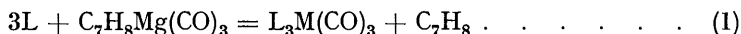


### 467. *Substituted Carbonyl Compounds of Chromium, Molybdenum, Tungsten, and Manganese.*

By E. W. ABEL, M. A. BENNETT, and G. WILKINSON.

Complexes of the type  $L_3M(CO)_3$  ( $M = Cr, Mo, W$ ), where  $L$  represents various nitrogen, phosphorus, arsenic, and antimony donor compounds, have been prepared by the reaction of the ligand with either the metal hexacarbonyl or the cycloheptatrienemetal tricarbonyl. A cationic manganese compound  $[dienMn(CO)_3]^+$  has also been prepared (dien = diethylenetriamine,  $NH_2 \cdot [CH_2]_2 \cdot NH \cdot [CH_2]_2 \cdot NH_2$ ). The unusually large variations in the position of the C-O stretching frequencies in the infrared spectra are discussed.

UNTIL recently, when some *o*-phenylenebisdimethylarsine derivatives were briefly recorded,<sup>1</sup> excluding isocyanide complexes, the substituted carbonyls of the Group VI transition metals have been confined to compounds in which nitrogen was the donor atom.<sup>2</sup> In contrast a great variety of substituted products of the carbonyls of nickel, iron, and cobalt have been reported. We have now prepared a number of substituted chromium, molybdenum, and tungsten carbonyls, of the general formula  $L_3M(CO)_3$  in which the ligand donor atoms are nitrogen, phosphorus, arsenic, and antimony. Several of the compounds were prepared by the direct reaction of the ligand with the hexacarbonyl, but for the preparation of both these and similar derivatives, the cycloheptatrienemetal tricarbonyl<sup>3</sup> has proved a useful intermediate through reactions of the type:



The conditions for this reaction vary with the nature of the ligand; in some cases reaction was rapid in the cold but in others more vigorous conditions were required. Thus, triphenyl-phosphine, -arsine, and -stibine reacted in boiling benzene with cycloheptatrienemolybdenum tricarbonyl, whereas phosphorus trichloride reacted at once in the cold. The tridentate ligand, diethylenetriamine (dien), also reacted in the cold both with cycloheptatrienemolybdenum tricarbonyl and with mesitylenemolybdenum tricarbonyl;<sup>4</sup> the dien carbonyls,  $dienM(CO)_3$ , were also made directly from the Group VI hexacarbonyls.

#### EXPERIMENTAL

Microanalyses and molecular-weight determinations were by the Microanalytical Laboratories, Imperial College.

*Preparations.*—Tripyridinemolybdenum tricarbonyl was prepared by the method of Hieber and Mühlbauer<sup>5</sup> and was recrystallised from pyridine (Found: C, 51.3; H, 4.0; N, 10.2; O, 11.4. Calc. for  $C_{18}H_{19}O_3N_3Mo$ : C, 51.8; H, 3.6; N, 10.1; O, 11.5%).

*Diethylenetriaminemolybdenum tricarbonyl.* (Method 1.) The triamine (1.1 g.) in ether (5 ml.) was added dropwise to cycloheptatrienemolybdenum tricarbonyl<sup>3</sup> (0.73 g.) in ether (5 ml.). After removal of ether (20°/0.2 mm.) the product was washed with water (5 × 10 ml.) and chloroform (3 × 2 ml.). Removal of excess of solvent (at 20°/0.1 mm.) left fine yellow crystals (0.67 g.) (Found: C, 29.1; H, 4.8; N, 14.4; O, 17.2.  $C_7H_8O_3N_3Mo$  requires C, 29.7; H, 4.6; N, 14.8; O, 17.0%). Under the same conditions, mesitylenemolybdenum tricarbonyl<sup>4</sup> gave the same product (yield, 77%) (Found: C, 29.3; H, 4.9%).

