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REACTIONS OF (CYCLOPENTADIENYL)NITROSYLDICARBONYLMANGANESE CATION WITH AMINES

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Summary

The $[(XC_5H_4)Mn(CO)(NO)L]^+$ complexes react with primary alkylamines to give carboxamido complexes, where $X = H, CH_3$; $L = CO, P(C_6H_5)_3$. In the case of $L = CO$, the carboxamido complexes may be isolated, whereas with $L = P(C_6H_5)_3$ the reversibility of the reactions permits the isolation only of the starting materials when the solutions are evaporated to dryness. This diminished tendency to form carboxamido complexes is related to the decreased electron density on the carbonyl carbon going from $L = CO$ to $L = P(C_6H_5)_3$. The presence of the coordinated NO group does not change the reactivity of the cationic complexes towards amines.

Introduction

The reactions of a variety of cationic metal carbonyl complexes with primary and secondary amines, hydrazines, alkoxide and azide ions have been recently reported [1 - 7]. In all these studies, nucleophilic attack at the carbon atom of a coordinated carbon monoxide molecule has been suggested. In contrast, this type of reaction has rarely been observed for the coordinated NO group in nitrosyl complexes.

With the objective of bringing about reactions between amines and the coordinated NO group, we have examined the interaction of nitrosyl-cation complexes of the type $[(XC_5H_4)Mn(CO)(NO)L]^+$ [$X = H, CH_3$; $L = CO, P(C_6H_5)_3$] with primary amines. We have found that the amines react at the carbonyl in preference to the nitrosyl group, in agreement with the known

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behaviour of the methoxide ion towards mixed nitrosyl carbonyl cationic complexes [8 - 11].

Experimental

The hexafluorophosphate salts of the cations $[(C_5H_5)Mn(CO)_2(NO)]^+$ [12], $[(CH_3C_5H_4)Mn(CO)_2(NO)]^+$ [12], $[(C_5H_5)Mn(CO)(NO)P(C_6H_5)_3]^+$ [9], $[(CH_3C_5H_4)Mn(CO)(NO)P(C_6H_5)_3]^+$ [13] were prepared by published methods.

All syntheses were carried out under nitrogen in dry solvents. Infrared and proton NMR spectra were respectively recorded on Perkin—Elmer 457 and Jeol T-60 spectrometers. The mass spectra were obtained with an Atlas CH-4.

Preparation of $(C_5H_5)Mn(CO)(NO)(CONHCH_3)$

The complex $[(C_5H_5)Mn(CO)_2(NO)]PF_6$ (1.00 mmole) was suspended in 20 ml of ethyl ether. Methylamine was slowly bubbled into this suspension for about 10 min. The resulting red solution was filtered, and the solvent removed with a stream of nitrogen. The residue was dissolved in a CH_2Cl_2/hexane mixture (1/2) and the solution was filtered. On cooling the solution to — 78°, the orange $(C_5H_5)Mn(CO)(NO)(CONHCH_3)$ (41% yield) m.p. 88 - 90° (dec.) separated out. (Found; C, 39.0; H, 3.54; N, 10.8 $(C_5H_5)Mn(CO)(NO)$-$(NO)(CONHCH_3)$ calcd.: C, 40.6; H, 3.84; N, 11.2%.)

Its proton NMR spectrum in $CDCl_3$ solution shows a doublet at δ 2.76 ppm downfield from tetramethylsilane due to the methyl protons, and a singlet at 5.12 ppm due to the five ring protons.

Preparation of $(CH_3C_5H_4)Mn(CO)(NO)(CONHCH_3)$

The title compound was prepared in 40% yield, by the procedure described above. It is orange, and melts with decomposition at 87 - 90°. (Found: C, 43.1; H, 4.3; N, 10.6. $(CH_3C_5H_4)Mn(CO)(NO)(CONHCH_3)$ calcd.: C, 43.20; H, 4.38; N, 11.16%.)

Its proton NMR spectrum in $CDCl_3$ solution shows a singlet at 1.95 ppm due to the methyl protons of the methyl on the cyclopentadienyl ring, a doublet at 2.75 ppm due to the CH_3 protons of the methyl carbamoyl moiety, and a broad line at 4.92 ppm due to the four ring protons.

Reactions of $[C_5H_5Mn(CO)_2(NO)]PF_6$ with other primary amines

In the case of liquid amines a slight variation on the method used for the gaseous methylamine was required. A ten-fold excess of the amine was added to an ether suspension of the $[(C_5H_5)Mn(CO)_2(NO)]PF_6$, and after 30 min the solvent was evaporated to dryness under vacuum. Recrystallization by the method described above, from CH_2Cl_2 and hexane, give the carboxamido products, contaminated with $(NH_3R)PF_6$ as indicated from the presence of absorptions due to the PF_6 group at 835 cm^{-1} in the IR spectra of the final products. The carboxamido products were identified by their IR spectra (Table 1).

