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LIGAND REACTIONS OF MANGANESE CARBONYL—ISOCYANIDE COMPLEXES WITH AMINES

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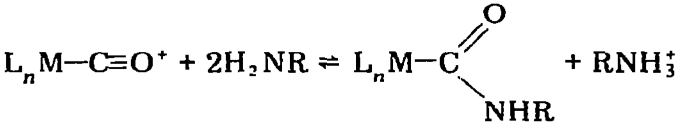
Summary

The complex, *cis*-$Mn(CO)_4(CNCH_3)_2^+$, I, reacts rapidly with excess CH_3NH_2 at 25° to form the carbamoyl complex *fac*-$Mn(CO)_3(CONHCH_3)(CNCH_3)_2$, II. On standing, the carbamoyl complex slowly disappears and the chelated amidinium complex, $(OC)_4MnC(NHCH_3)N(CH_3)C(NHCH_3)^+$, VI, may be isolated. On reaction with bases such as CH_3NH_2 or $(C_2H_5)_3N$, complex VI is deprotonated to give $(OC)_4MnC(=NCH_3)N(CH_3)C(NHCH_3)$, V. Passage of VI through a silica gel chromatography column leads to some rearrangement and the isolation of *cis*-$Mn(CO)_4(CNCH_3)[C(NHCH_3)_2]^+$, III, which is an isomer of VI containing $CNCH_3$ and monodentate amidinium ligands. When treated with base, III is rapidly converted to the chelated form, V. The complex, *mer*-$Mn(CO)_3(CNCH_3)_3^+$, VII, reacts rapidly in neat n-$BuNH_2$ to give the carbamoyl complex $Mn(CO)_2(CNCH_3)_3(CONHR)$ (VIII, R = Bu) and no further reaction occurs. At lower concentrations of amine, VIII does not form, but in a slow reaction the chelated amidinium complex, *mer*-$(OC)_3(CH_3NC)MnC(NHCH_3)N(CH_3)C(NHCH_3)^+$, IX, is produced. The isomer of VII, *fac*-$Mn(CO)_3(CNCH_3)_3^+$, has also been prepared and it appears to react with CH_3NH_2 giving an amidinium complex which was too unstable to be isolated. Factors affecting the relative reactivities of CO and $CNCH_3$ ligands with amines are discussed.

Introduction

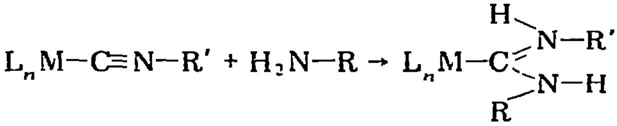
Carbonyl ligands in many metal carbonyl complexes react with aliphatic amines to give carbamoyl complexes according to eqn. 1 [1].



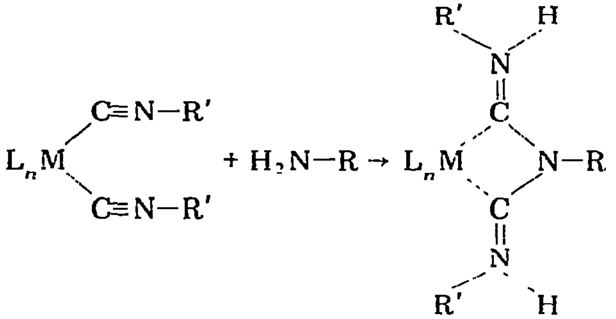
$$L_nM{-}C{\equiv}O^+ + 2H_2NR \rightleftharpoons L_nM{-}C(=O)NHR + RNH_3^+ \qquad (1)$$

The extent to which this reaction occurs has been correlated [2] with the C≡O stretching force constant of the reacting CO group.

In a similar manner (eqn. 2), isocyanide ligands react with amines to yield amidinium (also called carbene) ligands [3, 4]. In cases where *cis* isocyanide ligands are present in the complex, the amine may react with both isocyanide ligands to generate a chelated amidinium ligand (eqn. 3). An example of this type of reaction has been reported for $Fe(CNCH_3)_6^{2+}$ [5, 6].



$$L_nM{-}C{\equiv}N{-}R' + H_2N{-}R \rightarrow L_nM{-}C(NHR')(NHR) \quad (2)$$



(3)

In an earlier study [7], we sought to compare and contrast the reactivities of CO and CNR ligands in complexes containing both types of ligands. For a series of π-cyclopentadienyl iron complexes, we found that the following reactions took place:

$$(C_5H_5)Fe(CO)_2(CNCH_3)^+ + 2CH_3NH_2 \rightleftharpoons (C_5H_5)Fe(CO)(CNCH_3)CONHCH_3 + CH_3NH_3^+ \quad (4)$$

$$(C_5H_5)Fe(CO)(CNCH_3)_2^+ + CH_3NH_2 \rightarrow (C_5H_5)Fe(CO)(CNCH_3)\text{-}[C(NHCH_3)_2]^+ \quad (5)$$

$$(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+ + CH_3NH_2 \rightarrow (C_5H_5)Fe(PPh_3)(CO)\text{-}[C(NHCH_3)_2]^+ \quad (6)$$

