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GROUP VI METAL HEXACARBONYL DERIVATIVES OF SOME NEW FLUORINE SUBSTITUTED DITERTIARY PHOSPHINES

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Summary

Complexes of the type $[M(CO)_4(P-P')]$ (M = Cr, Mo, W; P–P′ = $R_2PCH_2CH_2PPh_2$, R = *m*-FC_6H_4 (**1a**), R = *p*-FC_6H_4 (**1b**), R = *m*-$CF_3C_6H_4$ (**1c**)) have been obtained from the reaction of appropriate metal hexacarbonyl with the corresponding ditertiary phosphine in methylcyclohexane/xylene. The order of ease of replacement of carbonyl by these phosphines was found in the sequence Mo > Cr > W. The complexes $[M(CO)_4(P-P')]$ react with excess of pyridine to yield the trisubstituted complexes $[M(CO)_3(py)(P-P')]$ (M = Cr, Mo, W; py = pyridine; P–P′ = **1a**, **1b** or **1c**). All the complexes have been characterized by elemental analysis and IR and ^1H NMR spectroscopy, and are assigned octahedral structures. Carbonyl force constants have been calculated from the ν(CO) stretching frequencies. $^{31}P\{^1H\}$NMR spectra of $[M(CO)_4(P-P')]$ complexes reveal unusually large downfield shifts upon coordination, and these are explained in terms of a ring contribution. The values of the tungsten–phosphorus $J(^{183}W-^{31}P)$ and phosphorus–phosphorus $J(^{31}P-^{31}P')$ coupling constants are discussed.

Introduction

Although symmetrical ditertiary phosphine complexes of Group VI metal hexacarbonyls have been extensively investigated [1–11], very few studies have been made of such complexes containing unsymmetrical ditertiary phosphines [12,13]. Since such unsymmetrical ditertiary phosphines provide additional information, such as $^{31}P-^{31}P'$ couplings and the effect of substituents on the ^{31}P chemical shifts, it was considered of interest to synthesize Group VI metal hexacarbonyl complexes containing some new fluorine-substituted ditertiary phosphines. The introduction of a fluorine substituent into phenyl ring is expected to modify the electronic properties of the phosphine and also to increase the solubility characteristic of the resulting complexes, thereby facilitating the ^{31}P NMR studies.

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Results and discussion

The reaction of ligand **1a**, **1b** or **1c** with chromium or molybdenum hexacarbonyls in 1/1 molar ratio in methylcyclohexane yields complexes of the type $[M(CO)_4(P\text{–}P')]$ (M = Cr, Mo). For tungsten hexacarbonyl, the reaction was found to be slow in methylcyclohexane, and so in this case xylene was used as solvent. Additional mixed-ligand complexes $[M(CO)_3(py)(P\text{–}P')]$ (M = Cr, Mo, W; P–P' = **1a**, **1b** or **1c**) were prepared by refluxing the $[M(CO)_4(P\text{–}P')]$ complexes with an excess of pyridine. Table 1 presents the analytical data, Table 2 the ^{31}P NMR data, and Table 3 the IR fequencies and force constants.

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF METAL CARBONYL COMPLEXES [a]

