980. *The Reactions of Di- and Tri-tertiary Phosphines with the Hexacarbonyls of Metals of Group VI.*

By J. Chatt and H. R. Watson.

Ditertiary phosphines react with the hexacarbonyls of chromium, molybdenum, and tungsten, replacing either two or four carbon monoxide molecules. Tritertiary phosphines replace three. Complete expulsion of carbonyl groups was not achieved. *cis-trans*-Isomerism is exhibited by the substituted chromium derivatives, but not by those of molybdenum or tungsten. The carbonyl absorption frequencies in the 1700—2100 cm.$^{-1}$ range, and dipole moments, are recorded.

In view of the relative ease with which tertiary diphosphines replace all of the carbon monoxide from nickel carbonyl,[1] we have examined their reactions with the carbonyls of the metals of Group VI. The reactions of monodentate tertiary phosphines and phosphites with carbonyls of Group VI metals are referred to in papers by Abel, Bennett, and Wilkinson [2] and by Matthews, Magee, and Wotiz.[3] They show that replacement of one or two carbonyl groups by monodentate ligands proceeds readily, whereas a third carbonyl group is expelled only with difficulty. Further replacement has not been effected.

Using *o*-phenylenebisdimethylarsine, Nigam, Nyholm, and Stiddard [4] were able to displace four carbonyl groups from chromium, molybdenum, and tungsten carbonyls. We now report similar results with the ditertiary phosphines (I), (II; R = Et or Ph), and (III), and also our examination of the replacement of carbon monoxide by the tridentate tertiary phosphines (IV—VI). In every case simple replacement of carbon monoxide by the chelating tertiary phosphines [with *m* phosphorus(III) atoms] occurred as follows, yielding the mixed derivatives listed in Table 1.

$$n\,\text{Polyphosphine} + \text{M(CO)}_6 \longrightarrow [\text{M(Polyphosphine)}_n\text{(CO)}_{6-nm}] + nm\text{CO}$$

$CH_2(PPh_2)_2$ (I)	$(CH_2{\cdot}PR_2)_2$ (II)	$o\text{-}C_6H_4(PEt_2)_2$ (III)
$Ph{\cdot}P(o\text{-}C_6H_4{\cdot}PEt_2)_2$ (IV)	$Ph{\cdot}P(C_2H_4{\cdot}PPh_2)_2$ (V)	$Me{\cdot}C(CH_2{\cdot}PPh_2)_3$ (VI)

Ease of Replacement of Carbonyl Groups.—Previous work suggests that expulsion of carbonyl groups by tervalent phosphorus compounds proceeds stepwise with increasing difficulty, until there remain three carbonyl groups which cannot be removed by monodentate ligands. Electronegative substituents on the phosphorus atom favour this replacement.

Ditertiary phosphines react similarly. Replacement of two carbonyl groups occurs readily, and with the diphosphine (II; R = Et) no further replacement occurs. The more electronegative diphosphines (II; R = Ph) and (III) replace a third carbonyl, and even a fourth carbonyl group; the remaining two carbonyl groups are very strongly bound and have resisted all our attempts to replace them. With the tetracarbonyl derivatives of chromium replacement is difficult to effect and, under the experimental conditions used for the molybdenum and tungsten analogues, only minute yields of dicarbonyl derivatives were obtained. Therefore they were prepared by using the relatively ready displacement of mesitylene from mesitylenechromium tricarbonyl. When the arenemetal tricarbonyl was heated at atmospheric pressure with two equivalents of the diphosphines (I), (II; R = Ph), or (III) it gave the dicarbonyls in fair yield, with considerable proportions of

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[1] Chatt and Hart, *J.*, 1960, 1378.

[2] Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

[3] Matthews, Magee, and Wotiz, *J. Amer. Chem. Soc.*, 1959, **81**, 2273.

[4] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803.

tetracarbonyl derivatives. This was unexpected because nitrogen was passed rapidly through the reaction mixture to strip away mesitylene and would also have removed any free carbon monoxide. Apparently these carbonyl compounds can take part in reactions in which a carbonyl group of one molecule undergoes exchange with a ligand of another molecule.

The tritertiary phosphines (IV—VI) readily expel three molecules of carbon monoxide, to give the triphosphinemetal tricarbonyls, but further replacement does not occur in the presence of an excess of the phosphine, even at 250°. The strong bonding of the remaining three carbonyl groups is shown further by the reaction of the tritertiary phosphine (VI) with the tetracarbonyl (XVII) (Table 1) to give the tricarbonyl (XXXIII). The triphosphine presumably replaces one carbonyl group and then it expels the chelated ditertiary phosphine, in preference to the remaining carbonyls. No reaction occurs between the triphosphine (VI) and the dicarbonyl (XXVII).

We believe that total replacement in carbonyls of Group VI metals by di- or tri-tertiary phosphines is not possible. Nevertheless, products of the formula [M(diphosphine)$_3$] (M = Cr, Mo, and W) have been obtained by other methods[5] and are thermally stable.

General Properties of the Derivatives.—All crystallise well from solution. The tetracarbonyls are more soluble in non-polar than in polar solvents, being very soluble in chloroform or benzene, and sparingly so in ethanol or methanol. Solubility decreases with rising molecular weight of the component tertiary phosphine but does not appear to vary much between the corresponding derivatives of the three metals. The dicarbonyls and tricarbonyls have solubility characteristics similar to those of the tetracarbonyls, but in general are much less soluble. The compounds are non-conductors in nitrobenzene solution.

