Structure and Stereodynamics of $[M(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ (M = Cr, Mo or W) and $[Cr(CO)_3\{P(C_6H_4Me\text{-}o)_3\}]$†

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The crystal structure of $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ has been determined. It reveals an exo_2 conformation for the phosphine ligand, in agreement with molecular mechanics calculations. Barriers to P–C rotation in the series $[M(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ (M = Cr, Mo or W) are in the range 36–42 kJ mol^{-1}; restricted M–P rotation is also evident in the low-temperature ^{13}CO NMR spectrum of $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$. The crystal structure of the π complex $[Cr(CO)_3\{P(C_6H_4Me\text{-}o)\}_3]$ is most consistent with an electron-acceptor character for the $P(C_6H_4Me\text{-}o)_2$ substituent. Crystal data: $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$, monoclinic, space group $P2_1/n$, a = 10.774(2), b = 14.951(5), c = 14.687(7) Å, β = 91.45(2)°, Z = 4, R' = 0.0980 for 209 variable parameters and 2326 observed reflections; $[Cr(CO)_3\{P(C_6H_4Me\text{-}o)_3\}]$, monoclinic, space group $P2_1/a$, a = 16.725(2), b = 7.340(1), c = 17.675(4), β = 92.66(2)°, Z = 4, R' = 0.1187 for 263 variable parameters and 1848 observed reflections.

As ancillary ligands in transition-metal complexes, phosphines provide great potential for control of structure and reactivity through variation of steric and electronic properties. Though conformational isomerism in free triarylphosphines and related compounds has been extensively investigated,[1a,b] much less is known about the stereodynamics of metal–phosphine complexes. As part of a developing interest in this subject,[2a–f] we describe here experimental and molecular mechanics studies of the M–P and P–C rotational processes in the series $[M(CO)_5L]$ **1a**–**1c** (M = Cr, Mo or W) containing the sterically demanding $P(C_6H_4Me\text{-}o)_3$ ligand, together with the crystal and molecular structure of the η^6-bound complex $[Cr(CO)_3\{P(C_6H_4Me\text{-}o)_3\}]$ **2**. Part of this work has been reported as a preliminary communication.[3]

Results and Discussion

As previously described,[4] the $[M(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ series was prepared photolytically from $[M(CO)_6]$; $[Cr(CO)_3\{P(C_6H_4Me\text{-}o)_3\}]$ was prepared by reflux of $[Cr(CO)_6]$ with $P(C_6H_4Me\text{-}o)_3$ in decane.

(*a*) *Solid-state and Solution Studies of* $[M(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ *Complexes*.—The solid-state structure of $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ is shown in Fig. 1. The Cr–P bond length (Table 1) is elongated relative to those in other reported $[Cr(CO)_5(PR_2R')]$ structures (R = R' = Ph, Me, CH_2CH_2CN; R = Me, R' = SH) (2.36–2.42 Å).[2a,5a–c] The phosphine adopts an exo_2 conformation‡ in which the distal ring approximately bisects one OC–Cr–CO angle. This bisecting orientation is also common to other reported $[Cr(CO)_5(PR_3)]$ and $[M(CO)_5(PR_3)]$ structures (M = Mo, R = Ph or CH_2CH_2CN; M = W, R = Me),[5a,6] which also show a slight tilting with respect to the Cr–P axis such that the P–M–CO angles for the *cis*-$(CO)_2$ pair whose angle is bisected are less than 90°. In contrast, in $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$, a significant bending away from the phosphorus is observed for the *trans*-$(CO)_2$ pair [C(24), C(25)] which exhibit the closest non-bonded interaction with the methyl groups of the proximal *o*-tolyl rings (3.0–3.3 Å). A linear OC(*trans*)–Cr–P geometry is observed. The cone angle measured for the phosphine in $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$ is 160°,§ while that for the phosphine in $[Fe(CO)_4\{P(C_6H_4Me\text{-}o)_3\}]$, which contains an exo_3 conformation, is 166°.[3] Calculation of cone angles from the published structures of *trans*-$[PtI_2\{P(C_6H_4Me\text{-}o)_2\}_3]$[8a] and *trans*-$[Ir\{P(C_6H_4Me\text{-}o)_3\}_2(CO)Cl]$[8b] which contain the exo_2 conformation yield values of approximately 163°. These values are substantially less than the quoted literature value[9] of 194°. Indeed, if an iron atom is attached to free $P(C_6H_4Me\text{-}o)_3$ generated from the literature coordinates[10] at the standard M–P distance of 2.28 Å, a cone angle of 184° may be calculated. The reduction in cone angle in geniune complexes may be attributed to a flattening of the phosphine which is manifest in the increase in torsion angle lone pair/Fe–P–C(*ipso*)–C(Me) from 42° in the free ligand to 53° in $[Fe(CO)_4\{P(C_6H_4Me\text{-}o)_3\}]$.

