Chemistry of the Metal Carbonyls. Part LVI.[1] Reactions of Bis(pentafluorophenyl)phosphine and Tetrakis(pentafluorophenyl)diphosphine with Group VI Metal Hexacarbonyls

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Reactions between bis(pentafluorophenyl)phosphine and Group VI metal carbonyls have been investigated and the mono-, di- and tri-substituted complexes $[(C_6F_5)_2PH]M(CO)_5$ (M = Cr, Mo, W), $[(C_6F_5)_2PH]_2M(CO)_4$ (M = Cr, Mo), and $[(C_6F_5)_2PH]_3Mo(CO)_3$ characterised. Treatment of the monosubstituted chromium and molybdenum complexes with n-butyl-lithium affords $(C_6F_5)_2P(Li)M(CO)_5$ (M = Cr, Mo). Reaction of tetrakis-(pentafluorophenyl)diphosphine with $Cr(CO)_6$ and $Mo(CO)_6$ gave polymeric complexes $[(C_6F_5)_4P_2M(CO)_4]_n$ (M = Cr, Mo), and small yields of the monosubstituted complexes $[(C_6F_5)_2PH]Mo(CO)_5$. The anions $[M(CO)_5]^{2-}$ (M = Cr, Mo) react with $(C_6F_5)_2PCl$ to give the monosubstituted diphosphine complexes $(C_6F_5)_4P_2M(CO)_5$. The chromium complex was also prepared from $(C_6F_5)_2P(Li)Cr(CO)_5$ and $(C_6F_5)_2PCl$.

UNTIL recently [2] the transition-metal chemistry of tervalent pentafluorophenylphosphorus compounds had been relatively unexplored. Herein we report reactions of bis(pentafluorophenyl)phosphine and tetrakis(pentafluorophenyl)diphosphine with Group VI metal carbonyls.

Bis(pentafluorophenyl)phosphine reacts with $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in methylcyclohexane to afford the air-stable crystalline complexes $[(C_6F_5)_2PH]M(CO)_5$ (M = Cr, Mo, W) (I)—(III). Although di- and tri-substituted complexes (IV)—(VI) can be obtained by further reaction, these compounds are obtained more satisfactorily by displacement of an olefin from an olefin-substituted carbonyl complex. Treatment of bis(pentafluorophenyl)phosphine with norbornadiene–tetracarbonylmolybdenum in benzene affords the disubstituted complex (V). The tri-substituted complex (VI) was obtained on refluxing the phosphine and cycloheptatriene–tricarbonylmolybdenum in benzene. The disubstituted chromium complex (IV) was obtained by a different route. When complex (I) is heated *in vacuo* it decomposes forming (IV) and chromium hexacarbonyl.

TABLE 1

Microanalytical data for the complexes

Complex		Colour	Yield	M.p.	Found C (%)	Found H (%)	Found F (%)	Found P (%)	M *	Required C (%)	Required H (%)	Required F (%)	Required P (%)	M
$[(C_6F_5)_2PH]Cr(CO)_5$	(I)	Yellow	39	90—91°	36·4	0·2	34·0	5·7	543	36·6	0·2	34·1	5·5	558
$[(C_6F_5)_2PH]Mo(CO)_5$	(II)	White	33	95—96	34·1	0·3	32·2	5·2	581	33·9	0·2	31·6	5·2	602
$[(C_6F_5)_2PH]W(CO)_5$	(III)	White	34	94—95	29·6	0·3	27·8	4·4	712	29·6	0·2	27·6	4·5	690
$[(C_6F_5)_2PH]_2Cr(CO)_4$	(IV)	Yellow	3	118—120	37·6	0·4	42·8	6·6	912	37·5	0·2	42·4	6·9	896
$[(C_6F_5)_2PH]_2Mo(CO)_4$	(V)	White	72	131—132	36·0	0·3	40·7	6·7	916	35·8	0·2	40·4	6·6	940
$[(C_6F_5)_2PH]_3Mo(CO)_3$	(VI)	Buff	28	150 dec.	35·6	0·5	44·2	7·0	1334	36·6	0·2	44·6	7·3	1278
$Li(C_6F_5)_2PCr(CO)_5$	(VII)	Yellow	95	280 dec.	36·1	—	34·1	5·6	—	36·1	—	33·7	5·5	—
$Li(C_6F_5)_2PMo(CO)_5$	(VIII)	White	94	300 dec.	33·7	—	31·1	5·3	—	33·6	—	31·2	5·1	—
$[(C_6F_5)_4P_2Cr(CO)_4]_n$	(IX)	White	54	350	37·4	—	42·7	7·0	—	37·5	—	42·5	6·9	—
$[(C_6F_5)_4P_2Mo(CO)_4]_n$	(X)	White	38	350	36·4	—	40·7	6·5	—	35·8	—	40·5	6·6	—
$(C_6F_5)_4P_2Cr(CO)_5$	(XI)	Yellow	31	83—85	37·7	—	41·2	7·2	932	37·7	—	41·1	6·9	922
$(C_6F_5)_4P_2Mo(CO)_5$	(XII)	White	17	75—76	36·8	—	39·6	6·5	979	36·0	—	39·4	6·4	966

