195. *Dinuclear Phosphorus- and Arsenic-bridged Carbonyl Compounds of Iron, Chromium, Molybdenum, and Tungsten.*

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The reactions of organic diphosphines and diarsines, $R_2E \cdot ER_2$ (E = P or As, R = alkyl or aryl), with carbonyls of iron, chromium, molybdenum, and tungsten provide two types of dinuclear phosphorus- and arsenic-bridged compounds. One type (A) can be formulated $[M_2(ER_2)_2(CO)_n]$ (M = Fe, n = 6; M = Cr, Mo, or W, n = 8), with the metal formally in the monovalent state and bridging phosphido- or arsenido-groups; and the second type (B) $[M_2(CO)_n(E_2R_4)]$ (M = Fe, n = 8; M = Cr, Mo, or W, n = 10) with zero-valent metal atoms and bridging $R_2E \cdot ER_2$ groups. Dipole moments and other physical properties are given.

MANY dinuclear transition-metal complexes having carbon, sulphur, and halogen atoms as bridging atoms exist, but very little is known about those containing atoms of Group V. Interest has been stimulated by the development of easier preparations of tetra-alkyl- and tetra-aryl-diphosphines and of secondary phosphines. The subject has recently been summarised by Hayter,[1] who also described an extensive series of diphenylphosphido-bridged compounds of palladium. Here we describe the reactions of a number of diphosphines [$R_2P \cdot PR_2$; R = Me, Et, or Ph] and some analogous diarsines with the carbonyls of iron, chromium, molybdenum, and tungsten. These have yielded a variety of phosphorus- and arsenic-bridged dinuclear carbonyls of two types, designated as (A) and (B), which can be formulated on the basis of the inert gas rule: (A) as phosphido- and arsenido-bridged carbonyls and (B) as diphosphine- and diarsine-bridged carbonyls. To type (A) we assign structures (I) and (II) and to type (B) structures (III) and (IV) (E = P or As; M = Cr, Mo, or W). Type (A) compounds were to be expected since analogous thio-complexes (V) are well known,[2] and Lambert [3] has shown that triphenyl-arsine with manganese carbonyl in boiling tetrahydronaphthalene gives the compound (VI).

Type (B) compounds were unexpected, but there is precedence for bridging by other types of diphosphines; thus a binuclear compound $[(CO)_2Ni(Et_2P \cdot CH_2 \cdot CH_2 \cdot PEt_2)_2Ni(CO)_2]$ was obtained by Chatt and Hart, amongst other products, when $Et_2P \cdot CH_2 \cdot CH_2 \cdot PEt_2$

[1] Hayter, *J. Amer. Chem. Soc.*, 1962, **84**, 3046, and references therein.
[2] (*a*) Hieber and Spacu, *Z. anorg. Chem.*, 1937, **233**, 353; (*b*) Kettle and Orgel, *J.*, 1960, 3890; (*c*) King, *J. Amer. Chem. Soc.*, 1962, **84**, 2460.
[3] Lambert, *Chem. and Ind.*, 1961, 830.

was treated with nickel carbonyl.[4] Similarly, Zingales *et al.* have obtained binuclear carbonyls of Group VI metals by reaction of $Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2$ with the corresponding carbonyls.[5]
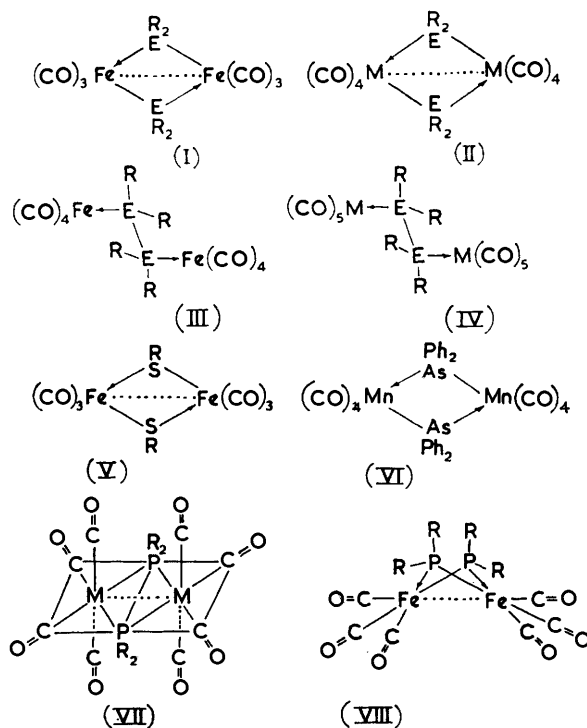
Compounds of both types derived from the Group VI metal carbonyls, should be considered separately from those derived from iron carbonyl (cf. the compounds listed in Table 1).

