formed. After stirring for 2.5 hr, it was filtered off and dried under vacuum.

Anal. Calcd for C$_6$(CH$_3$)$_6$Mn(CO)$_2$CONH$_2$: C, 56.8; H, 6.35. Found: C, 56.8; H, 6.14.

The analogous (mesitylene)Mn(CO)$_2$CONH$_2$ was prepared in the same way; however, the compound decomposes during the

period of a day even in the dark under a nitrogen atmosphere. It was identified by its infrared spectrum (Table I).

[(C$_6$H$_{11}$NH$_2$)$_3$Mn(CO)$_3$]PF$_6$.—As soon as 0.202 g (0.558 mmol) of [(C$_6$H$_6$)Mn(CO)$_3$]PF$_6$ had dissolved in 2 ml (20 mmol) of cyclohexylamine, the solution was evaporated to dryness. The residue was dissolved in a minimum of CH$_2$Cl$_2$ and hexane was added to precipitate 0.219 g (68%) of the greenish yellow product.

Anal. Calcd for [(C$_6$H$_{11}$NH$_2$)$_3$Mn(CO)$_3$]PF$_6$: C, 43.4; H, 6.76; N, 7.23. Found: C, 43.8; H, 6.64; N, 7.21.

The analogous complex, {[(CH$_3$)$_2$CHNH$_2$]$_3$Mn(CO)$_3$}PF$_6$, was prepared in the same way using isopropylamine and was identified by its ir spectrum (Table II).

{[(CH$_3$)$_2$CHNH$_2$]$_3$Re(CO)$_3$}PF$_6$.—The complex [C$_6$(CH$_3$)$_6$Re-(CO)$_3$]PF$_6$ (0.08 g, 0.14 mmol) was dissolved in 2 ml (35 mmol) of isopropylamine. After 15 min, the amine was evaporated under vacuum. The solid was washed with cyclohexane, leaving the white product.

Anal. Calcd for {[(CH$_3$)$_2$CHNH$_2$]$_3$Re(CO)$_3$}PF$_6$: C, 24.3; H, 4.59. Found: C, 24.1; H, 4.75.

C$_6$(CH$_3$)$_6$Mn(CO)$_2$(NCO).—CH$_2$Cl$_2$ (10 ml) was distilled onto 0.528 g (1.18 mmol) of [C$_6$(CH$_3$)$_6$Mn(CO)$_3$]PF$_6$ at −196°. To this was added 0.5 ml (16 mmol) of NH$_2$NH$_2$. As the solution warmed to room temperature it became dark red. After 3 hr the mixture was filtered and evaporated to an orange-red solid. Hexamethylbenzene was removed by sublimation at 50–60° for 15 hr. The red residue was dissolved in about 6 ml of CHCl$_3$. Upon adding 50 ml of hexane, 0.080 g (yields ranged from 20 to 30%) of the red product precipitated.

Anal. Calcd for C$_6$(CH$_3$)$_6$Mn(CO)$_2$(NCO): C, 57.1; H, 5.76; N, 4.44. Found: C, 55.5; H, 5.80; N, 4.44. This compound decomposes even under a nitrogen atmosphere. Its characterization also rests on its infrared spectrum (Table I; see Discussion). The same product was obtained by allowing methyl-substituted hydrazines, CH$_3$NHNH$_2$ and (CH$_3$)$_2$NNH$_2$, to react with [C$_6$(CH$_3$)$_6$Mn(CO)$_3$]PF$_6$.