(Method 2.) *Diethylenetriamine-chromium, -molybdenum, and -tungsten tricarbonyls.* The hexacarbonyl (ca. 1 g.) and the triamine (ca. 5 ml.) were heated together. When no more gas was evolved, the mixture was poured into cold water (100 ml.). The crystals were removed

<sup>1</sup> Nigam and Nyholm, *Proc. Chem. Soc.*, 1957, 321.

<sup>2</sup> For references see Hieber, Abeck, and Platzner, *Z. anorg. Chem.*, 1955, 280, 252.

<sup>3</sup> Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.

<sup>4</sup> Nicholls and Whiting, *J.*, 1959, 551.

<sup>5</sup> Hieber and Mühlbauer, *Z. anorg. Chem.*, 1935, 221, 337.

by filtration and washed with water (50 ml.) and alcohol (20 ml.). Removal of solvent (20°/0.1 mm.) left the pure products  $\text{dienM}(\text{CO})_3$  (Table). The compounds darken with decomposition above 230°; they are insoluble in common organic solvents.

	Yield (%)	Colour	Found (%)					Required (%)				
			C	H	N	O	M	C	H	N	O	M
Cr	73	Pale brown	35.5	5.8	18.6	20.3	20.9	35.2	5.4	17.6	20.1	21.8
Mo	87	Pale yellow	29.7	4.7	14.8	16.9	33.9	29.7	4.6	14.8	17.0	34.0
W	81	Dark yellow	22.3	3.6	—	12.8	49.6	22.6	3.5	—	12.9	49.6

*Tri(phosphorus Trichloride)molybdenum Tricarbonyl.*—Cycloheptatrienemolybdenum tricarbonyl (0.62 g.) and phosphorus trichloride (10 ml.) were heated (80°) under nitrogen (15 min.). Excess of trichloride was removed (30°/5 mm.), and the residue extracted with light petroleum (b. p. 40–60°) (2 × 10 ml.). The resulting yellow solution was filtered and cooled (–80°). The yellow crystals were filtered off and recrystallised from petrol (0.56 g.), m. p. 85° (decomp.) (Found: C, 7.0; P, 16.1; Cl, 55.1.  $\text{C}_3\text{O}_3\text{Cl}_9\text{MoP}_3$  requires C, 6.1; P, 15.7; Cl, 53.9%).

Similar reactions with arsenic or antimony trichloride occurred, but it was impossible to isolate a pure product, although infrared spectra of the yellow solutions formed indicated the presence of arsenic and antimony analogues of the phosphorus trichloride complex. The latter is soluble in light petroleum and several other organic solvents. Like  $\text{Ni}(\text{PCl}_3)_4$ <sup>6</sup> the compound is fairly stable to cold water but decomposes slowly on warming. On storage even in vacuum it becomes pink and loses phosphorus trichloride.

*Tri(triphenylphosphine)molybdenum Tricarbonyl, and Arsenic and Antimony Analogues.*—Cycloheptatrienemolybdenum tricarbonyl (0.37 g.) and triphenylphosphine (2.0 g.) in benzene (5 ml.) were heated under reflux until the red colour of the cycloheptatriene complex had completely disappeared (15 min.). Cooling, filtration, and repeated washing with benzene, followed by evacuation (20°/0.1 mm.), left fine yellow crystals (0.34 g.), darkening 145°, decomp. 160° (Found: C, 70.9; H, 5.4; P, 9.1.  $\text{C}_{57}\text{H}_{45}\text{O}_3\text{MoP}_3$  requires C, 70.8; H, 4.7; P, 9.6%). Prepared similarly, *tris(triphenylarsine)molybdenum tricarbonyl*, darkening 150°, decomp. 170° (Found: C, 63.4; H, 5.0; O, 3.6.  $\text{C}_{57}\text{H}_{45}\text{O}_3\text{As}_3\text{Mo}$  requires C, 62.3; H, 4.1; O, 4.4%), and *tris(triphenylstibine)molybdenum tricarbonyl*, darkening 210°, decomp. 220° (Found: C, 56.1; H, 4.0; O, 4.6.  $\text{C}_{57}\text{H}_{45}\text{O}_3\text{MoSb}_3$  requires C, 55.3; H, 3.7; O, 3.9%), were obtained as yellow crystals. These products were insoluble in organic solvents other than warm chloroform, dichloromethane, and acetone, and these solutions darkened rapidly owing to decomposition.