In the absence of light, the compounds are not obviously oxidised by air, even in solution, and in this respect differ from the corresponding ditertiary arsine derivatives.[4] In light and air, the solids darken slowly, and in solution they slowly deposit oxidised material. The derivative (XXIX) is oxidised faster than the others and had to be recrystallised in a nitrogen atmosphere. Light, in the absence of oxygen, appears to have no effect on the compounds: under nitrogen their solutions are unchanged when illuminated by a strong ultraviolet source for long periods.

The compounds are oxidised when heated in air, and therefore melting points were determined in evacuated tubes. In the absence of air they are thermally stable and most of them, even those of high m. p., appear to melt without decomposition. In attempts to achieve complete replacement we have heated dicarbonyls such as (XXVII) with the component ditertiary phosphine *in vacuo* for two weeks at 200°, or at this temperature for some days in a quartz vessel with strong ultraviolet illumination; the reactants were unchanged.

Configurations of Derivatives.—Dipole moments and infrared spectra have been used to elucidate the configurations of the tetra-, tri-, and di-carbonyl complexes.

All of the derivatives of molybdenum and tungsten have configurations with the greatest possible number of carbonyl groups in relative *cis*-positions. In the tetracarbonyl series, the chelate ligands impose such a configuration, but the molybdenum and tungsten derivatives (XX and XXI) of the monodentate phosphine (PPhEt$_2$) also have *cis*-phosphorus configurations. Their dipole moments in benzene are constant, indicating no spontaneous isomerisation, and the values are close to those of the corresponding derivatives of the chelating diphosphine (III).

The dicarbonyl complexes of molybdenum and tungsten have dipole moments in the region 6·15—6·7 D, in accordance with the *cis*-dicarbonyl structure. No evidence of a *trans*-configuration has been observed.

In order to satisfy the steric requirements of the triphosphine (VI) the three carbonyl

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[5] Chatt and Watson, *Proc. Chem. Soc.*, 1960, 243, and unpublished work.

groups in the derivatives (XXXII), (XXXIII), and (XXXIV) must occupy positions mutually at right angles. The observed dipole moment, 8·75 D, of the tricarbonyl (XXXIII) supports this conclusion. The infrared spectra of the derivatives (XXX) and (XXXI) indicate that these also have the carbonyl groups in *cis*-positions although the constituent triphosphines (IV) and (V) are able to span either edge or face positions.

In contrast to the molybdenum and tungsten derivatives, all of the chromium compounds in which *cis-trans*-isomerism is possible have shown evidence of such isomerism, by spontaneous change of dipole moment or of infrared spectrum in solution.

Where two values of the dipole moment are quoted in Table 1, they represent, respectively, the moment obtained by extrapolation to zero time of dissolution of the sample, and the apparent moment when equilibrium has been reached. Measurements at timed intervals show that intermediate values lie on an exponential curve. The isomerisation is shown clearly by the dicarbonyl derivatives (XXV) and XXVI). The moment of the pure *cis*-isomer, 6·2 D, decreases to a value of 4·85 D, whereas that of the *trans*-isomer, initially 0·95 D, increases to 4·1 D, indicating that the equilibrium mixture contains about equal amounts of both isomers.

TABLE 1.

Some physical properties of new phosphorus-substituted group VI carbonyls.

Compound		M. p.	Colour	Dipole moment (D)
$[Cr(CO)_4C_2H_4(PEt_2)_2]$	VII	116—116·5°	White	—
$[Mo(CO_4C_2H_4(PEt_2)_2]$	VIII	106·5—107	,,	—
$[W(CO)_4C_2H_4(PEt_2)_2]$	IX	121·5—122	Pale yellow	—
$[Cr(CO)_4$*o*-$C_6H_4(PEt_2)_2]$	X	162—164·5	White	7·6
$[Mo(CO)_4$*o*-$C_6H_4(PEt_2)_2]$	XI	181·5—182	,,	7·8
$[W(CO)_4$*o*-$C_6H_4(PEt_2)_2]$	XII	190·5—191	,,	8·25
$[Cr(CO)_4CH_2(PPh_2)_2]$	XIII	170·5—171·5	Yellow	—
$[Mo(CO)_4CH_2(PPh_2)_2]$	XIV	195·5—196	Pale yellow	—
$[W(CO)_4CH_2(PPh_2)_2]$	XV	200·5—201·5	,,	—
$[Cr(CO)_4C_2H_4(PPh_2)_2]$	XVI	211—212	,,	—
$[Mo(CO)_4C_2H_4(PPh_2)_2]$	XVII	193—194	White	—
$[W(CO)_4C_2H_4(PPh_2)_2]$	XVIII	208—209	Pale yellow	—
cis-$[Cr(CO)_4(PPhEt_2)_2]$	XIX	95—95·5	Lemon-yellow	~5·0 ⟶ 3·3
cis-$[Mo(CO)_4(PPhEt_2)_2]$	XX	98·5—99	Pale buff	6·95
cis-$[W(CO)_4(PPhEt_2)_2]$	XXI	104	Pale yellow	7·25
cis-$[Cr(CO)_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	XXII	263·5—266·5	Orange	—
cis-$[Mo(CO)_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	XXIII	257—258	Bright yellow	6·4
cis-$[W(CO)_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	XXIV	270—272	,,	6·6
cis-$[Cr(CO)_2\{C_2H_4(PPh_2)_2\}_2]$	XXV	280—280·5	Pale orange	6·2 ⟶ 4·85
trans-$[Cr(CO)_2\{C_2H_4(PPh_2)_2\}_2]$	XXVI	279—280	Vermilion red	0·95 ⟶ 4·1
cis-$[Mo(CO)_2\{C_2H_4(PPh_2)_2\}_2]$	XXVII	324—325	Yellow	6·15
cis-$[W(CO)_2\{C_2H_4(PPh_2)_2\}_2]$	XXVIII	320—323	Bright yellow	6·7
cis-$[Cr(CO)_2\{CH_2(PPh_2)_2\}_2]$	XXIX	289	Orange	6·55 ⟶ 5·4
$[Mo(CO)_3Ph\cdot P(o\text{-}C_6H_4\cdot PEt_2)_2]$	XXX	268·5—269	Pale yellow	—
$[Mo(CO)_3Ph\cdot P(C_2H_4\cdot PPh_2)_2]$	XXXI	261·5—263	White	—
$[Cr(CO)_3Me\cdot C(CH_2\cdot PPh_2)_3]$	XXXII	362 *	Pale yellow	—
$[Mo(CO)_3Me\cdot C(CH_2\cdot PPh_2)_3]$	XXXIII	378—380 *	White	8·75
$[W(CO)_3Me\cdot C(CH_2\cdot PPh_2)_3]$	XXXIV	>400 *	,,	—

