Substituted Group VI Metal Carbonyl Complexes with the Ligands Trimethylphosphine, Dimethylphenylphosphine, Dimethylphenylarsine, and Dimethyl Phenylphosphonite

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Series of substituted metal carbonyls of the types $[M(CO)_{6-x}L_x]$ [M = Cr, Mo, or W; x = 1, 2, or 3; L = PMe_3, PMe_2Ph, $P(OMe)_2Ph$, or $AsMe_2Ph$] are described. I.r. and n.m.r. spectral data and dipole moment results are given and discussed. The methyl resonance patterns of the tertiary phosphine or phosphonite complexes are not particularly useful in determining stereochemistry since they are of the type corresponding to intermediate phosphorus–phosphorus coupling.

WE have made extensive use of the methyl ^1H n.m.r. patterns of dimethylphenylphosphine or dimethylphenylarsine as ligands to study the stereochemistry of their complexes (refs. 1—6 and unpublished work.) For example, in complexes of the Group VIII metals two dimethylphenylphosphine ligands in mutual *trans*-positions usually give a well defined 1 : 2 : 1 triplet for the methyl resonance pattern due to very strong phosphorus–phosphorus coupling across the metal atom. In contrast, a dimethylphenylphosphine ligand with some ligand other than dimethylphenylphosphine in the *trans*-position gives a well defined 1 : 1 doublet methyl-resonance pattern; *i.e.*, the dimethylphenylphosphine ligand is not coupling sufficiently strongly with the P-atom of another dimethylphenylphosphine in *cis*-position to give an observed effect.

It seemed of interest to extend our n.m.r. study of dimethylphenylphosphine and dimethylphenylarsine complexes to the substituted Group VI metal carbonyls, to see if one could use the method for determining stereochemistry.

Complexes of the type $[M(CO)_4(PMe_2Ph)_2]$ (M = Cr, Mo, or W) were readily prepared by heating the hexacarbonyl with dimethylphenylphosphine in a sealed tube. The complexes were shown to have the *cis*-configuration by dipole-moment measurements (Table 3) but some isomerisation to the *trans*-isomer occurred in solution for chromium (as shown by n.m.r. and dielectric measurements). The ^1H (methyl) n.m.r. patterns of the complexes in chloroform solution were complicated and consisted of a rather broad central resonance flanked by a 1 : 1 doublet of separation 6 Hz (*i.e.* the pattern was no longer the simple 1 : 1 doublet or 1 : 2 : 1 triplet found for many Group VIII metal–PMe_2Ph complexes, but an intermediate pattern). Harris[7,8] has developed the theory of nuclear spin systems of the type $X_nAA'X_n'$ (*i.e.* X = H, A = P for our compounds) and has shown that a simple 1 : 2 : 1 triplet resonance will be observed when $|J(A-A')| \gg |J(A-X) + J(A'-X)|$ (*i.e.* when phosphorus–phosphorus coupling is strong). His equations show that when phosphorus–phosphorus coupling is small a 1 : 1 doublet would be observed; *i.e.*, the ^1H dimethylphenylphosphine ligand resonance is not split by other phosphorus nuclei. When phosphorus–phosphorus coupling is intermediate, however, several methyl absorption resonances would be expected and would appear as an unresolved, broad resonance lying between a 1 : 1 doublet of separation $J(A-X) + J(A'-X)$.[7,8] Thus, for complexes of the type *cis*-$[M(CO)_4(PMe_2Ph)_2]$ phosphorus–phosphorus coupling is sufficiently large to give these broad resonances and not large enough to give 1 : 2 : 1 triplets or small enough to make the dimethylphenylphosphine ligands behave independently and give 1 : 1 methyl resonance patterns.

TABLE 1

^1H (Methyl) n.m.r. data for some complexes of the type $[M(CO)_{6-x}L_x]$ {M = Cr, Mo, or W; x = 1, 2, or 3; L = PMe_3, PMe_2Ph, $AsMe_2Ph$, or $P(OMe)_2Ph$} in chloroform solution. 'J' values (in Hz) refer to the separation of the two outer peaks; *i.e.*, 'J' = $|J(P-H) + J'(P'-H)|$. s = singlet; d = doublet; i = intermediate pattern