Variable-temperature NMR spectra of complexes **1a**–**1c** reveal a restricted P–C rotational process which is most clearly evident in the collapse of the single room-temperature *o*-tolyl methyl resonance to three at low temperature (Fig. 2; complexes of Mo and W are similar). Line-shape analysis yields the activation parameters in Table 2. The $\Delta G^{\ddagger}$ values are slightly lower for the complexes of Mo and W, most likely as a result of the elongation of the M–P by about 0.15 Å in each case.[2a,5a,6] The barriers are comparable to those observed for $XP(C_6H_4Me\text{-}o)_3$ (X = S or Se, $\Delta G^{\ddagger}_{273}$ = 38, 40 kJ mol^{-1})[11] in which the exo_2 isomer predominates in solution, but lower than the value for

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ If a regular trigonal bipyramid is constructed from a metal as apex and three *para* ring carbons as the base, a proximal (exo) substituent will point away from the base while a distal (endo) substituent will point towards the base. The terms exo_3 and exo_2 define the number of proximal *o*-methyl groups.

§ Calculated from the crystal structure using CHEM-X[7] and values of 1.2 and 2.0 Å respectively for the van der Waals radii of hydrogen and the methyl group.

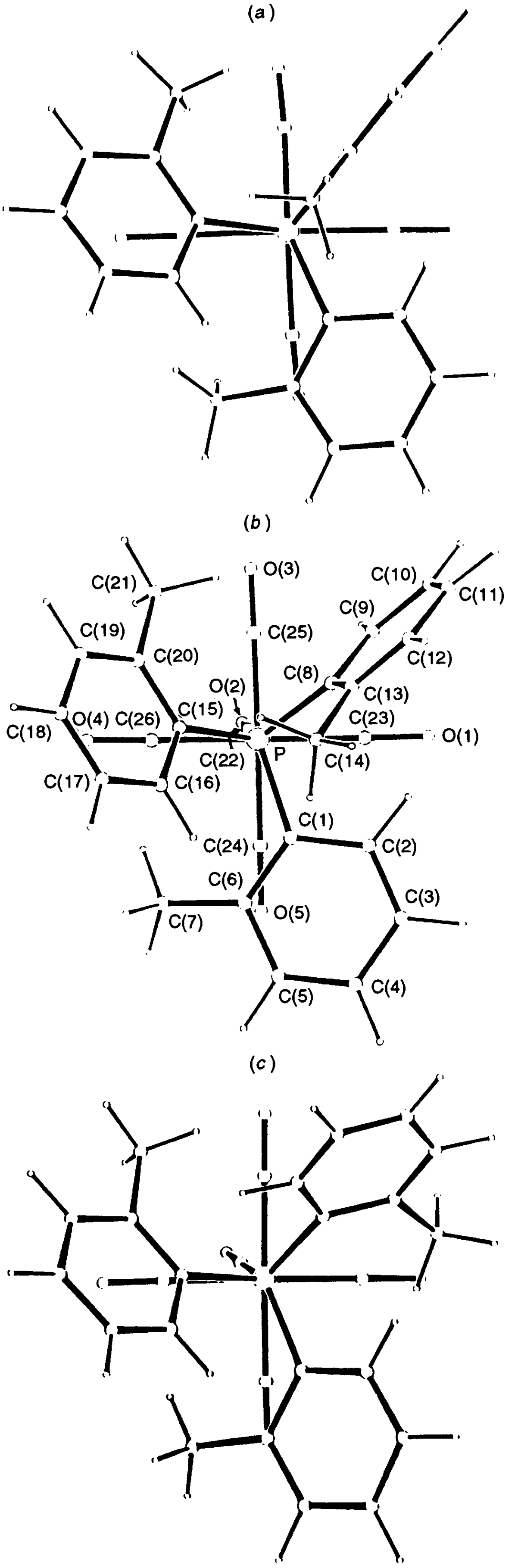


Fig. 1 Experimental (*a*) and computed structures (*b*) (minimised exo$_2$) and (*c*) (minimised exo$_3$) for [Cr(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]

Table 1 Experimental and computed geometries (distances in Å, angles in °) for exo$_2$ and exo$_3$ [Cr(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]

		Computed	
	Experimental	exo$_2$	exo$_3$
Cr–P	2.469(2)	2.473	2.478
Cr–CO(*cis*)(average)	1.91(1)	1.89	1.89
Cr–CO(*trans*)	1.85(1)	1.88	1.88
P–Cr–CO(22)	179.1(3)	173.0	164.1
P–Cr–CO(23)	88.4(3)	93.0	103.9
P–Cr–CO(24)	95.0(3)	95.4	97.8
P–Cr–CO(25)	97.9(3)	88.2	83.9
P–Cr–CO(26)	88.6(3)	87.2	81.8
OC(22)–Cr–CO(23)	91.4(3)	91.8	89.5
OC(22)–Cr–CO(24)	84.1(3)	89.9	91.2
OC(22)–Cr–CO(25)	83.0(3)	86.5	87.4
OC(22)–Cr–CO(26)	91.6(3)	88.0	85.0
OC(23)–Cr–CO(25)	91.1(3)	91.7	90.6
OC(25)–Cr–CO(26)	91.6(3)	88.2	90.5
OC(26)–Cr–CO(24)	90.0(3)	91.1	91.0
OC(24)–Cr–CO(23)	87.9(3)	88.9	87.8
P–C(average)	1.855(8)	1.861	1.870
C(8)–P–C(15)	101.7(4)	99.0	101.9
C(8)–P–C(1)	102.8(4)	102.0	99.3
C(1)–P–C(15)	106.0(4)	103.9	100.2
Cr–P–C(*ipso*)–C(Me)	173	166	42
	66	66	61
	73	78	65
C(8)–P–Cr–C(25)	40	55	43