* Measured in chloroform solution, with a Mechrolab vapour pressure osmometer.

The mononuclear complexes are all air-stable crystalline solids, and were characterised by elemental analysis (Table 1), i.r. spectroscopy (Table 2), ^{19}F n.m.r. spectroscopy, and in some cases by mass spectroscopy.

The monosubstituted complexes (I)—(III) show five bands in the terminal carbonyl i.r. region corresponding to C_s symmetry, the lowering of the symmetry from the customary C_{4v} for $LM(CO)_5$ complexes [3] presumably being due to the unsymmetrical character of the phosphine ligand.[4,5] The disubstituted complexes (IV) and (V) show five carbonyl stretching bands in cyclohexane solution. The presence of five bands in the solution spectrum of each complex suggests the presence of isomers. Recrystallisation of the complexes from benzene, ether–benzene, or chloroform–pentane had no effect on the relative intensities of the bands. It is noteworthy that the analogous complex $(Ph_2PH)_2Mo(CO)_4$ exists in two isomeric forms.[6]

The mass spectra of the complexes (I)—(III) show peaks corresponding to molecular ions, as well as ions $[(C_6F_5)_2PHM(CO)_n]^+$ (n = 0—4) corresponding to successive loss of carbonyl groups. Ions corresponding to the species $[C_{12}F_9PHM(CO)_n]^+$ (n = 0—5) are also visible

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[1] Part LV, D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 502.

[2] A. G. Ang and J. M. Miller, *Chem. and Ind.*, 1966, 945; M. Cooke, M. Green, and D. Kirkpatrick, *J. Chem. Soc.* (*A*), 1968, 1507; R. D. W. Kemmitt, D. I. Nichols, and R. D. Peacock, *J. Chem. Soc.* (*A*), 1968, 1898, 2149; M. G. Hogben, R. S. Gay, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1966, **88**, 3457.

[3] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

[4] J. B. Wilford and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 371; *Inorg. Chem.*, 1965, **4**, 389.

[5] J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1195; and refs. therein.

[6] J. G. Smith and D. T. Thompson, *J. Chem. Soc.* (*A*), 1967, 1694.

in the spectra. In the spectrum of (III) ions corresponding to the breakdown of the phosphine ligand, by loss of fluorine, carbon, and hydrogen, while still attached to the metal are very abundant. Indeed the ion $[C_6F_5PW]^+$ is the base peak in this spectrum. The relative intensities of the peaks due to the ion $[C_6F_5M]^+$ increase in the spectra of (I)—(III) from Cr to W, and those due to the ion $[M]^+$ decrease in the same order. The spectra of the disubstituted complexes (IV) and (V) show similar cracking patterns. Weak ions due to $[(C_6F_5)_2PH]_2M(CO)_4^+$ are observed, and peaks corresponding to the successive loss of four carbonyl groups.

The metallation [7] of primary and secondary phosphines is well known; however, the corresponding reaction of a phosphine co-ordinated to a transition metal has not been previously investigated. The complexes (I) and (II) reacted with one equivalent of n-butyl-lithium in tetrahydrofuran to form the crystalline solids (VII) and (VIII), respectively. The air-stable involatile solids decomposed *in vacuo* without melting at temperatures above 300°. The ^{19}F n.m.r. spectra in acetone solution showed the expected three peaks due to the *ortho*-, *para*- and *meta*-fluorine nuclei.