Complex	Colour	M.p. (°C)	Analysis (Found (calcd.)(%))		
			C	H	P
$[Cr(CO)_4$(**1a**)$]$	Yellow	120–122	60.0 (60.2)	3.6 (3.7)	10.1 (10.3)
$[Mo(CO)_4$(**1a**)$]$	Yellow	128–129	55.8 (56.1)	3.5 (3.4)	9.5 (9.6)
$[W(CO)_4$(**1a**)$]$	Light-yellow	135–136	49.4 (49.3)	3.1 (3.0)	8.2 (8.5)
$[Cr(CO)_3(py)$(**1a**)$]$	Yellow	140–142	62.9 (62.9)	4.3 (4.2)	9.4 (9.6)
$[Mo(CO)_3(py)$(**1a**)$]$	Brown	135–136	58.8 (58.9)	3.6 (3.9)	8.7 (8.9)
$[W(CO)_3(py)$(**1a**)$]$	Yellow	142–145	52.4 (52.3)	3.6 (3.5)	8.8 (8.6)
$[Cr(CO)_4$(**1b**)$]$	Yellow	128–129	60.0 (60.2)	3.4 (3.7)	10.1 (10.4)
$[Mo(CO)_4$(**1b**)$]$	Yellow	143–144	55.9 (56.1)	3.2 (3.4)	9.3 (9.6)
$[W(CO)_4$(**1b**)$]$	Light-yellow	156–158	49.0 (49.3)	3.2 (3.0)	8.3 (8.5)
$[Cr(CO)_3(py)$(**1b**)$]$	Yellow	150–151	62.6 (62.9)	4.0 (4.2)	9.3 (9.6)
$[Mo(CO)_3(py)$(**1b**)$]$	Brown	145–147	58.5 (58.9)	3.5 (3.9)	8.7 (8.9)
$[W(CO)_3(py)$(**1b**)$]$	Red	162–163	52.3 (52.3)	3.2 (3.1)	8.1 (8.6)
$[Cr(CO)_4$(**1c**)$]$	Yellow	103–104	54.8 (55.0)	3.0 (3.1)	8.5 (8.9)
$[Mo(CO)_4$(**1c**)$]$	Yellow	112–114	51.4 (51.7)	2.6 (2.9)	8.0 (8.3)
$[W(CO)_4$(**1c**)$]$	Yellow	126–127	46.0 (46.3)	2.4 (2.7)	7.2 (7.5)
$[Cr(CO)_3(py)$(**1c**)$]$	Yellow	114–116	57.5 (57.7)	3.4 (3.7)	8.0 (8.3)
$[Mo(CO)_3(py)$(**1c**)$]$	Yellow	129–130	54.3 (54.5)	3.1 (3.4)	7.4 (7.8)
$[W(CO)_3(py)$(**1c**)$]$	Yellow	142–143	48.7 (49.0)	2.8 (3.0)	6.7 (7.0)

[a] **1a** = $(m\text{-}FC_6H_4)_2PCH_2CH_2PPh_2$; **1b** = $(p\text{-}FC_6H_4)_2PCH_2CH_2PPh_2$; **1c** = $(m\text{-}CF_3C_6H_4)_2PCH_2CH_2PPh_2$.

TABLE 2

$^{31}P\{^{1}H\}$ NMR DATA FOR $[M(CO)_4(P-P')]$ COMPLEXES

Complex	Chemical shift (ppm)		Coordination chemical shift		Ring contribution [d], Δ_R		
	$\delta(PPh_2)$	$\delta(PR_2)$	Δ PPh_2	Δ PR_2	Δ PPh_2	Δ PR_2	J(P–P') (Hz)
$[Cr(CO)_4$(**1a**)]	79.27	79.82	91.40	90.92	30.4	29.92	8.40
$[Mo(CO)_4$(**1a**)]	55.21	56.25	67.34	67.35	24.44	24.45	6.92
$[W(CO)_4$(**1a**)] [a]	40.16	41.27	52.29	52.37	26.99	27.07	5.15
$[Cr(CO)_4$(**1b**)]	80.80	81.08	93.0	95.56	32.0	34.56	9.24
$[Mo(CO)_4$(**1b**)]	54.23	54.74	66.43	69.22	23.53	26.32	7.00
$[W(CO)_4$(**1b**)] [b]	40.27	41.21	52.47	55.69	27.17	30.39	6.25
$[Cr(CO)_4$(**1c**)]	80.01	84.57	92.21	95.77	31.31	34.87	10.6
$[Mo(CO)_4$(**1c**)]	56.04	59.82	68.24	71.02	25.34	28.12	7.58
$[W(CO)_4$(**1c**)] [c]	40.20	43.15	52.40	54.35	27.10	29.05	6.80