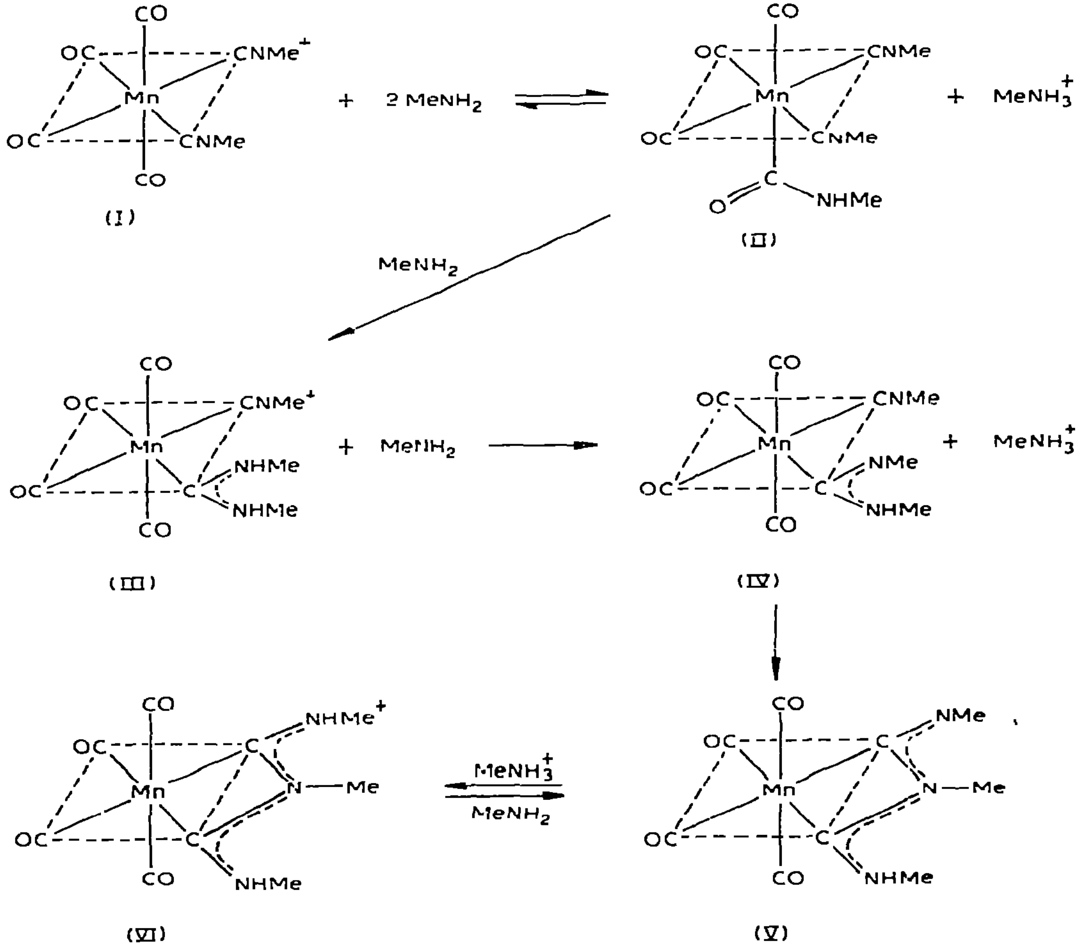
Although the starting complex in reaction 5 contained *cis*-isocyanide ligands, products containing chelated amidinium ligands were not observed. Some tentative conclusions about the relative reactivities of the CO and CNR ligands were made. In the present study, we sought to determine the validity of those conclusions for reactions of amines with the carbonyl—isocyanide complexes of Mn^I, *cis*-$Mn(CO)_4(CNCH_3)_2^+$, *mer*-$Mn(CO)_3(CNCH_3)_3^+$ and *fac*-$Mn(CO)_3(CNCH_3)_3^+$

Results and discussion

cis-$Mn(CO)_4(CNCH_3)_2^+$ *with* CH_3NH_2

The reaction of *cis*-$Mn(CO)_4(CNCH_3)_2^+$, I (Roman numerals refer to structures in Schemes 1 or 2), with excess CH_3NH_2 over a 24 hour period gives complex VI, $(OC)_4\overline{MnC(NHCH_3)N(CH_3)C}(NHCH_3)^+$ which contains a chelated amidinium ligand (eqn. 3). It was characterized by elemental analysis and its infrared spectrum (Table 1) which showed no isocyanide $\nu(C{\equiv}N)$ bands near 2200 cm^{-1}. While only 3 $\nu(C{\equiv}O)$ bands are observed, the strong, broad absorption at 2011 cm^{-1} could conceal a fourth band which is expected for the C_{2v} symmetry of the compound.

SCHEME 1.



The proton NMR spectrum (Table 2) of VI exhibited a broad peak at τ 0.26 corresponding to the two NH protons, while a singlet at τ 6.77 corresponds to the CH_3 group on the central N atom. A singlet at τ 6.52 integrates correctly for the 6 protons of the two CH_3 groups on the terminal N atoms. The positions of these resonances are very similar to those observed for the chelated amidinium complex [5], $(CH_3NC)_4FeC(NHCH_3)N(CH_3)C(NHCH_3)^{2+}$, which has bands at τ 1.62 (NH), 6.92 (central CH_3), and 6.50 (doublet, terminal CH_3 groups). It is not clear why the terminal CH_3 groups in compound VI are not split into a doublet by coupling to the NH proton, as is found in the Fe compound [5].

An X-ray structural analysis [5] of the Fe compound shows the ligand to have the planar geometry pictured in eqn. 3, with both terminal CH_3 groups directed away from the central group. The NMR spectrum of VI suggests that it also has this structure.