* After decomposition.

The intensely vermilion-red *trans*-compound (XXVI) is the only isolated *trans*-dicarbonyl of a Group VI metal. It is isomerised by adding an excess of methanol to its red solution in benzene or chloroform. The solution becomes yellow immediately and the *cis*-isomer separates completely. This change is accompanied by some side reaction, since no *trans*-isomer remains and the yield of *cis*-isomer is variable. On the other hand, complete reconversion of the *cis*- into the *trans*-isomer is attained by heating its yellow solution in benzene, toluene, or chloroform, whereupon it rapidly becomes deep red; the *trans*-isomer may then be recovered by evaporation. When the solid *cis*-compound is heated *in vacuo* it gradually becomes red and melts finally at the m. p. of the *trans*-compound. The change from *trans* to *cis* is very rapid at room temperature in 1,2-dichloroëthane.

Rapid dissolution of a sample of the *trans*-compound in this solvent, followed by immediate inspection of the carbonyl infrared stretching frequencies, has shown that although the intensities of the carbonyl absorption bands of the *cis*-isomer increase slightly during measurement, no band attributable to a *trans*-isomer is detectable. Both the potassium bromide disc and the Nujol mull prepared from the *trans*-compound are yellow, and both transmit the spectrum of the *cis*-compound.

The *cis*-derivative (XXIX) of the methylene diphosphine (I) undergoes similar changes. However, the colour changes are reversible, and attempts to isolate the *trans*-isomer failed. The *cis–trans* change of the dicarbonyl (XXII) has been inferred from its infrared absorption characteristics (see below).

The few dicarbonyl derivatives of Group VI metals which have been reported previously appear to have only *cis*-carbonyl configurations.[6,7] Even dicarbonylbis-(*o*-phenylenebisdimethylarsine)chromium, similar in constitution to the dicarbonyl derivatives of our series, appears only in the *cis*-form.[4]

The apparent dipole moment of the *cis*-chromium tetracarbonyl (XIX) in benzene solution decreases with time, finally attaining a steady value, but no *trans*-isomer has been isolated. Different samples of this compound, of the same m. p., give different values of dipole moment (the highest obtained are recorded in Table 1) and it is probable that these samples contained different proportions of *trans*-isomer as impurity. The *cis*-molybdenum and tungsten analogues (XX) and (XXI), show no signs of isomerisation, but a few examples of isomerisation of this type of derivative have appeared recently. The *cis*-forms of the Group VI tetracarbonyls, $M(CO)_4L_2$, are usually isolated, but Poilblanc and Bigorgne[8] were able to isolate pure *cis*- and *trans*-forms of $Mo(CO)_4(PEt_3)_2$ and obtained

TABLE 2.

Carbonyl infrared absorption frequencies (cm.$^{-1}$) in 1,2-dichloroethane.

Formula	M = Mo	M = W	M = Cr
$[M(CO)_4C_2H_4(PPh_2)_2]$	2020s	2016s	2009s
	1919sh	1912sh	1914sh
	1907vs	1901vs	1899vs
	1881s	1876s	1877s
$[M(CO)_4CH_2(PPh_2)_2]$	2020s	2013s	2006s
	1920sh	1909sh	1915s
	1907vs	1902vs	1897vs
	1879s	1871s	1875s
$[M(CO)_4o\text{-}C_6H_4(PEt_2)_2]$	2014s	2011s	2001s
	1912sh	1905sh	1906sh
	1896vs	1887vs	1884vs
	(—)sh	(—)sh	(—)sh
$[M(CO)_4(PPhEt_2)_2]$	2012s	2008s	1999
	1907sh	1900sh	1897sh
	1895vs	1885vs	1873vs
	1866s	1862s	(—)sh
$[M(CO)_4C_2H_4(PEt_2)_2]$	2012s	2008s	2000s
	1909sh	1901sh	1905s
	1891vs	1882vs	1880vs
	(1873)sh	(1866)sh	(—)sh
$[M(CO)_2\{C_2H_4(PPh_2)_2\}_2]$	1852s	1847s	1848s
	1786s	1782s	1708s
$[M(CO)_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$	1843s	1832s	1826s
	1774s	1766s	1760s
$[M(CO)_3Me{\cdot}C(CH_2{\cdot}PPh_2)_3]$	1930s	1930s	1905s
	1834s	1834s	1830s
$[Mo(CO)_3Ph{\cdot}P(C_2H_4{\cdot}PPh_2)_2]$	1937s		
	1848s		
$[Mo(CO)_3Ph{\cdot}P(o\text{-}C_6H_4{\cdot}PEt_2)_2]$	1937s		
	1844s		