Ligand L	Stereochemistry	Chromium		Molybdenum		Tungsten	
		τ	'J'	τ	'J'	τ	'J'
			$[M(CO)_5L]$				
PMe_2Ph				8·19d	7·0		
$P(OM)_2Ph$				6·42d	12·5		
			$[M(CO)_4L_2]$				
PMe_3	*cis*	8·58i	6·9	8·57i	6·6	8·41i	7·0
PMe_3	*trans*	8·53i	7·2				
PMe_2Ph	*cis*	8·53i	6·9	8·52i	6·0	8·69 *	6·2 *
$AsMe_2Ph$	*cis*	8·47s		8·58s		8·47s	
$P(OMe)_2Ph$	*cis*	6·51i	11·1				
$P(OMe)_2Ph$	*trans*	6·41i	10·9	6·44i	11·6	6·45i	12·4
			$M(CO)_3L_3$				
PMe_3	*fac*	8·63i	5·6	8·62i	5·2		
PMe_2Ph	*fac*	8·57i	5·1	8·58i	4·3	8·46i	4·7
PMe_2Ph	*mer*			8·36i	5·2		
				9·01d	5·6		
$AsMe_2Ph$	*fac*	8·68s		8·67s		8·59s	
$P(OMe)_2Ph$	*mer*	6·51i	11·1	6·64i	10·8		
		6·67d	11·4				

* In benzene solution.

We have also prepared other complexes of the type $[M(CO)_4L_2]$ (M = Cr, Mo, or W and L = PMe_3, $P(OMe)_2Ph$, or $AsMe_2Ph$) generally by displacing a chelating

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† No reprints available.

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diene such as cyclo-octa-1,5-diene or norbornadiene from a diene complex of the type [M(CO)$_4$(diene)] with the ligand L. After this work was completed Jenkins and Verkade[9] described the trimethylphosphine complexes of the type *cis*-[M(CO)$_4$(PMe$_3$)$_2$] (M = Cr, Mo, and W) and also *trans*-[Cr(CO)$_4$(PMe$_3$)$_2$] and gave the carbonyl stretching frequencies exhibited by the solid complexes but not the n.m.r. data (which we give in Table 1). Our assigned stereochemistries for these complexes are based mainly on the number and relative intensities of the carbonyl stretching frequencies in the near i.r. regions (Table 2). (Jenkins and Verkade's were similarly based).

TABLE 2

Carbonyl stretching frequencies for some pentacarbonyl, tetracarbonyl, or tricarbonyl complexes of chromium, molybdenum, or tungsten in chloroform solution

	ν(CO) (cm.$^{-1}$)			
[Mo(CO)$_5$(PMe$_2$Ph)]	2068w	1982w		1940vs
[Mo(CO)$_5${P(OMe)$_2$Ph}]	2070w	1988w		1946vs
[Cr(CO)$_4$(PMe$_3$)$_2$] †	2001s	1901 *	1873vs	1866 *
[Cr(CO)$_4$(PMe$_2$Ph)$_2$] †	2003s	1905 *	1880vs	1866 *
[Cr(CO)$_4${P(OMe)$_2$Ph}$_2$] ‡	2014w	1952w	1902vs	
cis-[Cr(CO)$_4$(AsMe$_2$Ph)$_2$]	2008s	1904 *	1893vs	1873 *
cis-[Mo(CO)$_4$(PMe$_3$)$_2$]	2016s	1910vs	1896vs	1874 *
cis-[Mo(CO)$_4$(PMe$_2$Ph)$_2$]	2011s	1912 *	1895vs	1878 *
trans-[Mo(CO)$_4${P(OMe)$_2$Ph}$_2$]	2028w	1961m	1908vs	
trans-[Mo(CO)$_4${P(allyl)$_2$Ph}$_2$]	2020w	1946m	1890vs	
cis-[Mo(CO)$_4$(AsMe$_2$Ph)$_2$]	2016s	1912 *	1898vs	1869 *
cis-[W(CO)$_4$(PMe$_3$)$_2$]	2008s	1898 *	1880vs	1862 *
cis-[W(CO)$_4$(PMe$_2$Ph)$_2$]	2008s	1901 *	1883vs	1873 *
trans-[W(CO)$_4${P(OMo)$_2$Ph}$_2$]	2028vw	1953w	1901vs	
cis-[W(CO)$_4$(AsMe$_2$Ph)$_2$]	2012s	1908 *	1887vs	1862 *
trans-[W(CO)$_4${P(allyl)$_2$Ph}$_2$]	2010w	1938m	1880vs	
fac-[Cr(CO)$_3$(PMe$_3$)$_3$]	1923s	1821vs		
fac-[Cr(CO)$_3$(PMe$_2$Ph)$_3$] *	1920s	1920vs		
mer[Cr(CO)$_3${P(OMe)$_2$Ph}$_2$]	1969w	1866vs		
fac-[Cr(CO)$_3$(AsMe$_2$Ph)$_3$]	1923s	1818vs		
fac-[Mo(CO)$_3$(PMe$_3$)$_3$]	1927s	1828vs		
fac-[Mo(CO)$_3$(PMe$_2$Ph)$_3$]	1939s	1832vs	1824sh	
mer-[Mo(CO)$_3$(PMe$_2$Ph)$_3$]	1955w	1846vs		
mer-[Mo(CO)$_3${P(OMe)$_2$Ph)$_3$]	1980w	1957vw	1880vs	
fac-[Mo(CO)$_3$(AsMe$_2$Ph)$_3$]	1932s	1828vs		
fac-[W(CO)$_3$(PMe$_2$Ph)$_3$]	1932s	1926vs		
fac-[W(CO)$_3$(AsMe$_2$Ph)$_3$]	1932s	1832vs		

