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AMINEMOLYBDENUM CARBONYLS

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SUMMARY

Ethylamine, isopropylamine, butylamine, benzylamine, and cyclohexylamine react with molybdenum hexacarbonyl to give simple substitution products, $[L_nMo(CO)_{6-n}]$, where L is an amine molecule, and $n = 1,2$ and 3. Diisopropylamine, quinoline and α-picoline yield only monosubstituted derivatives, $[L\ Mo(CO)_5]$. Piperazine gives a novel compound bis(piperazine)molybdenum tricarbonyl; 2,2'-biquinoline displaces only two CO molecules from molybdenum hexacarbonyl under all conditions of reactions. The IR spectra of the complexes have been measured and assignments made, and the CO stretching force constants and stretch–stretch interaction constants have been evaluated.

INTRODUCTION

We describe below the preparation and characterisation of several new substituted molybdenum carbonyl derivatives containing nitrogen donor ligands. Stretching force constants of CO groups of various sites with respect to other substituents, and stretch–stretch interaction constants have been deduced from the IR spectra. To our knowledge, few workers[1,2] have paid attention to relate the CO force constants to the structures of the substituted metal carbonyl derivatives.

The presence of ligands such as substituted phosphines, arsines, stibines, sulphides, ethers, amines etc. causes lowering of the C–O frequencies in the metal carbonyls and enhances π-bonding between the metal and the remaining carbonyl groups in the molecule. In amines and similar compounds the nitrogen atom can act only as a donor, since it has no orbitals to interact with filled metal d_π orbitals. Since the remaining carbonyl groups will accept more negative charge than in the unsubstituted metal carbonyls, complete substitution of carbon monoxide in carbonyls should not take place, and this agrees with our results. Direct reactions between molybdenum hexacarbonyl and the bases having monodentate groups yielded derivatives up to the trisubstituted stage. Further carbonyl groups could not be replaced. Almost all the possible $[Mo(CO)_4L_2]$ and $[Mo(CO)_3L_3]$ complexes (L = nitrogen donor ligands) were obtained in the *cis* form. It has previously been thought that amines can displace

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a maximum of two carbon monoxide molecules in molybdenum hexacarbonyl by direct reactions[3,4], and the trisubstituted molybdenum carbonyls have generally been prepared by displacement of arene group in arene molybdenum tricarbonyls, [(arene)-$Mo(CO)_3$][3]. Preliminary accounts of the work are given in refs. 5 and 6.

RESULTS AND DISCUSSION

Ethyl-, isopropyl- or cyclohexylamine reacted with molybdenum hexacarbonyl on heating in evacuated sealed tubes to give mono-, di- and trisubstituted derivatives depending on the temperature and time. Further replacement of carbon monoxide could not be achieved even under drastic conditions (temperature above 220°). Butyl- and benzylamine yielded only mono- and disubstituted products in evacuated sealed tubes under all conditions but gave trisubstituted products in reactions involving reflux under nitrogen. In addition to piperazinedimolybdenum decacarbonyl[3] and tris(piperazine)molybdenum tricarbonyl[3], sealed tube reactions with piperazine yielded the novel compound bis(piperazine)molybdenum tricarbonyl. In this compound only one piperazine molecule acts as a bidentate ligand the other being monodentate; similar behaviour is found with ethylenediamine in bis(ethylenediamine)-molybdenum tricarbonyl[7].

Quinoline displaced only one CO molecule under both sets of conditions. Diisopropylamine reacted with molybdenum hexacarbonyl to give a blue-black decomposition product under both sets of conditions but no substituted molybdenum carbonyls were isolated. However, ultraviolet irradiation under nitrogen gave the low-melting monosubstituted derivative, $[(C_3H_7)_2NHMo(CO)_5]$, in low yield (14.8%). α-Picoline did not react with molybdenum hexacarbonyl in sealed tubes or under reflux, but a small quantity of α-picolinemolybdenum pentacarbonyl, $[(\alpha\text{-}C_5H_4\text{-}NCH_3)Mo(CO)_5]$ was obtained by a 40 h ultraviolet irradiation of a solution of molybdenum hexacarbonyl and α-picoline in hexane under nitrogen. Increase in the irradiation time gave no appreciable increase in yield. 2.2'-Biquinoline, like o-phenanthroline and 2,2'-bipyridine[8], could replace only two CO molecules, to form 2,2'-biquinolinemolybdenum tetracarbonyl, $[(C_{18}H_{12}N_2)Mo(CO)_4]$; this complex gave a violet solution in xylene, toluene, or benzene and a red-violet solution in acetone.

