rate constant as measured for the 2-carboxybenzoate is not the rate constant applying to adjacent attack alone. Introduction of the second ester group, while decreasing the rate of adjacent attack, increases the possibilities of remote attack: the reductant has twice the opportunities for forming the binuclear complex. If the two ligands investigated have the same affinity for the extra proton, this advantage decreases with increasing temperature, as shown by the second term in the rate laws.

The reason given in the past for the absence of remote attack when the ligand is phthalic acid was that the two carboxyl groups cannot lie in the same plane. If protonation of the coordinated carboxyl occurs, coplanarity becomes possible. A very small amount of conjugation between the two metal centers should provide a sufficient path for the reduction to occur, but even so it is unlikely that the remote attack can ever be detected experimentally. The term for remote attack will probably be small in comparison with those for the adjacent attack and the deprotonated path, and no side reactions can be induced to yield additional evidence. Nor does a plot of ΔH^* against ΔS^* resolve the problem as it did in the case of the fumarate complexes[7]: the values fall on the line of the other *ortho*-substituted complexes, which have an isokinetic temperature of 70°.[10]

---

[10] J. E. Leffler, *J. Org. Chem.*, **20**, 122 (1955).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF SOUTHAMPTON, SOUTHAMPTON, ENGLAND

The Reactions of Group VI Metal Carbonyls with Pyrrolidine, Piperazine, and Morpholine

BY G. W. A. FOWLES AND D. K. JENKINS

Received August 19, 1963

Pyrrolidine and morpholine react with group VI metal carbonyls to give simple substituted products $L_nM(CO)_{6-n}$, where $n = 1$ and 2. Piperazine reacts with excess of $Mo(CO)_6$ and $W(CO)_6$ to give $(C_4H_{10}N_2)[M(CO)_5]_2$. The trisubstituted carbonyls $L_3Mo(CO)_3$ have been prepared for L = piperazine and morpholine by displacement of either toluene or mesitylene from the π-complexes. The infrared spectra of the complexes have been measured and assignments made.

Morpholine complexes have been prepared previously from the carbonyls of iron, cobalt, and nickel,[1-3] but the preparation involved the disproportionation of the carbonyls with the formation of complexes that were ionic in nature, *e.g.*, $[Fe(C_4H_8NO)_6]Fe_4(CO)_{13}]$. In this paper we report on products obtained by the reaction of pyrrolidine, piperazine, and morpholine with the group VI metal carbonyls. These compounds are diamagnetic and appear to be simple substitution complexes analogous to the various amine complexes prepared photochemically by Strohmeier and co-workers.[4-6] Thus, in reactions involving excess of carbonyl, morpholine displaced one mole of carbon monoxide to give the adducts $M(CO)_5(C_4H_8NO)$; the chromium and molybdenum compounds were monomeric in benzene solution. When morpholine was used in excess, two moles of carbon monoxide were displaced from both molybdenum and tungsten hexacarbonyls, giving the disubstituted products which were insoluble in nonpolar solvents but sparingly soluble in nitromethane; the corresponding chromium compound could not be isolated, but when the reaction was carried out in toluene solution the π-complex $(CH_3C_6H_5)Cr(CO)_3$ was isolated as well as $(C_4H_8NO)Cr(CO)_5$.

Both the mono- and disubstituted complexes were obtained from the reactions of the molybdenum and tungsten hexacarbonyls with pyrrolidine. The monosubstituted complexes were monomeric in benzene solution. In the corresponding reactions involving piperazine with the carbonyl in excess, the only products that could be isolated were the compounds $(C_4H_{10}N_2)[M(CO)_5]_2$.

Trisubstituted complexes could not be prepared from the carbonyls themselves, but the molybdenum compounds $Mo(CO)_3L_3$ were readily prepared by displacing mesitylene or toluene from the π complexes π-(arene)-$Mo(CO)_3$[7] by either morpholine or piperazine.