The analogous (mesitylene)Mn(CO)$_2$(NCO) was prepared by the same method, but it was even less stable than the hexamethylbenzene derivative. It was identified only by its infrared spectrum (Table I).
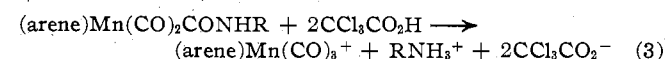
Results and Discussion

Carboxamido Complexes.—The (arene)Mn(CO)$_3$$^+$ complexes react with amines to form carboxamido complexes according to the equation

$$\text{(arene)Mn(CO)}_3{}^+ + 2\text{RNH}_2 \rightleftharpoons$$
$$\text{(arene)Mn(CO)}_2\text{CONHR} + \text{RNH}_3{}^+ \quad (2)$$
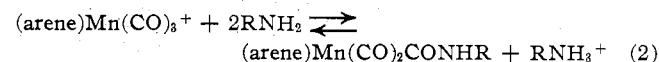
For arene = C$_6$(CH$_3$)$_6$ and R = H or C$_6$H$_{11}$, the product precipitates from the amine solution. The cyclohexyl derivative is the more stable, yet even it rapidly decomposes in CHCl$_3$, CCl$_4$, CH$_2$Cl$_2$, dimethyl sulfoxide, and acetone solutions usually giving a precipitate. It is stable but not very soluble in cyclohexane, while it is quite soluble and relatively stable in dry deaerated benzene. The infrared spectrum (Table I) of C$_6$-(CH$_3$)$_6$Mn(CO)$_2$CONHC$_6$H$_{11}$ is characterized by two terminal C–O stretching absorptions and a weaker absorption at 1589 cm^{-1} which corresponds to a combination of the carboxamido C–O stretching mode and an N–H bending mode.[6] The proton nmr spectrum of C$_6$-(CH$_3$)$_6$Mn(CO)$_2$CONHC$_6$H$_{11}$ in benzene solvent shows a singlet at τ 7.87 for the CH$_3$ groups and a very broad resonance at about τ 8 due to the C$_6$H$_{11}$ group. We attribute the poor resolution to the presence of small amounts of paramagnetic Mn(II).

Both C$_6$(CH$_3$)$_6$Mn(CO)$_2$CONHC$_6$H$_{11}$ and C$_6$(CH$_3$)$_6$-Mn(CO)$_2$CONH$_2$ react rapidly with trichloroacetic acid in hexane solvent as follows

$$\text{(arene)Mn(CO)}_2\text{CONHR} + 2\text{CCl}_3\text{CO}_2\text{H} \longrightarrow$$
$$\text{(arene)Mn(CO)}_3{}^+ + \text{RNH}_3{}^+ + 2\text{CCl}_3\text{CO}_2{}^- \quad (3)$$

The reaction of carboxamido complexes with strong acids to produce cationic carbonyl complexes appears

(9) T. H. Coffield, V. Sandel, and R. D. Closson, *J. Amer. Chem. Soc.*, **79**, 5826 (1957).

(10) G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961).

(11) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 2323 (1959).

(12) G. Winkhaus and H. Singer, *Z. Naturforsch. B*, **18**, 418 (1963).

(13) H. Behrens and P. Pässler, *Z. Anorg. Allg. Chem.*, **365**, 128 (1969).

TABLE I
IR SPECTRA OF COMPOUNDS IN CH_2Cl_2 SOLVENT

Compd	ν(C–O), cm^{-1}
$[(C_6H_6)Mn(CO)_3]PF_6{}^a$	2079 s, 2024 s
$(Toluene)Mn(CO)_2CONHC_6H_{11}$	1968 vs, 1912 s
$(p\text{-Xylene})Mn(CO)_2CONHC_6H_{11}$	1964 vs, 1905 s
$(Mesitylene)Mn(CO)_2CONHC_6H_{11}$	1957 vs, 1902 s
$(Mesitylene)Mn(CO)_2CONH_2{}^b$	1965 s, 1910 s^c
$(Durene)Mn(CO)_2CONHC_6H_{11}$	1951 vs, 1893 s
$C_6(CH_3)_6Mn(CO)_2CONHC_6H_{11}$	1943 vs, 1882 s
$C_6(CH_3)_6Mn(CO)_2CONHC_6H_{11}$	1961 s, 1886 s^d
$C_6(CH_3)_6Mn(CO)_2CONH_2$	1939 s, 1875 s^e
$(Mesitylene)Mn(CO)_2CONHNH_2$	1964 s, 1906 s
$C_6(CH_3)_6Mn(CO)_2CONHNH_2$	1948 s, 1888 s
$(Mesitylene)Mn(CO)_2(NCO)$	1997 s, 1951 s^f
$C_6(CH_3)_6Mn(CO)_2(NCO)$	1982 s, 1927 s^g

