Crystal Structures of $[W(CO)_5(PPh_3)]$, $[M(CO)_5(AsPh_3)]$ and $[M(CO)_5(SbPh_3)]$ (M = Mo or W): A Comparative Study of Structure and Bonding in $[M(CO)_5(EPh_3)]$ Complexes (E = P, As or Sb; M = Cr, Mo or W)†

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Crystal structures have been determined for $[W(CO)_5(PPh_3)]$, $[M(CO)_5(AsPh_3)]$ and $[M(CO)_5(SbPh_3)]$ (M = Mo or W) as part of a systematic study of a series of nine $[M(CO)_5(EPh_3)]$ complexes (M = Cr, Mo or W; E = P, As or Sb). Trends in bond lengths and angles are rationalised in terms of steric and electronic interactions between the bonded $M(CO)_5$ and EPh_3 fragments. Comparison is made between the solid-state geometry of the free and co-ordinated EPh_3. Torsion angles defining the disposition of the EPh_3 groups in relation to $M(CO)_5$ show little variation within the $[M(CO)_5(EPh_3)]$ series. For all nine complexes the EPh_3 groups have propeller geometry with small deviations from symmetric C_3 structures. The studies were extended to include other related $[M(CO)_5L]$ complexes. Trends in the structural parameters of 29 such compounds are related to the steric behaviour and π-acceptor capacity of the ligands L. It is shown that M–P bond dimensions are not adequately explained by hybridisation changes of the phosphorus atom in the ligand L.

This work is part of a continuing programme of study of the electronic and steric factors which affect metal–ligand interactions in $[M(CO)_5L]$ transition-metal complexes.[1–5] Knowledge of such factors can be important in understanding the course of metal-centred reactions in complexes and in the design and fine-tuning of organometallic catalytic systems.

In this paper crystal structure determinations are reported for the complexes $[W(CO)_5(PPh_3)]$, $[Mo(CO)_5(AsPh_3)]$, $[W(CO)_5(AsPh_3)]$, $[Mo(CO)_5(SbPh_3)]$ and $[W(CO)_5(SbPh_3)]$. The structures presented complete a series of nine having the general formula $[M(CO)_5(EPh_3)]$ (E = P, As or Sb; M = Cr, Mo or W). Variations in M–E, M–C and CO bond lengths, in bond angles about E and M, and in the torsion angles defining molecular conformations about rotation axes M–E and E–C_{ar} are examined in relation to the donor atom E and the metal M. Comparison is made between the solid-state geometry of the free EPh_3 molecule and that of the corresponding ligand bonded to M. Finally, the structures described are compared with those of other related $[M(CO)_5L]$ complexes to gauge trends in the structural parameters across a series of twenty-nine compounds and to rationalise these in terms of the more important factors contributing to the M–L bonding.

Experimental

Synthesis.—All the complexes $[M(CO)_5(EPh_3)]$ were prepared by photolysis of $[M(CO)_6]$ under nitrogen in sodium-dried tetrahydrofuran (thf). Addition of EPh_3 to the resulting $[M(CO)_5(thf)]$ solution produced the required complexes in high yield.[6,7] They were purified by evaporation of the solvent *in vacuo* followed by vacuum sublimation at 60 °C to remove unreacted $[M(CO)_6]$. The residue was rinsed with cold hexane to dissolve unreacted EPh_3, then chromatographed on a silica column (Keiselgel 60, mesh 70–230). Hexane eluted $[M(CO)_5(EPh_3)]$ as a slow band. Further elution with benzene gave *cis*-$[M(CO)_4(EPh_3)_2]$ in trace amounts. The compounds were recrystallised from hexane and the purity was determined in each case by comparison of the melting point and of the carbonyl infrared spectra with those reported.[8–10]

X-Ray Analysis.—Crystals of the $[M(CO)_5(EPh_3)]$ complexes were grown from hexane at 0 °C over a period of several days. Lattice parameters at 293 K were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf–Nonius CAD4F four-circle diffractometer employing graphite-monochromated Mo-Kα (λ 0.710 69 Å) radiation. Data were collected over the range $0 < 2\theta < 50°$. The scan modes and widths used are listed in Table 1. N Independent reflections were obtained and N_o with $I > 2.5\sigma(I)$ were considered observed and used in the full-matrix least-squares refinement after numerical absorption correction.[11]