The lithium complex (VIII) reacted with hydrogen chloride in chloroform solution to give (II) but in low yield. Refluxing the lithium complex in methyl

$$[(C_6F_5)_2PH]Mo(CO)_5 \underset{+HCl}{\overset{+BunLi}{\rightleftharpoons}} (C_6F_5)_2P(Li)Mo(CO)_5 \qquad (1)$$

iodide gave only a low yield of the complex $[(C_6F_5)_2P(CH_3)]Mo(CO)_5$. These observations show that (VII) and (VIII) are of little value as synthetical reagents, although as discussed later the reaction with bis(pentafluorophenyl)phosphinous chloride affords a new type of complex.

TABLE 2

I.r. spectra of the complexes (cm.$^{-1}$)

Complex	Carbonyl bands [a]	Other bands [b]
(I)	2078m, 2003w, 1975s, 1965s, 1959s	1664m, 1515s, 1481s, 1398m, 1388m, 1296m, 1149w, 1124vw, 1099s, 1089s, 1011vw, 994s, 922m, 904m, 845w, 645s
(II)	2085m, 2003w, 1973s, 1965s, 1963s	1644m, 1516s, 1483s, 1399m, 1389m, 1297m, 1149w, 1122vw, 1098s, 1089s, 1013vw, 994s, 930m, 897m, 846w, 630s
(III)	2085m, 2005w, 1975s, 1967s, 1963s	1643m, 1515s, 1484s, 1397m, 1387m, 1296m, 1147w, 1122vw, 1098s, 1090s, 1012vw, 994s, 920m, 896m, 846w, 633s
(IV)	2041m, 1969s, 1951s, 1939s, 1934s	[a] 1640m, 1515s, 1481s, 1395m, 1385m, 1296m, 1147w, 1110w,sh, 1090s, 1020vw, 994s, 925w, 841vw, 630s
(V)	2052m, 1973s, 1961s, 1949s, 1942s	1644m, 1515s, 1483s, 1398m, 1388m, 1297m, 1148w, 1122vw, 1012vw, 998s, 994s, 989s, 918m, 898m, 844w, 630s
(VI) [b]	2085vw, 2047m, 1959sh, 1937s	1643m, 1516s, 1482s, 1387m, 1302m, 1146w, 1100s, 1013vw, 986s, 915vw, 899vw, 843vw, 630m
(VII) [b]	2079m, 2038vw, 2006w, 1957s	1643m, 1517s, 1478s, 1454s, 1388w, 1293w, 1241m, 1093s, 1018vw, 983s, 963m, 918w, 890w, 640m
(VIII) [b]	2087m, 2049vw, 2005w, 1965s	1642m, 1516s, 1478s, 1453s, 1387w, 1293w, 1243m, 1093s, 983s, 962m, 919w, 826w
(IX) [c]	2069w, 2013m, 1945s, 1920m	1646m, 1525s, 1304m, 1190m, 1110m, 1080m, 979m, 884m, 767w, 730m, 662m, 640m
(X) [c]	2087w, 2016m, 1941s, 1923m	1645m, 1520s, 1300m, 1200m, 1105m, 1075m, 976m, 841m, 762w, 736m, 635m
(XI)	2079m, 2002w, 1974s, 1963s, 1958s	1641m, 1515s, 1479s, 1384m, 1295m, 1149w, 1091s, 1014vw, 994m, 980s, 920w, 904w, 840w, 649w
(XII)	2085m, 2007w, 1973s, 1966s, 1963s	1641m, 1514s, 1483s, 1395w, 1384m, 1292m, 1145w, 1090s, 991m, 979s, 890w, 840w

[a] Cyclohexane solution unless otherwise stated. [b] Chloroform solution. [c] Nujol mull.