* Shoulder. † From the i.r. spectrum largely *cis* in the solid state but gives some *trans*-isomer in solution (n.m.r. evidence). ‡ From the i.r. spectrum largely *trans* in the solid state but gives some *cis*-isomer in solution (n.m.r. evidence).

cis-Complexes of this type show a sharp band at highest frequency followed by a complex of three bands which may not be completely resolved and at least one of which will be intense.[10-12] *trans*-Complexes show only one intense band and two weaker ones at higher frequencies.[10-12] For the complex [Cr(CO)$_4${P(OMe)$_2$Ph}$_2$] the configuration was also shown to be *trans* by the dipole moment (Table 3) and for the dimethylphenylarsine and dimethylphenylphosphine complexes *cis* for all three metals by dipole measurements. For the chromium complex *cis*-[Cr(CO)$_4$(PMe$_2$Ph)$_2$] the dielectric 'constant' of its benzene solution changed with time, corresponding to isomerisation to the *trans*-isomer. At 20° equilibrium was reached after *ca.* 30 min. and corresponded to *ca.* 25% *trans*- and 75% *cis*-isomer; the values of $\Delta\varepsilon/w$ used to calculate the dipole moment (6·3 D) were obtained by extrapolation to zero time.

Several tricarbonyl complexes of the type [M(CO)$_3$L$_3$] [M = Cr or Mo; L = PMe$_3$, PMe$_2$Ph, AsMe$_2$Ph, or P(OMe)$_2$Ph] were prepared by displacing cycloheptatriene from the cycloheptatriene complex [M(CO)$_3$-(C$_7$H$_8$)]. [W(CO)$_3$(AsMe$_2$Ph)$_3$] was similarly made from the mesitylene complex. The P(OMe)$_2$Ph complexes showed only one strong carbonyl absorption band in the i.r. region, indicating the *mer*-configuration. The remainder showed one intense and one very intense band, indicative of a *fac*-stereochemistry (Table 2).[12] Measurement of the dipole moments of several of these complexes of type [M(CO)$_3$L$_3$] confirmed that they were facial isomers (Table 3). (The *mer*-isomers would be expected to have considerably smaller moments than the *cis*-isomers of type [M(CO)$_4$L$_2$], whereas the observed moments are greater.) The methyl resonances of these *fac*-isomers consisted of a broad, central peak with two partially resolved side peaks (Table 1). The complex *mer*-[Cr(CO)$_3${P(OMe)$_2$Ph}$_3$] showed two methyl resonances, relative intensities 2 : 1; one a triplet characteristic of intermediate phosphorus–phosphorus coupling and the less intense resonance a well defined 1 : 1 doublet due to the P(OMe)$_2$Ph ligand *trans* to carbonyl. The complex *mer*-[Mo(CO)$_3${P(OMe)$_2$Ph}$_3$], however, showed only one resonance, probably due to accidental overlap since the *mer*-configuration was clearly indicated by its i.r. spectrum (Table 2). We have also prepared the *mer*-isomer of [Mo(CO)$_3$(PMe$_2$Ph)$_3$] by the sodium borohydride reduction of [MoCl$_2$(CO)$_2$(PMe$_2$Ph)$_3$]MeOH in the presence of an excess of carbon monoxide. The methyl resonance pattern of this complex showed a triplet at τ 8·36 of total relative intensity 2 and a 1 : 1 doublet resonance of intensity 1 at τ 9·01, clearly indicating the *mer*-configuration. The i.r. spectrum (Table 2) showed only one intense carbonyl absorption band, again indicative of the *mer*-configuration.