TABLE 1.

Infrared carbonyl stretching frequencies (cm.$^{-1}$) in chloroform of compounds of general formula $[M_2(CO)_nL]$.

Formula				Formula				
$[Cr_2(CO)_8(PMe_2)_2]$	2011s	1952vs, b		$[Mo_2(CO)_{10}(PMe_2)_2]$	2079w, sh	2069m	1990w	1954vs, b
				$[W_2(CO)_{10}(PMe_2)_2]$	2079w, sh	2068m	1981w	1946vs, b
$[Cr_2(CO)_8(PEt_2)_2]$	2003s	1942vs, b						
$[Mo_2(CO)_8(PEt_2)_2]$	2019s	1948vs, b		$[Mo_2(CO)_{10}(PEt_2)_2]$	2076w, sh	2068m	1988w	1950vs, b
$[W_2(CO)_8(PEt_2)_2]$	2024s	1946vs, b		$[W_2(CO)_{10}(PEt_2)_2]$	2075w, sh	2067m	1980w	1944vs, b
$[Mo_2(CO)_8(AsMe_2)_2]$	2026s	1960vs, b		$[Mo_2(CO)_{10}(AsMe_2)_2]$	2077w, sh	2069m	1992w	1954vs, b
$[W_2(CO)_8(AsMe_2)_2]$	2018s	1946vs, b		$[W_2(CO)_{10}(AsMe_2)_2]$	2079w, sh	2070m	1985w	1947vs, b
$[Mo_2(CO)_8(PPh_2)_2]$	2035s	1969vs, b						
$[W_2(CO)_8(PPh_2)_2]$	2034s	1961vs, b						
$[Mo_2(CO)_8(AsPh_2)_2]$	2033s	1965vs, b						
$[Fe_2(CO)_6(PMe_2)_2]$	2047s	2009vs	1976s	1963s				
$[Fe_2(CO)_6(PEt_2)_2]$	2045s	2007vs	1972s	1962s				
$[Fe_2(CO)_6(AsMe_2)_2]$	2037s	2024vw	1998vs	1965s	1958s			
$[Fe_2(CO)_8(PMe_2)_2]$	2059sh	2049s	1982w-m	1947vs, b				

Compounds Derived from Chromium, Molybdenum, and Tungsten Carbonyls.—Alkyl derivatives of types (A) and (B) were usually obtained by heating the metal carbonyl with

[4] Chatt and Hart, *J.*, 1960, 1378.
[5] Zingales and Canziani, *Gazzetta*, 1962, **92**, 343; Zingales, Canziani, and Ugo, *ibid.*, p. 761.

the tetra-alkyl-diphosphine or -diarsine (0·5 mole) in a sealed tube; the product depended on the temperature, the carbonyl, and the diphosphine or diarsine. Generally, at 180—200° compounds of type (B) were obtained and at higher temperatures (240—260°) compounds of type (A), but it was not always possible to obtain both types of derivative. Thus, molybdenum and tungsten hexacarbonyls gave only type (B) products with tetra-methyldiphosphine at all temperatures up to 320°, whereupon severe decomposition occurred, whereas chromium hexacarbonyl would not react below 260° and then formed only products of type (A). Sometimes compounds of higher carbonyl content could be converted into those of lower carbonyl content by heating them under reduced pressure. Thus, $[M_2(CO)_{10}(PEt_2)_2]$ (M = Mo or W) were converted into $[M_2(CO)_8(PEt_2)_2]$, but a corresponding conversion of the tetra-alkylarsines could not be effected.

The tetra-aryl-diphosphines and -diarsines underwent extensive decomposition under similar conditions. Boiling benzene as medium gave purer products, but these were of type (A) and no aromatic derivatives of type (B) were obtained. Type (A) compounds are orange to red materials, whereas type (B) compounds containing phosphorus are colourless and those containing arsenic are pale yellow.