When compound VI is treated with $(C_2H_5)_3N$, one proton is removed (Scheme 1) to give the neutral complex V, $(OC)_4MnC(=NCH_3)N(CH_3)C(NHCH_3)$. This deprotonation is also effected by CH_3NH_2 and n-BuLi but not by pyridine.

TABLE 1. INFRARED SPECTRA IN CARBONYL STRETCHING REGION

Compound	$\nu(C{=}NCH_3)$ [a] (cm^{-1})	$\nu(C{-}O)$ [a] (cm^{-1})
cis-[$Mn(CO)_4(CNCH_3)_2$]PF_6, [b] I	2256 (sh), 2243 m	2123 s, 2070 (sh) [c], 2048 vs, 2033 (sh)
fac-[$Mn(CO)_3(CNCH_3)_3$]SO_3F	2246 (sh), 2222 m	2067 vs, 2010 vs, (br) [d]
mer-[$Mn(CO)_3(CNCH_3)_3$]PF_6, [e] VII	2239 w, 2218 (sh), 2199 s	2089 w, 2018 vs, (br) [f]
fac-$Mn(CO)_3(CONHCH_3)(CNCH_3)_2$, [g] II	2210 m, 2182 m	2019 s, 1951 (sh), 1931 s
cis-$(OC)_4MnC(=NCH_3)N(CH_3)C(NHCH_3)$, V		2065 m, 1975 vs (br), 1934 s
cis-{$Mn(CO)_4(CNCH_3)[C(NHCH_3)_2]$}$PF_6$, III	2234 m	2104 m, 2033 s, 2019 vs, 1999 s
cis-[$(OC)_4MnC(NHCH_3)N(CH_3)C(NHCH_3)$]$PF_6$, VI		2095 m, 2011 vs (br), 1977 s
mer-[$(OC)_3(CH_3NC)MnC(NHCH_3)N(CH_3)C(NHCH_3)$]$PF_6$, IX	2175 m	2052 w, 1975 vs, 1952 s

[a] In CH_2Cl_2 solution. Abbreviations: w, weak; m, medium, s, strong; (sh), shoulder; v, very. [b] Reported values in ref. 8 are 2249, 2221, 2125, 2064, 2051, and 2036 cm^{-1} in CH_2Cl_2. [c] CO stretch force constants calculated according to ref. 18 are: k_1 (*trans* to $CNCH_3$) 17.0; k_2 (*trans* to CO) 17.4 mdyne/Å. [d] CO stretch force constant calculated similarly to that in c; k 16.6 mdyne/Å. [e] Reported values in ref. 8 are 2215, 2220, 2202, 2090 and 2020 cm^{-1} in CH_2Cl_2. [f] CO stretch force constant calculated according to ref. 19 are k_1 (*trans* to $CNCH_3$) 16.6, k_2 (*trans* to CO) 17.0 mdyne/Å. [g] Not isolated.

TABLE 2. PROTON NMR SPECTRA [a]

Compound	Assignment	τ (ppm) [b]
cis-[$Mn(CO)_4(CNCH_3)_2$]PF_6, I	$CNCH_3$	6.37 t [c]
fac-[$Mn(CO)_3(CNCH_3)_3$]SO_3F	$CNCH_3$	6.40 s (br)
mer-[$Mn(CO)_3(CNCH_3)_3$]PF_6, VII	$CNCH_3$	6.40 s
cis-$(OC)_4MnC(=NCH_3)N(CH_3)C(NHCH_3)$, V		6.83 (6) s
		7.09 (3) s
cis-{$Mn(CO)_4(CNCH_3)[C(NHCH_3)_2]$}$PF_6$, III	NH	2.36 (2) br
	$CNCH_3$	6.35 (3) s (br)
	$C(NHCH_3)_2$	6.66 (3) d [d]
		7.03 (3) d [d]
cis-[$(OC)_4MnC(NHCH_3)N(CH_3)C(NHCH_3)$]$PF_6$, VI	NH	0.26 (2) (br)
	$NHCH_3$	6.52 (6) s
	$>NCH_3$	6.77 (3) s
mer-[$(OC)_3(CH_3NC)MnC(NHCH_3)N(CH_3)C(NHCH_3)$]$PF_6$, IX	NH	0.78 (2) (br)
	$CNCH_3$	6.44 (3) s
	$NHCH_3$	6.62 (6) d [e]
	$>NCH_3$	6.88 (3) s

[a] All spectra were obtained in acetone-d_6 except for *fac*-[$Mn(CO)_3(CNCH_3)_3$]SO_3F which was taken in $CDCl_3$. [b] Tetramethylsilane used as internal standard (τ 10.0). Relative intensities are in parentheses. Abbreviations: s, singlet, d, doublet; t, triplet; (br), broad. [c] $J(NCH)$ 2.3 Hz. [d] $J(HNCH)$ 5.0 Hz. [e] $J(HNCH)$ 4.0 Hz.

Solvents such as CH_2Cl_2, THF or CH_3CN have been used in these reactions. The neutral V can be re-protonated by CCl_3CO_2H in CH_2Cl_2 to give VI. Isolation of the protonated form VI rather than V in the original reaction of I with excess CH_3NH_2 is apparently due to the lower solubility of VI.