^{a} In acetone solvent. ^{b} In CHCl$_3$ solvent. ^{c} Carboxamido ν(C–O) and δ(N–H) at 1575 (m) cm^{-1}. ^{d} In cyclohexane; carboxamido ν(C–O) and δ(N–H) at 1589 (w, br) cm^{-1}. ^{e} In Nujol; carboxamido ν(C–O) and δ(N–H) at 1546 (m) cm^{-1}. ^{f} Asymmetric NCO stretching absorption at 2243 (m) cm^{-1}. ^{g} Asymmetric NCO stretching absorption at 2244 (m) cm^{-1}.

to be a general one[3-7] and is a convenient chemical means of confirming the presence of a carboxamido complex.

Attempts to isolate other (arene)Mn(CO)$_2$CONHR complexes were frustrated by their extreme instability and the reversibility of reaction 2. To illustrate the latter point, when $[C_6(CH_3)_6Mn(CO)_3]PF_6$ and $C_6H_{11}NH_2$ were allowed to react in CH_2Cl_2, the carboxamido product was present as indicated by ir and nmr spectra of the solution. Yet on evaporating the solution to dryness, only the starting $[C_6(CH_3)_6Mn(CO)_3]$-PF$_6$ was obtained.

This equilibrium was further confirmed by adding increasing amounts of $C_6H_{11}NH_2$ to a CH_2Cl_2 solution of $[C_6(CH_3)_6Mn(CO)_3]PF_6$. This caused the carboxamido ir bands (1943, 1882 cm^{-1}) to be augmented at the expense of those of the starting cation (2064, 2059, 2003 cm^{-1}). The same behavior was observed for the other cations $[(durene)Mn(CO)_3]I$,[14] $[(mesitylene)Mn$-$(CO)_3]PF_6$,[14] $[(p\text{-xylene})Mn(CO)_3]PF_6$, and $[(toluene)$-$Mn(CO)_3]PF_6$ (see Tables I and II for ir spectra of these reactants and products).

Likewise, nmr spectra of CH_2Cl_2 solutions of $[C_6$-$(CH_3)_6Mn(CO)_3]PF_6$ containing increasing concentrations of $C_6H_{11}NH_2$ showed an increase of the $C_6(CH_3)_6$-$Mn(CO)_2CONHC_6H_{11}$ methyl resonance (τ 7.80) with a simultaneous decrease of the $[C_6(CH_3)_6Mn(CO)_3]PF_6$ methyl resonance (τ 7.55). It was necessary to record these spectra quickly to avoid broadening caused by decomposition to paramagnetic Mn(II).

Attempts were made to determine an equilibrium constant for reaction 2 with $[C_6(CH_3)_6Mn(CO)_3]PF_6$ and $C_6H_{11}NH_2$. However, constant values were not obtained for reasons which are not clear; it may be that ion pairing was responsible for the deviations observed. Nevertheless, it was of interest to determine semiquantitatively what effect the number of methyl groups in the arene ligand had on the position of the equilibrium. Because only $[C_6(CH_3)_6Mn(CO)_3]PF_6$, $[(durene)Mn$-$(CO)_3]I$, and $[(p\text{-xylene})Mn(CO)_3]PF_6$ were sufficiently soluble in CH_2Cl_2, only these complexes were used. For each of these complexes, solutions containing initial concentrations of 1.6×10^{-2} M (arene)Mn(CO)$_3{}^+$

(14) Durene is 1,2,4,5-tetramethylbenzene. Mesitylene is 1,3,5-trimethylbenzene.