Table 2 Kinetic data for ring exchange in complexes **1a**–**1c**

Complex	T/K	Rate constant/s^{-1}	$\Delta G^‡$/kJ mol^{-1}
1a	183	39	38.5
	193	135	38.9
	213	1 500	38.5
	233	10 500	38.5
	253	33 000	39.7
	273	60 000	41.8
1b	173	51	35.9
	183	180	36.4
	193	810	35.9
	203	2 400	35.9
	213	7 500	35.9
	223	18 000	35.9
	233	36 000	36.4
1c	183	105	36.8
	193	420	36.8
	203	1 440	36.8
	213	4 350	36.8
	233	36 000	36.4

[Fe(CO)$_4${P(C$_6$H$_4$Me-*o*)$_3$}] ($\Delta G^‡_{273}$ = 46 kJ mol^{-1}) in which the exo$_3$ isomer dominates.

A second fluxional process is evident at lower temperatures involving restriction of rotation about the Cr–P bond. Thus, the room-temperature doublet assigned to the *cis* carbonyls exhibits substantial broadening relative to the *trans* resonance (Fig. 3). The quality of the spectra is limited by the low solubility of complex **1a**. Though a low-temperature limiting spectrum is not obtained, realistic assumptions regarding chemical shift differences place the barrier to Cr–P rotation at $\leqslant$32 kJ mol^{-1}. Barriers to Cr–P rotation in a series of sterically hindered [Cr(CO)$_2$(PPh$_3$)(arene)] complexes are approximately 37 kJ mol^{-1}.[12a,b]

(*b*) *Molecular Mechanics Studies of Complex* **1a**.—We have used recently reported parameters for molecular mechanics

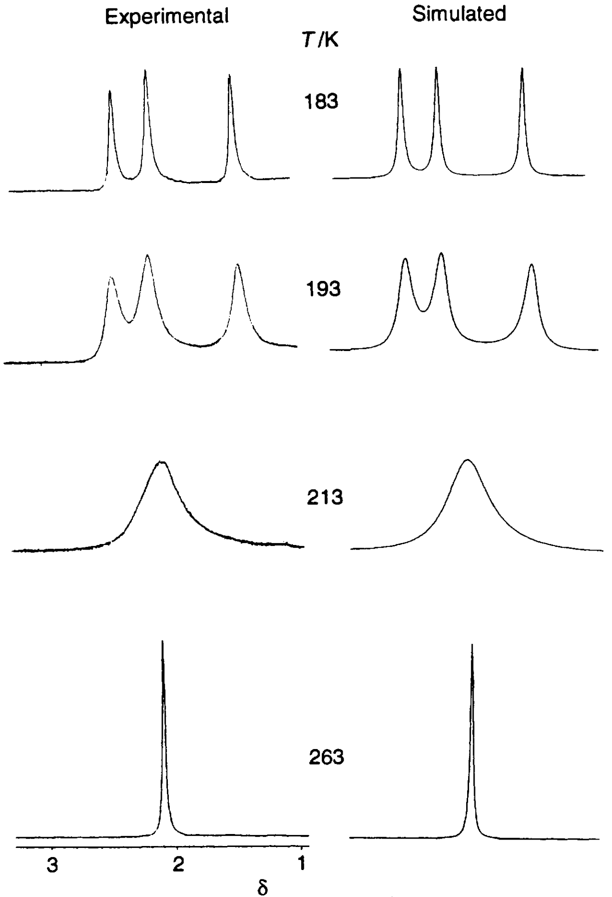


Fig. 2 Experimental and simulated ^1H NMR spectra for $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$

studies of $Cr(CO)_5$(phosphine) complexes[2b,c] to evaluate the relative energies of the exo_2 and exo_3 conformations of $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$. Minimisation starting from the experimentally determined structure maintains an exo_2 configuration (Table 1) in which the bond lengths and intraphosphine bond angles and torsion angles agree closely with observed values. A slight rotation of 15° about the Cr–P axis is accompanied by an equalisation of OC(*trans*)–Cr–CO(*cis*) angles and a relief of steric strain by bending of the phosphine into the octant defined by the *cis*-$(CO)_2$ pair [C(25), C(26)] in which methyl–carbonyl interactions are minimised. Though less, this bending distortion is common to other $Cr(CO)_5$(phosphine) complexes (see above). The origin of the difference between the experimental and minimised exo_2 configurations is not clear. In view of the molecular complexity, it is reasonable to expect that the energy profile may contain several minima of very similar energy, and that *inter*molecular forces may determine the finer details of the observed conformation. The more substantial departure of the minimised structure from octahedral symmetry [P–Cr–C(22) 173°] may also result from assignment of a zero bending force constant for the P–Cr–CO(*trans*) fragment. Such an assignment may overemphasise minimisation of interligand repulsions at the expense of loss of electronic energy in a strictly octahedral configuration.