Compounds Derived from Iron Carbonyl.—These derivatives were prepared similarly under milder conditions, and most conveniently in benzene. Tetramethyldiphosphine at 160° yielded the octacarbonyl compound, type (B), and at 180° the hexacarbonyl compounds, type (A). However, both tetraethyldiphosphine and tetramethyldiarsine yielded only products of type (A). All the iron compounds were yellow or orange.

Structures of the Phosphorus- and Arsenic-bridged Compounds.—The compounds are diamagnetic substances, stable to air and moisture, and with considerable thermal stability. The compounds of type (A) are given structures (I) and (II) on the basis of the inert gas rule and the formulation of analogous thio-compounds of iron. The metal–metal bond is essential to account for the diamagnetism of the complexes and its presence receives support from some anomalies in the dipole moments.

If the compounds of type (B) were given exactly analogous structures to (I) and (II), but with an additional carbon monoxide molecule attached to each metal atom, the effective atomic number of the metal atoms would exceed that of the next inert gas. Electrons would thus have to be accommodated in high-energy orbitals. Since the ligands are all of high ligand-field strengths, these additional electrons, one for each metal atom, should be readily removed by oxidation. The facts that the compounds are not oxidised by air, and that the derivatives of the chromium Group are colourless lend support to the formulation of the compounds of type (B) as (III) and (IV), in which the phosphorus–phosphorus and arsenic–arsenic bonds remain intact and there is no metal–metal bond. These formulations are supported by both dipole-moment and infrared-spectral measurements.

Infrared Spectra (By D. M. Adams).—The carbonyl stretching frequencies, v_{CO} (Table 1), in chloroform show that all the carbonyl groups are in terminal positions. The carbonyl absorption patterns of the compounds containing Group VI metals are similar to those normally observed for compounds of types cis-$[M(CO)_4L_2]$ [6] (type A) and $[M(CO)_5L]$ [7] (type B) (L = monodentate phosphine) which are in good agreement with the suggested structures. The carbonyl stretching frequencies of the iron compounds $[Fe_2(CO)_6L]$ exhibited a pattern different from that normally associated with the tricarbonyl iron group, indicating probable coupling between the two $Fe(CO)_3$ groups. This suggests that the iron compounds of type (A) are not exactly analogous in structure to the compounds of type (A) formed by the Group VI metals.

The spectra of the complexes containing the $(PMe_2)_2$-bridging group are sufficiently simple to allow them to be divided, on infrared evidence alone, into the two types (A)

[6] Chatt and Watson, *J.*, 1961, 4980.
[7] Poilblanc and Bigorgne, *Compt. rend.*, 1960, **250**, 1064.

and (B) (Table 2).   The spectra of type (B) are the simpler.   In them the symmetric deformation of the methyl groups, $\delta_{Me(s)}$ appears as an intense sharp doublet, whereas the chromium type (A) compound yields two bands of unequal intensity, and the tricarbonyl iron type (A) compound exhibits three bands.   Furthermore, the type (B) compounds exhibit P–CH_3 stretching bands $\nu_{P-C(as)}$ and $\nu_{P-C(s)}$ of equal intensities at nearly identical frequencies, whereas in the spectra of the type (A) compounds the bands are close together, broader, and differ in intensities (Table 2).   Finally, the methyl rocking frequencies, ρ_{Me} found near 940 cm.$^{-1}$ and 890 cm.$^{-1}$ show a slight splitting in the type (A) compounds, which is not observed in the spectra of the type (B).   These features indicate an element of dissymmetry in the structure of the chromium and tricarbonyl iron compounds which is also apparent from their dipole moments.

TABLE 2.

Phosphorus–methyl stretching frequencies (cm.$^{-1}$) in chloroform of compounds
containing the $(PMe_2)_2$-bridging group.

Compound	Type	$\nu_{P-C(as)}$	$\nu_{P-C(s)}$
$[Fe_2(CO)_6(PMe_2)_2]$	A	722s	705s
$[Cr_2(CO)_8(PMe_2)_2]$	A	731m	712vs
$[Fe_2(CO)_8(PMe_2)_2]$	B	745m	693m
$[Mo_2(CO)_{10}(PMe_2)_2]$	B	735m	684m
$[W_2(CO)_{10}(PMe_2)_2]$	B	736m	684m

Dipole Moments.—The aromatic derivatives were too insoluble in benzene for the measurement of dipole moments, but those of the aliphatic compounds were measured (Table 3; Experimental section).   The compounds of chromium, molybdenum, and tungsten fall sharply into the two types: type (A) with moments of about 1 D and type (B) with moments of about 4 D.   The iron compounds present an exactly opposite pattern, the compounds of the type (A) having the higher moment of about 4 D and the only example of type (B) having an intermediate moment of 2·5 D.   All except this latter moment can be easily explained on the basis of suggested structures.