Reactions of the hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) with tetra-alkyl- or tetra-aryl-diphosphines have been previously investigated.[8] Treatment of tetrakis(pentafluorophenyl)diphosphine, $(C_6F_5)_2P{\cdot}P(C_6F_5)_2$, with hexacarbonyl chromium gave two products. One was identified as $[(C_6F_5)_2PH]Cr(CO)_5$ (I) by comparison (i.r. and n.m.r.) with an authentic sample. The other product (IX) was polymeric. It is unchanged on heating to 360°, and is only slightly soluble in acetone and chloroform. A similar reaction of $(C_6F_5)_2P{\cdot}P(C_6F_5)_2$ with $Mo(CO)_6$ gave $[(C_6F_5)_2PH]Mo(CO)_5$ (II) and (X). We suggest that (IX) and (X) have structures similar to those put forward for the products of the reactions of tetramethyldiphosphine with $Cr(CO)_6$ and $Mo(CO)_6$.[8]

The formation of (I) and (II) in these reactions merits further comment. It is suggested that the dinuclear complexes $[(OC)_5M{\cdot}P(C_6F_5)_2{\cdot}P(C_6F_5)_2{\cdot}M(CO)_5]$ (M = Cr, Mo) are first formed, but owing to steric interactions are unstable. Homolysis occurs forming the radicals $[(C_6F_5)_2PM(CO)_5]^{\cdot}$ which abstract hydrogen to form (I) and (II). An *X*-ray diffraction study [9] has shown that in the complex $(CO)_3Ni{\cdot}Ph_2P{\cdot}PPh_2{\cdot}Ni(CO)_3$ the phosphorus–phosphorus bond is significantly longer than in other diphosphines, which can be understood in terms of steric strain owing to interaction between bulky phenyl groups. Such an effect would be expected to be even more important with dinuclear pentacarbonyl chromium and molybdenum complexes, particularly with the more bulky pentafluorophenyl groups.

Treatment of the anion $[Cr(CO)_5]^{2-}$ with bis(penta-

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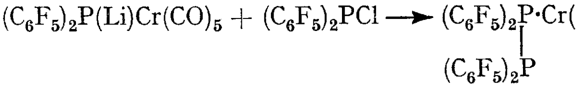
[7] L. Maier, *Progr. Inorg. Chem.*, 1963, **5**, 27.

[8] R. G. Hayter, *Preparative Inorganic Reactions*, 1965, **2**, 211.

[9] R. H. B. Mais, P. G. Owston, D. T. Thompson, and A. M. Wood, *J. Chem. Soc.* (*A*), 1967, 1744.

fluorophenyl)phosphinous chloride in tetrahydrofuran gave a pale yellow crystalline complex (XI). This was shown by elemental analysis and by mass, i.r., and ^{19}F n.m.r. spectroscopy to be the new type of complex $(C_6F_5)_2P{\cdot}P(C_6F_5)_2{\cdot}Cr(CO)_5$, in which the diphosphine behaves as a unidentate ligand. A similar reaction of $[Mo(CO)_5]^{2-}$ with $(C_6F_5)_2PCl$ yielded the analogous molybdenum complex (XII). The chromium complex (XI) was also obtained by treating the lithium complex (VII) with bis(pentafluorophenyl)phosphinous chloride (reaction 2). The molybdenum complex (XII) was also prepared by the reaction of $[(C_6F_5)_2PH]Mo(CO)_5$ (II) with $(C_6F_5)_2PCl$ in the presence of triethylamine.



$$(C_6F_5)_2P(Li)Cr(CO)_5 + (C_6F_5)_2PCl \longrightarrow \begin{array}{l}(C_6F_5)_2P{\cdot}Cr(CO)_5\\ \quad\;| \\ (C_6F_5)_2P\end{array} \qquad (2)$$

The complexes (XI) and (XII) decompose on standing, liberating the free diphosphine. The i.r. spectra of the complexes show five terminal carbonyl bands consistent with C_s symmetry. The ^{19}F n.m.r. spectrum of the molybdenum complex shows two equal groups of three peaks (with relative intensities 2 : 1 : 2) corresponding to two different environments for the pentafluorophenyl groups. In the spectrum of the chromium complex, the peaks due to the *ortho*-fluorines in the two rings coincide. The mass spectra show very weak parent ions, $[(C_6F_5)_4P_2M(CO)_5]^+$, followed by peaks corresponding to loss of five carbonyl groups. Peaks corresponding to the ions $[(C_6F_5)_2PCF{\cdot}M(CO)_n]^+$ (n = 0—5) are also observed.