Thus the ^{1}H (methyl) resonance patterns of these tertiary phosphine substituted Group VI carbonyls are not generally useful in determining their stereochemistry since the patterns are of the intermediate type (*i.e.*, neither well defined 1 : 2 : 1 triplets nor 1 : 1 doublets). Similarly, intermediate coupling patterns have been obtained for tris(dimethylamino)phosphine[13] or phosphite ester[14] derivatives of Group VI carbonyls and also for some dimethylphosphido-bridged complexes.[15]

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TABLE 3

Dipole moment data in benzene at 20°

Complex	10^3w	$\Delta\varepsilon/w$	$10^2\Delta n/w$	$-\Delta v/w$	$_{\mathrm{T}}P$	$_{\mathrm{E}}P$	$_{\mathrm{O}}P$	μ(D)
$[\mathrm{Cr(CO)_4(PMe_2Ph)_2}]$	2·307	10·4 †						
	2·791	10·6 †		(0·37)	965 †	(119)	829 †	6·3 †
cis-$[\mathrm{Mo(CO)_4(PMe_2Ph)_2}]$	2·152	10·98						
	2·983	11·12		(0·39)	1108	(129)	959	6·8 *
cis-$[\mathrm{W(CO)_4(PMe_2Ph)_2}]$	2·380	10·20						
	3·141	10·19		(0·46)	1206	(134)	1051	7·1
cis$[\mathrm{Cr(CO)_4(AsMe_2Ph)_2}]$	2·061	9·92						
	2·951	9·69		(0·37)	1086	(139)	927	6·7 *
cis-$[\mathrm{Mo(CO)_4(AsMe_2Ph)_2}]$	2·343	9·36						
	3·550	9·41		(0·39)	1131	(149)	959	6·8 *
cis-$[\mathrm{W(CO)_4(AsMe_2Ph)_2}]$	1·336	9·18						
	1·390	8·92						
	2·519	8·80						
	3·253	8·96						
	3·130	9·15		(0·46)	1216	(154)	1038	7·1 *
trans-$[\mathrm{Cr(CO)_4\{P(OMe)_2Ph\}_2}]$	2·106	1·64						
+ a little *cis*-impurity	2·894	1·58		(0·37)	267	(125)	123	2·4 *
trans-$[\mathrm{W(CO)_4\{P(allyl)_2Ph\}_2}]$	2·053	0·822		(0·46)	242	(188)	25	1·1 *
fac-$[\mathrm{Cr(CO)_3(PMe_2Ph)_3}]$	2·110	11·29						
	3·159	11·24						
	7·185		12·52					
	11·900		10·92					
	5·642			0·39				
	10·007			0·40	1279	152	1104	7·3
fac-$[\mathrm{Mo(CO)_3(PMe_2Ph)_3}]$	2·735	11·17						
	2·915	11·19		(0·54)	1349	(146)	1181	7·5 *
fac-$[\mathrm{W(CO)_3(PMe_2Ph)_3}]$	2·407	10·91						
	3·074	11·03						
	23·65		11·00					
	26·56		11·68					
	11·72			0·56				
	14·77			0·56	1516	166	1325	8·0
fac-$[\mathrm{Cr(CO)_3(AsMe_2Ph)_3}]$	1·901	9·25						
	2·870	9·39						
	23·08		10·0					
	27·36		10·3	(0·39)	1340	182	1130	7·4 *
fac-$[\mathrm{Mo(CO)_3(AsMe_2Ph)_3}]$	1·938	9·80						
	2·969	9·65						
	24·71		10·1					
	28·78		10·4					
	9·656			0·54				
	15·27			0·55	1447	176	1245	7·7
fac-$[\mathrm{W(CO)_3(AsMe_2Ph)_3}]$	2·045	9·97						
	2·867	9·82		(0·56)	1646	(196)	1420	8·3 *

* Calc. by using estimated values of densities and refractivities, shown in parentheses. † Since in benzene solution this largely *cis*-complex partially isomerises with time to more of the *trans*-isomer these values were obtained by extrapolation to zero time.

From the resonance shapes for the complexes *cis*-$[\mathrm{M(CO)_4(PMe_2Ph)_2}]$ it is clear that [J(P–P′] increases along the series W < Mo < Cr although the differences are small. In contrast, for the series *trans*-$[\mathrm{M(CO)_4\{P(OMe)_2Ph\}_2}]$ the order of increasing J(P–P′) is Cr < Mo < W; this same order has been found for complexes of the type *trans*-$[\mathrm{M(CO)_4(PBu_3)(PPh_3)}]$.[16]

It is not clear why intermediate coupling patterns should be obtained for two tertiary phosphine (or phosphites, *etc.*) ligands, whether in mutual *cis*- or *trans*-positions in these substituted Group VI metal carbonyls whilst, in contrast, extreme resonance patterns (*i.e.*, 1 : 1 doublets or 1 : 2 : 1 triplets) are observed with Group VIII metal complexes in oxidation states $\geqslant 1$. Grim and his co-workers [16] have shown that phosphorus–phosphorus couplings in complexes of the type *cis*- and *trans*-$[\mathrm{M(CO)_4(PPh_3)(PBu_2Ph)}]$ are respectively 21 and 49 Hz. In contrast phosphorus–phosphorus coupling in *trans*-$[\mathrm{PdI_2(PMe_3)(PEt_3)}]$ is 565 Hz but only 8·0 Hz in *cis*-$[\mathrm{PdCl_2(PMe_3)_2}]$.[17] In other complexes of type *trans*-$[\mathrm{PdI_2(PR^1_3)(PR^2_3)}]$ the coupling is several hundreds of Herz.[18] It will be of interest to discover the factors responsible for the large variations in phosphorus–phosphorus couplings in these complexes.