The structures of $[W(CO)_5(PPh_3)]$ and $[W(CO)_5(SbPh_3)]$ were solved by heavy-atom methods and the other three by direct methods using SHELXS 86[12] and the solutions were extended by Fourier-difference methods. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions with isotropic thermal parameters. The weighting schemes employed for each complex along with R and R' are listed in Table 1. Maximum excursions in the final difference maps are also in Table 1. Scattering factors and anomalous dispersion terms for Mo and W were taken from ref. 13 and all others used were supplied in SHELX 76.[12] The calculations were carried out using SHELX 76 and plots were drawn using ORTEP.[14]

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

Results and Discussion

All five $[M(CO)_5(EPh_3)]$ complexes examined are isostructural in the triclinic space group $P\bar{1}$. No unusually close contacts between molecules are observed. Crystal data are summarised in Table 1. Fractional atomic coordinates are listed in Table 7. An ORTEP plot of $[W(CO)_5(AsPh_3)]$ with atomic numbering

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Crystal data, experimental conditions and refinements *

	[W(CO)$_5$(PPh$_3$)]	[Mo(CO)$_5$(AsPh$_3$)]	[W(CO)$_5$(AsPh$_3$)]	[Mo(CO)$_5$(SbPh$_3$)]	[W(CO)$_5$(SbPh$_3$)]
Empirical formula	$C_{23}H_{15}O_5PW$	$C_{23}H_{15}AsMoO_5$	$C_{23}H_{15}AsO_5W$	$C_{23}H_{15}MoO_5Sb$	$C_{23}H_{15}O_5SbW$
M	586.19	542.23	630.145	586.17	674.08
Colour, habit	Yellow plates	Colourless prisms	Yellow plates	Colourless, plates	Cream, columnar
Crystal size/mm	0.22 × 0.10 × 0.32	0.21 × 0.24 × 0.28	0.188 × 0.075 × 0.125	0.175 × 0.320 × 0.048	0.26 × 0.22 × 0.09
a/Å	9.468(2)	9.496 6(10)	9.490 1	9.526(1)	9.509(2)
b/Å	9.657(1)	9.712 6(6)	9.743 9	9.814(2)	9.845(2)
c/Å	12.232(5)	12.415(2)	12.350	12.591(2)	12.546(2)
α/°	74.51(2)	105.08(1)	105.46	104.60(1)	104.88(1)
β/°	89.19(2)	90.56(1)	90.43	92.96(1)	92.75(2)
γ/°	84.40(1)	95.16(1)	95.12	93.80(1)	93.83(2)
U/Å^3	1072.5	1100.5(2)	1095.72	1133.6(3)	1129.96
D_c/g cm^{-3}	1.815	1.635	1.913	1.724	2.343
μ(Mo-Kα)/cm^{-1}	55.70	21.0	68.82	17.66	32.24
F(000)	564	535.88	599.87	571.91	623.99
Scan type	ω–1.33θ	ω–1.33θ	ω–2θ	ω–0.67θ	ω–1.33θ
Scan width	0.90 + 0.35 tan θ	0.90	1.00	0.95 + 0.35 tan θ	0.8 + 0.35 tan θ
hkl ranges	0–11, −11 to 11, −14 to 14	−12 to 12, −12 to 12, 0–16	−11 to 11, −11 to 11, 0–14	−11 to 11, −11 to 11, 0–15	−11 to 11, −11 to 11, 0–14
Reflections collected, *N*	4025	5283	4052	4192	4174
Reflections observed, N_o	3517	3987	3306	3433	3738
Minimum, maximum transmission		0.485–0.704	0.272–0.600	0.748 3–0.919 8	0.510 2–0.730 9
Quantity minimised		4647	3636	3758	3900
Extinction correction		0.001 29(2)	−0.001 7(2)	0.000 27(2)	0.000 32(3)
Weighting scheme		1.5165 1.01 × 10^{-4}	1.0815 8.16 × 10^{-4}	1.2091 1.17 × 10^{-4}	5.055 57 7.61 × 10^{-4}
R	0.020	0.0227	0.0285	0.0231	0.0482
R′	0.022	0.0251	0.0345	0.0264	0.0491

* Details in common: triclinic, space group $P\bar{1}$; $Z = 2$; 2θ 2–50°; $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w F_o{}^2)]^{\frac{1}{2}}$.