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[6] Weiss and Hübel, *J. Inorg. Nuclear Chem.*, 1959, **11**, 42.
[7] Fischer, Palm, and Fritz, *Chem. Ber.*, 1959, **92**, 2645.
[8] Poilblanc and Bigorgne, *Compt. rend.*, 1960, **250**, 1064.

evidence of isomeric change of $Mo(CO)_4(PPh_3)_2$ and $W(CO)_4(PEt_3)_2$. These compounds isomerise in solution. Hieber and Peterhans [9] have also shown that the bistriphenylphosphine tetracarbonyls of chromium, molybdenum, and tungsten exist in the *trans*-form.

Infrared Absorption Spectra (with D. M. ADAMS).—The infrared absorption spectra of the substituted carbonyls in 1,2-dichloroethane solution have been measured in the 1700—2100 cm.$^{-1}$ region (Table 2). The main features of the infrared spectra of metal carbonyls and their derivatives have already been determined but this work presents the first detailed series of Group VI carbonyls, containing the same ligand atom as substituent.

Table 2 is laid out so that the carbonyl frequencies ($\nu_{C=O}$) decrease downwards and to the right in each half of the Table. In corresponding compounds of these series of di- and tetra-carbonyls the carbonyl frequencies decrease in the order Mo > W > Cr. This does not parallel that (Cr > Mo > W) shown by the related tricarbonyl derivatives studied by Wilkinson and his colleagues,[2] or that of the hexacarbonyls in 1,2-dichloroethane (Mo > Cr > W). The differences between the corresponding frequencies in the compounds of these three metals are small, and these differences in sequence probably have little significance.

Electronegative groups attached to the phosphorus atoms cause progressive decrease in $\nu_{C=O}$, presumably by withdrawing electrons from the metal and so increasing the contribution of the triply bonded resonance form, $M^{-}C\equiv O$, relative to the doubly-bonded form M=C=O. This effect is a general effect.[1,2,10]

Tetracarbonyl Complexes.—The symmetry of these complexes is C_{2v}, the four carbonyl stretching vibrations being distributed amongst the symmetry classes of the point group as follows: [7] $\tau = 2A_1 + B_1 + B_2$. All are infrared active.

These vibrations may be considered as two pairs, originating from (i) symmetric (A_1) and antisymmetric (B_1) modes of the two *trans*-carbonyl groups, and (ii) symmetric (A_1) and antisymmetric (B_2) modes of the two *cis*-carbonyl groups. There will however be some interaction between these modes and this will be greatest in the case of the two A_1 modes. The antisymmetric modes are expected to lie at higher frequencies than their corresponding A_1 modes, which will probably be quite close together. It is found in practice that one sharp band is present near 2000 cm.$^{-1}$ and a broad band showing indications of three contributions centred near 1850 cm.$^{-1}$. The 2000 cm.$^{-1}$ band must be due to either the B_1 or the B_2 mode, the other antisymmetric mode being part of the broad band, in which the A_1 components will probably have been mutually shifted by Fermi resonance.

Since interaction of the B_1 and the B_2 mode with each other or with A_1 modes will be slight, the single band near 2000 cm.$^{-1}$ indicates that one of the pairs of carbonyl groups has a higher force constant than the other. On the basis that carbonyl groups have a large *trans*-effect it seems likely that this is the *trans*-pair.

Dicarbonyl Derivatives.—In the *cis*-dicarbonyl derivatives two strong carbonyl frequencies are observed. These are lowered very considerably with respect to the parent carbonyl and are within the range usually attributed to bridging carbonyls (the same effect has been noted [2] with tricarbonyl derivatives of Group VI). It is apparent that the two remaining carbonyl groups are able to share a much greater proportion of the available metal *d*-electrons; the resulting strong bonding to the metal explains their great resistance to substitution.

The chromium dicarbonyl (XXII) gives a spectrum containing three carbonyl absorption bands. Two, at 1826 and 1760 cm.$^{-1}$, decrease in intensity with time, and the third, at 1844 cm.$^{-1}$, increases in intensity. The highest value is probably the single absorption band of the (unisolated) *trans*-dicarbonyl, and it increases in intensity during a change in solution from pure *cis*- to an equilibrium mixture of *cis*- and *trans*-forms.

Tricarbonyl Derivatives.—Absorption frequencies of tricarbonyl derivatives of Group

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[9] Hieber and Peterhans, *Z. Naturforsch*, 1959, **14**b, 462.
[10] Meriwether and Fiene, *J. Amer. Chem. Soc.*, 1959, **81**, 4200.

VI metals have been discussed previously.[2] The compounds of the present series are of unequivocal structure and the results obtained from them are in accord with previous work.