Minimisation of an exo_3 conformation [generated from the experimental structure by setting of all Cr–P–C(*ipso*)–C(Me) angles to 55°] retains this essential structure, but with a greater bending of the phosphine and consequent bending of C(25), C(26) towards the *trans* CO ligand. In all three structures, approximately 90° interactions between the *cis* CO ligands are maintained. The energy of the minimised exo_3 conformation lies approximately 42 kJ mol^{-1} higher than the minimised exo_2 conformation. The agreement with the measured P–C rotational barrier may be fortuitous, but may indicate that the exo_3 conformation lies at or near the transition state for P–C exchange. The lowest-energy process which results in complete ring exchange in systems of this type has been shown to be the two-ring flip mechanism (Scheme 1), in which ring exchange occurs *via* an exo_3 intermediate.

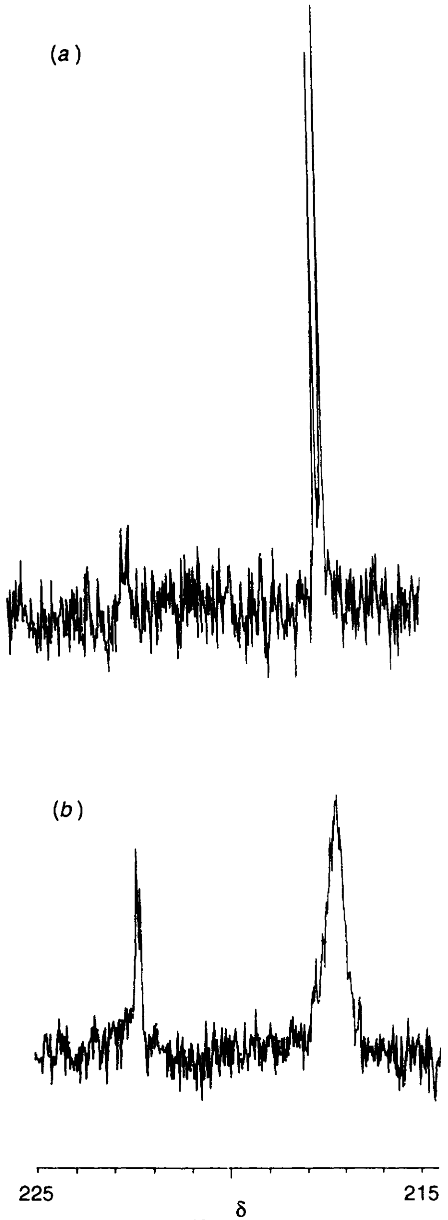
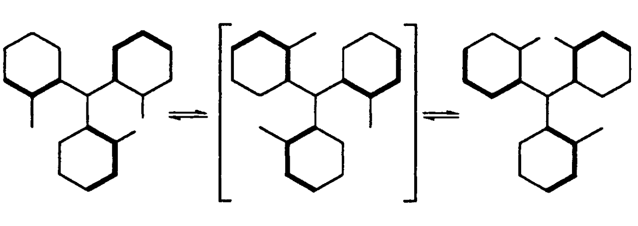
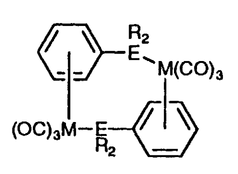


Fig. 3 Variable-temperature ^{13}CO NMR spectra of $[Cr(CO)_5\{P(C_6H_4Me\text{-}o)_3\}]$: (*a*) 293, (*b*) 183 K

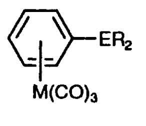


Scheme 1

(*c*) *Molecular Structure of Complex* **2**.—In addition to $[M(CO)_5(ER_3)]$ (R = aryl), the thermal reaction of $[M(CO)_6]$ with ER_3 is known to yield compounds having structures **A** and



A M = Cr, E = P



B M = Cr or Mo
E = P or As

B.[4,13a–f] Complex **B** (M = Cr, E = P) has also been prepared by reaction of [Cr(CO)$_3$(C$_6$H$_5$Li)] with PPh$_2$Cl.[14]

The structure of [Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}] **2** (Fig. 4) resembles that reported for [Cr(CO)$_3$(AsPh$_3$)].[13e] The phosphine retains the exo$_3$ conformation of the free phosphine[10] in which the Cr(CO)$_3$ moiety is bound to the exo surface of the cone. The lp–P–C(11)–C(12) torsion angle (lp = putative lone pair on phosphorus) is particularly diminished to accommodate the Cr(CO)$_3$ group. A simple P–C rotational process does not interconvert the non-complexed rings, and three ^{1}H methyl resonances are retained in C$_6$D$_6$ at temperatures up to +90 °C. Both ^{1}H and ^{31}P NMR spectra are temperature independent down to −90 °C, indicating that only the exo$_3$ conformer is populated.

