

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

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Summary

Complexes of the type $[M(CO)_4(P-P')]$ ($M = Cr, Mo, W$; $P-P' = R_2PCH_2CH_2-PPh_2$, $R = m-FC_6H_4$ (**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 $\nu(CO)$ 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.

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 $[M(CO)_4(P-P')]$ ($M = Cr, Mo$). 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 $[M(CO)_3(py)(P-P')]$ ($M = Cr, Mo, W$; $P-P' = 1a, 1b$ or **1c**) were prepared by refluxing the $[M(CO)_4(P-P')]$ complexes with an excess of pyridine. Table 1 presents the analytical data, Table 2 the ^{31}P NMR data, and Table 3 the IR frequencies 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*-FC₆H₄)₂PCH₂CH₂PPh₂; **1b** = (*p*-FC₆H₄)₂PCH₂CH₂PPh₂; **1c** = (*m*-CF₃C₆H₄)₂-PCH₂CH₂PPh₂.

TABLE 2
 $^{31}\text{P}\{^1\text{H}\}$ NMR DATA FOR $[\text{M}(\text{CO})_4(\text{P}-\text{P}')] \text{ COMPLEXES}$

Complex	Chemical shift (ppm)		Coordination chemical shift		Ring contribution ^d , Δ_R		
	$\delta(\text{PPh}_2)$	$\delta(\text{PR}_2)$	ΔPPh_2	ΔPR_2	ΔPPh_2	ΔPR_2	$J(\text{P}-\text{P}')$ (Hz)
$[\text{Cr}(\text{CO})_4(\mathbf{1a})]$	79.27	79.82	91.40	90.92	30.4	29.92	8.40
$[\text{Mo}(\text{CO})_4(\mathbf{1a})]$	55.21	56.25	67.34	67.35	24.44	24.45	6.92
$[\text{W}(\text{CO})_4(\mathbf{1a})]^a$	40.16	41.27	52.29	52.37	26.99	27.07	5.15
$[\text{Cr}(\text{CO})_4(\mathbf{1b})]$	80.80	81.08	93.0	95.56	32.0	34.56	9.24
$[\text{Mo}(\text{CO})_4(\mathbf{1b})]$	54.23	54.74	66.43	69.22	23.53	26.32	7.00
$[\text{W}(\text{CO})_4(\mathbf{1b})]^b$	40.27	41.21	52.47	55.69	27.17	30.39	6.25
$[\text{Cr}(\text{CO})_4(\mathbf{1c})]$	80.01	84.57	92.21	95.77	31.31	34.87	10.6
$[\text{Mo}(\text{CO})_4(\mathbf{1c})]$	56.04	59.82	68.24	71.02	25.34	28.12	7.58
$[\text{W}(\text{CO})_4(\mathbf{1c})]^c$	40.20	43.15	52.40	54.35	27.10	29.05	6.80

^a $J(^{183}\text{W}-^{31}\text{PPh}_2)$ 228.50, $J(^{183}\text{W}-^{31}\text{PR}_2)$ 234.42 Hz (R = *m*-FC₆H₄). ^b $J(^{183}\text{W}-^{31}\text{PPh}_2)$ 229.03 Hz; $J(^{183}\text{W}-^{31}\text{PR}_2)$ 231.63 Hz (R = *p*-FC₆H₄). ^c $J(^{183}\text{W}-^{31}\text{PPh}_2)$ 230.63 Hz, $J(^{183}\text{W}-^{31}\text{PR}_2)$ 238.80 Hz (R = *m*-FC₃C₆H₄). ^d Δ_R = Coordination chemical shift of *cis*-chelated disubstituted phosphine (Δ) - Coordination chemical shift of an equivalent phosphorus in a non-chelate complex (Δ). Δ *cis*- $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PBu}^n)_2]$ 61.0; Δ *cis*- $[\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PBu}^n)_2]$ 42.9; Δ *cis*- $[\text{W}(\text{CO})_4(\text{Ph}_2\text{PBu}^n)_2]$ 25.3 and ^{31}P chemical shifts reported for ditertiary phosphines [21] were used in Δ_R calculations.

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

The observed increase in the tungsten-phosphorus couplings (Table 2) in the sequence $\text{P}(\text{C}_6\text{H}_4\text{F-}p)_2 < \text{P}(\text{C}_6\text{H}_4\text{F-}m)_2 < \text{P}(\text{C}_6\text{H}_4\text{CF}_3-m)_2$ can be ascribed to the increased electron withdrawing ability of the substituents attached to phosphorus atom [15].