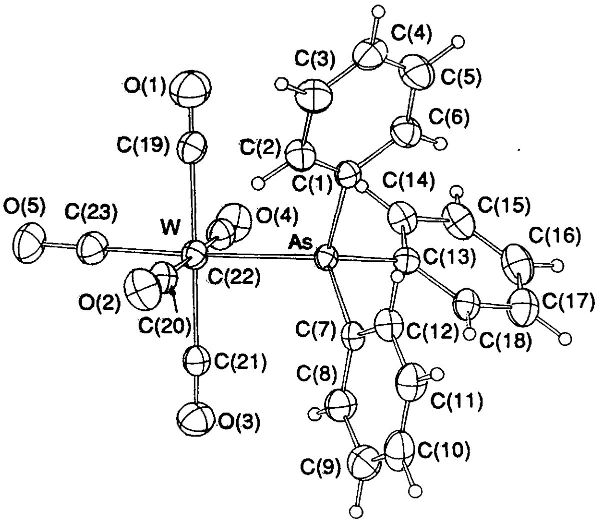

Fig. 1 An ORTEP[14] plot (30% thermal ellipsoids) of [W(CO)$_5$(AsPh$_3$)] with atomic numbering

is shown as an example in Fig. 1. Selected bond lengths and angles are given in Table 2. The crystal structures of the other four members of the series, [Cr(CO)$_5$(PPh$_3$)], [Mo(CO)$_5$(PPh$_3$)], [Cr(CO)$_5$(AsPh$_3$)] and [Cr(CO)$_5$(SbPh$_3$)], have been reported previously.[15–18]

Bond Distances.—Comparisons of selected bond distances within the group of nine complexes are given in Table 3. The M–E bond lengths increase with increasing donor atom size (*i.e.* P < As < Sb). Those for the chromium complexes are appreciably shorter than for those of the molybdenum and tungsten analogues which are similar. The Mo–P bond is slightly longer than W–P despite the closeness in atom size of Mo and W. The difference may be due to variations in metal–phosphorus overlap, though this is not reflected in the infrared carbonyl stretching frequencies which are almost identical for the two complexes.[5]

For each of the complexes studied the distance from M to the carbonyl *trans* to EPh$_3$ (M–C$_{ax}$) is shorter than that from M to the *cis* carbonyl groups (M–C$_{eq}$); the differences are greater than the uncertainties in the experimental data. Such observations accord with the notion that M–C π bonding is more pronounced for the M–CO bond which is *trans* to L and that the EPh$_3$ ligands are weaker π acceptors than is CO.

Both the M–C$_{ax}$ and M–C$_{eq}$ bond distances show small variations with change of ligand donor atom E; M–C increases in the order P < As < Sb (Cr–C$_{ax}$), P < As ≈ Sb (Cr–C$_{eq}$), As < Sb ⩽ P (Mo–C$_{ax}$ and W–C$_{ax}$), P ≈ As ≈ Sb (Mo–C$_{eq}$ and W–C$_{eq}$). No overall consistent pattern emerges. It has been shown by Cotton and Wing[19] that CO bond lengths in metal carbonyl complexes are relatively insensitive to subtle changes in CO bond order. The CO lengths axial and equatorial to EPh$_3$ are generally found to be in close agreement for each complex. The maximum deviation from equality of the *cis* and *trans* CO bond lengths occurs in [W(CO)$_5$(AsPh$_3$)] where that for the *trans* CO is 3% longer than the average of those for *cis* CO.

The E–C$_{ar}$ bond lengths for the co-ordinated EPh$_3$ (column 7 of Table 3) increase from P to Sb and are comparable with the analogous bond distances in the crystal structures of the non-complexed EPh$_3$ molecules. The crystal structure of PPh$_3$, first determined by Daly,[20] has since been reinvestigated by Dunne and Orpen[21] at 200 K who found the P–C$_{ar}$ bond distances to be approximately equal at 1.831(2) Å. The average As–C$_{ar}$ bond length in AsPh$_3$ was reported by Sobolev *et al.*[22] to be 1.957(8) Å and that of Sb–C$_{ar}$ in SbPh$_3$ is 2.120(7) Å.[23]

Bond Angles.—The bond angles M–E–C$_{ar}$ (θ) and the torsion angles M–E–C$_{ar}$–C$_{ar}$ (φ) and C$_{eq}$–M–E–C$_{ar}$ (ω) are listed in Tables 4 and 5 and depicted in Fig. 2. In the crystal structures of all the [M(CO)$_5$(EPh$_3$)] compounds the three M–E–C$_{ar}$ bond angles are unequal. The average M–E–C$_{ar}$ angle is found to be dependent upon the donor atom of the EPh$_3$ ligand and largely independent of the metal. Mean values are 115.6° for [M(CO)$_5$(PPh$_3$)], 116.6° for [M(CO)$_5$(AsPh$_3$)] and 118.0° for