[a] $J(^{183}W-^{31}PPh_2)$ 228.50, $J(^{183}W-^{31}PR_2)$ 234.42 Hz (R = *m*-FC_6H_4). [b] $J(^{183}W-^{31}PPh_2)$ 229.03 Hz; $J(^{183}W-^{31}PR_2)$ 231.63 Hz (R = *p*-FC_6H_4). [c] $J(^{183}W-^{31}PPh_2)$ 230.63 Hz, $J(^{183}W-^{31}PR_2)$ 238.80 Hz (R = *m*-$CF_3C_6H_4$). [d] ΔR = Coordination chemical shift of *cis*-chelated disubstituted phosphine (Δ) – Coordination chemical shift of an equivalent phosphorus in a non-chelate complex (Δ). Δ *cis*-$[Cr(CO)_4(Ph_2PBu^n)_2]$ 61.0; Δ *cis*-$[Mo(CO)_4(Ph_2PBu^n)_2]$ 42.9; Δ *cis*-$[W(CO)_4(Ph_2PBu^n)_2]$ 25.3 and ^{31}P chemical shifts reported for ditertiary phosphines [21] were used in ΔR calculations.

The $^{31}P\{^{1}H\}$ NMR spectra of $[M(CO)_4(P-P')]$ (M = Cr, Mo; P–P' = **1a**, **1b** or **1c**) complexes exhibit a pair of doublets (AB pattern), and those of the analogous tungsten complexes $[W(CO)_4(P-P')]$ have the expected satellites on each side of a quartet due to tungsten–phosphorus nuclear spin couplings $J(^{183}W-^{31}P)$. The higher downfield shifts were assigned to the phosphorus attached to the fluorophenyl group. All these complexes of the type $[M(CO)_4(P-P')]$ show unusually large downfield coordination chemical shifts which are not consistent with the linear $\Delta = A\delta(F) + B$ relationship [14] and so are interpreted in terms of a ring contribution (Δ_R).

The observed increase in the tungsten–phosphorus couplings (Table 2) in the sequence $P(C_6H_4F\text{-}p)_2 < P(C_6H_4F\text{-}m)_2 < P(C_6H_4CF_3\text{-}m)_2$ can be ascribed to the increased electron withdrawing ability of the substituents attached to phosphorus atom [15].

TABLE 3A

IR ν(CO) FREQUENCIES (in benzene) (cm^{-1}) AND FORCE CONSTANTS (in mdynes $Å^{-1}$)

Complex	Modes of carbonyl stretching				Force constants		
	A_1^1	A_1^2	B_1	B_2	K_1	K_2	K_i
$[Cr(CO)_4$(**1a**)]	2007	1912	1896	1875	14.45	15.02	0.25
$[Mo(CO)_4$(**1a**)]	2005	1918	1905	1880	14.55	15.22	0.28
$[W(CO)_4$(**1a**)]	2018	1920	1900	1877	14.50	15.24	0.32
$[Cr(CO)_4$(**1b**)]	2002	1915	1900	1855	14.61	15.11	0.27
$[Mo(CO)_4$(**1b**)]	2015	1920	1905	1890	14.72	15.25	0.30
$[W(CO)_4$(**1b**)]	2012	1910	1902	1886	14.66	15.20	0.29
$[Cr(CO)_4$(**1c**)]	2011	1937	1902	1876	14.51	15.21	0.30
$[Mo(CO)_4$(**1c**)]	2021	1945	1908	1890	14.74	15.32	0.31
$[W(CO)_4$(**1c**)]	2018	1940	1905	1880	14.59	15.29	0.32

TABLE 3B

IR ν(CO) FREQUENCIES (in $CHCl_3$) (cm^{-1}) AND FORCE CONSTANTS (in mdynes $Å^{-1}$)