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded in $CDCl_3$ or $CHCl_3$ on a Varian Associates HA100 spectrometer at 100 Mc./sec. and 94·1 Mc./sec. respectively. ^{19}F chemical shifts are relative to CCl_3F (0·0 p.p.m.). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on an AEI MS9 double-focusing spectrometer operating at an ionizing potential of 70 v.

Reactions of Bis(pentafluorophenyl)phosphine.[10]—(*a*) *With hexacarbonylchromium.* Hexacarbonylchromium (0·60 g., 2·73 mmoles) and bis(pentafluorophenyl)phosphine (1·0 g., 2·73 mmoles) dissolved in methylcyclohexane (5 ml.) were introduced into a Carius tube which was sealed *in vacuo*. After 20 hr. at 160° solvent was partially removed *in vacuo*, and the residue recrystallised from n-hexane giving yellow *crystals* of (I) (0·60 g., 39%). The mass spectrum showed peaks corresponding to the ions $[Cr(CO)_5PC_{12}F_{10}H]^+$ (20·3%), $[Cr(CO)_5PC_{12}F_9H]^+$ (0·1%), $[Cr(CO)_4PC_{12}F_{10}H]^+$ (4·8%), $[Cr(CO)_4PC_{12}F_9H]^+$ (0·3%), $[Cr(CO)_3PC_{12}F_{10}H]^+$ (1·1%), $[Cr(CO)_3PC_{12}F_9H]^+$ (0·2%), $[Cr(CO)_2PC_{12}F_{10}H]^+$ (7·7%), $[Cr(CO)_2PC_{12}F_9H]^+$ (0·3%), $[Cr(CO)PC_{12}F_{10}H]^+$ (29·8%), $[Cr(CO)PC_{12}F_9H]^+$ (1·0%), $[CrPC_{12}F_{10}H]^+$ (75·4%), and $[Cr]^+$ (32·9%). Fluorine-19 signals occured at 129·4 (2F), 158·0 (2F), and 146·1 (1F) p.p.m. The ^{1}H n.m.r. spectrum showed a single resonance at τ 2·67(d), J_{PH} 372 c./sec.

(b) *With hexacarbonyl molybdenum.* A similar reaction with hexacarbonylmolybdenum (0·72 g., 2·73 mmoles) and bis(pentafluorophenyl)phosphine (1·0 g., 2·73 mmoles) gave on recrystallisation from n-hexane white *crystals* of (II) (0·53 g., 33%); the mass spectrum showed peaks corresponding to the ions $[Mo(CO)_5PC_{12}F_{10}H]^+$ (2·8%), $[Mo(CO)_5PC_{12}F_9H]^+$ (vw), $[Mo(CO)_4PC_{12}F_{10}H]^+$ (2·2%), $[Mo(CO)_4PC_{12}F_9H]^+$ (0·1%), $[Mo(CO)_3PC_{12}F_{10}H]^+$ (3·6%), $[Mo(CO)_3PC_{12}F_9H]^+$ (0·2%), $[Mo(CO)_2PC_{12}F_{10}H]^+$ (4·3%), $[Mo(CO)_2PC_{12}F_9H]^+$ (0·3%), $[Mo(CO)PC_{12}F_{10}H]^+$ (0·8%), $[Mo(CO)PC_{12}F_9H]^+$ (0·2%), $[MoPC_{12}F_{10}H]^+$ (17·5%), $[MoPC_6F_5]^+$ (23·1), and $[Mo]^+$ (7·4%). Fluorine-19 resonances occurred at 130·1 (2F), 158·5 (2F), and 146·8 (1F) p.p.m. The ^{1}H n.m.r. spectrum showed a single absorption at τ 2·71(d), J_{PH} 367 c./sec.