We have also prepared two pentacarbonyl complexes of molybdenum $[\mathrm{Mo(CO)_5L}]$ (L = $\mathrm{PMe_2Ph}$ or $\mathrm{P(OMe)_2Ph}$) by treating $[\mathrm{Mo(CO)_6}]$ with the ligand L in boiling, light petroleum (b.p. 100—120°) (see Experimental section and physical properties in the Tables).

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Operations involving tertiary phosphines or tertiary arsines were carried out under nitrogen. Molecular weights were determined on a Hitachi–Perkin-Elmer osmometer in chloroform.

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Pentacarbonyl(dimethylphenylphosphine)molybdenum(0), [Mo(CO)$_5$(PMe$_2$Ph)].—A mixture of hexacarbonylmolybdenum(0) (4·00 g.), dimethylphenylphosphine (3·05 g.), and light petroleum (b.p. 100—120°) (40 ml.) was boiled under reflux for 2 hr. The solvent was removed under reduced pressure to leave a solid, mainly [Mo(CO)$_4$(PMe$_2$Ph)$_2$]. This solid was washed with light petroleum (b.p. 30—40°) (20 ml.), and the washings were cooled to −70° to give white crystals which when sublimed (20°/0·1 mm.) gave the *product* as white prisms (0·20 g.), m.p. 26—28° (Found: C, 41·8; H, 3·15. $C_{13}H_{11}MoO_5P$ requires C, 41·7; H, 3·0%).

Pentacarbonyl(dimethyl phenylphosphonite)molybdenum(0), [Mo(CO)$_5${P(OMe)$_2$Ph}].—A mixture of hexacarbonylmolybdenum(0) (2·00 g.), dimethyl phenylphosphonite (1·29 g.), and light petroleum (b.p. 100—120°) (20 ml.) was boiled under reflux for 45 min. The solvent was removed under reduced pressure to leave a yellow oil which crystallised from light petroleum (b.p. 30—40°) to give the *product* as white plates (1·68 g.), m.p. 54—55° (Found: C, 38·5; H, 2·65. $C_{13}H_{11}MoO_7P$ requires C, 38·4; H, 2·7%).

Tetracarbonyl Complexes

Tetracarbonylbis(dimethylphenylphosphine)chromium(0), [Cr(CO)$_4$(PMe$_2$Ph)$_2$]: *cis–trans*-Mixture.—A mixture of hexacarbonylchromium(0) (1·20 g.) and dimethylphenylphosphine (1·34 g.) was heated in a sealed, evacuated tube at 150° for 5 hr. Yellow crystals formed when the tube was cooled and gave the product as lemon-yellow prisms (1·47 g.), m.p. 101—103° (from ethanol); the product was shown from its n.m.r. spectrum to be a mixture of *cis*- and *trans*-isomers (Found: C, 54·4; H, 5·1. $C_{20}H_{22}CrO_4P_2$ requires C, 54·5; H, 5·0%).

cis-*Tetracarbonylbis(dimethylphenylarsine)chromium*(0), [Cr(CO)$_4$(AsMe$_2$Ph)$_2$].—This was prepared in a similar fashion to the preceding compound from hexacarbonylchromium(0) (1·40 g.) and dimethylphenylarsine (2·34 g.) (150° for 2½ hr.). The *product* formed lemon-yellow needles (130 g.), m.p. 92—94° [from light petroleum (b.p. 60—80°)] (Found: C, 45·5; H, 4·4. $C_{20}H_{22}As_2CrO_4$ requires C, 45·5; H, 4·2%).

cis-*Tetracarbonylbis(dimethylphenylphosphine)molybdenum*(0), [Mo(CO)$_4$(PMe$_2$Ph)$_2$].—This was prepared in a similar fashion to the preceding two compounds from hexacarbonylmolybdenum(0) (1·40 g.) and dimethylphenylphosphine (1·33 g.) (150—160° for 5 hr.). The product formed white needles (1·61 g.), m.p. 110—112·5° and was identified by its i.r. spectrum (Found: C, 49·8; H, 4·7%; *M*, 445. $C_{20}H_{22}MoO_4P_2$ requires C, 49·6; H, 4·6%; *M*, 484).

