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COMPETITIVE REACTIONS OF COORDINATED CARBON MONOXIDE AND METHYL ISOCYANIDE WITH AMINES

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Summary

The relative reactivities of CO and C≡N—R ligands with CH_3NH_2 were investigated in complexes which contained both ligands. Like $(C_5H_5)Fe(CO)_3{}^+$, the $(C_5H_5)Fe(CO)_2(CNCH_3)^+$ complex reacts with CH_3NH_2 to give the carbamoyl complex $(C_5H_5)Fe(CO)(CNCH_3)(CONHCH_3)$; this is a readily reversible reaction. In contrast, $(C_5H_5)Fe(CO)(CNCH_3)_2{}^+$ reacts with CH_3NH_2 to give the amidinium or carbene complex, $(C_5H_5)Fe(CO)(CNCH_3)[C(NHCH_3)_2]^+$. In a slow reaction, $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$ forms the amidinium complex, $(C_5H_5)Fe(PPh_3)(CO)[C(NHCH_3)_2]^+$. Factors that affect the site of CH_3NH_2 reaction are discussed. The complexes have been characterized by IR and NMR spectroscopy; a variable temperature NMR study of $(C_5H_5)Fe(CO)(CNCH_3)[C(NHCH_3)_2]^+$ indicates restricted rotation around the C—N bonds of the amidinium ligand.

Introduction

Many metal carbonyl complexes are known [1] to react with primary and secondary amines to give carbamoyl complexes. An early example of the reaction was [2]:

$$(C_5H_5)Fe(CO)_3{}^+ + 2CH_3NH_2 \rightarrow (C_5H_5)Fe(CO)_2(CONHCH_3) + CH_3NH_3{}^+ \quad (1)$$

We also carried out the reaction of an analogous isocyanide complex to determine whether the electronically similar isocyanide ligand would react in the

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same manner. The reaction proceeded to give an amidinium or "carbene" complex [3]:

$$(C_5H_5)Fe(C{\equiv}N{-}R)_3{}^+ + CH_3NH_2 \rightarrow (C_5H_5)Fe(C{\equiv}N{-}R)_2[C(NHCH_3)NHR]^+ \quad (2)$$

where R = *p*-methoxyphenyl. Now many examples are known [4] of reactions of isocyanide complexes with amines to give amidinium complexes.

Since both ligands undergo amine addition, we sought to determine whether the CO or the isocyanide ligand was more reactive in a complex which contained both ligands. In the present paper, we report the reactions of $(C_5H_5)Fe(CO)_2(C{\equiv}N{-}CH_3)^+$, $(C_5H_5)Fe(CO)(C{\equiv}N{-}CH_3)_2{}^+$, and $(C_5H_5)Fe(CO)(C{\equiv}N{-}CH_3)(PPh_3)^+$ with primary amines.

Results

The complex $(C_5H_5)Fe(CO)_2(C{\equiv}N{-}CH_3)^+$ reacts with CH_3NH_2 as follows:

$$(C_5H_5)Fe(CO)_2(CNCH_3)^+ + 2CH_3NH_2 \rightleftharpoons (C_5H_5)Fe(CO)(CNCH_3)(CONHCH_3) + CH_3NH_3{}^+ \quad (3)$$

After bubbling CH_3NH_2 through a CH_2Cl_2 solution of the complex for 1 hour at 25°, the reactant infrared bands at 2079, 2037 (C≡O stretches) and 2242 cm^{-1} (C≡N stretch) disappeared leaving product absorptions at 1951 (C≡O) and 2163 cm^{-1} ($C{\equiv}N{-}CH_3$). The 107 cm^{-1} decrease of $\nu(CO)$ from an average 2058 cm^{-1} for the reactant to 1951 cm^{-1} for the product is typical of these reactions [5]. A decrease of only 79 cm^{-1} occurs in the C≡N stretching frequency of the $CNCH_3$ ligand.

As has been found with some other metal carbonyl reactions with amines [5], this reaction is readily reversible. On evaporating a solution of the carbamoyl product, only the starting $(C_5H_5)Fe(CO)_2(CNCH_3)^+$ was recovered. Likewise, attempted precipitation with non-polar solvents such as pentane or ether yielded only the starting cation. Cyclohexylamine reacted similarly. Although there is little doubt about the structure of the carbamoyl product based on its infrared spectrum, products could not be isolated in either reaction.