(c) *With hexacarbonyltungsten.* Similarly, reaction of hexacarbonyltungsten (0·96 g., 2·73 mmoles) with bis(pentafluorophenyl)phosphine (1·0 g., 2·73 mmoles) gave on recrystallisation from n-hexane white *crystals* of (III) (0·64 g., 34%); the mass spectrum showed peaks corresponding to the ions $[W(CO)_5PC_{12}F_{10}H]^+$ (23·8%), $[W(CO)_5PC_{12}F_9H]^+$ (0·7%), $[W(CO)_4PC_{12}F_{10}H]^+$ (10·5%), $[W(CO)_4PC_{12}F_9H]^+$ (0·3%), $[W(CO)_3PC_{12}F_{10}H]^+$ (20%), $[W(CO)_3PC_{12}F_9H]^+$ (0·3%), $[W(CO)_2PC_{12}F_{10}H]^+$ (1·5%), $[W(CO)_2PC_{12}F_9H]^+$ (0·5%), $[W(CO)PC_{12}F_{10}H]^+$ (3·8%), $[W(CO)PC_{12}F_9H]^+$ (0·7%), $[WPC_{12}F_{10}H]^+$ (2·9%), and $[WPC_6F_5]^+$ (100%). Fluorine-19 resonances occurred at 130·5 (2F), 157·1 (2F), and 145·6 (1F) p.p.m. The ^{1}H n.m.r. spectrum showed a single resonance at τ 2·29(d), J_{PH} 382 c./sec.

Preparation of Di(bispentafluorophenylphosphine)tetracarbonylchromium.— Bis(pentafluorophenyl)phosphine(pentacarbonyl)chromium (0·41 g., 0·74 mmole) contained in a tube was heated *in vacuo* at 140° (3 days) then at 190° (2 days). Sublimation (20°/10^{-2} mm.) of the products gave $(C_6F_5)_2PH$ (0·15 g., 55%), and $Cr(CO)_6$ (0·015 g., 9%). Further sublimation (100°/10^{-2} mm.) gave (I) (0·062 g., 15%). The residue in the sublimation apparatus was recrystallised from n-hexane–ether to yield yellow *crystals* of (IV) (0·01 g., 3·0%); the mass spectrum showed peaks at $[Cr(CO)_4P_2(C_6F_5)_4H_2]^+$ (0·2%), $[Cr(CO)_3P_2(C_6F_5)_4H_2]^+$ (vw), $[Cr(CO)_2P_2(C_6F_5)_4H_2]^+$ (vw), $[Cr(CO)P_2(C_6F_5)_4H_2]^+$ (vw), $[CrP_2(C_6F_5)_4H_2]^+$ (0·9%), $[Cr(CO)_5P(C_6F_5)_2H]^+$ (1·81%), $[Cr(CO)_4P(C_6F_5)_2H]^+$ (0·3%), $[Cr(CO)_3P(C_6F_5)_2H]^+$ (0·1%), $[Cr(CO)_2P(C_6F_5)_2H]^+$ (0·7%), $[Cr(CO)P(C_6F_5)_2H]^+$ (2·3%) and $[CrP(C_6F_5)_2H]^+$ (8·9%). Fluorine-19 signals occurred at 129·6 (2F), 157·6 (2F), and 146·0 (1F) p.p.m.

Preparation of Di(bispentafluorophenylphosphine)tetracarbonylmolybdenum.— Bis(pentafluorophenyl)phosphine (1·50 g., 4·10 mmoles) in benzene (10 ml.) was added dropwise with stirring to a solution of bicyclo[2,2,1]heptadiene(tetracarbonyl)molybdenum (0·70 g., 2·33 mmoles) in benzene (10 ml.) cooled in ice-water. After 3 hr. at room temperature, solvent was removed *in vacuo* and the residue recrystallised from n-hexane–chloroform to give white *crystals* of (V) (1·39 g., 72%). The mass spectrum showed peaks at $[Mo(CO)_4P_2(C_6F_5)_4H_2]^+$ (0·1%), $[Mo(CO)_3P_2(C_6F_5)_4H_2]^+$ (vw), $[Mo(CO)_2P_2(C_6F_5)_4H_2]^+$ (0·1%), $[Mo(CO)P_2(C_6F_5)_4H_2]^+$ (vw), $[MoP(C_6F_5)_4H_2]^+$ (vw), $[Mo(CO)_5P(C_6F_5)_2H]^+$ (1·8%), $[Mo(CO)_4P(C_6F_5)_2H]^+$ (1·1%), $[Mo(CO)_3P(C_6F_5)_2H]^+$ (2·0%), $[Mo(CO)_2P(C_6F_5)_2H]^+$ (1·5%), $[Mo(CO)P(C_6F_5)_2H]^+$ (0·3%), and $[MoP(C_6F_5)_2H]^+$ (5·9%). Fluorine-19 and ^{1}H n.m.r. resonances occurred at 130·1 (2F), 158·1 (2F), and 146·7 (1F) p.p.m., and τ 2·83 (poorly resolved XAA′X′ spin system, separation of outer lines 361 c./sec.), respectively.