cis-*Tetracarbonylbis(dimethylphenylarsine)molybdenum*(0), [Mo(CO)$_4$(AsMe$_2$Ph)$_2$].—This was prepared in similar fashion to the above compounds from hexacarbonylmolybdenum(0) (1·32 g.) and dimethylphenylarsine (1·62 g.) (150° for 19 hr.). The *product* formed off-white needles (1·30 g.), m.p. 82—83° [from light petroleum (b.p. 60—80°)] (Found: C, 42·1; H, 3·9. $C_{20}H_{22}As_2MoO_4$ requires C, 42·0; H, 3·9%).

cis-*Tetracarbonylbis(dimethylphenylphosphine)tungsten*(0), [W(CO)$_4$(PMe$_2$Ph)$_2$].—This was prepared in a similar way to the above compounds from hexacarbonyltungsten(0) (1·80 g.) and dimethylphenylphosphine (1·33 g.) (150° for 7 hr.). The *product* formed yellow needles (1·88 g.), m.p. 115—117° (from ethanol) (Found: C, 42·1; H, 3·9%; *M*, 587. $C_{20}H_{22}O_4P_2W$ requires C, 42·0; H, 3·9%; *M*, 637).

cis-*Tetracarbonylbis(dimethylphenylarsine)tungsten*(0), [W(CO)$_4$(AsMe$_2$Ph)$_2$].—This compound was prepared from hexacarbonyltungsten(0) (1·55 g.) and dimethylphenylarsine (1·58 g.) (150° for 19 hr.). The *product* formed pale yellow needles (0·62 g.), m.p. 97—98° (Found: C, 36·65; H, 3·4. $C_{20}H_{22}As_2O_4W$ requires C, 36·4; H, 3·4%).

trans-*Tetracarbonylbis(diallylphenylphosphine)tungsten*(0), [W(CO)$_4${P(allyl)$_2$Ph}$_2$].—This was prepared in a similar fashion to the above compounds from hexacarbonyltungsten(0) (1·85 g.) and diallylphenylphosphine (2·00 g.) (130—140° for 5 hr.). The *product* formed yellow needles (0·33 g.), m.p. 101—105° [from light petroleum (b.p. 40—60°)] (Found: C, 50·0; H, 4·75. $C_{28}H_{30}O_4P_2W$ requires C, 49·7; H, 4·5%).

Tetracarbonylbis(trimethylphosphine)chromium(0), [Cr(CO)$_4$(PMe$_3$)$_2$].—A solution of trimethylphosphine (0·11 g.) in diethyl ether (20 ml.) was added to a solution of tetracarbonylnorbornadienechromium(0) (0·18 g.) in benzene (10 ml.) and the mixture was boiled under reflux for 5 hr. The solvent was removed under reduced pressure and the resulting yellow solid was crystallised from light petroleum (b.p. 40—60°) to give the product as pale yellow needles (0·16 g.), m.p. 79—84°; the product was shown to be a mixture of *cis*- and *trans*-isomers by n.m.r. spectroscopy (Found: C, 37·9; H, 5·8. Calc. for $C_{10}H_{18}CrO_4P_2$: C, 38·0; H, 5·7%).

Tetracarbonylbis(dimethyl phenylphosphonite)chromium(0), [Cr(CO)$_4${P(OMe)$_2$Ph}$_2$].—This was prepared in a similar fashion to the preceding compound from tetracarbonylnorbornadienechromium(0) (0·40 g.), dimethyl phenylphosphonite (0·56 g.), and dry benzene (15 ml.) (3 hr. reflux). The product formed pale yellow needles (0·61 g.), m.p. 99—101° [from light petroleum (b.p. 60—80°)]; it was shown to be a mixture of *cis*- and *trans*-isomers (Found: C, 47·8; H, 4·6. $C_{20}H_{22}CrO_6P_2$ requires C, 47·6; H, 4·4%).

cis-*Tetracarbonylbis(trimethylphosphine)molybdenum*(0), [Mo(CO)$_4$(PMe$_3$)$_2$].—This was prepared in a similar fashion by heating tetracarbonylcyclo-octa-1,5-dienemolybdenum(0) (0·11 g.), a solution of trimethylphosphine (0·05 g.) in diethyl ether (10 ml.), and light petroleum (b.p. 40—60°) under reflux for 3 hr. The product formed white needles (0·09 g.), m.p. 93—95° [from light petroleum (b.p. 40—60°)] (Found: C, 33·55; H, 5·3. Calc. for $C_{10}H_{18}MoO_4P_2$: C, 33·3; H, 5·0%) (lit., m.p. 95—96°).