We would expect the compounds of type (A) containing the Group VI metals to have a configuration as shown in (VII).   If the molecule were flat (as drawn) the compounds would have zero dipole moments, but there is the possibility of folding about the P–P line. The phosphorus atoms must carry an appreciable positive charge relative to the rest of the molecule; this, if the molecule were folded, would cause the development of a considerable dipole moment.   Such folding would also bring the metal atoms closer, so facilitating metal–metal bonding, but would also cause steric interference of the carbonyl groups perpendicular to the plane containing the phosphorus atoms.   Some compromise between these tendencies may prevail, leading to a slight folding to account for the moments of about 1 D.

In the iron compounds of type (A) with only five ligands to each metal atom, there is no steric reason why folding about the P–P line should be resisted, and the molecule can fold until each iron atom fills approximately the sixth co-ordination position on the other, as in (VIII), cf. $[Rh_2Cl_2(CO)_4]$.[8]   Such folding would explain the rather high dipole moments of the iron compounds of type (A).

We would expect the compounds of type (B) to have molecules shaped as in (III) and (IV) with free rotation about the P–P bonds, and the observed dipole moments of the Group VI metal compounds of type (B) are consistent with this.   The moment of the iron compound of type (B) [2·5 D] is about 1·0 D lower than expected on the basis of the structure (III; E = P, R = Me) but the difference may not be significant.

The properties of the compounds of the Group VI metals fit well the proposed structures (II) and (IV).   Those of the iron compounds show some slight anomalies: type (A) in the

[8] Dahl, Martell, and Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

infrared spectra and type (B) in the dipole moment. They may have some new and more exotic structures but at present there seem no logical alternatives to those suggested.

TABLE 3.

Dipole moments in benzene (25°) of dinuclear carbonyl compounds of general formula $[M_2(CO)_nL]$.

M	n	L	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$_{T}P$	$_{E}P$	$_{O}P$	$\mu(D)$
Cr	8	$(PMe_2)_2$	3·067	0·790						
			2·417	0·760						
			12·23		3·90					
			19·44		3·18					
			1·744			0·401				
			2·280			0·395	166·4	108·4	41·7	1·4
Cr	8	$(PEt_2)_2$	2·484	0·484						
			1·936	0·499		(0·390)	161·0 *	(126·9)	15·1 *	0·9 *
Mo	8	$(PEt_2)_2$	4·498	0·542						
			2·814	0·536						
			28·15		9·41					
			39·05		9·71					
			5·708			0·508				
			8·190			0·501	173·9	144·5	7·8	0·6
W	8	$(PEt_2)_2$	3·541	0·457						
			4·244	0·475						
			19·39		6·94					
			21·88		7·11					
			4·575			0·656				
			6·370			0·644	181·5	143·2	16·8	0·9
Mo	8	$(AsMe_2)_2$	0·975	0·475						
			3·000	0·470		(0·505)	175·4 *	(132·0)	23·6 *	1·1 *
W	8	$(AsMe_2)_2$	2·481	0·410						
			1·824	0·411		(0·650)	180·6 *	(135·7)	24·6 *	1·1 *
Mo	10	$(PMe_2)_2$	2·652	3·005						
			4·109	3·000						
			12·25		9·59					
			23·41		9·47					
			3·116			0·481				
			5·182			0·444	457·5	151·7	283·1	3·7
W	10	$(PMe_2)_2$	5·464	2·526						
			7·516	2·521						
			23·48		6·35					
			20·36		6·87					
			6·823			0·586				
			6·874			0·582	495·1	156·4	315·1	3·9
Mo	10	$(PEt_2)_2$	2·932	2·486						
			4·806	2·496		(0·463)	437·5 *	(133·2)	284·35 *	3·7 *
W	10	$(PEt_2)_2$	5·743	2·161						
			3·151	2·129		(0·584)	472·2 *	(174·9)	271·1 *	3·6 *
Mo	10	$(AsMe_2)_2$	3·191	2·563						
			2·631	2·579		(0·463)	469·2 *	(157·7)	311·5 *	3·9 *
W	10	$(AsMe_2)_2$	5·475	1·501						
			4·839	1·525		(0·584)	388·15 *	(162·4)	201·4 *	3·1 *
Fe	6	$(PMe_2)_2$	3·078	3·889						
			6·809	3·885						
			33·01		8·50					
			20·28		8·51					
			4·800			0·479				
			5·865			0·460	375·4	99·5	260·95	3·6
Fe	6	$(PEt_2)_2$	2·504	3·968						
			2·836	3·983		(0·470)	429·6 *	(118·0)	293·95 *	3·8 *
Fe	6	$(AsMe_2)_2$	1·940	4·185						
			2·611	4·151		(0·470)	477·2 *	(105·5)	355·9 *	4·2 *
Fe	8	$(PMe_2)_2$	2·896	1·834						
			3·166	1·831						
			18·36		6·01					
			19·45		5·98					
			5·136			0·467				
			3·821			0·445	252·3	108·65	127·3	