Table 2 Selected bond lengths (Å) and angles (°) for $[M(CO)_5(EPh_3)]$ complexes

	$[W(CO)_5(PPh_3)]$	$[Mo(CO)_5(AsPh_3)]$	$[W(CO)_5(AsPh_3)]$	$[Mo(CO)_5(SbPh_3)]$	$[W(CO)_5(SbPh_3)]$
M–E	2.545(1)	2.612(0)	2.617(1)	2.756(0)	2.753(0)
M–C(19)	2.027(5)	2.046(3)	2.038(7)	2.037(4)	2.022(7)
M–C(20)	2.046(6)	2.028(3)	2.015(7)	2.031(4)	2.046(8)
M–C(21)	2.044(6)	2.036(3)	2.031(6)	2.032(3)	2.048(7)
M–C(22)	2.015(5)	2.046(3)	2.038(7)	2.058(4)	2.022(7)
M–C(23)	2.006(5)	1.975(3)	1.961(7)	1.989(4)	1.993(7)
E–C(1)	1.829(4)	1.952(2)	1.947(6)	2.131(3)	2.134(6)
E–C(7)	1.832(4)	1.941(2)	1.949(6)	2.133(3)	2.146(6)
E–C(13)	1.832(4)	1.948(2)	1.954(5)	2.132(3)	2.132(6)
C(19)–O(1)	1.135(7)	1.132(3)	1.111(8)	1.137(4)	1.147(8)
C(20)–O(2)	1.134(7)	1.134(3)	1.143(8)	1.134(4)	1.142(9)
C(21)–O(3)	1.129(7)	1.141(3)	1.116(8)	1.139(4)	1.122(9)
C(22)–O(4)	1.142(7)	1.133(3)	1.140(8)	1.133(4)	1.130(9)
C(23)–O(5)	1.125(6)	1.129(3)	1.164(9)	1.142(4)	1.147(9)
C(19)–M–E	94.2(1)	88.0(1)	87.9(2)	88.2(1)	91.1(2)
C(20)–M–C(19)	88.6(2)	91.5(1)	91.9(3)	91.0(2)	88.3(3)
C(21)–M–C(19)	177.3(2)	177.8(1)	178.0(2)	177.9(1)	177.4(3)
C(22)–M–E	87.4(2)	95.0(1)	95.6(2)	93.5(1)	87.0(2)
C(22)–M–C(20)	176.6(2)	177.1(1)	176.6(2)	178.8(1)	179.2(3)
C(23)–M–E	174.2(2)	174.6(1)	174.0(2)	174.8(1)	174.1(2)
C(23)–M–C(20)	88.6(2)	87.8(1)	87.7(3)	87.9(2)	91.8(3)
C(23)–M–C(22)	88.2(2)	89.5(1)	89.3(3)	91.0(2)	88.0(3)
C(7)–E–M	116.3(1)	116.8(1)	116.8(2)	117.8(1)	117.7(2)
C(13)–E–M	118.4(1)	120.6(1)	120.6(2)	122.7(1)	122.4(2)
C(13)–E–C(7)	102.0(2)	100.2(1)	100.2(2)	98.0(1)	98.1(2)
C(6)–C(1)–E	118.6(4)	122.3(2)	123.0(5)	118.0(3)	121.6(5)
C(12)–C(7)–E	119.1(4)	121.7(2)	122.0(5)	121.7(4)	118.4(5)
C(18)–C(13)–E	119.5(4)	122.1(2)	122.3(4)	121.1(3)	119.0(5)
O(2)–C(20)–M	175.9(5)	178.4(2)	178.2(6)	179.0(4)	178.3(7)
O(4)–C(22)–M	177.9(5)	177.0(3)	178.1(6)	178.5(4)	177.7(7)
C(20)–M–E	95.8(2)	87.8(1)	87.5(2)	87.6(1)	93.2(2)
C(21)–M–E	87.5(2)	93.1(1)	93.1(2)	91.6(1)	88.1(2)
C(21)–M–C(20)	89.3(2)	90.4(1)	89.9(2)	91.1(1)	89.3(3)
C(22)–M–C(19)	90.1(2)	89.2(1)	89.6(3)	89.5(2)	91.0(3)
C(22)–M–C(21)	91.9(2)	88.9(1)	88.6(2)	88.5(1)	91.5(3)
C(23)–M–C(19)	89.5(2)	89.0(1)	88.8(3)	89.3(1)	92.3(3)
C(23)–M–C(21)	88.9(2)	90.1(1)	90.4(3)	91.0(2)	88.8(3)
C(1)–E–M	111.6(1)	112.1(1)	112.8(2)	114.0(1)	113.8(2)
C(7)–E–C(1)	103.0(2)	101.8(1)	101.4(2)	99.1(1)	99.4(2)
C(13)–E–C(1)	103.6(2)	102.7(1)	102.2(2)	101.4(1)	101.9(2)
C(2)–C(1)–E	123.4(4)	118.3(2)	118.3(4)	122.6(3)	118.0(5)
C(8)–C(7)–E	122.5(4)	118.9(2)	119.0(5)	118.9(3)	121.3(5)
C(14)–C(13)–E	121.9(4)	118.8(2)	117.8(5)	119.8(2)	121.0(5)
O(1)–C(19)–M	176.9(5)	179.2(3)	179.1(7)	179.7(2)	177.8(6)
O(3)–C(21)–M	178.3(6)	177.3(2)	177.8(6)	178.5(3)	178.5(8)
O(5)–C(23)–M	177.9(5)	178.2(3)	178.6(6)	178.0(4)	178.4(7)