*Tri(diphenylphosphorus Chloride)molybdenum Tricarbonyl.*—The cycloheptatriene complex (0.7 g.) in ether (5 ml.) was added to diphenylphosphorus chloride (2 ml.) in ether (5 ml.). After ½ hour's shaking, the mixture was filtered and the crystals were washed with ether (20 ml.). Removal of excess of solvent in vacuum gave the product (1.3 g.), m. p. 148° (efferv.) (Found: C, 56.4; H, 4.0; P, 10.5%; M, 839.  $\text{C}_{39}\text{H}_{30}\text{O}_3\text{Cl}_3\text{MoP}_3$  requires C, 55.6; H, 3.6; P, 11.0%; M, 842). The compound is insoluble in light petroleum, alcohol, and carbon tetrachloride but is moderately soluble in benzene, dichloromethane, chloroform, and carbon disulphide. On being warmed in these solvents, some decomposition occurs.

*Tri(phenylphosphorus Dichloride)molybdenum Tricarbonyl.*—To cycloheptatrienemolybdenum tricarbonyl (0.845 g.) in ether (10 ml.) was added phenylphosphorus dichloride (1 ml.). After the mixture had been shaken for 1 hr. the ether was removed in vacuum. The residue was extracted with light petroleum (b. p. 40–60°) (4 × 20 ml.), and the filtered solution concentrated to 20 ml. and cooled to –78°. The yellow crystals were removed, and after being washed with petroleum and dried in vacuum, had m. p. 106–110° (decomp.) (Found: C, 35.3; H, 2.8; P, 12.7.  $\text{C}_{21}\text{H}_{15}\text{O}_3\text{Cl}_6\text{MoP}_3$  requires C, 35.2; H, 2.1; P, 13.0%).

*Diethylenetriaminemanganese Tricarbonyl Iodide.*—The triamine (0.9 g.) was added to mesitylenemanganese carbonyl iodide<sup>7</sup> (0.93 g.), and the mixture warmed (60°). Although no evolution of gas was observed, yellow crystals were deposited and a strong smell of mesitylene was noted. The product was washed with ether (5 × 2 ml.) and recrystallised from chloroform (0.49 g.) (Found: C, 23.4; H, 3.6; N, 11.8; O, 13.6; I, 34.9.  $\text{C}_7\text{H}_{13}\text{O}_3\text{N}_3\text{I}_3\text{Mn}$  requires C, 22.8; H, 3.5; N, 11.4; O, 13.0; I, 34.5%). The yellow crystals dissolve in water to a pale

<sup>6</sup> Irvine and Wilkinson, *Science*, 1951, **113**, 742.

<sup>7</sup> Coffield, Sandel, and Closson, *J. Amer. Chem. Soc.*, 1957, **79**, 5286.

yellow solution from which the iodide is immediately precipitated by silver ion. The hydroxide is soluble in water. The cation can be precipitated from aqueous solutions by large anions such as reineckate, tetraphenylborate, etc.