* Calculated by using estimated values of densities and refractivities.[13]

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are corrected. Normal combustion of compounds containing chromium, molybdenum, or tungsten gave low carbon values probably owing to partial formation of stable metal carbides; admixture of the sample with potassium dichromate overcame this difficulty. Reactions involving phosphines or arsines were carried out under nitrogen.

Tetraethyldiphosphine was prepared by Hewertson and Watson's method.[9] Tetramethyldiarsine was prepared by reaction of lithium with chlorodimethylarsine. Tetramethyldiphosphine was prepared by Parshall's method.[10]

Tetraphenyldiphosphine.—Diphenylphosphine (18·6 g., 1 mol.) was slowly added with stirring to a solution of sodium (2·3 g., 1 atom-equiv.) in liquid ammonia (250 ml.) cooled in carbon dioxide–acetone. The initial blue colour was discharged by the last few drops of the phosphine, yielding an orange solution of sodium diphenylphosphide. Chlorodiphenylphosphine (22·1 g., 1 mol.) in dry ether (30 ml.) was slowly added with stirring. The ammonia was allowed to evaporate overnight. The dark product was dissolved in benzene (200 ml.), and water (100 ml.) was added. The benzene layer was evaporated at atmospheric pressure and the residual viscous liquid transferred to a nitrogen-filled dry-box. Addition of ether caused crystallisation. After filtration and drying, the compound (8·0 g., 22%) had m. p. 118—120° (vac.) (lit.,[11] 118—120°).

Tetraphenyldiarsine.—Triphenylarsine (24·5 g., 1 mol.) was added during 10 min. to a stirred solution of sodium (3·7 g., 2 atom-equiv.) in liquid ammonia (2·0 ml.) as above, giving a red solution. Phenylsodium was destroyed by the addition of ammonium chloride (4·3 g., 1 mol.), and chlorodiphenylarsine (21·2 g., 1 mol.) in dry ether (100 ml.) was slowly added. After several hours' stirring, the ammonia was allowed to evaporate overnight. The product, worked up as described above, had m. p. 127—128° (vac.) (lit.,[12] 129—130°).

General Method of Preparation of Dinuclear Carbonyl Complexes.—The metal carbonyl (2 mol.) was placed in a Carius tube. The diphosphine or diarsine (1 mol.) in a sealed glass ampoule was added to the tube followed by a small steel cylinder encased in glass. The tube was swept out with nitrogen and sealed so that the final length was *ca.* 400 mm. The ampoule was broken by means of the steel cylinder and the tube heated in a Carius furnace. In some cases it was desirable to carry the reaction out in the presence of benzene. In the following preparations of *complexes*, the temperature of reaction, the period for which the tube was heated, and the volume of benzene employed (if any) are given:

Di-μ-dimethylphosphido-bis(tetracarbonylchromium). 260° for 20 hr., red crystals (from benzene) unmolten at 350° (Found: C, 32·3; H, 2·8. $C_{12}H_{12}Cr_2O_8P_2$ requires C, 32·0; H, 2·7%).

Di-μ-diethylphosphido-bis(tetracarbonylchromium). 240° for 96 hr., maroon crystals (from light petroleum, b. p. 60—80°), unmolten at 350° (Found: C, 38·1; H, 4·0. $C_{16}H_{20}Cr_2O_8P_2$ requires C, 38·0; H, 4·0%).