Table 3 Average bond lengths (Å) for the $[M(CO)_5(EPh_3)]$ complexes

Compound	M–E	$M-C_{ax}$	$M-C_{eq}$	$C-O_{ax}$	$C-O_{eq}$	$E-C_{ar}$	$C_{ar}-C_{ar}$
$[Cr(CO)_5(PPh_3)]$[15,16]	2.422(1)	1.845(4)	1.880(4)	1.154(5)	1.147(6)	1.828(4)	1.373
$[Mo(CO)_5(PPh_3)]$[18]	2.560(1)	1.995(3)	2.046(8)	1.142(4)	1.134(6)	1.832(4)	1.377
$[W(CO)_5(PPh_3)]$	2.545(1)	2.006(5)	2.033(5)	1.125(6)	1.135(6)	1.831(4)	1.377
$[Cr(CO)_5(AsPh_3)]$[17]	2.4972(5)	1.859(3)	1.897	1.147(4)	1.139	1.947(3)	1.375
$[Mo(CO)_5(AsPh_3)]$	2.612(0)	1.975(3)	2.039(3)	1.129(3)	1.135(3)	1.947(5)	1.377
$[W(CO)_5(AsPh_3)]$	2.617(1)	1.961(7)	2.031(7)	1.164(9)	1.125(9)	1.950(6)	1.374
$[Cr(CO)_5(SbPh_3)]$[17]	2.6170(3)	1.865(3)	1.899	1.136(4)	1.140	2.133(3)	1.375
$[Mo(CO)_5(SbPh_3)]$	2.756(0)	1.989(4)	2.040(4)	1.142(4)	1.136(3)	2.132(3)	1.376
$[W(CO)_5(SbPh_3)]$	2.753(0)	1.993(7)	2.035(7)	1.147(8)	1.135(8)	2.137(6)	1.382

$[M(CO)_5(SbPh_3)]$ showing a progressive closing up of the $E(C_{ar})_3$ pyramid with increasing size of E. A commensurate decrease occurs in the angles C_{ar}–E–C_{ar}, the average values of which are listed in column 8 of Table 4. For the free EPh_3 in the solid state the C_{ar}–E–C_{ar} bond angles are 102.8 ± 0.9 (P), 100.1 ± 0.4 (As) and 97.8 ± 1.0° (Sb),[20–23] *i.e.* very little change is observed upon complexation with $[M(CO)_5]$.

From Table 4 it is seen that the average C_{eq}–M–E bond angles for the $[M(CO)_5(EPh_3)]$ complexes deviate by less than 2° from the 90° expected for regular octahedral geometry about M. The EPh_3 ligand is tilted relative to the $M(CO)_5$ moiety with the C_{ax}–M–E bond angle 174.5 ± 0.5° throughout. The C_{eq}–M–E angles are marginally greater for the chromium complexes. Reasons advanced to explain such tilting include symmetry mismatch between ER_3 and the $M(CO)_4$ plane,[24] the alleviation of steric interactions between the groups,[18] and intermolecular interactions in the crystal lattice.