Compound V has been characterized by elemental analysis and shows a parent ion peak at *m/e* 279 in its mass spectrum. Like its protonated precursor (VI), V has the same pattern of 3 $\nu(C{\equiv}O)$ bands in its IR spectrum (Table 1) but they occur about 35 cm^{-1} lower than observed for VI. There are no $\nu(C{\equiv}N)$ absorptions.

The proton NMR spectrum of V showed a singlet at τ 7.09 (3 protons) assignable to the CH_3 group on the central N atom. Another singlet at τ 6.83 may be assigned to the terminal CH_3 groups. The NH proton has not been located by NMR although the presence of an N—H band (ν(N—H) at 3340 cm^{-1} in $CHCl_3$) in the IR spectrum indicates its presence. Structure V would suggest that the terminal CH_3 groups are different and should occur as separate peaks in the NMR spectrum. That only 1 peak is observed suggests that the proton is rapidly moving from one terminal N to the other (perhaps via solvent protonation), thereby making the CH_3 groups equivalent on the NMR time scale. This movement might also lead to broadening of the N—H proton resonance accounting for the fact that it is not observed.

When the chelated amidinium complex, VI, $[(CO)_4\overline{MnC(NHCH_3)N(CH_3)C}(NHCH_3)]PF_6$ was passed through a silica gel column, two yellow bands were eluted. The slower moving band was simply VI; the fast-moving band was a new compound which had the same elemental composition as VI but a structure, III, *cis*-$Mn(CO)_4(CNCH_3)[C(NHCH_3)_2]^+$, which contained an isocyanide and a monodentate amidinium ligand. Since compound III was not present in the original sample of VI placed on the column, it must have been formed on the column via an unknown route by cleavage of the chelate ring in VI.

The IR spectrum (Table 1) of III showed a $\nu(C{\equiv}N)$ band and 4 $\nu(C{\equiv}O)$ bands, which support the proposed structure. Its proton NMR spectrum (Table 2) showed a singlet at τ 6.35 which may be assigned to the $CNCH_3$ ligand protons. A broad band at τ 2.36 may be assigned to the two N—H protons, and the two sets of doublets at τ 6.66 and 7.03 are expected for the two CH_3 groups in the amidinium ligand. The non-equivalence of these CH_3 groups apparently arises from the planar ligand structure shown in eqn. 2 and from restricted rotation around the carbene C—N bonds due to partial double bonding. This has been noted in other amidinium complexes [3, 4, 7, 9, 10].

Since Doonan and Balch [6] had previously suggested that the chelated amidinium ligand in $(CH_3NC)_4\overline{FeC(NHCH_3)N(CH_3)C}(NHCH_3)^{2+}$ reversibly opens and closes, it was of interest to determine if compounds III and VI could be interconverted. When heating either III or VI at 55° in THF for 24 h, no interconversion was observed. Neither did heating solid samples of III or VI to 150° produce any conversion. However, when III was treated with bases such as CH_3NH_2 or $(C_2H_5)_3N$ in CH_2Cl_2 at room temperature, it was immediately converted to the deprotonated amidinium chelate complex V. On evaporating the solution, the protonated form VI was recovered, as expected (see above). Only on the silica gel column was it possible to convert some of VI to III, as described above.

The base-catalyzed conversion of III to V probably proceeds by initial deprotonation of III to give the amidine IV, (Scheme 1) which rapidly ring-closes by intramolecular attack of the deprotonated N on the adjacent isocyanide ligand. There is no spectroscopic evidence for the presence of IV in the reaction solutions.

Having only isolated compound VI from the reaction of *cis*-$Mn(CO)_4$-$(CNCH_3)_2^+$ with CH_3NH_2, we examined the reaction more carefully using IR spectroscopy to identify possible intermediates. When I was treated with CH_3NH_2, in CH_2Cl_2, THF, or CH_3CN at room temperature, the absorptions of I disappeared and new absorptions appeared almost instantaneously at 2210 m and 2182 m, assigned to $\nu(C{\equiv}N)$, and at 2019 s, 1951 (sh) and 1934 s cm^{-1}, assigned to $\nu(C{\equiv}O)$. If this solution is immediately evaporated to dryness under vacuum, only the starting complex I is recovered. When the reaction was run in CH_2Cl_2 and immediately treated with a large excess of pentane, a white precipitate (presumably $[CH_3NH_3]PF_6$) separated. The solution was filtered and evaporated to dryness under vacuum to give a complex which we believe to be the carbamoyl complex, *fac*-$(OC)_3(CH_3NC)_2MnCONHCH_3$, II. It was extremely unstable in air, even as the solid, and could not be purified. Its IR spectrum, which was the same as observed in the reaction mixture, is consistent with the presence of two $CNCH_3$ ligands and 3 terminal CO ligands. When treated with an acid (e.g., CCl_3CO_2H) in solution, II was immediately converted to the starting cation I. This acid reaction and the reversible regeneration of I on evaporating the original reaction are common reactions of carbamoyl compounds [1, 2, 11, 12]. Neither reaction has been observed for amidinium complexes.

If the reaction solution of I with CH_3NH_2 was allowed to continue at 25°, a new set of bands at 2065 m, 1975 vs (br) and 1934 s slowly appeared over the next 5 h while those of II disappeared. These new absorptions were identical to those of the deprotonated chelated amidinium complex, V. On evaporating this solution to dryness, only the protonated form, VI, was isolated. During the reaction, no IR bands due to unidentified species were observed.