and 2.7×10^{-1} M $C_6H_{11}NH_2$ were prepared. Using experimentally determined molar extinction coefficients of 42.2, 37.1, and 39.6[15] l./(mol cm) for the lowest frequency C–O stretching absorption of $[C_6(CH_3)_6Mn$-$(CO)_3]PF_6$, $[(durene)Mn(CO)_3]I$, and $[(p\text{-xylene})Mn$-$(CO)_3]PF_6$, respectively, the concentrations of carboxamido complex present in each case were calculated as 0.13×10^{-2}, 1.0×10^{-2}, and 1.2×10^{-2} M, respectively. Thus a decreasing number of CH$_3$ groups in the arene ring favors carboxamido formation. This may be rationalized in terms of the electron-releasing ability of methyl groups; they cause an increase of electron density at both the manganese and the CO groups. Thus the CH$_3$ groups make the carbon of the CO ligands less positive and less likely to bind the basic amine. Later in this paper, it will be shown that a knowledge of the charge on the carbonyl carbon atom is very useful in predicting which metal carbonyls will form carboxamido complexes and which will not.

$(RNH_2)_3Mn(CO)_3{}^+$.—Contrary to the reactions of (arene)Mn(CO)$_3{}^+$, where arene = $C_6(CH_3)_6$, durene, mesitylene, p-xylene, and toluene, the analogous benzene complex reacts by ring displacement

$$(C_6H_6)Mn(CO)_3{}^+ + 3RNH_2 \longrightarrow$$
$$cis\text{-}(RNH_2)_3Mn(CO)_3{}^+ + C_6H_6 \quad (4)$$
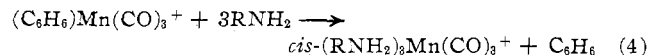
That benzene is displaced and the methyl-substituted benzenes are not is consistent with the known[16,17] increase in rate of arene displacement from (arene)Mo-(CO)$_3$ as the number of methyl groups decreases.

Complexes where R = C_6H_{11} and $-CH(CH_3)_2$ have been isolated; their infrared spectra (Table II) are very similar to those of $(NH_3)_3Mn(CO)_3{}^+$ (2038, 1921–1932 (br) cm^{-1} in KBr),[18] $[(pip)_3Mn(CO)_3]Br$ (2023, 1912 cm^{-1} in KBr),[19] and $[(dien)Mn(CO)_3]I$ (2034, 1904 cm^{-1} in KBr).[20] The cations (RNH$_2$)$_3$Mn(CO)$_3{}^+$ do not form carboxamido complexes with excess RNH$_2$. Infrared spectra of the cations even in liquid RNH$_2$ show only the presence of the cation.

$(RNH_2)_3Re(CO)_3{}^+$.—In an attempt to prepare arene carboxamido complexes of Re, $C_6(CH_3)_6Re(CO)_3{}^+$ was allowed to react with $(CH_3)_2CHNH_2$. Unfortunately only hexamethylbenzene displacement occurred.

$$C_6(CH_3)_6Re(CO)_3{}^+ + 3(CH_3)_2CHNH_2 \longrightarrow$$
$$cis\text{-}[(CH_3)_2CHNH_2]_3Re(CO)_3{}^+ + C_6(CH_3)_6 \quad (5)$$
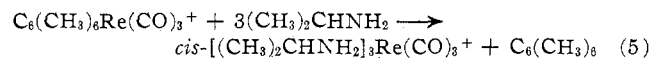
The infrared spectrum (Table II) of the product is very similar to those of $(NH_3)_3Re(CO)_3{}^+$ (2024, 1894 cm^{-1} in acetone)[13] and (pyrrolidine)$_3$Re(CO)$_3{}^+$ (2021, 1898 cm^{-1} in CH_2Cl_2).[20] Like the analogous Mn cation, $[(CH_3)_2CHNH_2]_3Re(CO)_3{}^+$ does not form a carboxamido complex even in liquid isopropylamine.