The reaction of $(C_5H_5)Fe(CO)(CNCH_3)_2{}^+$ with CH_3NH_2 in CH_2Cl_2 for 1 hour at 25° yielded the carbene product:

$$(C_5H_5)Fe(CO)(CNCH_3)_2{}^+ + CH_3NH_2 \rightleftharpoons (C_5H_5)Fe(CO)(CNCH_3)[C(NHCH_3)_2]^+ \quad (4)$$

It was isolated and characterized by its elemental analysis and infrared spectrum which showed $\nu(CO)$ at 1995 cm^{-1} and $\nu(C{\equiv}N)$ at 2190 cm^{-1} (Table 1). In going from the starting complex to the cationic carbene complex, $\nu(CO)$ decreases by only 36 cm^{-1} and $\nu(C{\equiv}N)$ decreases by 30 cm^{-1}.

In addition to the C_5H_5 protons at τ5.09, the NMR spectrum (Table 2) of the product showed a singlet at τ6.55 for the $CNCH_3$ methyl group, a broad band at τ2.20—2.60 for the N—H protons and two doublets (*J*(HNCH)4.7 Hz)

TABLE 1

INFRARED SPECTRA IN CARBONYL STRETCHING REGION

Compound	$\nu(C{\equiv}NCH_3)^a$ (cm^{-1})	$\nu(C{\equiv}O)^a$ (cm^{-1})	$k(C{\equiv}O)^e$ (mdynes/Å)
$[(C_5H_5)Fe(CO)_3]PF_6$		2120, 2070^b	17.6
$[(C_5H_5)Fe(CO)_2CNCH_3]PF_6$	2242	2079, 2037	17.1
$[(C_5H_5)Fe(CO)_2(PPh_3)]Cl$		2065, 2030	16.9
$(C_5H_5)Fe(CO)_2CN$		2062, 2016^c	16.8
$(C_5H_5)Fe(CO)_2Cl$		2050, 2010	16.6
$[(C_5H_5)Fe(CO)(CNCH_3)_2]BPh_4$	2229, 2210	2031	16.6
$[(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)]BPh_4$	2194	1999	16.1
$\{(C_5H_5)Fe(CO)(CNCH_3)[C(NHCH_3)_2]\}BPh_4$	2190	1995	16.0
$(C_5H_5)Fe(PPh_3)(CO)CN$		1972^d	15.7
$\{(C_5H_5)Fe(PPh_3)(CO)[C(NHCH_3)_2]\}BPh_4$		1960	15.5
$[(C_5H_5)Fe(CO)(CNCH_3)(CONHCH_3)$	2163	1951	15.4
$[(C_5H_5)Fe(CO)(CNCH_3)(CONHC_6H_{11})$	2165	1950	15.4

[a] In CH_2Cl_2 solvent. [b] Ref. 17. [c] $\nu(CN) = 2124\ cm^{-1}$. [d] $\nu(CN) = 2099\ cm^{-1}$. [e] Calculated by the methods given in ref. 18.

at $\tau 6.99$ and $\tau 7.28$ for the two methyl groups of the carbene ligand. The non-equivalence of the carbene methyl groups almost certainly results from the existence of the ligand in the following planar form:

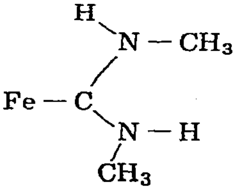

Fig. 1

Partial double bonding between the carbene C and the N atoms leads to significant barriers to rotation around those bonds.

As the temperature of the complex is increased, the carbene ligand CH_3 group resonances change (Fig. 2). First the doublet character disappears indicating a loss of coupling between the CH_3 and NH protons. This is probably due to exchange of the NH protons with the small amount of H_2O in the DMSO-d_6 solvent. At slightly higher temperatures, the two CH_3 resonances coalesce (coalescence temperature of approximately 72°) into one peak which sharpens up to the maximum temperature (92°) studied. All of these changes are reversible by lowering the temperature. The coalescence of the two CH_3 resonances indicates that these groups are becoming equivalent most probably by a mechanism involving rotation around the C—N bonds. Hammond and Neuman [6] previously observed similar changes in the N—H proton resonances of the acetamidinium ion, $CH_3C(NHCH_3)_2^+$. Although the value is not directly comparable with our value, they obtained a coalescence temperature of approximately 96° for rotation around the C—N bonds. Little is known about the factors which influence such barriers to rotation, although it has been noted that steric effects of the other ligands bound to the metal contribute significantly to the barrier in carbamoyl M—C(O)N$(CH_3)_2$ complexes [7].