The more highly-substituted derivatives were of lighter colour than the less substituted. Most of the monoaminemolybdenum pentacarbonyls were dark yellow or orange red solids, which melted or decomposed without melting at low temperatures. The trisubstituted derivatives were pale yellow or white in colour. Both di- and trisubstituted derivatives were very air-sensitive, but decomposed less rapidly in the solid state than in solution. Compounds of the type $[LMo(CO)_5]$ were soluble in polar and nonpolar organic solvents, but the $[L_3Mo(CO)_3]$ complexes were practically insoluble in nonpolar solvents and only sparingly soluble in polar solvents. The $[L_2Mo(CO)_4]$ compounds were of intermediate solubility and stability.

IR spectra

Since most of the above complexes decomposed in solution rapidly their IR spectra were measured on mulls (Nujol mull). The carbonyl stretching frequencies of the substituted molybdenum carbonyl complexes have been assigned on the basis of work by Orgel[9] and Cotton and Kraihanzel[1]. The two CO stretching force constants

k_1 and k_2, *i.e.* the force constants of CO groups *cis* and *trans* to substituent nitrogen donors, respectively, for mono- and disubstituted derivatives, and k_i, the stretch–stretch interaction constant for mono-, di- and trisubstituted derivatives have also been evaluated by Cotton and Kraihanzel's factored secular equations[1]. In the case of trisubstituted derivatives the value of k_1 and k_2 are equal, so that only one constant k is required.

In the complexes of the type [LMo(CO)$_5$] each spectrum showed a single weak band (1) arising from the A_1 mode of the *trans* pair of carbonyl groups. A second band (2) was assigned due to the B_1 mode, which should be only Raman active but show up also in the IR because the structures of the ligands interfere with perfect C_{4v} symmetry. Band (3) may be due to the E mode, and band (4), which was just visible as a shoulder or weak peak, to the A_1 mode of *cis*-carbonyls.

TABLE 1

CO STRETCHING FREQUENCIES FOR [LMo(CO)$_5$] COMPLEXES

Complex	Band	Frequency[a] (cm^{-1})	Mode	k_1 (mdynes/Å)	k_2	k_i
[($C_2H_5NH_2$)Mo(CO)$_5$]	1	2062 w	A_1	14.56	15.70	0.38
	2	1972 (sh)	B_1			
	3	1923 s	E			
	4	1887 (sh)	A_1			
[(i-$C_3H_7NH_2$)Mo(CO)$_5$]	1	2062 w	A_1	14.54	15.54	0.30
	2	1961 (sh)	B_1			
	3	1923 s	E			
	4	1887 w	A_1			
{[(CH_3)$_2$CH]$_2$NH Mo(CO)$_5$}	1	2062 w	A_1	14.54	15.54	0.30
	2	1961 m	B_1			
	3	1923 s	E			
	4	1887 (sh)	A_1			
[($C_4H_9NH_2$)Mo(CO)$_5$]	1	2062 w	A_1	14.54	15.54	0.30
	2	1961 m	B_1			
	3	1923 s	E			
	4	1887 (sh)	A_1			
[($C_7H_7NH_2$)Mo(CO)$_5$]	1	2075 w	A_1	14.55	15.75	0.34
	2	1975 m	B_1			
	3	1931 s	E			
	4	1887 mw	A_1			
[(α-$C_5H_4NCH_3$)Mo(CO)$_5$]	1	2075 w	A_1	14.58	15.54	0.35
	2	1961 w	B_1			
	3	1915 m	E			
	4	1887 (sh)	A_1			
[(C_9H_7N)Mo(CO)$_5$]	1	2062 w	A_1	14.44	15.56	0.30
	2	1963 w	B_1			
	3	1924 s	E			
	4	1883 (sh)	A_1			

[a] Accuracy ±5 cm^{-1}.