In both complex **2** and [Cr(CO)$_3$(AsPh$_3$)] the orientation of Cr(CO)$_3$ relative to the ring lies between eclipsed and staggered [OC–Cr–Z–C(ring) 16°, where Z = centroid of co-ordinated ring]. While the bound ring is planar (±0.01 Å), the phosphorus and arsenic atoms are displaced from this plane towards the chromium by 4–5°. While these effects may be steric in origin, there are similar conformations and displacement of substituent towards the metal by 2–3° in other complexes containing the π-accepting CO$_2$Me substituent[15a–e] (in agreement with theoretical prediction).[16] In contrast, in the structures of complexes containing π-donor NR$_2$ or OR substituents[15e,17a,b] the Cr(CO)$_3$ moiety eclipses the π-donor substituent which is bent away from the metal by 3–6°. Distinct deviations from ring planarity are also observed. The results thus seem most consistent with a π-acceptor character for the ER$_2$ substituent.

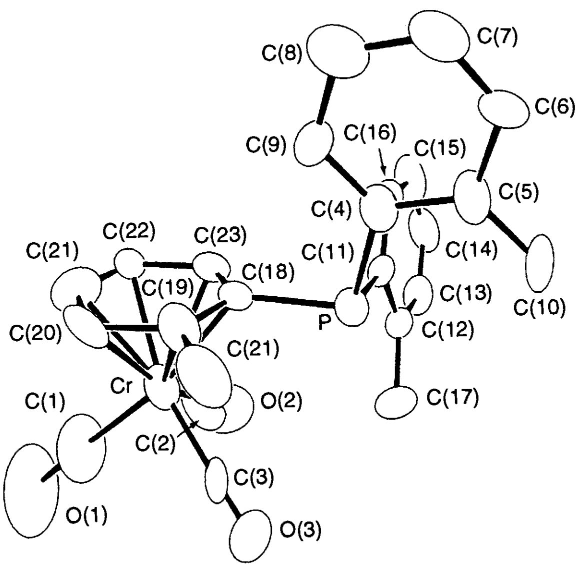


Fig. 4 Molecular structure of [Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}]. Important bond lengths (Å) and angles (°): Cr–CO(average) 1.81(2), Cr–C(ring)-(average) 2.22(1), P–C(18) 1.85(1), P–C(11)/C(4)(average) 1.86(1) and Cr–Z 1.70; OC–Cr–CO(average) 87.6(8), Z–Cr–CO(average) 127.3, C(4)–P–C(11) 100.8(5), C(18)–P–C(4)/C(11)(average) 101.4(6), lp–P–C(4)–C(5) 47.7, lp–P–C(11)–C(12) 28.7 and lp–P–C(18)–C(19) 42.5; Z is the centroid of the co-ordinated ring and lp is the putative lone pair on phosphorus

Experimental

The NMR spectra were recorded using a JEOL GSX 270 spectrometer; temperatures were measured using the in-built copper–constantan thermocouple. Line-shape analyses were performed using the EXCHANGE program.[18] The compound P(C$_6$H$_4$Me-*o*)$_3$ was prepared by a literature method.[19] All solvents were dried and degassed before use.

Syntheses.—[M(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]. Following Bowden and Colton,[4] [Cr(CO)$_6$] (1.0 g, 4.55 mmol) was dissolved in heptane–tetrahydrofuran (thf) (1 : 1, 230 cm^3) and irradiated for 1 h under a flow of nitrogen using a 90 W mercury arc lamp (254 nm). The compound P(C$_6$H$_4$Me-*o*)$_3$ (1.38 g, 4.55 mmol) was added, and after stirring for 30 min the solution was filtered through Celite and solvent removed under reduced pressure. The residue was recrystallised from thf–light petroleum (b.p. 60–80 °C) to give [Cr(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}] as a pale yellow solid (1.4 g, 62%). A crystal suitable for X-ray analysis was grown from ethyl acetate. The molybdenum and tungsten complexes were prepared similarly.

[Cr(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]: m.p. 139–141 °C (Found: C, 62.8; H, 4.15. Calc.: C, 62.9; H, 4.25%); infrared (hexane) 2055, 1947 and 1939 cm^{-1}; δ(^{13}C) 130.0 (36, C^1), 141.4 (8, C^2), 125.0 (10), 130.2, 132.4 (7), 134.3 (14.8) (C$^{3-6}$), 23.8 (5, Me), 216.9 (12, equatorial CO) and 221.8 (6, axial CO); δ(^{1}H) 7.9–7.2 (aryl) and 2.13 (Me); δ(^{31}P) 52.9.