The reaction of $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$ with CH_3NH_2 proceeds slowly with carbene formation (eq. 5).

TABLE 2

PROTON NMR SPECTRA

Compound	Solvent	Assignment	τ(ppm)[a]
$(C_5H_5)Fe(PPh_3)(CO)(CN)$	$CDCl_3$	C_5H_5	5.47(d)[b]
		C_6H_5	2.60(m)
$[(C_5H_5)Fe(CO)_2(CNCH_3)]PF_6$	Acetone-d_6	C_5H_5	4.29(s)
		$CNCH_3$	6.35(s)
$[(C_5H_5)Fe(CO)(CNCH_3)_2]BPh_4$	Acetone-d_6	C_5H_5	4.88(s)
		$CNCH_3$	6.63(s)
		C_6H_5	2.5 - 3.5(m)
$[(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)]BPh_4$	Acetone-d_6	C_5H_5	4.90(d)[b]
		$CNCH_3$	6.76(d)[b]
		C_6H_5	2.50 - 3.50(m)
$\{(C_5H_5)Fe(CO)(CNCH_3)[C(NHCH_3)_2]\}BPh_4$	Acetone-d_6	C_5H_5	5.26(s)
		$CNCH_3$	6.69(s)
		C_6H_5	2.60 - 3.50(m)
		$C(NHCH_3)_2$	6.98(d)[c] 7.32(d)[c]
	DMSO-d_6	C_5H_5	5.09(s)
		$CNCH_3$	6.55(s)
		C_6H_5	2.70 - 3.33(m)
		NH	2.20 - 2.60 (br)
		$C(NHCH_3)_2$	6.99(d)[c] 7.28(d)[c]
$\{(C_5H_5)Fe(PPh_3)(CO)[C(NHCH_3)_2]\}BPh_4$	Acetone-d_6	C_5H_5	5.05(d)[b]
		C_6H_5	2.5(m), 3.1(m)
		$C(NHCH_3)_2$	6.72(d)[c] 7.42(d)[c]

[a] Tetramethylsilane used as internal standard (τ10.0). Multiplicities are indicated in parentheses: s, singlet; d, doublet; m, multiplet; br, broad. [b] J(PFeCH)1.5Hz. [c] J(HNCH)4.7Hz.

$$(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+ + CH_3NH_2 \rightarrow (C_5H_5)Fe(PPh_3)(CO)[C(NHCH_3)_2]^+ \quad (5)$$

Its elemental analysis and infrared spectrum with ν(CO) at 1959 cm^{-1} and no ν(CN) confirms this structure. As in reaction 4, ν(CO) is lowered by 39 cm^{-1} on going to the carbene product. Its proton NMR spectrum showed C_5H_5 protons at τ5.05 and the non-equivalent methyl groups of the carbene ligand as doublets (J(HNCH) 4.7 Hz) at τ6.72 and τ7.42 as in Fig. 1.

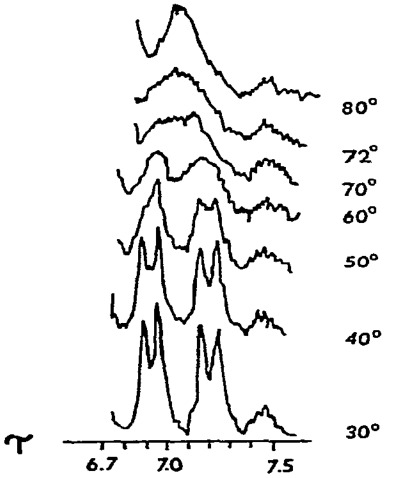

Fig. 2. Temperature-dependent NMR spectra of the amidinium CH_3 groups in $(C_5H_5)Fe(CO)(CNCH_3)$-$[C(NHCH_3)_2]^+$ in DMSO-d_6.

As commonly observed for metal carbonyl complexes, the C—O stretching frequencies and their associated force constants depend on the nature of the other ligands in the complex. The changes for the complexes described in this paper (Table 1) may be summarized by noting the increasing tendency of the following ligands to increase the C—O force constant: $CONHCH_3^- < C(NHCH_3)_2 < CN^- \sim PPh_3 < CNCH_3 < CO$.