Reactions of $[(XC_5H_4)Mn(CO)(NO)P(C_6H_5)_3]PF_6$ with CH_3NH_2

These reactions were carried out in CH_2Cl_2. The yellow solution of the

TABLE 1

IR SPECTRA (cm^{-1}) OF COMPOUNDS IN CH_2Cl_2

Compound	ν(C—O)	ν(N—O)	ν(C=O)
$[(-C_5H_5)Mn(CO)_2(NO)]PF_6$[a]	2119s, 2079s	1852s	
$[(-C_5H_5)Mn(CO)(NO)P(C_6H_5)_3]PF_6$[a]	2042s	1801s	
$[(CH_3C_5H_4)Mn(CO)_2(NO)]PF_6$[b]	2116s, 2078s	1847s	
$[(CH_3C_5H_4)Mn(CO)(NO)P(C_6H_5)_3]PF_6$[b]	2039s	1794s	
$(C_5H_5)Mn(CO)(NO)(CONHCH_3)$	2006s	1746s	1617m
$(C_5H_5)Mn(CO)(NO)(CONHC_2H_5)$	2006s	1748s	1618m
$(C_5H_5)Mn(CO)(NO)(CONHC_3H_7)$	2006s	1750s	1606m
$(C_5H_5)Mn(CO)(NO)(CONHC_4H_9)$	2008s	1748s	1619m
$(C_5H_5)Mn(CO)(NO)(CONHC_6H_{11})$	206s	1753s	1625m
$(C_5H_5)Mn(CO)(NO)(CONHCH_2C_6H_5)$	2010s	1753s	1622m
$(CH_3C_5H_4)Mn(CO)(NO)(CONHCH_3)$[c]	2010s	1736s	1600m
$(CH_3C_5H_4)Mn(NO)P(C_6H_5)_3(CONHCH_3)$		1669s	1600m
$(C_5H_5)Mn(NO)P(C_6H_5)_3(CONHCH_3)$		1679s	1611m

[a] In acetonitrile, ref. [9]. [b] In acetone, ref. [13]. [c] In carbon tetrachloride.

starting cationic complex immediately turned red-orange upon bubbling in CH_3NH_2. Removal of the solvent with a stream of nitrogen afforded the starting complex in an almost quantitative yield. The IR spectrum of the reaction mixture showed the characteristic absorption peaks of the cationic complexes, together with those of the $(XC_5H_4)Mn(NO)P(C_6H_5)_3(CONHCH_3)$ (see results and discussion).

Reactions of $(XC_5H_4)Mn(CO)(NO)(CONHR)$ with HCl

Gaseous HCl was bubbled into a solution of 0.1 g of $(XC_5H_4)Mn(CO)(NO)(CONHR)$ dissolved in 30 ml of ether; after a few minutes a pale-yellow precipitate appeared. After 10 min the reaction was stopped, and the solid was filtered off under nitrogen and dissolved in water. The product $[(XC_5H_4)Mn(CO)_2(NO)]^+PF^-$ was precipitated by addition of an aqueous solution of NH_4PF_6.

Results and discussion

The reaction of $[(XC_5H_4)Mn(CO)(NO)L]^+$ complexes with primary amines, RNH_2, yields $(XC_5H_4)Mn(NO)(L)(CONHR)$ according to eqn. (1).

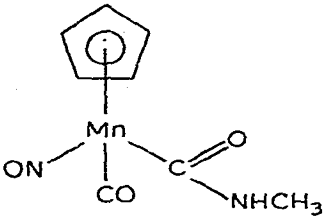
$$[(XC_5H_4)Mn(CO)(NO)L]^+ + 2NH_2R \rightarrow (XC_5H_4)Mn(NO)(L)(CONHR) + RNH_3^+ \qquad (1)$$

($X = H, CH_3$; $L = CO, P(C_6H_5)_3$; $R = CH_3, C_2H_5, (CH_3)_2CH, C_4H_9, CH_2C_6H_5, C_6H_{11}$).

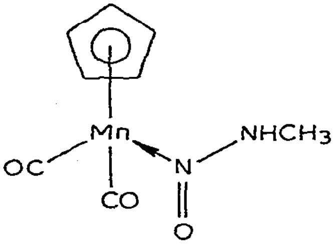
All the $(XC_5H_4)Mn(CO)(NO)(CONHR)$ are orange solids, soluble in all the common organic solvents. Their stability in solution decreases as the size of the R group increases. In the solid state they decompose even if stored under nitrogen. The broadening of the NMR signals suggests that the decomposition product may contain paramagnetic Mn^{II} species.