*Tetracarbonyl Derivatives.*—For comparison with the tricarbonyls and for spectral measurements the following derivatives were made. *o*-Phenanthroline-molybdenum tetracarbonyl was prepared by Hieber's method;<sup>4</sup> it was impossible to purify it by repeated crystallisation as claimed, but chromatography on Grade H (Spence) alumina yielded the pure red crystalline complex (Found: C, 49.8; H, 2.6%; *M*, 406. Calc. for  $C_{16}H_8O_4N_2Mo$ : C, 49.6; H, 2.1%; *M*, 388). 2,2'-Dipyridyl-molybdenum tetracarbonyl. Molybdenum hexacarbonyl (0.7 g.) and the dipyridyl (0.4 g.) in toluene (5 ml.) were heated under reflux until evolution of gas ceased. The product crystallised on cooling and removal of excess of solvent and molybdenum carbonyl at  $40^\circ/10^{-3}$  mm. left the pure *product* as red crystals, decomp.  $150-170^\circ$  (Found: C, 46.2; H, 2.7; N, 7.8; O, 17.8.  $C_{14}H_8O_4N_2Mo$  requires C, 46.2; H, 2.2; N, 7.7; O, 17.6%). It is insoluble in petrol but soluble in carbon tetrachloride, chloroform, ethanol, and acetone, giving orange-red solutions.

*Infrared Spectra.*—Measurements were made by using a Perkin-Elmer Model 21 instrument with sodium chloride and calcium fluoride optics. Spectra were taken in carbon tetrachloride, chloroform, and petroleum solutions and also in Nujol mulls. The bands in the carbonyl region

Compound	cm. <sup>-1</sup>		
	2100	1900	1700
Py <sub>3</sub> Mo(CO) <sub>3</sub>			
dienCr(CO) <sub>3</sub>			
dienMo(CO) <sub>3</sub>			
dienW(CO) <sub>3</sub>			
dienMn(CO) <sub>3</sub> I			
<i>Infrared spectra of carbonyl stretching region</i>			
(Ph <sub>3</sub> P) <sub>3</sub> Mo(CO) <sub>3</sub>			
(Ph <sub>3</sub> As) <sub>3</sub> Mo(CO) <sub>3</sub>			
(Ph <sub>3</sub> Sb) <sub>3</sub> Mo(CO) <sub>3</sub>			
(PCl <sub>3</sub> ) <sub>3</sub> Mo(CO) <sub>3</sub>			
(AsCl <sub>3</sub> ) <sub>3</sub> Mo(CO) <sub>3</sub>			
(SbCl <sub>3</sub> ) <sub>3</sub> Mo(CO) <sub>3</sub>			
(PCl <sub>2</sub> ) <sub>3</sub> Mo(CO) <sub>3</sub>			
(PhPCl <sub>2</sub> ) <sub>3</sub> Mo(CO) <sub>3</sub>			
(Ph <sub>2</sub> PCl) <sub>3</sub> Mo(CO) <sub>3</sub>			
(Ph <sub>3</sub> P) <sub>3</sub> Mo(CO) <sub>3</sub>			