EXPERIMENTAL

M. p.s are corrected and were determined in evacuated tubes. Molecular weights were determined ebullioscopically and in acetone unless otherwise stated. Microanalyses were carried out in these laboratories; normal combustion frequently gave low carbon values, probably caused by partial formation of stable metal carbides; admixture of the sample with potassium dichromate overcame this difficulty. The diphosphines $(CH_2{\cdot}PR_2)_2$ (R = Et or Ph) were prepared as described by Chatt and Hart,[11] o-$C_6H_4(PEt_2)_2$ and $Ph{\cdot}P(o\text{-}C_6H_4PEt_2)_2$ as described by Hart,[12] and $CH_2(PPh_2)_2$ by a modification of Issleib and Muller's method.[13] The preparation of $Me{\cdot}C(CH_2{\cdot}PPh_2)_3$ and $Ph{\cdot}P(C_2H_4{\cdot}PPh_2)_2$ will be detailed later.[14] A representative selection of the carbonyl compounds was shown to be electrically non-conducting in nitrobenzene.

Tetracarbonyl Derivatives.—These were prepared by heating a slight excess of the metal hexacarbonyl with the tertiary phosphine in a sealed evacuated tube of such dimensions that at the temperature used the final pressure of evolved carbon monoxide did not exceed 10 atm.

*Tetracarbonyl-*1,2*-bisdiethylphosphinoethanechromium* (VII). A mixture of chromium carbonyl and the phosphine was heated at 150—160° for 4·5 hr., and the cooled crystalline mass was recrystallised from ethanol to yield the *tetracarbonyl* (85%) (Found: C, 45·2; H, 6·7%; *M*, 355. $C_{14}H_{24}CrO_4P_2$ requires C, 45·4; H, 6·5%; *M*, 370). The compound distils unchanged at 140° (bath)/0·02 mm. The following compounds were similarly prepared; the heating periods are in parentheses.

*Tetracarbonyl-*1,2*-bisdiethylphosphinoethanemolybdenum* (VIII) (6 hr.) The cooled brown crystalline mass recrystallised from light petroleum (b. p. 80—100°), to give a yellow solid (68%) which on recrystallisation from methanol yielded the pure *tetracarbonyl* (Found: C, 40·4; H, 5·8%; *M*, 360. $C_{14}H_{24}MoO_4P_2$ requires C, 40·6; H, 5·8%; *M*, 414).

*Tetracarbonyl-*1,2*-bisdiethylphosphinoethanetungsten* (IX) (12 hr.). The cooled product, when recrystallised from ethanol, gave the *tetracarbonyl* (79%). Further recrystallisation followed by elution in ether through alumina afforded the pure compound (Found: C, 33·3; H, 4·8. $C_{14}H_{24}O_4P_2W$ requires C, 33·5; H, 4·8%).

*Tetracarbonyl-*o*-phenylenebisdiethylphosphinechromium* (X) (5 hr.). Crystallisation of the product from ethanol gave the *tetracarbonyl* (62%), purified by repeated recrystallisation from light petroleum (b. p. 80—100°) (Found: C, 51·7; H, 5·9. $C_{18}H_{24}CrO_4P_2$ requires C, 51·7; H, 5·8%).

*Tetracarbonyl-*o*-phenylenebisdiethylphosphinemolybdenum* (XI) (3 hr.). An excess of molybdenum carbonyl was sublimed from the product, and recrystallisation from light petroleum (b. p. 80—100°) gave the pure *tetracarbonyl* (70%) (Found: C, 47·1; H, 5·35%; *M*, 450. $C_{18}H_{24}MoO_4P_2$ requires C, 46·8; H, 5·2%; *M*, 462).

*Tetracarbonyl-*o*-phenylenebisdiethylphosphinetungsten* (XII) (7 hr.). The product (77%) gave the *tetracarbonyl* which was purified by repeated recrystallisation from methanol (Found: C, 38·7; H, 4·5. $C_{18}H_{24}O_4P_2W$ requires C, 39·3; H, 4·4%).

Tetracarbonylbisdiphenylphosphinomethanechromium (XIII) (12 hr.) The *tetracarbonyl* (77%) was purified by repeated recrystallisation from light petroleum (b. p. 80—100°) (Found: C, 63·6; H, 4·15%; *M* in chloroform, 559. $C_{29}H_{22}CrO_4P_2$ requires C, 63·5; H, 4·0%; *M*, 548·5).

Tetracarbonylbisdiphenylphosphinomethanemolybdenum (XIV) (8 hr.). Recrystallisation from acetone gave the *tetracarbonyl* (97%) which repeatedly recrystallised from light petroleum (b. p. 80—100°) (Found: C, 58·65; H, 4·0%; *M* in chloroform, 600. $C_{29}H_{22}MoO_4P_2$ requires C, 58·8; H, 3·7%; *M*, 592).

Tetracarbonylbisdiphenylphosphinomethanetungsten (XV) (8 hr.). Recrystallisation from acetone gave the *tetracarbonyl* (93%) (Found: C, 50·55; H, 3·3; *M*, 654, 647. $C_{29}H_{22}O_4P_2W$ requires C, 51·2; H, 3·3%; *M*, 680).

*Tetracarbonyl-*1,2*-bisdiphenylphosphinoethanechromium* (XVI) (12 hr.). Recrystallisation from acetone gave the *tetracarbonyl* (71%), which was purified by further recrystallisation from

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[11] Chatt and Hart, *J.*, 1960, 1378.

[12] Hart, *J.*, 1960, 3324.

[13] Issleib and Muller, *Chem. Ber.*, 1959, **92**, 3175.

[14] Hewertson and Watson, unpublished work.

acetone (Found: C, 64·3; H, 4·6%; *M*, 539. $C_{30}H_{24}CrO_4P_2$ requires C, 64·1; H, 4·3%; *M*, 562·5).