The bands in the IR spectra of the $[L_2Mo(CO)_4]$ complexes having C_{2v} symmetry agree well with expectation for *cis*-configurations. Band (1) might be due to the mode A_1 which mainly involved *trans*-carbonyl groups. Bands (2), (3) and (4) may be attributable to modes A_1, B_1, and B_2, respectively.

TABLE 2

CO STRETCHING FREQUENCIES FOR *cis*-$[L_2Mo(CO)_4]$ COMPLEXES

Complex	Band	Fraquency[a] (cm^{-1})	Mode	k_1 (mdynes/Å)	k_2 (mdynes/Å)	k_i
$[(C_2H_5NH_2)_2Mo(CO)_4]$	1	2000 w	A_1	13.87	14.80	0.52
	2	1923 (sh)	A_1			
	3	1869 m	B_1			
	4	1818 m	B_2			
$[(i\text{-}C_3H_7NH_2)_2Mo(CO)_4]$	1	2012 w	A_1	13.82	14.95	0.48
	2					
	3	1862 s	B_1			
	4	1818 w	B_2			
$[(C_4H_9NH_2)_2Mo(CO)_4]$	1	2000 w	A_1	13.87	14.80	0.52
	2	1923 (sh)	A_1			
	3	1869 m	B_1			
	4	1818 m	B_2			
$[(C_7H_7NH_2)_2Mo(CO)_4]$	1	2000 w	A_1	13.21	14.46	0.56
	2	1894 s	A_1			
	3	1818 m	B_1			
	4	1770 s	B_2			
$[(C_6H_{11}NH_2)_2Mo(CO)_4]$	1	2000 w	A_1	13.33	14.47	0.56
	2	1869 s	A_1			
	3	1818 m	B_1			
	4	1779 s	B_2			

[a] Accuracy ±5 cm^{-1}.

The IR spectra of the $[L_3Mo(CO)_3]$ complexes indicated that they were *cis*-derivatives, having C_{3v} symmetry. Bands (1) and (2) were assigned for A_1 and E modes respectively.

It will be seen that the CO stretching force constants decrease steadily as the CO groups are successively replaced by nitrogen donor ligands. The values of k_1 and k_2 are in the ranges of 14.54–14.58 and 15.54–15.75 mdynes/Å, respectively, in case of monosubstituted derivatives, and the corresponding ranges are 13.21–13.87 and 14.46–14.95 mdynes/Å for disubstituted derivatives. With trisubstituted derivatives k is in the range of 12.50–12.79 mdynes/Å. Cotton and Kraihanzel[2] have recorded the values of k_1 and k_2 for some nitrogen-donor substituted metal carbonyl derivatives; for $[(\text{pyridine})M(CO)_5]$ (M = Cr, Mo and W), the values of k_1 and k_2 are 14.56–14.59 and 15.83–15.93 mdynes/Å, respectively; for $[(\text{ethylenediamine})M(CO)_4]$, they are 13.68–13.72 and 15.01–15.25 mdynes/Å, while k for $[(\text{diethylenetriamine})M(CO)_3]$ is 13.13 mdynes/Å. The values of k_i are 0.34–0.38, 0.42–0.47 and 0.70–0.73 mdynes/Å, respectively, for mono-, di-, and trisubstituted compounds, which are a little low compared with our ranges of 0.30–0.38, 0.48–0.56 and 0.73–0.82, respectively.