Proton NMR spectra of reactants and products are given in Table 2. When $(C_5H_5)Fe(CO)(CNCH_3)_2^+$ and $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$ react with CH_3NH_2 to form the corresponding carbene complexes (equations 4 and 5), the C_5H_5 proton resonances move to higher field. This suggests that the carbene ligand is a better electron donor than the $CNCH_3$ group. This evidence, together with the trend in ν(CO) values, suggests that the $C(NHCH_3)_2$ group acts as a much poorer π-acceptor (and/or a better σ-donor) of electron density than does the $CNCH_3$ ligand. This is consistent with conclusions for Pt—carbene complexes [4] for which there is little evidence for π-bonding in the Pt—C bond. Thus the ligand would be more accurately described as an amidinium group rather than a carbene.

Discussion

CO versus $CNCH_3$ reaction

Since more is known about the reactivity of CO than isocyanides with nucleophilic amines, it is instructive to ask why the CO group reacts in $(C_5H_5)Fe(CO)_3^+$, $(C_5H_5)Fe(CO)_2(PPh_3)^+$, and $(C_5H_5)Fe(CO)_2(CNCH_3)^+$ but not in $(C_5H_5)Fe(CO)(CNCH_3)_2^+$ or $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$. In general, the reaction of amines with coordinated CO appear [2,3] to be much more rapid [8] than those with isocyanides [9]. Thus it would be expected that the CO would have the first opportunity to react with the amine. As has been noted previously [5], the tendency of a given CO in a complex to react with amines depends upon the electron density on the C atom, which is related to the C—O stretching frequency or force constant. Low C—O force constants indicate a relatively high electron density [10] on the C and thus a low tendency (i.e., small equilibrium constant) to react with electron donors such as amines. From previous studies [5], it was found that CO ligands with force constants greater than 17.0 mdyn/Å readily form carbamoyl complexes, those with force constants between 16.0 and 17.0 mdyn/Å give equilibrium mixtures of starting carbonyl and product carbamoyl complexes, and those with constants below 16.0 mdyn/Å showed no evidence for carbamoyl formation. In the present series of compounds, it is clear (Table 1) from the high C—O force constant (17.6 mdyn/Å) for $(C_5H_5)Fe(CO)_3^+$ that it will form a stable carbamoyl complex, as it does [2].

Both $(C_5H_5)Fe(CO)_2(CNCH_3)^+$ and $(C_5H_5)Fe(CO)_2(PPh_3)^+$ have force constants, 17.1 and 16.9, respectively, which are significantly lower. In CH_2Cl_2, both form carbamoyl complexes as indicated by infrared spectra, yet on evaporating the solutions to dryness, their equilibria shift back to give only the starting complexes. This behavior is typical of those complexes with force constants in this region. Our ability to isolate [2] the $(C_5H_5)Fe(CO)(PPh_3)CONHCH_3$ complex apparently resulted from its insolubility in the diethyl ether solvent used in its preparation.

Finally the two complexes, $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$ and $(C_5H_5)Fe(CO)(CNCH_3)_2^+$, that react with CH_3NH_2 addition to the $CNCH_3$ ligand, have still lower C—O force constants. For $(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)^+$ the force constant (16.1 mdyn/Å) is sufficiently low that the CO group may be unreactive; the $CNCH_3$ group, however, is still reactive although the reaction is much slower than with $(C_5H_5)Fe(CO)(CNCH_3)_2^+$. This latter complex has a C—O force constant (16.6 mdyn/Å) which suggests that the CO would still be able to react but reversibly. The fact that the isocyanide ligand reacts means that the equilibrium favors it over the CO group. The actual mechanism could involve initial amine attack at the CO followed by migration to the $CNCH_3$.

Our rationalization of the results might be summarized as follows: amine attack occurs preferentially at CO groups with high C—O force constants because of their higher rate of reaction and possibly also their higher thermodynamic stability. As the C—O force constant decreases, amine addition to CO becomes thermodynamically less favorable and amine addition to $CNCH_3$ predominates. Thus under conditions where CO is unreactive, $CNCH_3$ is still capable of undergoing amine addition. Since this is the first comparative study of CO and isocyanides, these tentative conclusions warrant investigation in other systems.

Experimental

The following compounds were prepared as described in the literature: $(C_5H_5)Fe(CO)_2Cl$ [11,12], $(C_5H_5)Fe(CO)_2(CN)$ [12], $[(C_5H_5)Fe(CO)_2(PPh_3)]Cl$ [13], and $[(C_5H_5)Fe(CO)(CNCH_3)_2]I$ [14]. The latter compound was converted to the PF_6^- or BPh_4^- salt by adding an aqueous solution of $[(C_5H_5)Fe(CO)(CNCH_3)_2]I$ to a saturated aqueous solution of NH_4PF_6 or $NaBPh_4$.