The infrared spectra of the morpholine complexes suggest that bonding is through nitrogen rather than oxygen. Thus in all the complexes the C–O–C stretches (found at 1079 and 875 cm.$^{-1}$ in morpholine itself) remain unchanged, while the N–H stretching frequency changes from 3320 cm.$^{-1}$ in morpholine to 3260 cm.$^{-1}$ in $(C_4H_8NO)_2Mo(CO)_4$; there is a similar lowering of the N–H stretching frequency of between 50 and 100 cm.$^{-1}$ in the other complexes, possibly resulting from electron withdrawal from nitrogen *via* the σ-bond upon coordination.

The carbonyl stretching frequencies of the $LM(CO)_5$ complexes can be assigned on the basis of work by Orgel[8] and Cotton and Kraihanzel.[9] Each spectrum

---

[1] W. Hieber and N. Kahlen, *Ber.*, **91**, 2223 (1958).
[2] W. Hieber, W. Kroder, and E. Zahn, *Z. Naturforsch.*, **15b**, 325 (1960).
[3] W. Hieber and R. Wiesboeck, *Ber.*, **91**, 1146 (1958).
[4] W. Strohmeier and D. von Hobe, *ibid.*, **94**, 761 (1961).
[5] W. Strohmeier, K. Gerlach, and D. von Hobe, *ibid.*, **94**, 164 (1961).
[6] W. Strohmeier and K. Gerlach, *ibid.*, **93**, 2087 (1960).
[7] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).
[8] L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).
[9] F. A. Cotton and C. S. Kraihanzel, *ibid.*, **2**, 533 (1963).

TABLE I
INFRARED SPECTRA

Complex	Assignment	Spectra (cm.$^{-1}$) Solution[a]	Nujol
$(C_4H_8NO)Cr(CO)_5$	A_1	2080 (w)	2049 (w)
	B_1	1992 (m)	1985 (s)
	E	1945 (s)	1942 (s)
	A_1	~1920 (sh)	
			1828 (m)
$(C_4H_8NO)Mo(CO)_5$	A_1	2074 (w)	2050 (m)
	B_1	1988 (m)	1980 (s)
	E	1943 (s)	1937 (s)
	A_1	~1915 (sh)	
			1824 (m)
$(C_4H_8NO)W(CO)_5$	A_1	2070 (w)	2050 (w)
	B_1	1979 (m)	1978 (s)
	E	1935 (s)	1940 (s)
	A_1	~1915 (sh)	
			1818 (m)
$(C_4H_9N)Mo(CO)_5$	A_1	2072 (w)	2048 (w)
	B_1	1982 (m)	1992 (m)
	E	1940 (s)	1938 (s)
	A_1	~1910 (sh)	1918 (m)
$(C_4H_9N)W(CO)_5$	A_1	2069 (w)	2047 (w)
	B_1	1980 (m)	1987 (m)
	E	1931 (s)	1936 (s)
	A_1	~1910 (sh)	1919 (m)
$(C_4H_8NO)_2Mo(CO)_4$	A_1	2009 (w)	2013 (m)
	B_1	1890 (s)	1877 (s)
	A_1	~1870 (sh)	1856 (s)
	B_2	1817 (s)	1789 (s)
$(C_4H_8NO)_2W(CO)_4$	A_1	2002 (w)	1992 (m)
	B_1	1888 (s)	1855 (s)
	A_1	~1865 (sh)	1825 (s)
	B_2	1810 (s)	1761 (s)
$(C_4H_9N)_2Mo(CO)_4$	A_1	2010 (w)	1995 (w)
	B_1	1888 (s)	1924 (m)
	A_1	~1870 (sh)	1887 (s)
	B_2	1815 (m)	1828 (s)
			1765 (s)
$(C_4H_9N)_2W(CO)_4$	A_1	2002 (w)	
	B_1	1875 (s)	
	A_1	~1870 (sh)	
	B_2	1808 (m)	
$(C_4H_8NO)_3Mo(CO)_3$			1870 (s)
			1840 (s)
$(C_4H_{10}N_2)_3Mo(CO)_3$			1878 (s)
			1737 (s)
$(C_4H_{10}N_2)Mo_2(CO)_{10}$	A_1	2079 (w)	2066 (w)
	B_1	~1980 (sh)	
	E	1940 (s)	1953 (s,br)
	A_1	1901 (m)	
			1821 (s)
$(C_4H_{10}N_2)W_2(CO)_{10}$	A_1	2077 (w)	2075 (w)
	B_1	~1970 (sh)	
$(C_4H_{10}N_2)W_2(CO)_{10}$	E	1933 (s)	1945 (s,br)
	A_1	1895 (m)	
			1818 (s)