1700—2100 cm.<sup>-1</sup> are: dipyMo(CO)<sub>4</sub>, 2022 (m), 1906 (vs), 1877 (s), 1826 (s) (in CHCl<sub>3</sub> soln.); *o*-phenMo(CO)<sub>4</sub>, 2025 (m), 1906 (vs), 1875 (s), 1826 (s) (in CHCl<sub>3</sub> soln.); py<sub>3</sub>Mo(CO)<sub>3</sub>, 1888 (s), 1850 (sh), 1818 (sh), 1746 (s, broad) (Nujol mull); dienCr(CO)<sub>3</sub>, 1881 (s), 1735 (s, broad) (Nujol mull); dienMo(CO)<sub>3</sub>, 1883 (s), 1723 (s, broad) (Nujol mull); dienW(CO)<sub>3</sub>, 1873 (s), 1718 (s, broad) (Nujol mull); dienMn(CO)<sub>3</sub>I, 2034 (s), 1903 (s, broad) (Nujol mull); (Ph<sub>3</sub>P)<sub>3</sub>Mo(CO)<sub>3</sub>, 1949 (s), 1908 (w), 1891 (w), 1835 (s) (Nujol mull); (Ph<sub>3</sub>As)<sub>3</sub>Mo(CO)<sub>3</sub>, 1957 (s), 1910 (w), 1889 (w), 1847 (s) (Nujol mull); (Ph<sub>3</sub>Sb)<sub>3</sub>Mo(CO)<sub>3</sub>, 1972 (s), 1945 (w, sh), 1875 (vs), 1850 (sh) (Nujol mull); (PCl<sub>3</sub>)<sub>3</sub>Mo(CO)<sub>3</sub>, 2041 (s), 1989 (s), 1960 (sh) (CCl<sub>4</sub> soln.); (AsCl<sub>3</sub>)<sub>3</sub>Mo(CO)<sub>3</sub>, 2031 (m), 1992 (m), 1958 (w) (petrol soln.); (SbCl<sub>3</sub>)<sub>3</sub>Mo(CO)<sub>3</sub>, 2045 (m), 1991 (m), 1953 (w) (petrol soln.); (Ph<sub>2</sub>PCl)<sub>3</sub>Mo(CO)<sub>3</sub>, 1977 (s), 1885 (s) (CHCl<sub>3</sub> soln.); (PhPCl<sub>2</sub>)<sub>3</sub>Mo(CO)<sub>3</sub>, 2016 (s), 1943 (s) (CHCl<sub>3</sub> soln.).

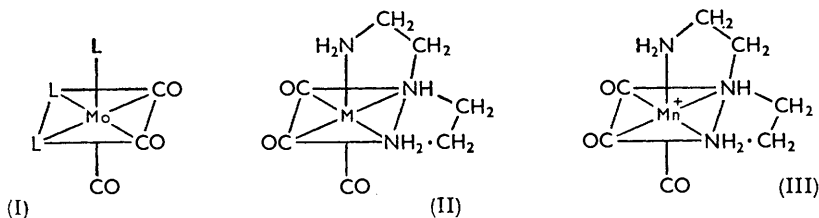
#### DISCUSSION

The formation of the compounds  $L_3Mo(CO)_3$  from cycloheptatriene- and mesitylene-molybdenum tricarbonyls suggests that the three carbon monoxide groups in the octahedral structure (I) are mutually *cis*. This configuration is also suggested by *trans*-effect arguments in the stepwise formation of the diethylenetriamine-chromium, -molybdenum,

and -tungsten tricarbonyls (II); the diethylenetriaminemanganese tricarbonyl ion will have a similar structure (III). The infrared spectra of the compounds  $L_3Mo(CO)_3$  all have two strong bands in the C-O stretching region in accordance with three mutually *cis*-carbonyl groups, since these molecules have a  $C_{3v}$  symmetry axis. The dienM(CO)<sub>3</sub> and dienMn(CO)<sub>3</sub>I spectra also have only two carbonyl modes despite the lower symmetry; the low-frequency band in each compound is very broad, however, but could not be resolved even with calcium fluoride optics. Since the donor atoms (N) are the same, a large splitting may well not occur.

Factors affecting the values of C-O stretching frequencies in metal carbonyls and substituted carbonyls as well as the nature and stabilities of the compounds, such as the extent of multiple bonding in the M-C bond and the influence thereon of the nature of other ligands present, have often been discussed.<sup>8,9</sup> In previous studies, however, the wide range of C-O stretching frequencies observed for the present compounds (Table) has not been observed; the variation in frequencies due to the factors discussed below we regard as being much greater than changes due to the effects of mass and the use of different media. It has often been assumed that C-O stretching frequencies of metal carbonyl compounds lying below  $\sim 1850$   $cm^{-1}$  were attributable to bridging carbon monoxide groups. However, in the present compounds bridging groups cannot be present.