Preparation of Tri(bispentafluorophenylphosphine)tricarbonylmolybdenum.— Cycloheptatriene(tricarbonyl)molybdenum (0·25 g., 0·91 mmole) and bis(pentafluorophenyl)phosphine (1·0 g., 2·73 mmoles) in benzene (30 ml.) were

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[10] H. B. Higson, Ph.D. Thesis, University of Manchester, 1966.

refluxed (30 min.). Solvent was removed *in vacuo*, and the residue recrystallised from n-hexane–chloroform to give (VI) (0·32 g., 28%). The ^{19}F n.m.r. spectrum showed peaks at 131·3 (2F), 158·6 (2F), and 143·9 (1F) p.p.m.

Preparation of the Lithium Derivative of Bis(pentafluorophenylphosphine)pentacarbonylchromium.— n-Butyl-lithium (0·8 ml., 0·454M hexane solution) was added dropwise to a stirred (−78°) solution of bis(pentafluorophenyl)phosphine-(pentacarbonyl)chromium (1·0 g., 1·79 mmoles) in tetrahydrofuran (10 ml.). After 2 hr. at room temperature, solvent was removed *in vacuo* and the residue recrystallised from n-hexane–chloroform to give (VII) (0·96 g., 95%). Fluorine-19 resonances (in acetone) occurred at 130·0 (2F), 162·5 (2F), and 149·0 (1F) p.p.m.

Preparation of Lithium Bis(pentafluorophenylphosphine)-pentacarbonylmolybdenum.—Reaction as above, with bis-(pentafluorophenylphosphine)pentacarbonylmolybdenum (0·75 g., 1·25 mmoles) and n-butyl-lithium (0·57 ml., 0·454M hexane solution) gave (VIII) (0·71 g., 94%). Fluorine-19 resonances (in acetone) occurred at 129·0 (2F), 161·7 (2F), and 149·2 (1F) p.p.m.

Reaction of the Lithium Salt of Bis(pentafluorophenylphosphine)pentacarbonylmolybdenum.—(a) *With hydrogen chloride.* Hydrogen chloride (dry) was bubbled for ½ hr. through a solution of (VIII) (0·02 g., 0·033 mmole) in methylene dichloride (5 ml.). Solvent was removed *in vacuo*, and the residue extracted with n-hexane (5 × 10 ml.). Removal of the n-hexane gave (II) (3 mg., 15%), identified by mass and i.r. spectroscopy.

(b) *With methyl iodide.* Complex (VIII) (0·015 g., 0·025 mmole) was refluxed (10 min.) in methyl iodide. The solution was filtered and the excess of methyl iodide removed *in vacuo*. Extraction of the product with cyclohexane afforded a few milligrams of $Me(C_6F_5)_2PMo(CO)_5$, identified by comparison of its m.p. and i.r. spectrum with an authentic sample.[11] The cyclohexane-insoluble residue was crystallised (hexane–chloroform) giving unchanged (VIII) (5 mg.).

Reactions of Tetrakis(pentafluorophenyl)diphosphine.—(a) *With hexacarbonylchromium.* Tetrakis(pentafluorophenyl)-diphosphine (1·50 g., 2·05 mmoles) and hexacarbonylchromium (0·91 g., 4·11 mmoles) in a Carius tube were heated (195°/21 hr.). The contents of the tube were extracted with chloroform. The complex (IX) (0·99 g., 54%) was collected as an off-white insoluble powder. Solvent was removed from the filtrate and the residue recrystallised from n-hexane to yield yellow crystals of (I) (0·12 g., 5%).

(b) *With hexacarbonylmolybdenum.* Reaction as above, with hexacarbonylmolybdenum (0·90 g., 3·42 mmoles) and tetrakis(pentafluorophenyl)diphosphine (1·25 g., 1·71 mmoles) afforded (X) (0·61 g., 38%) and white crystals of (II) (0·20 g., 10%).