[a] $CHCl_3$ for $LM(CO)_5$; CH_3NO_2 for $L_2M(CO)_4$; $(CH_3)_2CO$ for $LM_2(CO)_{10}$.

shows a single weak peak arising from the A_1 mode of the *trans* pair of carbonyl groups, stronger bands of the B_1 and E modes, and the A_1 mode from *cis* carbonyls which is just visible as a shoulder on the low frequency side of of the E mode. The frequencies observed for the peaks are of the same order as those obtained by Cotton for cyclohexylaminemolybdenum pentacarbonyl. These assignments are for the solution spectra; the Nujol mulls give rather more complex spectra (*cf.* Table I), presumably because of interactions in the solid.

The spectra of the tetracarbonyl complexes agree well with the assignments made for other $(amine)_2M(CO)_4$ complexes, and if the average frequency of the four peaks is taken as a guide, it is found to be similar to that found for the ethylenediamine complexes but lower than that for the dipyridyl derivatives. This suggests that the oxygen in the morpholine ring has no inductive effect on the nitrogen–metal bonding.

The reactions of piperazine with the hexacarbonyls could in theory give rise to several products: (a) $(C_4H_{10}N_2)_nM(CO)_{6-n}$, with piperazine functioning as a monodentate ligand, (b) $(C_4H_{10}N_2)M(CO)_4$, with the piperazine in the chair form and acting as a bidentate ligand, (c) $[(C_4H_{10}N_2)M(CO)_4]_n$, with piperazine a bidentate ligand in a polymeric chain, and (d) $(C_4H_{10}N_2)[M_2(CO)_{10}]$.

Strohmeier[10] examined the analogous reactions of 4-aminopyridine and *p*-phenylenediamine with molybdenum hexacarbonyl and obtained monomeric products $(C_5H_4NNH_2)_2Mo(CO)_4$ and $[C_6H_4(NH_2)_2]Mo(CO)_4$. In these reactions the amines function as monodentate groups.

In our experiments the carbonyls were used in 2-fold excess so that less replacement was to be expected. Compounds of type (d) were formed and their insolubility evidently prevented further replacement; the absence of tetracarbonyl derivatives was evident from the infrared spectra. Solution spectra were determined in acetone; to check that no reaction occurred in this solvent spectra were first run in Nujol, then in acetone, and the solid remaining after evaporation of the acetone was examined again in Nujol. The spectra are similar to those of the $(C_4H_8NO)M(CO)_5$ complexes, but both the B_1 and A_1 (*cis*) modes have been shifted to lower frequencies (relative to the other two peaks) so that the B_1 mode appears as a shoulder on the high frequency side of the main peak and the A_1 mode appears as a separate peak rather than a shoulder.

The infrared spectrum of the product formed by the displacement of toluene from π-$CH_3C_6H_5Mo(CO)_3$ shows the two strong peaks expected for a tricarbonyl derivative. Furthermore, it shows that both free and coordinated N–H groups are present, so that the piperazine molecules behave as monodentate ligands.

Experimental

Morpholine and pyrrolidine were dried over calcium hydride and piperazine was recrystallized from ethanol before use. All reactions were carried out under nitrogen and the products examined in a closed all-glass vacuum system.