TABLE 3A
 IR $\nu(\text{CO})$ FREQUENCIES (in benzene) (cm^{-1}) AND FORCE CONSTANTS (in $\text{mdynes } \text{\AA}^{-1}$)

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

TABLE 3B

IR $\nu(\text{CO})$ FREQUENCIES (in CHCl_3) (cm^{-1}) AND FORCE CONSTANTS (in $\text{mdynes } \text{\AA}^{-1}$)

Complex	Modes of carbonyl stretching			Force constants	
	A'	A''	A'	K_1	K_t
[Cr(CO) ₃ (py)(1a)]	1917	1833	1815	13.88	0.31
[Mo(CO) ₃ (py)(1a)]	1929	1842	1819	14.03	0.33
[W(CO) ₃ (py)(1a)]	1923	1836	1813	13.94	0.35
[Cr(CO) ₃ (py)(1b)]	1920	1815	1805	13.69	0.39
[Mo(CO) ₃ (py)(1b)]	1928	1820	1810	13.78	0.41
[W(CO) ₃ (py)(1b)]	1925	1832	1820	13.90	0.35
[Cr(CO) ₃ (py)(1c)]	1942	1838	1812	14.04	0.40
[Mo(CO) ₃ (py)(1c)]	1936	1826	1808	13.88	0.42
[W(CO) ₃ (py)(1c)]	1928	1815	1805	13.73	0.43

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

$${}^1J(\text{P-W}) = \gamma_{\text{P}} \gamma_{\text{W}} \frac{h}{2\pi} \frac{256}{g} \pi^2 \beta^2 |s_{\text{P}}(0)|^2 \frac{|s_{\text{W}}(0)|^2}{{}^3\Delta E} \frac{a^2(1-a^2)}{n} \alpha^2$$

where γ_{P} is the magnetogyric ratio of phosphorus nucleus, $|s_{\text{P}}(0)|^2$ 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 $|s_{\text{P}}(0)|^2$ and α^2 -terms.

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

The solution infrared spectra of $[\text{M}(\text{CO})_4(\text{P}-\text{P}')]_n$ 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 $[\text{M}(\text{CO})_3(\text{py})(\text{P}-\text{P}')]_n$ show three infrared active $\nu(\text{CO})$ bands corresponding to $2A'$ and A'' modes (Table 3B), as expected for similarly substituted *cis*- $[\text{X}_2\text{YM}(\text{CO})_3]$ complex having C_s symmetry [19]. The disappearance of one $\nu(\text{CO})$ band at ($\sim 2000 \text{ cm}^{-1}$) reflects the replacement of one of the carbonyl ligands of the parent complex $[\text{M}(\text{CO})_4(\text{P}-\text{P}')]_n$ by a pyridine ligand.

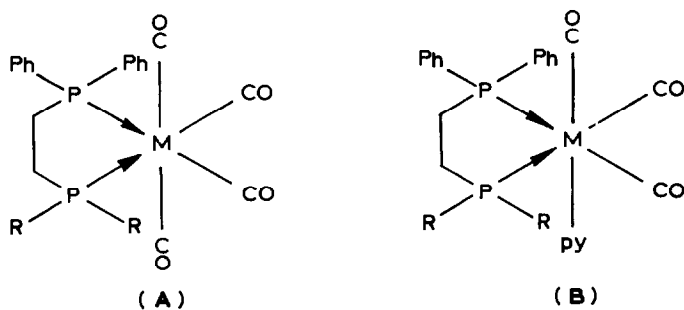
Carbonyl force constant calculations (Table 3A and 3B) show that: (i) the force constant for CO carbonyl *trans* to carbonyl (K_2) is always higher than for CO *trans* to the ligand (K_1) i.e. $K_2 > K_1$; (ii) all the CO stretch-stretch interaction constants (K_t) are positive.

The ${}^1\text{H}$ NMR spectra of the complexes $[\text{M}(\text{CO})_4(\text{P}-\text{P}')]_n$ 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 $J(\text{P-H})$ couplings. The complexes of the type $[\text{M}(\text{CO})_3(\text{py})(\text{P-P}')]$ 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 $[\text{M}(\text{CO})_4(\text{P-P}')]$ and $[\text{M}(\text{CO})_3(\text{py})(\text{P-P}')]$ can be assigned *cis*-octahedral structures **A** and **B**, respectively.



(M = Cr, Mo or W ;
 R = *m*-FC₆H₄, *p*-FC₆H₄ or *m*-CF₃C₆H₄ ;
 py = C₅H₅N)

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 CDCl₃ solution on a Varian A-60 instrument with TMS as internal standard. ³¹P {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% H₃PO₄.

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 crystals (yield 0.48 g, 80%).

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

A mixture of $\text{Mo}(\text{CO})_6$ (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 $\text{W}(\text{CO})_6$ 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 $[\text{M}(\text{CO})_3(\text{py})(\text{P}-\text{P}')]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{P}-\text{P}' = \mathbf{1a}, \mathbf{1b}$ or **1c**) were prepared by refluxing the appropriate $[\text{M}(\text{CO})_4(\text{P}-\text{P}')]$ with an excess of pyridine for ~ 40 h [17].

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