Preparation of Tetrakis(pentafluorophenyl)diphosphinepentacarbonylchromium.—(a) The pentacarbonylchromium dianion $[Cr(CO)_5]^{2-}$ was prepared from hexacarbonylchromium (0·82 g., 3·7 mmoles) and sodium amalgam (0·5 g. Na in 10 ml. of Hg) in tetrahydrofuran (40 ml.) under u.v. irradiation. The solution of the anion was added to a solution of bis(pentafluorophenyl)phosphinous chloride[12] (2·96 g., 7·4 mmoles) in tetrahydrofuran (−78°) (10 ml.). After 6 hr. at room temperature, solvent was removed *in vacuo*, and the residue chromatographed on Florisil. Elution with n-hexane gave a yellow band, which on recrystallisation gave yellow *crystals* of (XI) (0·70 g., 31%); the mass spectrum showed peaks at $[Cr(CO)_5P_2(C_6F_5)_4]^+$ (0·1%), $[Cr(CO)_4P_2(C_6F_5)_4]^+$ (0·1%), $[Cr(CO)_3P_2(C_6F_5)_4]^+$ (0·1%), $[Cr(CO)_2P_2(C_6F_5)_4]^+$ (vw), $[Cr(CO)P_2(C_6F_5)_4]^+$ (0·1%), $[Cr(CO)_5P(C_6F_5)_2H]^+$ (13·3%), $[Cr(CO)_2P(C_6F_5)_2H]^+$ (11·0%), $[Cr(CO)P(C_6F_5)_2H]^+$ (17·7%), $[CrPC_{12}F_9H_2]^+$ (61·3%), and $[Cr]^+$ (100%). The ^{19}F n.m.r. spectrum showed peaks 128·9 (2F), 158·5 (2F) p.p.m. and 146·5 (1F), and also at 128·9 (2F), 159·9 (2F), and 147·7 (1F) p.p.m.

(b) Bis(pentafluorophenyl)phosphinous chloride (0·36 g., 0·89 mmole) and lithium bis(pentafluorophenylphosphine)-pentacarbonylchromium (0·50 g., 0·89 mmole) were refluxed (8 hr.) in methylene dichloride (20 ml.) Solvent was removed *in vacuo* and the residue extracted with n-hexane to give yellow *crystals* of (XI) (0·13 g., 15%).

Preparation of Tetrakis(pentafluorophenyl)diphosphinepentacarbonylmolybdenum.—(a) Reaction as for (XI), using the anion $[Mo(CO)_5]^{2-}$ obtained from hexacarbonylmolybdenum (0·99 g., 3·70 mmoles) and sodium amalgam (0·60 g. Na in 10 ml. Hg), and bis(pentafluorophenyl)phosphinous chloride (3·01 g., 7·40 mmoles) afforded (XII) (0·29 g., 17%). The mass spectrum showed peaks at $[Mo(CO)_5P_2(C_6F_5)_4]^+$ (0·1%), $[Mo(CO)_4P_2(C_6F_5)_4]^+$ (0·2%), $[Mo(CO)_3P_2(C_6F_5)_4]^+$ (0·3%), $[Mo(CO)_2P_2(C_6F_5)_4]^+$ (0·2%), $[Mo(CO)P_2(C_6F_5)_4]^+$ (0·2%), $[Mo(CO)_5P(C_6F_5)_2H]^+$ (0·2%), $[Mo(CO)_2P(C_6F_5)_2H]^+$ (0·2%), $[Mo(CO)P(C_6F_5)_2H]^+$ (0·1%), $[MoPC_{12}F_9H_2]^+$ (0·6%), and $[Mo]^+$ (0·6%). The ^{19}F n.m.r. spectrum showed peaks at 130·4 (2F), 157·5 (2F), and 146·6 (1F) p.p.m. and also at 133·9 (2F), 159·2 (2F), and 148·8 (1F) p.p.m.

(b) A solution in methylene dichloride (20 ml.) of $(C_6F_5)_2PCl$ (0·13 g., 0·33 mmole), (II) (0·20 g., 0·33 mmole), and Et_3N (0·33 g., 0·33 mmole) was refluxed (1 hr.). Solvent was removed *in vacuo* and the residue chromatographed on Florisil. Elution with n-hexane gave (XII) (0·05 g., 16%).

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