(arene)Mn(CO)$_2$(NCO).—Cationic metal carbonyl complexes are known[4,6,21,22] to react with hydrazine and methyl-substituted hydrazines to convert one CO

(15) Because this complex is only sufficiently soluble for ir measurements when amine is present, this value was estimated by taking the average of the values for the other complexes.

(16) F. Zingales, A. Chiesa, and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 2707 (1966).

(17) A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc. A*, 872 (1967).

(18) H. Behrens, E. Ruyter, and H. Wakamatsu, *Z. Anorg. Allg. Chem.*, **349**, 241 (1967).
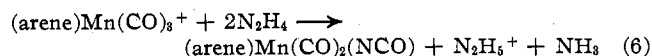
(19) W. Hieber and F. Stanner, *Chem. Ber.*, **102**, 2930 (1969).

(20) W. Hieber, W. Opavsky, and W. Rohm, *ibid.*, **101**, 2244 (1968).

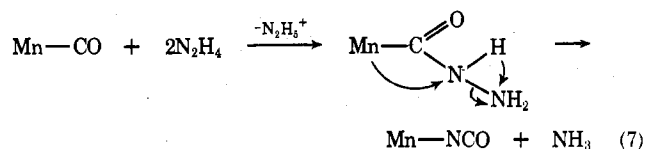(21) R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, **91**, 3197 (1969).

(22) R. J. Angelici and G. C. Faber, *Inorg. Chem.*, **10**, 514 (1971), and references therein.

group into an NCO^- ligand. In the same manner, $(arene)Mn(CO)_3^+$ reacts as follows

$$(arene)Mn(CO)_3^+ + 2N_2H_4 \longrightarrow$$
$$(arene)Mn(CO)_2(NCO) + N_2H_5^+ + NH_3 \quad (6)$$

The most stable product is obtained where the arene is $C_6(CH_3)_6$; the mesitylene analog is considerably less stable. Their infrared spectra (Table I) contain absorptions attributable to stretching modes of the two terminal CO groups and to the asymmetric NCO vibration; this is similar to the spectrum of (mesitylene)-$Mn(CO)_2(CN)$ ($\nu(C-O)$ at 2000 and 1954 cm^{-1} and $\nu(C-N)$ at 2103 cm^{-1}).[23]

The mechanism for reaction 6 is presumably similar to that discussed previously.[21]

$$Mn-CO + 2N_2H_4 \xrightarrow{-N_2H_5^+} Mn-C \overset{O}{\underset{N}{\diagdown}} \overset{H}{\underset{NH_2}{\diagdown}} \longrightarrow$$

$$Mn-NCO + NH_3 \quad (7)$$

In the reaction of $C_6(CH_3)_6Mn(CO)_3^+$ with hydrazine, an infrared spectrum of the solution after 10–15 min showed predominant absorptions at 1948 and 1888 cm^{-1} which we have attributed to the carbazoyl intermediate $C_6(CH_3)_6Mn(CO)_2CONHNH_2$ because of their similarity to those of the carboxamido complexes (Table I). Attempts to isolate the intermediate were unsuccessful. It disappeared with time to give rise to absorptions of the product $C_6(CH_3)_6Mn(CO)_2(NCO)$. In the reactions with the methyl-substituted hydrazines, CH_3NHNH_2 and $(CH_3)_2NNH_2$, there was no infrared evidence for a carbazoyl intermediate. This is presumably due to the faster decay of the carbazoyl intermediate to the product in these cases. This trend has previously been noted.[4,6,21] In the reaction of (mesitylene)Mn(CO)$_3^+$ with hydrazine, infrared absorptions due to a carbazoyl intermediate are also observed (Table I).

Isocyanate complexes have also been prepared[22] by the reaction of metal carbonyls with azide ion; however, neither $[C_6(CH_3)_6Mn(CO)_3]PF_6$ nor $[(mesitylene)-Mn(CO)_3]PF_6$ reacted with NaN_3 under conditions[21] which had been successful in previous reactions.