Tetracarbonyl-1,2-*bisdiphenylphosphinoethanemolybdenum* (XVII). The reactants were kept at 150° for 5 hr., then at 170° for 4 hr. The *tetracarbonyl* (67%) was obtained as prisms from acetone (Found: C, 59·3; H, 4·2. $C_{30}H_{24}MoO_4P_2$ requires C, 59·4; H, 4·0%).

Tetracarbonyl-1,2-*bisdiphenylphosphinoethanetungsten* (XVIII) (17 hr.). Recrystallisation from acetone–methanol gave the *tetracarbonyl* (67%), purified by further recrystallisation (Found: C, 52·1; H, 3·55%; *M*, 675. $C_{30}H_{24}O_4P_2W$ requires C, 51·9; H, 3·5%; *M*, 694).

cis-*Tetracarbonylbis*(*diethylphenylphosphine*)*chromium* (XIX) (8 hr.). Recrystallisation from ethanol–methanol gave the *tetracarbonyl* (XIX) (63%) which was purified by repeated recrystallisation (Found: C, 58·2; H, 6·3%; *M*, 489, 515. $C_{24}H_{30}CrO_4P_2$ requires C, 58·1; H, 6·1%; *M*, 496·5).

cis-*Tetracarbonylbis*(*diethylphenylphosphine*)*molybdenum* (XX) was prepared similarly (81%) and recrystallised from light petroleum (b. p. 60—80°) (Found: C, 53·5; H, 5·9. $C_{24}H_{30}MoO_4P_2$ requires C, 53·3; H, 5·6%).

cis-*Tetracarbonylbis*(*diethylphenylphosphine*)*tungsten* (XXI) was prepared similarly (58%) and repeatedly recrystallised from light petroleum (b. p. 60—80°) (Found: C, 45·6; H, 4·8%; *M*, 610, 606. $C_{24}H_{30}O_4P_2W$ requires C, 45·9; H, 4·8%; *M*, 628).

Dicarbonyl Derivatives.—cis-*Dicarbonyldi*-o-*phenylenebisdiethylphosphinechromium* (XXII). Tricarbonylmesitylenechromium and the ditertiary phosphine (2 equiv.) were mixed and heated in a nitrogen atmosphere at 195° for 5 hr.; recrystallisation of the product from ethanol gave a low yield of the *dicarbonyl* (Found: C, 58·6; H, 7·9. $C_{30}H_{48}CrO_2P_4$ requires C, 58·4; H, 7·85%).

cis-*Dicarbonyldi*-o-*phenylenebisdiethylphosphinemolybdenum* (XXIII). A mixture of the tetracarbonyl (XI) and the ditertiary phosphine (one equiv.), maintained under nitrogen and illuminated by a strong ultraviolet source, was heated at 220° for 16 hr., after which no gas evolution was discernible. Recrystallisation of the cooled mass from ethanol gave the *dicarbonyl* (51%) (Found: C, 54·55; H, 7·3%; *M* in chloroform, 653. $C_{30}H_{48}MoO_2P_4$ requires C, 54·55; H, 7·3%; *M*, 661).

cis-*Dicarbonyldi*-o-*phenylenebisdiethylphosphinetungsten* (XXIV). A mixture of the tetracarbonyl (XII) and the diphosphine (one equiv.) was heated in a sealed evacuated tube at 230° for 60 hr. Recrystallisation of the product from ethanol gave the bright yellow *dicarbonyl* (36%), m. p. 270—272° (becoming orange above 100°) after further recrystallisation (Found: C, 48·5; H, 6·5%; *M* in chloroform, 703. $C_{30}H_{48}O_2P_4W$ requires C, 48·1; H, 6·5%; *M*, 748·5).

trans-*Dicarbonyldi*-1,2-*bisdiphenylphosphinoethanechromium* (XXVI). Tricarbonylmesitylenechromium and the ditertiary phosphine (2 equiv.) were heated for 5 hr. at 190—195°. A slow nitrogen stream was passed through the fused mixture, which became deep red, and expelled mesitylene. Crystallisation of the cooled mass from toluene–light petroleum (b. p. 80—100°) gave a mixture of yellow and red crystals. This mixture was collected and washed with cold ethyl methyl ketone followed by a little cold toluene; only red crystals then remained (30%). These, when recrystallised as above, gave the trans-*dicarbonyl*, with one molecule of toluene of crystallisation, as very deep vermilion-red crystals, m. p. 279—280° (Found: C, 73·0; H, 5·8. $C_{54}H_{48}CrO_2P_4,C_7H_8$ requires C, 73·5; H, 5·7%). The compound was shaken repeatedly with portions of cold light petroleum (b. p. 40—60°), which removed toluene, leaving the trans-*dicarbonyl* as bright vermilion-red crystals, m. p. 279—280° (Found: C, 72·3; H, 5·35%; *M* in benzene, 1005. $C_{54}H_{48}CrO_2P_4$ requires C, 71·7; H, 5·35%; *M*, 905). The dicarbonyl is soluble in hot chloroform, benzene, or toluene to give deep cherry-red solutions from which it crystallises, with associated solvent, on cooling. With other solvents it undergoes change to the *cis*-isomer with partial decomposition. The ethyl methyl ketone washings from the initial product were evaporated to dryness and chromatographed on alumina in benzene. The operation afforded the tetracarbonyl (XVI) (36% based on tricarbonylmesitylenechromium), m. p. 210—212·5°, unchanged on admixture with the authentic sample.