[Mo(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]: m.p. 165 °C (decomp.) (Found: C, 57.8; H, 3.70. Calc.: C, 57.8; H, 3.90%; infrared (hexane) 2065, 1943 and 1932 cm^{-1}; δ(^{13}C) 130.4 (39, C^1), 141.7 (9, C^2), 125.3(10), 130.8, 132.6(7), 134.7 (11) (C$^{3-6}$), 24.0 (5, Me), 206.2 (8, equatorial CO) and 212.0 (22, axial CO); δ(^{1}H) 7.8–7.2 (aryl) and 2.14 (Me); δ(^{31}P) 37.7.

[W(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]: m.p. 194 °C (decomp.) (Found: C, 50.0; H, 3.30. Calc.: C, 49.7; H, 3.35%); infrared (hexane) 2065, 1939 and 1931 cm^{-1}; δ(^{13}C) 131.0 (35, C^1), 142.1 (9, C^2), 125.6(10), 131.0, 133.1 (7), 135.6 (15), (C$^{3-6}$), 24.3 (6, Me), 199.0 (6, equatorial CO) and 200.9 (22, axial CO); δ(^{1}H) 7.8–7.2 (aryl) and 2.15 (Me); δ(^{31}P) 17.9 (J_{WP} = 234 Hz).

[Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}]. The compound [Cr(CO)$_6$] (0.72 g, 3.3 mmol) and P(C$_6$H$_4$Me-*o*)$_3$ (1.0 g, 3.3 mmol) were refluxed in decane (30 cm^3) for 4 h. After filtration and removal of solvent, the residue was purified by preparative TLC (light petroleum, b.p. 40–60 °C) and recrystallised from light petroleum (b.p. 60–80 °C) to give [Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}] as yellow needles (0.3 g, 21%), m.p. 182–183 °C (Found: C, 64.9; H, 4.80. Calc.: C, 65.4; H, 4.75%); infrared (hexane) 1979 and 1911 cm^{-1}; δ(^{1}H) (unco-ordinated rings) 7.2–6.7 (aryl), 1.97 (1.0), 2.12 (2.0) (Me); (co-ordinated ring) 4.8–4.0 (aryl), 2.98 (Me); δ(^{31}P) −30.6.

The NMR spectra were recorded in CD$_2$Cl$_2$ for [M(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}] or C$_6$D$_6$ for [Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}]; chemical shifts are in ppm from SiMe$_4$ (^{13}C and ^{1}H) and 85% H$_3$PO$_4$ (^{31}P); *J*(P–C) and *J*(P–H) values are in parentheses.

Crystallography.—Data were collected on an Enraf-Nonius CAD4F diffractometer using Mo-Kα radiation (λ = 0.710 69 Å). Crystal data are given in Table 3. The structures were solved by direct methods (SHELX 86)[20] and refined by full-matrix least squares (SHELX 76).[21] Data were corrected for Lorentz and polarisation effects, but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. For [Cr(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}] all non-hydrogen atoms were refined anisotropically. For [Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}] the chromium, phosphorus, oxygen and carbon atoms of the methyl and carbonyl groups were refined anisotropically. Atomic scattering factors for non-hydrogen and hydrogen atoms were taken from refs. 22–24. Calculations were performed on a VAX 8700 computer. Atomic coordinates are listed in

Table 3 Crystal data for complexes **1a** and **3**

	[Cr(CO)$_5${P(C$_6$H$_4$Me-*o*)$_3$}]	[Cr(CO)$_3${P(C$_6$H$_4$Me-*o*)$_3$}]
Crystal symmetry	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
a/Å	10.774(2)	16.725(2)
b/Å	14.951(5)	7.340(1)
c/Å	14.687(7)	17.675(4)
β/°	91.45(2)	92.66(2)
U/Å^3	2365(3)	2167(2)
D_c/g cm^{-3}	1.39	1.35
Z	4	4
F(000)	1032	912
Crystal dimensions/mm	0.25 × 0.3 × 0.28	0.15 × 0.2 × 0.4
μ/cm^{-1}	6.83	5.70
2θ range/°	2–48	2–58
No. of unique data	4717	6148
Reflections with $I > 3\sigma(I)$	2326	1848
Variable parameters	209	263
Maximum shift/e.s.d.	< 0.001	< 0.005
Maximum, minimum electron density/e Å^3	0.44, −0.67	0.53, −0.52
R	0.0915	0.1121
R'	0.0980	0.1187

Table 4 Fractional atomic coordinates for [Cr(CO)$_5${P(C$_6$H$_4$-Me-*o*)$_3$}]