TABLE 3

CO STRETCHING FREQUENCIES FOR *cis*-$[L_3Mo(CO)_3]$ COMPLEXES

Complex	Band	Frequency[a] (cm^{-1})	Mode	k (mdynes/Å)	k_i
$[(C_2H_5NH_2)_3Mo(CO)_3]$	1	1862 s	A_1	12.50	0.73
	2	1709 s	E		
$[(i\text{-}C_3H_7NH_2)_3Mo(CO)_3]$	1	1862 s	A_1	12.50	0.73
	2	1709 s	E		
$[(C_4H_9NH_2)_3Mo(CO)_3]$	1	1869 s	A_1	12.64	0.73
	2	1718 s	E		
$[(C_7H_7NH_2)_3Mo(CO)_3]$	1	1887 s	A_1	12.79	0.79
	2	1724 s	E		
$[(C_6H_{11}NH_2)_3Mo(CO)_3]$	1	1862 s	A_1	12.50	0.73
	2	1709 s	E		
$[(C_4H_{10}N_2)_2Mo(CO)_3]$	1	1880 s	A_1	12.62	0.82
	2	1709 s	E		

[a] Accuracy ±5 cm^{-1}.

With mono- and disubstituted derivatives the value of k_2 is always higher than that of k_1, and in all cases the value of k_i increases with increasing replacement of CO.

Our results are in excellent agreement with Cotton and Kraihanzel's analyses.

EXPERIMENTAL

General

Molybdenum hexacarbonyl (Climax Molybdenum Co.) was sublimed before use. Ethylamine and isopropylamine were used as aqueous 50% and 70% solutions, respectively, but the other amines were used neat. Reactions and manipulations were carried out under dry nitrogen or *in vacuo*. Unchanged molybdenum hexacarbonyl was sublimed from the reaction product at 40°/1 mm. UV irradiation under nitrogen was performed in a quartz vessel fitted with accessories for gas measurement. The UV lamp (30 W) used was made by Philips Co., Holland. IR spectra were measured on a Perkin–Elmer spectrophotometer model 521.

Ethylamine reactions

(Ethylamine)molybdenum pentacarbonyl. Molybdenum hexacarbonyl (0.2 g) and ethylamine (0.5 ml of 50% aqueous solution) were heated in an evacuated sealed tube at 80° for 6 h. Bright yellow plates composed of very fine needles appeared in the tube. The product was removed from the tube with the help of a little pentane, and the solvent was evaporated under vacuum. Unreacted molybdenum hexacarbonyl was removed by sublimation to leave a yellow residue of (ethylamine)molybdenum pentacarbonyl (0.089g., 42%), m.p. 58°. (Found: C, 29.7; H, 2.1; N, 4.9. $C_7H_7MoNO_5$ calcd.: C, 29.8; H, 2.4; N, 4.9%.)

The compound was soluble in most organic solvents. Strohmeier and coworkers[10] reported the preparation of this product by UV irradiation method in poor yield (~7%) but gave no details.

Bis(ethylamine)molybdenum tetracarbonyl. Molybdenum hexacarbonyl (0.2 g) and ethylamine (1.0 ml of 50% aqueous solution) were heated in an evacuated sealed tube at 125° for 8 h. The yellow solid formed was washed with 5 ml portions of light petroleum (40°–60°) (20 ml) to remove unreacted molybdenum hexacarbonyl and any ethylaminemolybdenum pentacarbonyl. The residual yellow needles (0.150 g) decomposed above 114°. (Found: C, 32.1; H, 4.5; N, 9.4. $C_8H_{14}MoN_2O_4$ calcd.: C, 32.2; H, 4.6; N, 9.3%.)

The product, which was very unstable in air, was insoluble in hydrocarbons or light petroleum; it was soluble in diethyl ether, acetone, and dichloromethane, but the solutions decomposed rapidly.

Tris(ethylamine)molybdenum tricarbonyl. Molybdenum hexacarbonyl (0.2 g) and ethylamine (1.5 ml of 50% aqueous solution) were heated for 18 h at 155° in an