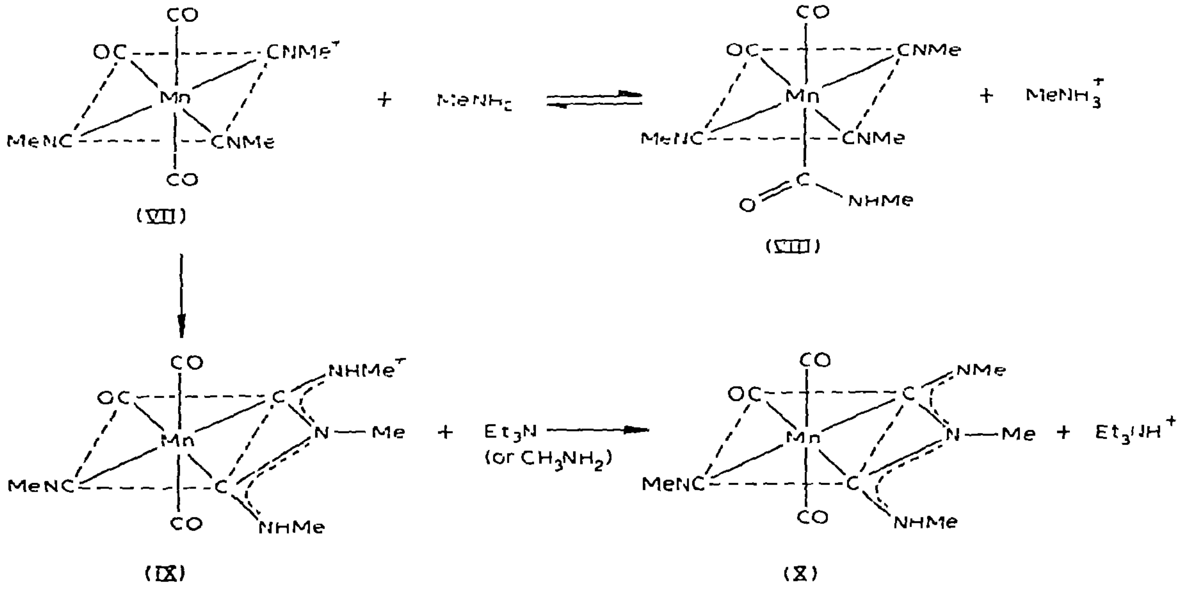
The conversion of II to V could proceed by two major routes: (1) $NHCH_3$ migration from the carbamoyl group to the isocyanide ligand to form IV which rapidly closes to yield V, or (2) attack of an amine molecule in solution on an isocyanide ligand of II to give III which we know is rapidly converted to V. Although there is no precedent for mechanism 1, mechanism 2 has been supported by a kinetic study [13] of the reactions of complexes such as *cis*-Pd-$(PPh_3)(CNPh)Cl_2$ with amines to give the corresponding amidinium complexes. Since these reactions have a first-order dependence on the amine concentration, the conversion of II to V should be faster at high amine concentration if mechanism 2 is involved.

This was investigated using n-$BuNH_2$ which like CH_3NH_2 immediately gives complex II on reaction with I. It was noted that the conversion of II to V was much faster in neat n-$BuNH_2$ than in a dilute solution of n-$BuNH_2$ in CH_2Cl_2. This observation supports mechanism 2 but does not necessarily rule out the migration mechanism 1 which could also be promoted by high amine concentrations.

mer-$Mn(CO)_3(CNCH_3)_3^+$ *with* CH_3NH_2

Reaction of *mer*-$Mn(CO)_3(CNCH_3)_3^+$, VII, with excess CH_3NH_2 in THF at room temperature for 24 h gave the chelated amidinium product, $[(OC)_3(CH_3NC)$-

SCHEME 2.



$\overline{\mathrm{MnC(NHCH_3)N(CH_3)C}}\mathrm{(NHCH_3)]PF_6}$, IX, (Scheme 2). The IR spectrum (Table 1) of this compound showed one ν(C≡N) band for the isocyanide ligand and three ν(C≡O) bands which are consistent with structure IX. Its proton NMR spectrum showed, apart from resonances at τ 0.78 and 6.44 for the NH and C≡NCH_3 protons, a singlet at τ 6.88 characteristic of the CH_3 on the central N of the chelate and a doublet at τ 6.62 for the CH_3 groups on the terminal N atoms of the ligand (eqn. 3). When $(C_2H_5)_3N$ or CH_3NH_2 was added to a solution of IX, the IR spectrum of IX shifted about 10 cm^{-1} to lower frequencies (2170 m, 2044 w, 1967 vs, and 1941 m cm^{-1} in CH_2Cl_2) suggesting that deprotonation of IX to give X had occurred. Attempts to purify X were unsuccessful.

Searching for intermediates in the conversion of VII to IX, we examined reaction solutions of VII with CH_3NH_2 by IR spectroscopy. They showed bands only for the starting complex VII and the deprotonated product X. However, when VII was dissolved in pure (neat) n-BuNH$_2$, bands for VII immediately disappeared and absorptions at 2189 m and 2128 s cm^{-1} for ν(C≡N) and 1948 s and 1895 m cm^{-1} for ν(C≡O) appeared. These absorptions together with the observation that evaporation of this solution yielded only the starting complex VII suggested that a carbamoyl complex, VIII, had formed. When the neat n-BuNH$_2$ solution was allowed to stand at room temperature for 4 h, the IR spectrum did not change except to show a gradual decrease in intensity as decomposition occurred. There was no evidence for the formation of IX or X.