(1) **Morpholine Reactions.** (i) **Morpholine Chromium Pentacarbonyl.**—Chromium hexacarbonyl (1 g.) was refluxed in a benzene (5 ml.)–toluene (20 ml.) mixture with morpholine (1 g.) for 48 hr. The resulting yellow solution was evaporated to dryness *in vacuo* and the yellow solid so obtained was dissolved in benzene and chromatographed on a silica-gel column. Two compounds were separated; one was the previously reported toluene

---

[10] W. Strohmeier and G. Schoenauer, *Ber.*, **95**, 1767 (1962).

product, $C_7H_8Cr(CO)_3$ (0.19 g.); the other was the morpholine product, $C_4H_9NOCr(CO)_5$. *Anal.* Calcd. for $C_9H_9CrNO_6$: C, 38.4; H, 3.2; N, 5.0; mol. wt., 281. Found: C, 38.4; H, 3.2; N, 5.6; mol. wt., 352.

(ii) **Morpholine Molybdenum Pentacarbonyl.**—Molybdenum hexacarbonyl (1 g.) was refluxed with morpholine (0.35 g.) in benzene for 6 hr.; the solution was cooled and filtered, and the filtrate was evaporated *in vacuo* to give a pale yellow solid (1.1 g.), m.p. 105–108°. *Anal.* Calcd. for $C_9H_9MoNO_6$: C, 33.4; H, 2.8; N, 4.3; mol. wt., 323. Found: C, 33.4; H, 3.1; N, 4.4; mol. wt., 362.

(iii) **Morpholine Tungsten Pentacarbonyl.**—Tungsten hexacarbonyl (1 g.) was refluxed with morpholine (0.25 g.) in toluene for 6 hr.; a pale yellow solid (0.9 g.), m.p. 139–141°, was obtained from the filtered reaction mixture. *Anal.* Calcd. for $C_9H_9WNO_6$: C, 26.9; H, 2.2; N, 3.4. Found: C, 26.7; H, 2.4; N, 3.5.

Bis-morpholine Molybdenum Tetracarbonyl.—Molybdenum hexacarbonyl (1 g.) was refluxed with excess morpholine in benzene until yellow crystals suddenly precipitated from solution. The crystals (1 g.) were filtered, washed twice with benzene, and kept *in vacuo*. *Anal.* Calcd. for $C_{12}H_{18}MoN_2O_6$: C, 37.7; H, 4.7; N, 7.3. Found: C, 37.2; H, 4.7; N, 7.4.

Bis-morpholine tungsten tetracarbonyl was prepared from tungsten hexacarbonyl by the method described for the molybdenum analog. *Anal.* Calcd. for $C_{12}H_{18}WN_2O_6$: C, 30.6; H, 3.8; N, 5.9. Found: C, 30.9; H, 3.8; N, 5.9.

Tris-morpholine Molybdenum Tricarbonyl.—Morpholine was distilled onto a frozen, evacuated benzene solution of π-$(CH_3)_3$-$C_6H_3Mo(CO)_3$.[7] The reactants were allowed to warm to room temperature, and the white, air-sensitive precipitate formed after 3 hr. was filtered and analyzed. *Anal.* Calcd. for $C_{15}H_{27}MoN_3O_6$: C, 40.8; H, 6.1; N, 9.6. Found: C, 40.3; H, 5.8; N, 9.8.

(2) **Pyrrolidine Reactions.**—These reactions were carried out under the same conditions as the morpholine reactions, and the following compounds were isolated.

(i) **Pyrrolidine Molybdenum Pentacarbonyl.**—Pale yellow powder, m.p. 53–55°, soluble in benzene. *Anal.* Calcd. for $C_9H_9MoNO_5$: C, 35.2; H, 2.9; N, 4.6; mol. wt., 307. Found: C, 35.0; H, 2.6; N, 4.6; mol. wt., 358.

(ii) **Pyrrolidine Tungsten Pentacarbonyl.**—Yellow powder, m.p. 71–73°, soluble in benzene. *Anal.* Calcd. for $C_9H_9WNO_5$: C, 27.3; H, 2.3; N, 3.5; mol. wt., 395. Found: C, 27.1; H, 2.0; N, 3.3; mol. wt., 417.