Correlation of the Metal Carbonyl–Amine Reactions with C–O Force Constants.—As noted earlier in this paper, the addition of electron-releasing groups (CH_3) to the arene ring of $(arene)Mn(CO)_3^+$ reduces the extent of carboxamido complex formation via eq 2. This is presumably due to an increase in electron density at the carbonyl carbon which makes it less likely to react with the basic amine. This is a thermodynamic property and not kinetic since all of these reactions occurred essentially instantaneously at room temperature even though the extent of carboxamido complex formation was small.

As pointed out by Darensbourg and Darensbourg[24] C–O stretching force constants can be used as a measure of the electron density at the carbon atom of a carbonyl ligand—the higher the force constant the lower the electron density on the carbon. Hence it seemed that a correlation should exist between C–O stretching force con-

stants and the tendency of carbonyl complexes to react with amines. In fact, this seems to be the case as indicated by the results in Table II, which include all reported attempts to prepare carboxamido complexes by reaction 1. Also included is carbon monoxide–borane, $H_3B \cdot CO$, which reacts analogously and behaves as predicted by the more general correlation. The compounds are listed in order of decreasing force constants. Except for those values taken from the literature, these force constants were calculated by the approximate methods of Cotton and Kraihanzel.[25] It should be emphasized that these force constants *are* approximate,[26,27] but they are not being used in this correlation to distinguish small differences in reactivity.

The reactivity of the complexes with alkylamines is indicated in the fourth column in three ways: *yes*, which means a carboxamido complex was isolated and there was no evidence for an equilibrium; *equil*, which means that the carbonyl compound was not completely converted to a carboxamido complex or that the carbonyl compound could be regenerated simply (*e.g.*, by evaporating the amine); or *no*, which means that there was no evidence for reaction at room temperature even when the compound was dissolved in pure alkylamine. The alkylamines have usually been methyl, ethyl, isopropyl, or cyclohexyl derivatives. Where investigated, NH_3 and secondary dialkylamines have been found to react similarly, but no carboxamido complexes have been obtained by reaction with the weakly basic aniline.[3,4,7]

The results in Table II indicate that *CO ligands with force constants greater than 17.0 mdyn/Å readily form carboxamido complexes, those with force constants between 16.0 and 17.0 mdyn/Å give equilibrium mixtures, and those with constants below 16.0 mdyn/Å show no evidence for carboxamido formation.* In terms of CO stretching frequencies, Table II shows that those *complexes which have terminal C–O stretching absorptions below 2000 cm^{-1} do not yield carboxamido complexes.* This last statement is less rigorous than those based on force constants, but it may be of some utility where force constant data are not available. The one apparent exception to the force constant correlation is $\{(C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$ for which an equilibrium reaction is predicted. The isolation of the carboxamido complex may simply reflect the insolubility of the product, as was observed with $C_6(CH_3)_6Mn(CO)_2-CONHC_6H_{11}$. The reaction was not examined for the existence of an equilibrium in solution.

Not only is this correlation useful in predicting the tendency of a carbonyl complex to form carboxamido complexes, but it also correctly predicts which CO will react with an amine in complexes where there is a choice of two kinds of CO ligands, as in $Fe(CO)_5$ and $(CH_3NH_2)M(CO)_5^+$, where M = Mn or Re. In these cases, the CO group with the highest force constant (Table II) is converted to a carboxamido ligand.

In a study involving the reaction of organolithium nucleophiles with metal carbonyl complexes, Darensbourg and Darensbourg[24] qualitatively correlated the

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TABLE II
CORRELATION OF C–O FORCE CONSTANTS WITH METAL CARBONYL–AMINE REACTIONS