Di-μ-diethylphosphido-bis(tetracarbonylmolybdenum). 240° for 96 hr., orange crystals (from light petroleum, b. p. 60—80°), slowly decomposes above 130° (Found: C, 32·6; H, 3·5. $C_{16}H_{20}Mo_2O_8P_2$ requires C, 32·3; H, 3·4%). ·

Di-μ-diethylphosphido-bis(tetracarbonyltungsten). 250° for 40 hr., orange crystals (from methanol), m. p. 146—149° (decomp.) (Found: C, 25·2; H, 2·8. $C_{16}H_{20}O_8P_2W_2$ requires C, 25·0; H, 2·6%).

Di-μ-dimethylarsenido-bis(tetracarbonylmolybdenum). 250° for 32 hr., orange crystals (from methanol), m. p. 310—315° (decomp.) (Found: C, 23·2; H, 1·9. $C_{12}H_{12}As_2Mo_2O_8$ requires C, 23·0; H, 1·9%).

Di-μ-dimethylarsenido-bis(tetracarbonyltungsten). 250° for 21 hr., orange crystals (from methanol), unmolten at 350° (Found: C, 18·25; H, 1·5. $C_{12}H_{12}As_2O_8W_2$ requires C, 18·0; H, 1·5%). The filtrate from the recrystallisation of μ-tetramethyldiarsine-bis(pentacarbonyltungsten), on evaporation, yielded an orange solid which, after recrystallisation from methanol, gave a further quantity of the *bistetracarbonyl* compound (Found: C, 18·2; H, 1·5%).

Di-μ-diphenylphosphido-bis(tetracarbonylmolybdenum). 190° for 30 hr., in benzene (10 ml.),

[9] Hewertson and Watson, *J.*, 1962, 1493.
[10] Parshall, *J. Inorg. Nuclear Chem.*, 1960, **14**, 291.
[11] Hoffmann, Grünewald, and Horner, *Chem. Ber.*, 1960, **93**, 861.
[12] Blicke, Weinkauff, and Hargreaves, *J. Amer. Chem. Soc.*, 1930, **52**, 780.

orange crystals (from ethyl methyl ketone), m. p. 290—305° [Found: C, 49·1; H, 2·75%; M (by X-ray method, density by flotation), 772 $\pm$ 12. $C_{32}H_{20}Mo_2O_8P_2$ requires C, 48·9; H, 2·6%; M, 786]. Crystal data: monoclinic, a sin β = 9·45 $\pm$ 0·02, b = 19·73 $\pm$ 0·03, c = 16·82 $\pm$ 0·03 Å, U = 3136 Å³, D_M = 1·635 $\pm$ 0·016, Z = 4, space group $P2_1/c$ (C^5_{2h}, No. 14).

Di-μ-diphenylphosphido-bis(tetracarbonyltungsten). 170° for 19 hr., in benzene (8 ml.), red crystals (from ethyl methyl ketone), unmolten at 350° (Found: C, 40·2; H, 2·3%; M, 942 $\pm$ 15. $C_{32}H_{20}O_8P_2W_2$ requires C, 39·95; H, 2·1%; M, 962). Crystal data: monoclinic, isomorphous with di-μ-diphenylphosphido-bis(tetracarbonylmolybdenum), a sin β = 9·48 $\pm$ 0·02, b = 19·64 $\pm$ 0·04, c = 16·85 $\pm$ 0·03 Å, U = 3137 Å³, D_M = 1·994 $\pm$ 0·02, Z = 4, space group $P2_1/c$ (C^5_{2h}, No. 14).

Di-μ-diphenylarsenido-bis(tetracarbonylmolybdenum). 185° for 21 hr., in benzene (7 ml.), orange crystals (from ethyl acetate), m. p. 277—279° (decomp.) (Found: C, 44·2; H, 2·5%; M, 849 $\pm$ 29. $C_{32}H_{20}As_2Mo_2O_8$ requires C, 44·0; H, 2·3%; M, 874). Crystal data: monoclinic, isomorphous with di-μ-diphenylphosphido-bis(tetracarbonylmolybdenum), a sin β = 9·52 $\pm$ 0·02, b = 20·13 $\pm$ 0·04, c = 16·81 $\pm$ 0·02 Å, U = 3221 Å³, D_M = 1·75 $\pm$ 0·05, Z = 4, space group $P2_1/c$ (C^5_{2h}, No. 14).