cis-*Dicarbonyldi*-1,2-*bisdiphenylphosphinoethanechromium* (XXV). Methanol (12 ml.) was added to a solution of the *trans*-compound (0·25 g.) in warm chloroform (2·5 ml.). The colour immediately changed to pale orange, and the cis-*dicarbonyl* separated (0·165 g., 66%) (Found: C, 71·6; H, 5·7%); *M*, cryoscopic in 1,2-dibromoethane, 975). No further crop could be isolated from the mother-liquor. When the *cis*-compound is heated *in vacuo*, it slowly becomes red; it melts at 280—280·5° to a red liquid. The m. p. is unchanged on admixture with the *trans*-compound. Cold solutions of the *cis*-compound in benzene or chloroform are orange, but when warmed they become deep red, and the *trans*-compound is deposited on cooling. The hot acetone solution is deep red-orange, but when cooled it becomes yellow-orange and deposits the pure *cis*-isomer.

cis-*Dicarbonyldi*-1,2-*bisdiphenylphosphinoethanemolybdenum*. A mixture of the tetracarbonyl (XVII) and the ditertiary phosphine (one equiv.) was heated at 210—220° for 60 hr. in an evacuated tube. The product, when recrystallised from benzene–methanol, gave the cis-*dicarbonyl* (XXVII) (72·5%), m. p. 324—325° (to a red liquid, reverting to a yellow solid on cooling) (Found: C, 68·75; H, 5·0%; *M*, 930. $C_{54}H_{48}MoO_2P_4$ requires C, 68·4; H, 5·1%; *M*, 949).

cis-*Dicarbonyldi*-1,2-*bisdiphenylphosphinoethanetungsten* (XXVIII). When this is prepared analogously to the molybdenum compound the yield is low. It is better obtained by heating the reactants in 1,2-dimethoxyethane under reflux in a nitrogen atmosphere, with strong ultraviolet illumination, for 35 hr. (silica flask). From the cooled mixture the *dicarbonyl* (47%) crystallised as plates, m. p. 320—323° (to a red liquid) after recrystallisation from the same solvent (Found: C, 62·5; H, 4·85%; *M* in chloroform, 979. $C_{54}H_{48}O_2P_4W$ requires C, 62·6; H, 4·7%; *M*, 1037). The dicarbonyl derivatives of molybdenum and tungsten give pale orange solutions in hot benzene or chloroform. No indication of the existence of *trans*-isomers has been observed.

TABLE 3.

Dipole moments.

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$
Compound (X)			
2·229	15·537	—	—
3·121	15·503	—	—
28·35	—	9·64	—
41·38	—	9·49	—
6·978	—	—	0·387
7·438	—	—	0·336
Compound (XI)			
1·954	14·879	—	—
3·179	14·860	—	—
30·74	—	10·16	—
38·94	—	10·01	—
4·760	—	—	0·420
6·615	—	—	0·438
Compound (XII)			
2·924	13·830	—	—
2·954	13·878	—	—
48·88	—	9·28	—
78·00	—	9·13	—
3·715	—	—	0·538
7·005	—	—	0·500
Compound (XIX)			
4·352	5·90	—	—
3·562	2·771	—	—
3·396	2·772	—	—
14·59	—	7·59	—
22·51	—	7·53	—
8·552	—	—	0·374
9·242	—	—	0·314
Compound (XX)			
3·035	10·354	—	—
4·380	10·153	—	—
39·30	—	10·47	—
43·43	—	10·66	—
6·870	—	—	0·393
6·952	—	—	0·432
Compound (XXI)			
3·457	9·585	—	—
4·636	9·582	—	—
18·98	—	8·94	—
30·07	—	9·28	—
5·605	—	—	0·517
6·136	—	—	0·456
Compound (XXIII)			
1·573	7·383	—	—
24·28	—	13·55	—
29·70	—	13·70	—
3·306	—	—	0·363
5·846	—	—	0·359
Compound (XXIV)			
2·754	6·832	—	—
3·864	6·826	—	—
17·31	—	12·45	—
18·63	—	12·36	—
4·999	—	—	0·580
7·369	—	—	0·556
Compound (XXV)			
0·9964	5·482	—	—
1·049	5·492	—	(0·35)
0·9964	3·645	—	—
1·049	3·699	—	(0·35)
Compound (XXVI)			
1·642	0·976	—	—
1·773	0·971	—	(0·35)
1·642	2·915	—	—
1·773	2·883	—	—
4·123	2·894	—	(0·35)
Compound (XXVII)			
0·9094	5·213	—	—
0·9102	5·242	—	(0·40)
Compound (XXVIII)			
1·050	5·511	—	—
1·160	5·504	—	(0·54)
Compound (XXIX)			
2·076	5·847	—	—
2·705	5·926	—	(0·35)
2·076	4·266	—	—
2·705	4·237	—	(0·35)
Compound (XXXIII)			
1·253	10·86	—	—
1·582	10·99	—	(0·32)