The nature of the carboxamido complexes was established from their IR spectra and, where possible, by elemental analysis. Owing to the difficulties in eliminating the $(NH_3R)PF_6$ salt from the reaction mixture, pure products were not isolated from the reactions of ethylamine, isopropylamine, n-butylamine, cyclohexylamine and benzylamine. The similarities of their IR spectra (Table 1) to those of the well characterized methylamine complexes in the C—O and N—O stretching region, strongly suggests that these products also have the composition of the type shown in eqn. (1).

The IR spectra (see Table 1) of all the compounds show one band in the range 2006 - 2010 cm^{-1} which is assigned to the terminal C—O, a strong band in the range 1736 - 1753 cm^{-1} attributable to the terminal ν(NO) and a medium intensity band in the range 1600 - 1622 cm^{-1} due to the ν(C=O) stretching frequencies of the carboxamido group. The mass spectrum of $(XC_5H_4)Mn(CO)(NO)(CONHCH_3)$ shows the parent ion peak followed by fragments corresponding to the loss of CO, $NHCH_3$, NO. These spectroscopic properties are in agreement with the proposed carboxamido formulation (I), unambiguously excluding alternative possibilities, such as nitroso-amino derivatives (II).



(I)



(II)

Although it has been recently observed that the NO coordinated in cationic complexes is susceptible to nucleophilic attack [14 - 16] to give nitroso compounds, the cationic complexes described here do not follow such a path in reactions with amines. The same behaviour has been found for other nitrosyl—carbonyl cations. In fact the methoxide ion fails to react with $\{(C_5H_5)Mn(NO)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]\}^+$ [9] while with $(C_6H_5)Mn(CO)(NO)P(C_6H_5)_3$ and $[Os(CO)_2(NO)P(C_6H_5)_3]^+$ [14] it attacks the carbonyl rather than at the nitrosyl group.

The nature of the carboxamido products is further confirmed from the reaction with HCl. The complex $(XC_5H_4)Mn(CO)(NO)(CONHR)$ reacts rapidly with anhydrous HCl in ether solution with loss of the NHR moiety from the carbamoyl group to yield the parent cationic complex, according to eqn. (2):

$$(XC_5H_4)Mn(CO)(NO)(CONHR) + 2H^+ \rightarrow [(XC_5H_4)Mn(CO)_2(NO)]^+ + NH_3R^+ \qquad (2)$$

The cation may be precipitated from water as the hexafluorophosphate salt.

Attempts to isolate complexes of the type $(XC_5H_4)Mn(NO)P(C_6H)_3(CONHCH_3)$ were frustrated by the reversibility of the reaction (1).

Only the starting material was recovered from the reactions between the $[(XC_5H_4)Mn(CO)(NO)P(C_6H_5)_3]^+$ and NH_2CH_3. The IR spectrum of the

CH_2Cl_2 solution of the reaction mixture containing $[(XC_5H_4)Mn(CO)(NO)P(C_6H_5)_3]^+$ and NH_2CH_3 shows the carboxamido band (1600 cm^{-1}) together with the terminal C—O stretching (2040 cm^{-1}) of the starting material. Increasing the amount of amine causes a decrease of the band at 2040 cm^{-1} with a simultaneous increase of the band at 1600 cm^{-1}. This decrease in the formation of carboxamido complexes is presumably due to an increase in electron density at the carbonyl carbon on replacing a CO by the more basic $P(C_6H_5)_3$ ligand. This trend of reactivity for the cationic nitrosyl—carbonyl complexes on going from dicarbonyl to carbonyl—phosphine derivatives, agrees with the predictions made by Angelici and Blacik [5]. They relate the probability of metal carbonyl/amine reactions with the C—O force constants. In our case, the force constants of the C—O ligand for $[(XCH_3C_5H_4)Mn(CO)_2(NO)]^+$, $[(C_5H_5)Mn(CO)_2)(NO)]^+$, $[(CH_3C_5H_4)Mn(CO)(NO)P(C_6H_5)_3]^+$, and $[(C_5H_5)Mn(CO)(NO)P(C_6H_5)_3]^+$, calculated by the approximate methods of Cotton and Kraihanzel [17], are 17.8 and 16.8 mdyn/Å respectively for the first and second pair of complexes. As pointed out by Angelici and Blacik, these values indicate that the $[(XC_5H_4)Mn(CO)_2(NO)]^+$ ($X = H, CH_3$) complexes should readily form carboxamido complexes, whereas $[(XC_5H_4)Mn(CO)(NO)P(C_6H_5)_3]^+$ ($X = H, CH_3$) should give an equilibrium mixture.

It is noteworth that the presence of the coordinated NO group is not effective in changing the reactivity toward amines of cationic carbonyl complexes. Since $[(C_5H_5)Mn(NO)(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]^+$ [9] also fails to react with amines or methoxide ion to give nitroso derivatives, this lack of reactivity is probably due to the inertness of coordinated NO in the $[(C_5H_5)Mn(CO)_2(NO)]^+$ complexes, rather than to a kinetic effect favouring the formation of carboxamido complexes.

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