When VII was treated with a dilute solution of n-BuNH$_2$ in CH_2Cl_2, there was no evidence for carbamoyl (VIII, R = Bu) formation, and the reaction proceeded to give X. Thus it appears that VII can react with n-BuNH$_2$ to give either VIII or IX. Since the formation of VIII is kinetically faster, it is the observed product at high n-BuNH$_2$ concentration where the equilibrium is also favorable. At low amine concentration, however, this equilibrium is not favorable and formation of IX occurs.

It should be noted that the carbamoyl complex, VIII, was not converted to the amidinium complex, IX. This suggests that $NHCH_3$ migration from the CO to a $CNCH_3$ group is not a kinetically favorable process. This result also suggests that conversion of the carbamoyl complex, II, to V (Scheme 1) probably proceeded via external amine attack on a $CNCH_3$ ligand of II. That a similar attack does not occur on VIII can be attributed to a higher electron density on the $CNCH_3$ ligands in VIII, resulting from the replacement of a CO in II by a $CNCH_3$ ligand in VIII.

fac-$Mn(CO)_3(CNCH_3)_3^+$ + CH_3NH_2

The starting complex was prepared by the alkylation of *fac*-$Mn(CO)_3(CN)_3^{2-}$ [14] according to the equation:

$$fac\text{-}Mn(CO)_3(CN)_3^{2-} + 3CH_3OSO_2F \rightarrow fac\text{-}Mn(CO)_3(CNCH_3)_3^+ + 3SO_3F^-$$

Its proton NMR spectrum showed a broad singlet at τ 6.40 as contrasted with a triplet for *cis*-$Mn(CO)_4(CNCH_3)_2^+$ [8]; the triplet apparently arises from coupling to the N atom as occurs in free CH_3NC [15].

A small quantity of [*fac*-$Mn(CO)_3(CNCH_3)_3$]SO_3F was dissolved in a solution containing 1 ml of n-$BuNH_2$ and 4 ml of CH_2Cl_2. Portions of this solution were periodically evaporated to dryness. IR spectra of the residues in CH_2Cl_2 showed only the starting *fac*-$Mn(CO)_3(CNCH_3)_3^+$ and additional bands at 2192 w (br), 2026 vs, 1959 s, and 1936 s. If the reaction was allowed to proceed for 20 h, only the 4 new bands remained. A similar result was found for the reaction of CH_3NH_2 with *fac*-$Mn(CO)_3(CNCH_3)_3^+$ in THF. Due to the extreme instability of the product in air, we were unable to purify and characterize the compound. However, the number and position of its $\nu(C{\equiv}N)$ and $\nu(C{\equiv}O)$ bands and its non-reversibility to the starting material suggest that addition of the amine to one or two isocyanide ligands has occurred to give either an amidinium complex analogous to III or IV or a chelated compound similar to V or VI.

Reactivity of CO versus $CNCH_3$

One major difference between the reactions of CO and $CNCH_3$ ligands with primary amines is the much higher rates of the CO reactions [12, 13]. Thus in complexes where both CO and CNR ligands are present, the CO group has the first opportunity to react.

As has been discussed previously [2], the thermodynamic tendency of a given CO ligand to react with amines depends upon the electron density on the C atom, which is related to its CO stretching frequency or force constant. Low C—O force constants indicate a relatively high electron density on the C and thus a low tendency (i.e., small equilibrium constant for eqn. 1) to react with electron donors such as amines. Conversely, CO groups with high CO force constants have a high tendency to react.

In both *cis*-$Mn(CO)_4(CNCH_3)_2^+$ and *mer*-$Mn(CO)_3(CNCH_3)_3^+$, reaction of one of the mutually *trans* CO groups is observed to occur. Carbamoyl formation occurs with *cis*-$Mn(CO)_4(CNCH_3)_2^+$ (k_{trans} 17.4 mdyne/Å) using relatively dilute solutions of CH_3NH_2 or n-$BuNH_2$, but neat n-$BuNH_2$ is required for *mer*-$Mn(CO)_3(CNCH_3)_3^+$ (k_{trans} 17.0 mdyne/Å). The greater tendency toward carbamoyl formation for *cis*-$Mn(CO)_4(CNCH_3)_2^+$ is consistent with its higher CO force constant.

Similarly, we had previously observed [7] that carbamoyl formation occurred in dilute CH_3NH_2 solution with $(C_5H_5)Fe(CO)_2(CNCH_3)^+$ (k 17.1 mdyne/Å), but not with $(C_5H_5)Fe(CO)(CNCH_3)_2^+$ (k 16.6 mdyne/Å) or $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$ (k 16.1 mdyne/Å).

Although the carbamoyl complexes, II and VIII, from *cis*-$Mn(CO)_4(CNCH_3)_2^+$ and *mer*-$Mn(CO)_3(CNCH_3)_3^+$ are the first to form, the final products in both cases are the deprotonated chelated amidinium derivatives, V and X. Thus the equilibria, II $\rightleftharpoons$ V (see Scheme 1) VIII $\rightleftharpoons$ X (see Scheme 2) clearly indicate that the chelated isocyanide addition products are thermodynamically favored (although the rearrangement may be kinetically slow) over the corresponding carbamoyl derivatives.