Where nitrogen atoms are the active donors in the chromium, molybdenum, and tungsten complexes, the frequencies of the two carbonyl modes are unusually low; in fact, the lower frequencies are the lowest non-bridging carbonyl frequencies to be observed so far. Since the donor nitrogen atoms have little or no acceptor property, higher *d* orbitals being unavailable, the resulting negative charge on the metal atom  $R_3N^{+}-M^{-}$  may, according to Pauling's electroneutrality principle, be dissipated by increasing the bond orders in the M-C-O system. This will lead to a lowering of the C-O stretching frequency. In the octahedral trisubstituted derivatives of nitrogen donors, the multiple-bond character in the metal-carbon bonds of the tricarbonyl residue will be at a maximum by arguments similar to those given previously for similar cases.<sup>10</sup>



In the diethylenetriaminemanganese tricarbonyl cation, which is isoelectronic with the neutral dienCr(CO)<sub>3</sub>, the positive charge on the ion reverses to some extent the flow of negative charge into the M-C-O system, and accordingly leads to a rise in the carbonyl frequencies of about 150  $cm^{-1}$ . This type of alteration in the C-O stretching frequencies and bond orders by changes in the charge on a particular species has already been illustrated<sup>11</sup> by the decrease in the C-O stretching frequencies in going from  $Fe(CO)_5$  to  $[HFe(CO)_4]^{-}$  and  $[Fe(CO)_4]^{2-}$ , the latter ion also showing an unusually low carbonyl frequency.

Considering the molybdenum tricarbonyl compounds with triphenyl-phosphine, -arsine, and -stibine as donors, a pronounced increase in the carbonyl frequencies compared to those of the nitrogen-donor derivatives is observed. This increase is conventionally attributed to  $\pi$  character in the metal-ligand bond, the  $3d$ ,  $4d$ , and  $5d$  orbitals in phosphorus, arsenic, and antimony being utilized as acceptor orbitals. It will be noted,

<sup>8</sup> See, e.g., Nyholm and Short, *J.*, 1953, 2670.

<sup>9</sup> Chatt and Hart, *Chem. and Ind.*, 1958, 1474.

<sup>10</sup> Abel, Hargreaves, and Wilkinson, *J.*, 1958, 3149.

<sup>11</sup> Stammreich, Sala, Tavares, Krumholtz, and Behmoiras, *J. Chem. Phys.*, in the press.

however, from the Table, that there is little difference in the values of the C-O stretching frequencies in the phosphine, arsine, and stibine complexes. This may be taken as indicating that the donor-acceptor properties of the ligand atoms, phosphorus, arsenic, and antimony, are essentially the same. A similar conclusion has very recently been reached<sup>9</sup> from dipole-moment measurements, which showed that the differences in multiple-bonding capacities of phosphorus and arsenic towards nickel were virtually negligible. It certainly appears from our results that any differences in the donor-acceptor properties of the donor atoms are much smaller than the effects due to changes in electronegativity of groups attached to the donor atom.

In the trihalide phosphorus, arsenic, and antimony complexes, the availability of the donor atom *d* orbitals is increased relative to the phenyl compounds by the greater electronegativity of the halogen; an increase in the C-O stretching frequencies in the halide complexes is the result. The effect of the attachment of chlorine to the donor atom is well illustrated by the steady rise in the carbonyl frequencies along the series:

$(\text{Ph}_3\text{P})_3\text{Mo}(\text{CO})_3$ ,  $(\text{Ph}_2\text{PCl})_3\text{Mo}(\text{CO})_3$ ,  $(\text{PhPCl}_2)_3\text{Mo}(\text{CO})_3$ , and  $(\text{PCl}_3)_3\text{Mo}(\text{CO})_3$ .

We are indebted to the Ethyl Corporation for financial support (E. W. A. and M. A. B.) and to the Climax Molybdenum Company, Albright and Wilson (Mfg.) Ltd., and The Shell Petroleum Co. Ltd. for generous gifts respectively of molybdenum carbonyl, substituted phosphines, and cycloheptatriene.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,  
IMPERIAL COLLEGE, LONDON, S.W.7.

[Received, December 29th, 1958.]

---