The compound, $(C_5H_5)Fe(PPh_3)(CO)(CN)$, was prepared by the general method given by Jennings and Wojcicki [15]. A mixture of 1.83 g (9.0 mmole) of $(C_5H_5)Fe(CO)_2CN$ and 11.0 g (42 mmole) of PPh_3 in 150 ml of benzene was refluxed under nitrogen for 70 h. After evaporating the benzene under reduced pressure, the resulting oil was made to crystallize by treatment with pentane. It was washed several times with warm pentane to remove excess PPh_3. The crude product, obtained in essentially quantitative yield, was used in the synthesis of $[(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)]BPh_4$ without further purification.

$[(C_5H_5)Fe(CO)_2(CNCH_3)]PF_6$

This compound was prepared previously by Treichel and Stenson [16]. The synthetic details cited here were kindly provided by Dr. Treichel. A solution of 2.2 g (11 mmole) of $(C_5H_5)Fe(CO)_2CN$ and 8 ml of CH_3I in 42 ml of CH_3CN was refluxed for 24 h. After evaporation to dryness under reduced pressure, the residue was extracted with 20 ml of boiling H_2O. The extract was suction-filtered directly into 30 ml of a saturated aqueous solution of NH_4PF_6. The pale yellow powder which precipitated was recrystallized by dissolving in a minimum of acetone and adding ice water. The precipitate was immediately filtered and dried (yield 43%). (Found: C, 30.16; H, 3.07; N, 3.72. $C_9H_8F_6O_2NPFe$ calcd.: C, 29.75; H, 2.20; N, 3.87.)

$[(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)]BPh_4$

A mixture of 3.90 g (8.93 mmole) of $(C_5H_5)Fe(PPh_3)(CO)CN$ and 25 ml of CH_3I in 250 ml of acetonitrile was refluxed under nitrogen for 5 h. After filtering, the solution was evaporated under reduced pressure to an oil, which was dissolved in acetone. The acetone solution was added to a 150 ml aqueous solution of $NaBPh_4$. The resulting yellow precipitate was dissolved in CH_2Cl_2; this solution was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Addition of diethyl ether and allowing the solution to stand at − 15° yielded 5.70 g (83%) of yellow $[(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)]BPh_4$. (Found: C, 77.13; H, 5.74. $C_{50}H_{43}BNFeOP$ calcd.: C, 77.9; H, 5.58.)

$\{(C_5H_5)Fe(CO)(CNCH_3)[C(NHCH_3)_2]\}BPh_4$

Methylamine was slowly bubbled through a stirred solution of 1.0 g (19 mmole) of $[(C_5H_5)Fe(CO)(CNCH_3)_2]BPh_4$ in 50 ml of CH_2Cl_2 at 25° for 1 h. The solution was evaporated to dryness under vacuum, and the residue was redissolved in 100 ml of CH_2Cl_2. After filtration, the volume was reduced under vacuum to ≈30 ml, and 100 ml of ether was added. The bright yellow product precipitated; it was recrystallized by dissolving in CH_2Cl_2 and precipitating with $(C_2H_5)_2O$ (Yield 44%). (Found: C, 71.80; H, 6.66; N, 7.20. $C_{35}H_{36}BN_3O$ calcd.: C, 72.31; H, 6.24; N, 7.23.)

$\{(C_5H_5)Fe(PPh_3)(CO)[C(NHCH_3)_2]\}BPh_4$

A solution of 2.0 g (4.58 mmole) of $[(C_5H_5)Fe(PPh_3)(CO)(CNCH_3)]BPh_4$ in 50 ml of CH_2Cl_2 was saturated with CH_3NH_2. After 6 h at 25° the infrared spectrum indicated that the reaction had gone to completion. The solution was evaporated to dryness, and the residue was redissolved in CH_2Cl_2. After drying over $MgSO_4$ and filtering, diethyl ether was added to this solution to give 1.9 g (92%) of $\{(C_5H_5)Fe(PPh_3)(CO)[C(NHCH_3)_2]\}BPh_4$. (Found: C, 77.53; H, 6.55. $C_{52}H_{48}BN_2FeOP$ calcd.: C, 76.4; H, 5.98.)

Infrared and NMR Spectra

Infrared spectra were recorded on Perkin—Elmer 137B or on Beckman IR-18A or IR-12 spectrophotometers, calibrated with gaseous CO and polystyrene film. A Varian Associates A-60 spectrometer was used for proton NMR spectra; a model V-6031 temperature controller unit was employed in the temperature dependence studies.

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