Compd	ν(C–O),[a] cm^{-1}	Force constant, mdyn/Å	Amine reaction
$\{[(C_6H_5)_3As]_2PtCl(CO)\}BF_4$[b]	2138 s[c]	18.5	yes[t]
$\{[(C_6H_5)_3P]_2PtCl(CO)\}BF_4$[b]	2120 s[c]	18.2	yes[t]
H_3BCO	2169 s[d]	18.0[d]	yes[e]
$[(C_5H_5)Ru(CO)_3]PF_6$	2125 s, 2075 s, 2066 s[f]	17.6	yes[g]
$[(C_5H_5)Fe(CO)_3]PF_6$	2120 s, 2070 s[h]	17.6	yes[i]
$[(CH_3NH_2)Mn(CO)_5]PF_6$	2141 w, 2055 s, 2032 m[i]	17.5 (eq) 16.8 (ax)	yes[i]
$[(CH_3NH_2)Re(CO)_5]PF_6$	2167 vw, 2052 s, 2023 m[k]	17.5 (eq) 16.5 (ax)	yes[k]
$Fe(CO)_5$	2023 s, 2000 vs[l]	17.0 (ax)[l] 16.4 (eq)	equil[m]
$\{[(C_6H_5)_3P]_2Mn(CO)_4\}PF_6$[b]	2092 vw, 2046 w, 2001 vs[n]	16.9[n]	equil[n]
$[(toluene)Mn(CO)_3]PF_6$	2082 s, 2024 s	16.9	equil
$[(p\text{-xylene})Mn(CO)_3]PF_6$	2079 s, 2021 s	16.8	equil
$[(mesitylene)Mn(CO)_3]PF_6$	2075 s, 2015 s	16.7	equil
$\{(C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$	2055 s, 2010 s	16.7	yes[i]
$[(durene)Mn(CO)_3]I$	2066 s, 2007 s	16.6	equil
$[C_6(CH_3)_6Mn(CO)_3]PF_6$	2064 s, 2059 s, 2003 s	16.5	equil
$[(C_6H_{11}NH_2)_3Mn(CO)_3]PF_6$	2032 s, 1936 s, br	15.7	no[s]
$(C_5H_5)Mn(CO)_3$	2029 s, 1946 vs[l]	15.6[p]	no[s]
$\{[(CH_3)_2CHNH_2]_3Mn(CO)_3\}PF_6$	2020 s, 1925 s, br[o]	15.5	no[s]
$\{[(CH_3)_2CHNH_2]_3Re(CO)_3\}PF_6$	2033 s, 1917 s, br	15.5	no[s]
$[(dien)Mn(CO)_3]I$	2034 s, 1903 s, br[q]	15.3	no[s]
$[(NH_3)_3Re(CO)_3]B(C_6H_5)_4$	2024 s, 1894 s, br[r]	15.2	no[s]

[a] Solvent is CH_2Cl_2 unless otherwise noted. [b] Trans geometry. [c] In CHCl$_3$: W. J. Cherwinski and H. C. Clark, *Can. J. Chem.*, **47**, 2665 (1969). [d] R. C. Taylor, *J. Chem. Phys.*, **26**, 1131 (1957). [e] R. W. Parry, C. E. Nordman, J. C. Carter, and G. Terhaar, *Advan. Chem. Ser.*, No. **42**, 302 (1964); J. C. Carter and R. W. Parry, *J. Amer. Chem. Soc.*, **87**, 2354 (1965). [f] Nujol mull: T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 2158 (1968). [g] Reference 4. [h] Nujol mull: ref 4. [i] Reference 3. [j] Reference 5. [k] Reference 6. [l] H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967). [m] W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 3080 (1965); W. F. Edgell and B. J. Bulkin, *ibid.*, **88**, 4839 (1966). [n] R. Brink and R. J. Angelici, unpublished results. [o] In CHCl$_3$. [p] Reference 24. [q] Nujol mull: ref 11. [r] In acetone. [s] No infrared evidence for reaction in solutions of $C_6H_{11}NH_2$ or $(CH_3)_2CHNH_2$. [t] Reference 7.

rates (although it is not clear that equilibrium considerations are not involved) of reaction with C–O stretching force constants. They observed that reaction to form the acyl (or carbene) product occurred when the force constant was greater than 15.3 mdyn/Å. This lower limit of reaction is lower than observed here with amines (16.0) as would be expected for the more nucleophilic organolithium reagents.