Complex	Modes of carbonyl stretching			Force constants	
	A′	A″	A′	K_1	K_i
$[Cr(CO)_3(py)(\mathbf{1a})]$	1917	1833	1815	13.88	0.31
$[Mo(CO)_3(py)(\mathbf{1a})]$	1929	1842	1819	14.03	0.33
$[W(CO)_3(py)(\mathbf{1a})]$	1923	1836	1813	13.94	0.35
$[Cr(CO)_3(py)(\mathbf{1b})]$	1920	1815	1805	13.69	0.39
$[Mo(CO)_3(py)(\mathbf{1b})]$	1928	1820	1810	13.78	0.41
$[W(CO)_3(py)(\mathbf{1b})]$	1925	1832	1820	13.90	0.35
$[Cr(CO)_3(py)(\mathbf{1c})]$	1942	1838	1812	14.04	0.40
$[Mo(CO)_3(py)(\mathbf{1c})]$	1936	1826	1808	13.88	0.42
$[W(CO)_3(py)(\mathbf{1c})]$	1928	1815	1805	13.73	0.43

The magnitude of tungsten–phosphorus coupling is mainly determined by the following expression [16]:

$$^1J(\mathrm{P{-}W}) = \gamma_P\gamma_W \frac{h}{2\pi} \frac{256}{g} \pi^2\beta^2 |s_P(0)|^2 \frac{|s_W(0)|^2}{^3\Delta E} \frac{a^2(1-a^2)}{n} \alpha^2$$

where γ_P is the magnetogyric ratio of phosphorus nucleus, $|s_P(0)|^2$ is the magnitude of the valence state *s*-orbital of phosphorus atom at the nucleus, a^2 is the degree of metal *s*-character in the bonding molecular orbital, α^2 is the *s*-character of phosphorus lone-pair hybrid, n is the number of ligands and $^3\Delta E$ is the average excitation energy. The observed increase in the coupling constants with increase in the electron-withdrawing ability of the substituent attached to phosphorus arises mainly from the variation in the $|s_P(0)|^2$ and α^2-terms.

The value of the phosphorus–phosphorus coupling constants $J(^{31}P{-}^{31}P')$ is highest for chromium complexes and lowest for tungsten complexes (Table 2). The observed J(P–P′) is expected to include contributions from coupling through both the ligand backbone J(P–P′(B)) and the metal centre J(P–P′(M)); we believe that a marked change in the coupling through the metal centre is mainly responsible for the observed decrease in J(P–P′) values (Table 2) in the sequence Cr > Mo > W.

The solution infrared spectra of $[M(CO)_4(P{-}P')]$ complexes exhibit four absorption bands in the carbonyl absorption region, corresponding to A_1^1, A_1^2, B_1 and B_2 modes of carbonyl stretching (Table 3A) and consistent with the C_{2v} symmetry of the molecule [17,18], thereby confirming the chelating behaviour of the ligand. Mixed ligand complexes of the type $[M(CO)_3(py)(P{-}P')]$ show three infrared active ν(CO) bands corresponding to 2A′ and A″ modes (Table 3B), as expected for similarly substituted *cis*-$[X_2YM(CO)_3]$ complex having C_s symmetry [19]. The disappearance of one ν(CO) band at ($\sim$ 2000 cm^{-1}) reflects the replacement of one of the carbonyl ligands of the parent complex $[M(CO)_4(P{-}P')]$ by a pyridine ligand.

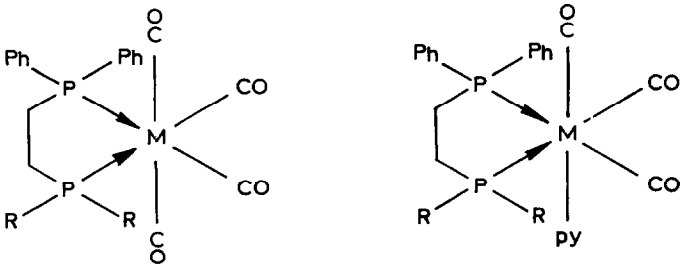
Carbonyl force constant calculations (Table 3A and 3B) show that: (i) the force constant for CO carbonyl *trans* to carbonyl (K_2) is always higher than for CO *trans* to the ligand (K_1) i.e. $K_2 > K_1$; (ii) all the CO stretch–stretch interaction constants (K_i) are positive.