All of the final amidinium products of the reactions reported in this paper have the chelated (eqn. 3) rather than the monodentate (eqn. 2) structure. That the chelated form is thermodynamically more stable is supported by the total conversion of III to V (with added base). The structurally similar $Fe(CNCH_3)_6^{2+}$ also gave the chelated product [5], but $Ru(CNCH_3)_6^{2+}$ [5] and $(C_5H_5)Fe(CO)(CNCH_3)_2^+$ [7] formed monodentate amidinium complexes. At this point, it is not clear what factors determine the form of the amidinium ligand.

Experimental

The isocyanide complexes, *cis*-$[Mn(CO)_4(CNCH_3)_2]PF_6$ and *mer*-$[Mn(CO)_3(CNCH_3)_3]PF_6$, were prepared according to the procedure of Treichel et al. [8]. All solvents were of reagent grade and were used without further purification, except for tetrahydrofuran which was dried over $LiAlH_4$ and freshly distilled before use. Methyl isocyanide was prepared according to the published method [17].

IR solution spectra were recorded on a Perkin—Elmer grating spectrophotometer model 337 using 1.0 mm NaCl cells and were calibrated against gaseous CO. Solid state spectra were obtained as either Nujol or hexachlorobutadiene (HCBD) mulls between NaCl plates on a Beckman IR-12 grating spectrophotometer. Proton NMR spectra were recorded on a Perkin—Elmer Hitachi R20B spectrometer and mass spectra were obtained on an Atlas CH4 mass spectrometer.

$[(OC)_4\overline{MnC(NHCH_3)N(CH_3)C}(NHCH_3)]PF_6$, VI

Into 0.200 g of *cis*-$[Mn(CO)_4(CNCH_3)_2]PF_6$ (0.51 mmoles) suspended in 25 ml of THF was bubbled gaseous CH_3NH_2 for 10 min. The flask was stoppered and the contents stirred at room temperature for 24 h. (Introduction of air during the reaction caused some decomposition, as evidenced by the formation of a red-brown precipitate. When, however, it was kept air-tight throughout the reaction, the solution remained clear yellow.) The reaction mixture was evaporated to dryness under vacuum. An IR spectrum showed the residue to be almost pure product. This oily lemon-yellow residue was allowed to stand in a large amount of ethyl ether for 30 min, giving a flaky solid. By triturating it with ethyl ether again, most of the yellow colored portion was removed, leaving an off-white precipitate. Recrystallization from CH_2Cl_2— ethyl ether gave white flaky crystals (0.160 g, 75%) of VI (m.p. 135—138°). (Found: C, 25.63; H, 2.44; N, 9.71. $C_9H_{11}F_6MnN_3O_4P$ calcd.: C, 25.41; H, 2.61; N, 9.89%.) The compound is readily soluble in CH_2Cl_2, THF and acetone, slightly soluble in $CHCl_3$, ethyl ether and benzene and insoluble in pentane and H_2O. In the solid state, VI is air-stable, but it slowly decomposes in solution.

IR spectrum in Nujol [or HCBD]: 3350 m (sh), 3340 m, [2970 m, 2932 vw (sh), 2880 vw] 1618 m, 1604 s [1465 w (sh), 1446 m, 1403 w, 1397 m, 1356 m] 1314 w (br), 1171 w (br), 1074 w, 1056 w (sh), 975 vw, 880 m (sh), 855 s, 845 s (sh), 758 w (sh), 740 m (sh), 722 s, 672 s, 650 s, 638 s.

Alternative purification method. The oily lemon-yellow residue obtained on evaporation of the reaction mixture was dissolved in CH_2Cl_2 and passed through a 12 X 250 mm silica gel column prepared in CH_2Cl_2. After the faster moving yellow band which exhibited only very weak ν(CO) bands was eluted with CH_2Cl_2, a second band, colored orange-yellow, was eluted with 1/1 CH_2Cl_2/THF giving a mixture rich in $\{Mn(CO)_4(CNCH_3)[C(NHCH_3)_2]\}PF_6$, III, but contaminated with VI The subsequent very poorly-defined yellow band was eluted with a THF—acetone mixture giving VI which was purified by recrystallization as described above. When the fraction rich in III was fractionally recrystallized from $CHCl_3$—ethyl ether, pure colorless crystals of III were obtained. Starting from 0.450 g (1.14 mmoles) of *cis*-$[Mn(CO)_4(CNCH_3)_2]$-PF_6, 0.038 g of pure III and 0.063 g of VI were obtained. Compound III (m.p., 130—136°) is readily soluble in CH_2Cl_2, THF and acetone, slightly soluble in $CHCl_3$, benzene and ether and insoluble in pentane and H_2O. (Found: C, 25.73; H, 2.59; N, 9.35. $C_9H_{11}F_6MnN_3O_4P$ calcd.: C, 25.41; H, 2.61; N, 9.89%.) In the solid state, III is air-stable, but it slowly decomposes in solution.

IR spectrum in Nujol [or HCBD]: 3460 vw, 3392 m [2968 w, 2930 w (sh), 2865 vw] 1578 m (br), 1524 m (br) [1490 w, 1462 w (br), 1453 w (sh), 1416 m, 1368 m] 1304 m (br), 1202 w (br), 1038 m, 978 vw, 877 m (sh), 848 s, 840 s (sh), 741 w, 720 m (sh), 712 m, 668 m (sh) 662 s, 640 s.