trans-*Tetracarbonylbis(diallylphenylphosphine)molybdenum*(0), [Mo(CO)$_4${P(allyl)$_2$Ph}$_2$].—This was prepared in a similar fashion from hexacarbonylmolybdenum(0) (1·67 g.), diallylphenylphosphine (1·55 g.) in light petroleum (b.p. 100—120°) (2·5 hr. reflux). The *product* formed pale yellow needles (0·10 g.), m.p. 101—103° [from light petroleum (b.p. 40—60°)] (Found: C, 56·95; H, 5·15. $C_{28}H_{30}MoO_4P_2$ requires C, 57·15; H, 5·10%).

trans-*Tetracarbonylbis(dimethyl phenylphosphonite)molybdenum*(0), [Mo(CO)$_4${P(OMe)$_2$Ph}$_2$].—This was prepared in a similar fashion from tetracarbonylcyclo-octa-1,5-dienemolybdenum(0) (0·60 g.), dimethyl phenylphosphinite (0·66 g.) and benzene (15 ml.) (3 hr. reflux). The *product* formed white needles (0·69 g.), m.p. 90—91° [from light petroleum (b.p. 40—60°)] (Found: C, 43·75; H, 3·9. $C_{20}H_{22}MoO_8P_2$ requires C, 43·8; H, 4·0%).

cis-*Tetracarbonylbis(trimethylphosphine)tungsten*(0), [W(CO)$_4$(PMe$_3$)$_2$].—This was prepared in a similar fashion from a solution of trimethylphosphine (0·05 g.) in diethyl ether (10 ml.), tetracarbonylcyclo-octa-1,5-dienetungsten(0).

(0·14 g.), and benzene (10 ml.) (4 hr. reflux). The product formed pale yellow needles (0·08 g.), m.p. 106—108° [from light petroleum (b.p. 30—40°)] (Found: C, 27·0; H, 4·1. Calc. *for* $C_{10}H_{18}O_4P_2W$: C, 26·8; H, 4·05%) (lit.,[9] m.p. 106—107°).

trans-*Tetracarbonylbis*(*dimethyl phenylphosphonite*)*tungsten*(0), $[W(CO)_4\{P(OMe)_2Ph\}_2]$.—This was prepared in a similar fashion from tetracarbonylcyclo-octa-1,5-dienetungsten(0) (0·20 g.), dimethyl phenylphosphonite (0·19 g.), benzene (10 ml.) (4 hr.). The *product* formed white needles (0·23 g.), m.p. 96—98° [from light petroleum (b.p. 40—60°)] (Found: C, 37·7; H, 3·45. $C_{20}H_{22}O_8P_2W$ requires C, 37·8; H, 3·5%).

Tricarbonyl Complexes

fac-*Tricarbonyltris*(*dimethylphenylarsine*)*chromium*(0), $[Cr(CO)_3(AsMe_2Ph)_3]$.—Dimethylphenylarsine (0·77 g.) was added to a solution of tricarbonylcycloheptatrienechromium(0) (0·32 g.) in benzene (10 ml.) and the mixture was boiled under reflux for 4 hr. The solvent was removed under reduced pressure to give a yellow solid which crystallised from benzene as lemon-yellow *prisms* (0·68 g.), m.p. 145—150° (decomp.) (Found: C, 47·7; H, 4·95. $C_{27}H_{33}As_3CrO_3$ requires C, 47·5; H, 4·9%).

fac-*Tricarbonyltris*(*trimethylphosphine*)*chromium*(0), $[Cr(CO)_3(PMe_3)_3]$.—This was prepared in a similar fashion from a solution of trimethylphosphine (0·10 g.) in diethyl ether (10 ml.), tricarbonylcycloheptatrienechromium(0) (0·10 g.), and benzene (10 ml.) (2 hr. reflux). The *product* formed pale yellow needles (0·10 g.), m.p. 132° (decomp.) (from ethanol) (Found: C, 39·55; H, 7·55. $C_{12}H_{27}CrO_3P_3$ requires C, 39·6; H, 7·5%).

mer-*Tricarbonyltris*(*dimethyl phenylphosphonite*)*chromium*(0), $[Cr(CO)_3\{P(OMe)_2Ph\}_3]$.—This was prepared in a similar fashion from dimethyl phenylphosphonite (0·51 g.), tricarbonylcycloheptatrienechromium(0) (0·23 g.), and dry benzene (15 ml.) (5 hr. reflux). The *product* formed pale yellow prisms (0·57 g.), m.p. 86—88° [from light petroleum (b.p. 40—80°)] (Found: C, 50·05; H, 5·15. $C_{27}H_{33}CrO_9P_3$ requires C, 50·2; H, 5·15%).