TABLE 4

Compound	Method	Reaction conditions (°C/h)	Colour[a] and m.p. (°C)	Yield (%)	Analysis found (calcd.) (%)		
					C	H	N
$[(i\text{-}C_3H_7NH_2)Mo(CO)_5]$	Sealed tube	80/6	Yellow dec. 62	36.7	32.1 (32.5)	2.9 (3.0)	4.6 (4.7)
$[(i\text{-}C_3H_7NH_2)_2Mo(CO)_4]$	Sealed tube	125/8	Pale yellow dec. 122	64.2	36.4 (36.8)	5.4 (5.5)	8.4 (8.5)
$[(i\text{-}C_3H_7NH_2)_3Mo(CO)_3]$	Sealed tube	155/20	Dirty white	75.8	40.1 (40.4)	7.4 (7.5)	11.6 (11.7)
$[(C_3H_7)_2NHMo(CO)_5]$	UV irr. in THF	/15	Yellow	14.8	39.0 (39.1)	3.8 (4.4)	4.0 (4.1)
$[(C_4H_9NH_2)Mo(CO)_5]$	Sealed tube	110/6	Yellow[b] dec. 69	38.9	34.8 (34.9)	3.4 (3.5)	4.5 (4.5)
$[(C_4H_9NH_2)_2Mo(CO)_4]$	Reflux in THF	$/1\frac{1}{2}$	Yellow[b] dec. 132	73.1	40.6 (40.6)	6.1 (6.2)	7.8 (7.9)
$[(C_4H_9NH_2)_3Mo(CO)_3]$	Reflux[c]	/3	White[d] dec. 155	80.0	44.6 (45.1)	8.0 (8.2)	10.4 (10.5)
$[(C_7H_7NH_2)Mo(CO)_5]$	Sealed tube	100/4	Yellow dec. 105	45.0	41.7 (41.9)	2.2 (2.6)	4.1 (4.0)
$[(C_7H_7NH_2)_2Mo(CO)_4]$	Sealed tube	155/10	Yellow dec. 137	70.4	50.6 (51.1)	3.9 (4.2)	6.6 (6.6)
$[(C_7H_7NH_2)_3Mo(CO)_3]$	Reflux in C_6H_6	/3	White[d] dec. 210	84.4	56.6 (57.4)	5.2 (5.3)	8.3 (8.3)
$[(C_6H_{11}NH_2)_2Mo(CO)_4]$	Sealed tube	110/6	Yellow dec. 137	68.3	46.6 (47.2)	6.6 (6.4)	6.7 (6.8)
$[(C_6H_{11}NH_2)_3Mo(CO)_3]$	Reflux[c]	/3	White dec. 230	79.9	52.6 (52.8)	7.9 (8.1)	8.6 (8.8)
$[(\alpha\text{-}C_5H_4NCH_3)Mo(CO)_5]$	UV in hexane	/40	Yellow dec. 152	15.0	39.8 (40.1)	1.9 (2.1)	4.3 (4.2)
$[(C_9H_7N)Mo(CO)_5]$[e]	Sealed tube	180/4	Yellow brown dec. 159	81.0	46.0 (46.0)	1.8 (1.9)	3.7 (3.8)
$[(C_4H_{10}N_2)_2Mo(CO)_3]$	Sealed tube	220/18	Pale yellow dec. 285	88.5	37.0 (37.5)	4.9 (5.6)	15.8 (15.9)
$[(C_{18}H_{12}N_2)Mo(CO)_4]$	Reflux in toluene	/2	Greenish black	86.8	56.4 (56.8)	2.1 (2.5)	6.0 (6.0)

[a] All compounds are solids. [b] Scales. [c] Without solvent. [d] Fibrous. [e] Ref. 11. No specific details are available in the literature.

evacuated pyrex tube. Pale-yellow crystals which formed on the walls of the tube were washed with light petroleum (40°–60°) followed by diethyl ether (15 ml) and then dried *in vacuo* (0.185 g). (Found: C, 34.0; H, 6.6; N, 13.4. $C_9H_{21}MoN_3O_3$ calcd.: C, 34.2; H, 6.6; N, 13.3%.)

The compound was insoluble in aliphatic and aromatic hydrocarbons, light petroleum, and diethyl ether. It dissolved in acetone, dichloromethane and tetrahydrofuran with immediate decomposition. The compound was also very air-sensitive in the solid state.

Complexes containing other ligands

Complexes containing other ligands generally resembled the corresponding ethylamine analogues in solubility and stability. Bis(piperazine)molybdenum tricarbonyl, however, was insoluble in practically all organic solvents and reasonably stable in air.

The methods of preparation, reaction conditions, characteristics, yields and analyses of the other substituted molybdenum carbonyl complexes are given in Table 4.

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