The ^1H NMR spectra of the complexes $[M(CO)_4(P{-}P')]$ show a slight downfield shift for the aromatic as well as the methylene protons. The signals from the

aromatic phenyl protons appear at δ 7.30–6.60 ppm as complex multiplets and those from the methylene protons at δ 2.60–2.20 ppm as broad peaks due to J(P–H) couplings. The complexes of the type $[M(CO)_3(py)(P-P')]$ exhibit a complex multiplet at δ 9.30–8.50 ppm because of additional signals from the pyridine protons.

Introduction of a fluorine group into a phenyl ring was found to increase the solubilities of the complexes.

On the basis of above results the complexes $[M(CO)_4(P-P')]$ and $[M(CO)_3(py)(P-P')]$ can be assigned *cis*-octahedral structures **A** and **B**, respectively.



(M = Cr, Mo or W ;
R = *m*-FC_6H_4, *p*-FC_6H_4 or *m*-$CF_3C_6H_4$;
py = C_5H_5N)

Experimental

Experimental techniques and physical measurements were as described elsewhere [21]. Elemental analyses were by the microanalytical laboratories of the Department of Chemistry, University of Delhi, and Australian National University, Canberra.

IR spectra were recorded in benzene or dichloromethane on a Perkin–Elmer-621 spectrophotometer. ^1H NMR were recorded in $CDCl_3$ solution on a Varian A-60 instrument with TMS as internal standard. $^{31}P\{^1H\}$ NMR spectra were measured in the FT mode on a Bruker WH-90 instrument operating at a frequency of 36.43 MHz and chemical shifts are relative to external 85% H_3PO_4.

Reactions involving ditertiary phosphines were carried out under purified nitrogen using standard Schlenk tube techniques. Solvents were dried in the usual way [20] and deoxygenated by distillation through a stream of nitrogen.

Chromium, molybdenum and tungsten hexacarbonyl were purchased from Pressure Chemical Co. Pittsburg, U.S.A. and used as such without further purification. The ligands were synthesised as described [21].

Synthesis of complexes

1-Diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethanetetracarbonylchromium-(0)

A mixture of $Cr(CO)_4$ (0.22 g, 1.0 mmol) and ligand **1a** (0.43 g, 1.0 mmol) in 50 ml of methylcyclohexane was boiled under reflux for 30 h to give a yellow solution. The solvent was then removed in vacuo to give a yellow powder, which was purified

on a silica column in chloroform then recrystallized from chloroform/hexane to give yellow crytals (yield 0.48 g, 80%).

1-Diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethanetetracarbonylmolybdenum(0)

A mixture of $Mo(CO)_6$ (0.28 g, 1.06 mmol) and ligand **1a** (0.46 g, 1.06 mmol) in 60 ml of methylcyclohexane was boiled under reflux for 25 h to give a deep yellow solution. The solvent was removed in vacuo to leave a yellow residue, which was purified and crystallized as described above to give yellow crystals (Yield 0.51 g, 75%).

1-Diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethanetetracarbonyltungsten(0)

A mixture of $W(CO)_6$ and ligand **1a** (0.44 g, 1.01 mmol) in 50 ml of xylene was boiled under reflux for 45 h to give a light yellow powder, which on recrystallization from chloroform/n-hexane gave light yellow crystals (Yield 0.38 g, 50%).

The analogous complexes containing ligands **1b** and **1c** were prepared by similar procedures. The complexes $[M(CO)_3(py)(P-P')]$ (M = Cr, Mo, W; P–P′ = **1a**, **1b** or **1c**) were prepared by refluxing the appropriate $[M(CO)_4(P-P')]$ with an excess of pyridine for ~ 40 h [17].

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