$(OC)_4MnC(=NCH_3)N(CH_3)C(NHCH_3)$, V

To 0.160 g (0.38 mmole) of $[(OC)_4MnC(NHCH_3)N(CH_3)C(NHCH_3)]PF_6$ dissolved in 5 ml of CH_2Cl_2 was added 2 ml (14 mmole) of $(C_2H_5)_3N$. After 10 min of reaction at 25°, 30 ml of ethyl ether was added to precipitate $(C_2H_5)_3$-$NH^+PF_6^-$. After filtration, the solution was evaporated to dryness in vacuum. The pale-yellow crude product which was contaminated with the starting material was sublimed at 80°/0.05 mm to give 0.077 g (73%) of V. A parent ion at *m/e* 279 was observed in its mass spectrum. The compound sublimes at atmospheric pressure at 100°C. It is readily soluble in CH_2Cl_2, THF, acetone, moderately soluble in $CHCl_3$, benzene, ethyl ether, and slightly soluble in pentane. It is stable in the solid state but decomposes slowly in solution. (Found: C, 38.77; H, 3.74; N, 15.32. $C_9H_{10}MnN_3O_4$ calcd.: C, 38.70; H, 3.61; N, 15.06%.)

IR spectrum in Nujol [or HCBD]: [~ 3110 w (br), 2900 m (br)] 1625 w (br), 1590 m (br) [1472 s, 1436 w, 1404 m, 1384 m, 1367 m, 1274 m] 1160 w (br), 1060 w, 1037 w, 980 w (br), 900 m, 723 w, 670 s, 635 s.

mer-$[(OC)_3(CH_3NC)MnC(NHCH_3)N(CH_3)C(NHCH_3)]PF_6$, IX

Into 0.284 g (0.70 mmole) of *mer*-$[Mn(CO)_3(CNCH_3)_3]PF_6$ suspended in 30 ml of THF was bubbled CH_3NH_2 for 50 min at room temperature. The resulting clear light-yellow solution was stirred for 5 h and then evaporated on a rotary vacuum evaporator. The brown residue, after being dried in vacuum, was extracted with acetone, and the product was precipitated with ethyl ether. White prismatic crystals of IX were obtained after recrystallization from acetone—ethyl ether. The yield was 0.176 g (58%). The product is slightly soluble in CH_2Cl_2 but readily soluble in acetone. It melted with gas evolution at 152—160°. (Found: C, 27.62; H, 3.23; N, 11.91, 12.48. $C_{10}H_{14}F_6MnN_4O_3P$ calcd.: C, 27.39; H, 3.22; N, 12.79%.)

IR spectrum in Nujol [or HCBD] : 3342 m, 3276 w [2960 m, 2935 w (sh), 2883 vw] 1640 vw, 1609 s, 1591 s [1455 w (br), 1421 m, 1396 m (sh), 1390 m] 1342 m, 1301 m (br), 1172 w (br), 1160 w (sh), 1054 w, 996 w, 893 m (sh), 860 s, 826 s, 745 m, 725 m (sh), 664 m, 650 m.

fac-$[Mn(CO)_3(CNCH_3)_3]SO_3F$

The starting complex, $[(C_2H_5)_4N]_2[Mn(CO)_3(CN)_3]$, was prepared from the reaction of 0.541 g (1.96 mmoles) of $Mn(CO)_5Br$, 0.766 g (11.7 mmoles) of KCN, and 0.657 g (10.8 mmoles) of $(C_2H_5)_4NCl$ in 30 ml of methanol under a nitrogen atmosphere. Although these conditions are much milder, they are similar to those used in the preparation of $K_2[Mn(CO)_3(CN)_3]$ as described by Behrens et al. [14]. After the initial vigorous evolution of CO gas, the solution turned from orange to lemon-yellow, and the solution was heated to reflux for 20 h. After the reaction, the excess salts were removed by filtration under nitrogen, and the filtrate was evaporated to dryness in vacuum, giving a chocolate-brown solid. It was redissolved in acetone and precipitated by adding ethyl ether giving a brown solid. No further purification was attempted at this stage. Its IR spectrum showed $\nu(C{\equiv}N)$ bands at 2105 (sh) and 2094 m, and $\nu(C{\equiv}O)$ bands at 2002 vs and 1911 vs (br) cm^{-1} in CH_2Cl_2 solvent; these values are similar to those reported [14] for $K_2[Mn(CO)_3(CN)_3]$ (2116 s, 2092 vs, 2015 s and 1937 vs in alcohol). The crude *fac*-$[Mn(CO)_3(CN)_3]^{2-}$ was dissolved in 20 ml of CH_2Cl_2 and 1.1 ml (13 mmoles) of CH_3SO_3F was added under nitrogen at room temperature. Reaction was continued for 20 min, and the mixture was evaporated to dryness under vacuum. The light-brown residue was recrystallized from $CHCl_3$—ethyl ether. White flaky crystals of product were obtained by a second recrystallization from acetone—ethyl ether to give 0.187 g (27% based on $Mn(CO)_5Br$ used) (m.p. 149—154°). (Found: C, 30.17; H, 2.92; N, 11.19. $C_9H_9FMnN_3O_6S$ calcd.: C, 29.90; H, 2.51; N, 11.63%.) The compound is air-stable as the solid but decomposes slowly in solution.

IR spectrum in Nujol [or HCBD] : [3025 w, 2965 w] 1655 w (br) [1456 m, 1416 m] 1275 s, 1222 s, 1196 s, 1125 m, 1073 w, 1052 s, 858 m, 725 m, 666 s, 638 s, 580 s.

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