fac-*Tricarbonyltris*(*dimethylphenylphosphine*)*molybdenum*(0), $[Mo(CO)_3(PMe_2Ph)_3]$.—This was prepared in a similar way from dimethylphenylphosphine (1·0 g.), tricarbonyltris(methylcyanide)molybdenum(0) (0·20 g.), and hexane (20 ml.) (2 hr. reflux). The product formed white needles (0·36 g.), m.p. 156—157° (from ethanol) (Found: C, 54·4; H, 5·4; *M*, 577. $C_{27}H_{33}MoOP_3$ requires C, 54·6; H, 5·6%; *M* 594).

fac-*Tricarbonyltris*(*dimethylphenylarsine*)*molybdenum*(0), $[Mo(CO)_3(AsMe_2Ph)_3]$.—This was prepared in a similar manner from dimethylphenylarsine (1·90 g.), tricarbonyl(cycloheptatriene)molybdenum(0) (0·96 g.), and benzene (15 ml.) (10 min. reflux). The *product* formed off-white plates (1·37 g.), m.p. 121—123° (from ethanol) (Found: C, 44·4; H, 4·65. $C_{27}H_{23}As_3MoO_3$ requires C, 44·7; H, 4·6%).

fac-*Tricarbonyltris*(*trimethylphosphine*)*molybdenum*(0), $[Mo(CO)_3(PMe_3)_3]$.—This was prepared in a similar way from a solution of trimethylphosphine (0·28 g.) in diethyl ether (20 ml.) and tricarbonylcycloheptatrienemolybdenum(0) (0·33 g.) (reflux 3 hr.); m.p. 155° (decomp.) (from ethanol) (Found: C, 35·1; H, 6·55. $C_{12}H_{27}MoO_3P_3$ requires C, 35·3; H, 6·7%).

Tricarbonyltris(*dimethyl phenylphosphonite*)*molybdenum*(0), $[Mo(CO)_3\{P(OMe)_2Ph\}_3]$.—This was prepared in a similar manner from dimethyl phenylphosphonite (0·83 g.), tricarbonylcycloheptatrienemolybdenum(0) (0·40 g.), and dry benzene (10 ml.) (40 min. reflux). The *product* formed white needles (0·78 g.), m.p. 121—123° (from methanol) (Found: C, 47·1; H, 4·9. $C_{27}H_{33}MoO_9P_3$ requires C, 47·0; H, 4·8%).

fac-*Tricarbonyltris*(*dimethylphenylarsine*)*tungsten*(0), $[W(CO)_3(AsMe_2Ph)_3]$.—This was prepared in a similar way from dimethylphenylarsine (2·20 g.), tricarbonylmesitylenetungsten(0) (1·50 g.), and benzene (40 ml.) (reflux 3 hr.). The *product* formed off-white prisms (1·48 g.), m.p. 133—135° (Found: C, 39·7; H, 3·95. $C_{27}H_{33}As_3O_3W$ requires C, 38·8; H, 4·1%).

Dichlorodicarbonyltris(*dimethylphenylphosphine*)*molybdenum*(II)-*Monomethanol*, $[MoCl_2(CO)_2(PMe_2Ph)_3]$–MeOH.—Chlorine was passed over finely powdered hexacarbonylmolybdenum(0) (2·30 g.) at −78° for 8 min. to give a yellow solid. The excess of chlorine was evaporated off under nitrogen and the residue was extracted with acetone (20 ml.). The solution was filtered into a solution of dimethylphenylphosphine (3·30 g.) in acetone (20 ml.). The solvent was then removed under reduced pressure to leave a yellow oil which crystallised upon addition of methanol. Recrystallisation of this solid from methanol gave the required *product* as yellow needles (2·81 g.), m.p. 90—120° (Found: C, 48·55; H, 5·75; Cl, 10·4%. $C_{27}H_{37}Cl_2MoO_3P_2$ requires C, 48·5; H, 5·6; Cl, 10·6%).

mer-*Tricarbonyltris*(*dimethylphenylphosphine*)*molybdenum*(0), $[Mo(CO)_3(PMe_2Ph)_3]$.—Carbon monoxide was bubbled through a suspension of dichlorodicarbonyltris(dimethylphenylphosphine)molybdenum(II)–methanol (0·193 g.) in methanol (15 ml.) for 10 min. Sodium borohydride (0·32 g.) was added to the mixture and carbon monoxide was bubbled through the solution for a further 30 min. The solution was filtered and when set aside −20° afforded the *product* as yellow plates (0·058 g.), m.p. 95—97° (from methanol) (Found: C, 54·4; H, 5·35. $C_{27}H_{33}MoO_3P_3$ requires C, 54·6; H, 5·6%).

N.m.r. Spectra.—These were recorded at 60 MHz and at 34° on a Perkin-Elmer R10 spectrometer.

Dipole Moments.—These were determined as described previously.[19]

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