Atom	x	y	z
Cr	0.239 28(12)	0.105 75(9)	0.422 01(9)
P	0.255 0(2)	0.267 3(1)	0.455 6(1)
O(1)	0.240 8(9)	0.148 7(6)	0.219 9(5)
O(2)	0.222 6(8)	−0.090 3(5)	0.381 3(6)
O(3)	−0.040 4(7)	0.082 6(5)	0.421 3(5)
O(4)	0.248 6(6)	0.070 0(5)	0.625 5(4)
O(5)	0.514 1(7)	0.066 1(5)	0.406 7(6)
C(7)	0.538 1(10)	0.226 1(8)	0.541 8(8)
C(14)	0.222 4(9)	0.489 2(6)	0.469 3(6)
C(21)	0.020 0(9)	0.246 4(7)	0.584 4(7)
C(22)	0.230 1(9)	−0.015 1(7)	0.396 4(7)
C(23)	0.239 9(10)	0.134 9(7)	0.294 5(7)
C(24)	0.412 8(10)	0.087 4(6)	0.416 5(7)
C(25)	0.063 0(10)	0.096 8(6)	0.418 7(6)
C(26)	0.246 5(8)	0.083 1(6)	0.550 0(7)
C(1)	0.406 5(8)	0.309 7(5)	0.416 4(5)
C(2)	0.404 3(9)	0.360 9(6)	0.336 8(6)
C(3)	0.513 5(10)	0.394 0(7)	0.299 7(7)
C(4)	0.623 9(11)	0.373 8(7)	0.345 1(7)
C(5)	0.627 8(10)	0.321 8(7)	0.418 9(7)
C(6)	0.520 3(9)	0.286 9(6)	0.458 9(6)
C(8)	0.141 9(7)	0.341 4(5)	0.395 9(5)
C(9)	0.055 7(8)	0.301 3(5)	0.337 3(5)
C(10)	−0.033 1(8)	0.349 6(6)	0.288 8(6)
C(11)	−0.038 2(9)	0.441 3(7)	0.299 1(7)
C(12)	0.045 6(9)	0.481 3(6)	0.358 6(6)
C(13)	0.137 0(8)	0.434 6(6)	0.408 4(6)
C(15)	0.242 3(7)	0.305 2(5)	0.575 4(5)
C(16)	0.339 7(8)	0.349 3(6)	0.619 2(6)
C(17)	0.335 5(9)	0.376 8(6)	0.709 3(6)
C(18)	0.233 6(9)	0.357 6(6)	0.759 0(7)
C(19)	0.132 7(9)	0.315 0(6)	0.715 7(6)
C(20)	0.134 4(8)	0.288 2(5)	0.625 0(6)

Table 5 Fractional atomic coordinates for [Cr(CO)$_3${P(C$_6$H$_4$-Me-*o*)$_3$}]

Atom	x	y	z
Cr	0.6420(1)	0.1232(3)	0.1276(1)
P	0.7962(2)	0.0709(5)	0.2786(2)
O(1)	0.5470(9)	0.2556(24)	−0.0076(9)
O(3)	0.7364(7)	0.4669(19)	0.1301(6)
O(2)	0.5210(8)	0.3050(21)	0.2195(9)
C(1)	0.5845(10)	0.2016(27)	0.0461(10)
C(2)	0.5689(9)	0.2348(29)	0.1840(9)
C(3)	0.6966(10)	0.3396(24)	0.1300(8)
C(4)	0.8665(6)	−0.1214(20)	0.2986(7)
C(5)	0.9298(7)	−0.0862(22)	0.3519(7)
C(6)	0.9839(8)	−0.2329(23)	0.3645(8)
C(7)	0.9774(8)	−0.3941(23)	0.3296(8)
C(8)	0.9140(9)	−0.4237(21)	0.2773(9)
C(9)	0.8589(8)	−0.2899(21)	0.2620(8)
C(10)	0.9397(9)	0.0863(23)	0.3933(9)
C(11)	0.7307(6)	0.0529(17)	0.3604(7)
C(12)	0.6912(7)	0.2060(19)	0.3842(7)
C(13)	0.6447(7)	0.1908(24)	0.4482(8)
C(14)	0.6409(9)	0.0301(31)	0.4864(8)
C(15)	0.6809(7)	−0.1187(23)	0.4631(7)
C(16)	0.7268(7)	−0.1071(20)	0.4000(7)
C(17)	0.6969(9)	0.3878(19)	0.3449(9)
C(18)	0.7316(7)	−0.0266(18)	0.2008(6)
C(19)	0.7599(8)	−0.0196(20)	0.1275(7)
C(20)	0.7100(8)	−0.0873(22)	0.0656(7)
C(21)	0.6321(9)	−0.1527(22)	0.0799(10)
C(22)	0.6067(10)	−0.1620(20)	0.1522(9)
C(23)	0.6542(7)	−0.0953(18)	0.2134(7)
C(24)	0.8411(8)	0.0527(25)	0.1085(8)

Tables 4 and 5. In both cases the crystals were of poor quality and diffracted weakly. The relatively high R factors are probably due to the relatively small proportion of observed data.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Molecular Mechanics Calculations.—Calculations were performed using the MM2(91) program[25] adapted for six-coordination and incorporating parameters reported for [Cr(CO)$_5$(phosphine)] complexes.[2b,c] Calculations were run on the Sequent Symmetry S81 computer at Keele University.

References

1 (*a*) K. Mislow, *Chemtracts: Org. Chem.*, 1989, **2**, 151; (*b*) K. Mislow, *Acc. Chem. Res.*, 1976, **9**, 26.