Compd.	${}_{\mathrm{T}}P$	${}_{\mathrm{E}}P$	${}_{\mathrm{O}}P$
X	1321	118	1185
XI	1394	123	1252
XII	1539	129	1390
XIX	670·5	137·2	512·7
	377·8	137·2	220·0
XX	1162	148	992
XXI	1258	153	1082
XXIII	1073	202	841
XXIV	1092	179	886
XXV	1149*	(314)	789*
	840	(314)	479*
XXVI	380*	(314)	19*†
	708*	(314)	347*
XXVII	1145 *	(318)	779 *
XXVIII	1262 *	(295)	922 *
XXIX	1180 *	(265)	875 *
	910 *	(265)	605 *
XXXIII	1854 *	(248)	1568 *

cis-*Dicarbonyldi(bisdiphenylphosphinomethane)chromium* (XXIX). This was prepared in the same way as the corresponding compound (XXV). The cooled reaction mixture, when crystallised from toluene–light petroleum (b. p. 80—100°), gave the cis-*dicarbonyl* (26%), m. p. 289° after recrystallisation from benzene under nitrogen followed by washing of the platy crystals by light petroleum (b. p. 40—60°) (they rapidly effloresced) (Found: C, 71·1; H, 5·2%; *M* in benzene, 918. $C_{52}H_{44}CrO_2P_4$ requires C, 71·2; H, 5·1%; *M*, 877). The solid is stable to air, but in solution the substance is oxidised, depositing a pale green sludge. Although solutions in chloroform or benzene become deep red-orange when warmed, the change is reversible, and no *trans*-isomer has been isolated.

Tritertiary Phosphine Complexes.—These were prepared in the same way as the tetracarbonyl derivatives, by heating the metal carbonyl and the phosphine in a sealed evacuated tube.

*Tricarbonylbis-(*o*-diethylphosphinophenyl)phenylphosphinemolybdenum* (XXX) was obtained from the hexacarbonyl and the triphosphine (2 equiv.) at 150° for 10 hr., then at 210° for 56 hr. The product was chromatographed in benzene on alumina; triphosphine followed by the tricarbonyl (68%), very pale yellow crystals from benzene–methanol, were eluted (Found: C, 56·5; H, 5·4. $C_{29}H_{33}MoO_3P_3$ requires C, 56·3; H, 5·4%).

Tricarbonylbis-(2-diphenylphosphinoethane)phenylphosphinemolybdenum (XXXI) was obtained from the carbonyl and triphosphine (one equivalent) at 150° for 15 hr. Recrystallisation from toluene gave the *tricarbonyl*, with one molecule of toluene of crystallisation (64%), as pale cream crystals, m. p. 265° (prior shrinking) (Found: C, 65·7; H, 4·8. $C_{37}H_{33}MoO_3P_3,C_7H_8$ requires C, 65·5; H, 5·1%). The unsolvated *tricarbonyl* was obtained as colourless crystals, m. p. 261·5—263° (much prior shrinking), from chloroform (Found: C, 62·5; H, 4·7. $C_{37}H_{33}MoO_3P_3$ requires C, 62·2; H, 4·7%).

Tricarbonyltris(diphenylphosphinomethyl)ethanechromium (XXXII). This was prepared from equimolar proportions of the reactants at 150° for 50 hr. (much of the chromium carbonyl was unchanged when the mixture was heated at 140° for 24 hr.). Recrystallisation from chloroform–light petroleum (b. p. 80—100°) gave the *tricarbonyl* (62%), m. p. 362° (prior decomp.) (Found: C, 68·8; H, 5·3. $C_{44}H_{39}CrO_3P_3$ requires C, 69·5; H, 5·2%).

Tricarbonyltris(diphenylphosphinomethyl)ethanemolybdenum (XXXIII) (prepared as above at 150° for 15 hr.). Recrystallisation from chloroform gave the *tricarbonyl* (49%) (Found: C, 65·8; H, 5·2. $C_{44}H_{39}MoO_3P_3$ requires C, 65·7; H, 4·9%).

Tricarbonyltris(diphenylphosphinomethyl)ethanetungsten (XXXIV). Preparations as above at 150° for 50 hr. gave the colourless *tricarbonyl* (38%), m. p. >400° (prior decomposition at 370°) (Found: C, 59·8; H, 4·6. $C_{44}H_{39}O_3P_3W$ requires C, 59·2; H, 4·4%).

Attempts to effect Further Replacement.—In attempts to effect complete expulsion of carbon monoxide and thus gain the compounds below, the dicarbonyl was heated with one equiv. or an excess of its constituent ditertiary phosphine. In all experiments there was no evidence of reaction, and the original components were recovered from the following experiments: $[Cr\{C_2H_4(PPh_2)_2\}_3]$, 50 hr., 195°.* $[Mo\{C_2H_4(PPh_2)_2\}_3]$, in decalin at reflux, 14 hr.; †‡ 60 hr., with an added 0·2 mole of $[Ni(CO)_2C_2H_4(PPh_2)_2]$.* $[W\{C_2H_4(PPh_2)_2\}_3]$, 330 hr., 225°.*

The tetracarbonyl (XVII) and the tritertiary phosphine (VI) (one equiv.) were heated *in vacuo* for 50 hr. at 210°, whereupon the tricarbonyl (XXXIII) (55%) (Found: C, 65·8; H, 4·9%) and the diphosphine (I; R = Ph) were formed. The dicarbonyl (XXVII) and the triphosphine (VI) did not react under these conditions.

Infrared Spectra.—These were measured on a Grubb–Parsons GS2A spectrometer.

Determination of Dipole Moments.—These were determined as described previously;[15] the same notations of measurements and estimated values have been used in Table 3.

Imperial Chemical Industries Limited,
Heavy Organic Chemicals Division,
Akers Research Laboratories, The Frythe,
Welwyn, Herts.

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* *In vacuo.* † Under nitrogen at atmospheric pressure. ‡ With strong ultraviolet illumination in a silica vessel.

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