(iii) **Bis-pyrrolidine Molybdenum Tetracarbonyl.**—Yellow crystals, insoluble in benzene, soluble in acetone, sparingly soluble in nitromethane. *Anal.* Calcd. for $C_{12}H_{18}MoN_2O_4$: C, 41.1; H, 5.1; N, 8.0. Found: C, 40.9; H, 5.2; N, 7.7.

(iv) **Bis-pyrrolidine Tungsten Tetracarbonyl.**—Yellow crystals, less easily oxidized than the Mo analog. *Anal.* Calcd. for $C_{12}H_{18}WN_2O_4$: C, 32.9; H, 4.1; N, 6.4. Found: C, 32.9; H, 4.05; N, 6.6.

(3) **Piperazine Reactions.** (i) **Piperazine Dimolybdenum Decacarbonyl.**—Molybdenum hexacarbonyl (4 g.) and piperazine (0.7 g.) were refluxed in benzene for 12 hr., when yellow crystals deposited together with a brown decomposition product. The crystals were dissolved in acetone, and the filtered solution was evaporated to yield a pale yellow powder (1.1 g.). *Anal.* Calcd. for $C_{14}H_{10}Mo_2N_2O_{10}$: C, 30.1; H, 1.8; N, 5.0. Found: C, 30.5; H, 1.9; N, 5.1.

(ii) **Piperazine Ditungsten Decacarbonyl.**—Tungsten hexacarbonyl (2.4 g.) and piperazine (0.3 g.) were refluxed in toluene for 6 hr. and the reaction products were worked up as for those of the analogous molybdenum reaction. *Anal.* Calcd. for $C_{14}H_{10}W_2N_2O_{10}$: C, 22.9; H, 1.4; N, 3.8. Found: C, 23.3; H, 1.5; N, 3.8.

(iii) **Tris-piperazine Molybdenum Tricarbonyl.**—Benzene was distilled onto a mixture of toluene molybdenum tricarbonyl (0.7 g.) and piperazine (0.7 g.) *in vacuo*, and the mixture was warmed to room temperature under nitrogen and shaken for 2 hr. The white precipitate (0.8 g.) was filtered, dried, and analyzed. *Anal.* Calcd. for $C_{15}H_{30}MoN_6O_3$: C, 41.1; H, 6.9; N, 19.2. Found: C, 40.1; H, 7.4; N, 19.3.

Reactivity of Complexes.—All the complexes were decomposed by air, very slowly in the solid state, but rapidly in solution. The molybdenum compounds were apparently less stable in this respect than the tungsten compounds, since the infrared spectra of solutions of the $L_2Mo(CO)_4$ complexes showed a new strong peak after the solutions had been exposed to air for a short time; similar bands were observed for the tungsten compounds only after exposure for 2–3 hr.

Infrared spectra were measured on Nujol mulls or solutions in various solvents using an SP 100 spectrophotometer.

Acknowledgment.—We greatly appreciate the award of a maintenance grant (to D. K. J.) by the Esso Petroleum Company.

Contribution from the Evans Laboratory of Chemistry,
The Ohio State University, Columbus 10, Ohio

Crystal Field Effects in Coordination Compounds. A Calorimetric Study of Some Hexacyano Metal Complexes[1]

By F. H. Guzzetta[2] and W. B. Hadley

Received October 1, 1963

The heats of complexation of cyanide ion with V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, and Fe^{+3} have been determined by direct calorimetry. The large excess of cyanide ion and the temperature at which the reactions were carried out (25.4°) ensure the formation of the hexacyano complex with the obvious exceptions being the zinc and cobaltous ions. The heats of complexation for V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, and Fe^{+3} are 47.0, 63.2, 34.5, 73.7, 74.4, 27.7, and 68.0 kcal./mole, respectively. The thermal data have been interpreted in terms of the ligand field theory and Dq values for some divalent ions have been estimated.

Introduction

The majority of ligands for which formation constants with different metal ions have been determined belong to structural types in which oxygen atoms, oxygen and nitrogen atoms, or only nitrogen atoms are

---

[1] Taken from the Ph.D. thesis of F. H. G. and presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] Knolls Atomic Power Laboratory, Schenectady, N. Y.