2 (*a*) T. L. Brown, *Inorg. Chem.*, 1992, **31**, 1286; (*b*) K. J. Lee and T. L. Brown, *Inorg. Chem.*, 1992, **31**, 289; (*c*) M. L. Caffery and T. L. Brown, *Inorg. Chem.*, 1991, **30**, 3907; (*d*) S. G. Davies, A. E. Derome and J. P. McNally, *J. Am. Chem. Soc.*, 1991, **113**, 2854; (*e*) S. C. Mackie and M. C. Baird, *Organometallics*, 1992, **11**, 3713; (*f*) J. Polowin, S. C. Mackie and M. C. Baird, *Organometallics*, 1992, **11**, 3724.

3 J. A. S. Howell, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. E. Gottlieb and D. Hezroni-Langerman, *Inorg. Chem.*, 1991, **30**, 4685.

4 J. A. Bowden and R. Colton, *Aust. J. Chem.*, 1971, **24**, 2471.

5 (*a*) F. A. Cotton, D. J. Darensbourg and W. H. Ilsley, *Inorg. Chem.*, 1981, **20**, 578; (*b*) W. P. Meier, J. Strahle and E. Lindner, *Z. Anorg. Allg. Chem.*, 1976, **424**, 154; (*c*) H. J. Plastas, J. M. Stewart and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.

6 F. A. Cotton, D. J. Darensbourg and B. W. S. Kolthammer, *Inorg. Chem.*, 1981, **20**, 4440.

7 CHEM-X, Chemical Design Limited, Oxford.

8 (*a*) E. C. Alyea, S. A. Dias, G. Ferguson and P. J. Roberts, *J. Chem. Soc., Dalton Trans.*, 1979, 948; (*b*) R. Brady, W. H. DeCamp, B. R. Flynn, M. I. Schneider, J. D. Scott, L. Vaska and M. F. Werneke, *Inorg. Chem.*, 1975, **14**, 2669.

9 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

10 T. S. Cameron and B. Dahlen, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1737.

11 J. A. S. Howell, M. G. Palin, P. C. Yates, P. McArdle, D. Cunningham, Z. Goldschmidt, H. E. Gottlieb and D. Hezroni-Langerman, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1769.

12 (*a*) J. A. Chudek, G. Hunter, R. L. MacKay, P. Kremminger, K. Schlogl and W. Weissensteiner, *J. Chem. Soc., Dalton Trans.*, 1990,

2001; (*b*) G. Hunter, T. J. R. Weakley and W. Weissensteiner, *J. Chem. Soc., Dalton Trans.*, 1987, 1545.

13 (*a*) J. A. Bowden and R. Colton, *Aust. J. Chem.*, 1973, **26**, 43; (*b*) G. B. Robertson and P. O. Whimp, *J. Organomet. Chem.*, 1973, **60**, C11; (*c*) C. E. Elschenbroich and F. Stohler, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 174; (*d*) G. B. Robertson and P. O. Whimp, *Chem. Commun.*, 1971, 573; (*e*) H. J. Wasserman, M. J. Wovkulich, J. D. Atwood and M. R. Churchill, *Inorg. Chem.*, 1980, **19**, 2831; (*f*) E. C. Alyea, G. Ferguson and A. Somogyvari, *Organometallics*, 1983, **2**, 669.

14 V. I. Losilkina, N. K. Estekhina, N. K. Baranetskaya and V. N. Setkina, *J. Organomet. Chem.*, 1986, **299**, 187.

15 (*a*) J. Y. Saillard and D. Grandjean, *Acta Crystallogr., Sect. B*, 1976, **32**, 2285; (*b*) J. Y. Saillard and D. Grandjean, *Acta Crystallogr., Sect. B*, 1978, **34**, 3773; (*c*) J. Y. Saillard, D. Grandjean, A. Le Beuze and G. Simmoneaux, *J. Organomet. Chem.*, 1981, **204**, 197; (*d*) J. Y. Saillard, G. Le Borgne and D. Grandjean, *J. Organomet. Chem.*, 1975, **94**, 409; (*e*) A. D. Hunter, L. Shilliday, W. S. Furey and M. J. Zaworotko, *Organometallics*, 1992, **11**, 1550.

16 E. L. Muetterties, J. R. Bleeke, E. J. Wucherer and T. A. Albright, *Chem. Rev.*, 1982, **82**, 499.

17 (*a*) P. Le Maux, J. Y. Saillard, D. Grandjean and G. Jaouen, *J. Org. Chem.*, 1980, **45**, 4526; (*b*) K. Schollkopf, J. J. Stezowski and F. Effenberger, *Organometallics*, 1985, **4**, 922.

18 R. E. D. McClung, EXCHANGE, University of Alberta.

19 T. Allmann and R. G. Goel, *Can. J. Chem.*, 1982, **60**, 716.

20 G. M. Sheldrick, SHELX 86, A Computer Program for Crystal Structure Determination, University of Göttingen, 1986.

21 G. M. Sheldrick, SHELX 76, A Computer Program for Crystal Structure Determination, University of Cambridge, 1976.

22 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

23 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

24 D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

25 N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.

Received 29th *April* 1993; *Paper* 3/02463F