μ-Tetramethyldiphosphine-bis(pentacarbonylmolybdenum). 180° for 19 hr., colourless crystals (from ethanol), m. p. 141—142° (Found: C, 28·4; H, 2·2%; M, 580 $\pm$ 12. $C_{14}H_{12}Mo_2O_{10}P_2$ requires C, 28·3; H, 2·0%; M, 594). Crystal data: monoclinic, a = 8·33 $\pm$ 0·02, b = 11·06 $\pm$ 0·02, c sin β = 12·20 $\pm$ 0·02 Å, U = 1124 Å³, D_M = 1·713 $\pm$ 0·005, Z = 2, space group $P2_1/n$ (C^5_{2h}, No. 14), molecular symmetry $\bar{1}$ (C_i).

μ-Tetramethyldiphosphine-bis(pentacarbonyltungsten). 200° for 17 hr., colourless crystals (from benzene), m. p. 162—163° (Found: C, 22·1; H, 1·7. $C_{14}H_{12}O_{10}P_2W_2$ requires C, 21·8; H, 1·6%).

μ-Tetraethyldiphosphine-bis(pentacarbonylmolybdenum). 190° for 23 hr., colourless crystals (from benzene) m. p. 157—159° (decomp.) (Found: C, 33·4; H, 3·2%; M, 640 $\pm$ 10. $C_{18}H_{20}Mo_2O_{10}P_2$ requires C, 33·25; H, 3·1%; M, 650). Crystal data: monoclinic, a = 18·67 $\pm$ 0·03, b = 15·00 $\pm$ 0·02, c sin β = 9·15 $\pm$ 0·02 Å, U = 2562 Å³, D_M = 1·658 $\pm$ 0·020, Z = 4, space group $P2_1/n$ (C^5_{2h}, No. 14).

μ-Tetraethyldiphosphine-bis(pentacarbonyltungsten). 190° for 45 hr., colourless crystals (from benzene), m. p. 188—189° (decomp.) (Found: C, 26·45; H, 2·5. $C_{18}H_{20}O_{10}P_2W_2$ requires C, 26·2; H, 2·4%).

μ-Tetramethyldiarsine-bis(pentacarbonylmolybdenum). 200° for 24 hr., yellow crystals (from ethanol), m. p. 116·5—117·5° (Found: C, 24·8; H, 1·9. $C_{14}H_{12}As_2Mo_2O_{10}$ requires C, 24·7; H, 1·8%).

μ-Tetramethyldiarsine-bis(pentacarbonyltungsten). 195° for 20 hr., yellow crystals (from light petroleum, b. p. 60—80°), m. p. 144—146° (Found: C, 20·0; H, 1·6. $C_{14}H_{12}As_2O_{10}W_2$ requires C, 19·6; H, 1·4%).

Di-μ-dimethylphosphido-bis(tricarbonyliron). 180° for 20 hr. in benzene (5 ml.), yellow crystals (from light petroleum, b. p. 60—80°), m. p. 170° (decomp.) [Found: C, 30·2; H, 3·1%; M (ebullioscopic in benzene), 382. $C_{10}H_{12}Fe_2O_6P_2$ requires C, 29·9; H, 3·0%; M, 402].

Di-μ-diethylphosphido-bis(tricarbonyliron). 165° for 24 hr. and 200° for 22 hr. in benzene (5 ml.), orange crystals (from benzene), m. p. 143—145° (Found: C, 36·85; H, 4·5. $C_{14}H_{20}Fe_2O_6P_2$ requires C, 36·7; H, 4·4%).

Di-μ-dimethylarsenido-bis(tricarbonyliron). 180° for 20 hr., in benzene (5 ml.), orange crystals (from methanol) unmolten at 350° (Found: C, 24·6; H, 2·5. $C_{10}H_{12}As_2Fe_2O_6$ requires C, 24·5; H, 2·5%).

μ-Tetramethyldiphosphine-bis(tetracarbonyliron). 165° for 24 hr., in benzene (8 ml.), orange crystals (from benzene), m. p. 146—148° (decomp.) (Found: C, 31·6; H, 2·8; M, 465. $C_{12}H_{12}Fe_2O_8P_2$ requires C, 31·5; H, 2·6%; M, 458].

Infrared Spectra were recorded on a Grubb-Parsons GS2A spectrometer.

Dipole Moments. The method of determination and significance of the symbols in Table 3 are given in ref. 13.

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[13] Chatt and Shaw, *J.*, 1959, 705.