The C_{eq}–M–E–C_{ar} torsion angles (ω) specify the disposition

Table 4 Bond angles (°) E–M–CO_{ax}, E–M–CO_{eq}, M–E–C_{ar} (θ) and C_{ar}–E–C_{ar} for [$M(CO)_5(EPh_3)$]

Compound	E–M–CO_{ax}	E–M–CO_{eq} (average)	θ_1	θ_2	θ_3	θ_{av}	C_{ar}–M–C_{ar} (average)
[$Cr(CO)_5(PPh_3)$][15,16]	174.3	91.6	118.1	116.6	112.3	115.7	102.6
[$Mo(CO)_5(PPh_3)$][18]	174.4	91.5	118.7	116.5	111.7	115.6	102.6
[$W(CO)_5(PPh_3)$]	174.2	91.7	118.4	116.3	111.6	115.4	102.9
[$Cr(CO)_5(AsPh_3)$][17]	174.7	91.0	119.7	118.4	112.9	116.6	101.4
[$Mo(CO)_5(AsPh_3)$]	174.6	91.0	120.6	116.8	112.1	116.5	101.6
[$W(CO)_5(AsPh_3)$]	174.0	91.0	120.6	116.8	112.8	116.7	101.3
[$Cr(CO)_5(SbPh_3)$][17]	175.0	90.1	121.8	117.9	114.1	117.9	99.2
[$Mo(CO)_5(SbPh_3)$]	174.8	90.2	122.7	117.8	114.0	118.2	99.5
[$W(CO)_5(SbPh_3)$]	174.1	89.9	122.4	117.7	113.8	118.0	99.8

Table 5 Dihedral (torsion) angles (°) C_{eq}–M–E–C_{ar} (ω) and M–E–C_{ar}–C_{ar} (φ) for [$M(CO)_5(EPh_3)$]

Compound	ω_1	φ_1	φ_2	φ_3	φ_{av}
[$Cr(CO)_5(PPh_3)$][15,16]	44.9	48.7	54.5	47.7	50.3
[$Mo(CO)_5(PPh_3)$][18]	47.2	47.0	56.0	44.5	49.2
[$W(CO)_5(PPh_3)$]	—	44.0	51.0	54.0	50.0
[$Cr(CO)_5(AsPh_3)$][17]	45.1	45.6	52.3	50.0	49.3
[$Mo(CO)_5(AsPh_3)$]	44.4	50.4	41.6	51.9	48.0
[$W(CO)_5(AsPh_3)$]	44.6	49.0	42.4	52.0	47.8
[$Cr(CO)_5(SbPh_3)$][17]	43.6	44.9	52.4	40.9	46.1
[$Mo(CO)_5(SbPh_3)$]	43.5	45.6	52.1	36.2	44.6
[$W(CO)_5(SbPh_3)$]	44.9	45.2	52.7	36.9	44.9

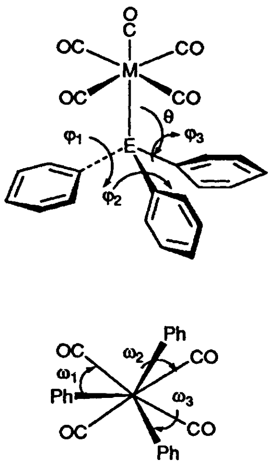

Fig. 2 Illustration of the angles θ, φ and ω for [$M(CO)_5(EPh_3)$]

of the EPh_3 group in relation to the near-planar $M(CO)_4$ moiety. In each of the nine [$M(CO)_5(EPh_3)$] complexes one M–E–C_{ar} plane bisects the angle between vicinal equatorial M–CO groupings so that the torsion angle ω_1 is approximately 45°, see Table 5; the other two E–C_{ar} bonds have ω_2 and ω_3 values of *ca.* ± 15° relative to $M(CO)_4$ as indicated in Fig. 1.

The M–E–C_{ar}–C_{ar} torsion angles (φ) in Table 5 depict the phenyl-ring orientations relative to a reference model, for which the φ values are 0°, having the ring planes parallel to the M–E bond axis. In all cases the torsion angles φ are unequal but deviations from regular C_3 propeller geometry for the M–EPh_3 fragments are not great. The PPh_3 ligand in these complexes differs in geometry from the solid-state configuration of molecular PPh_3 which is highly asymmetric with φ values of 25, 27 and 59°.[21] In the crystal, $AsPh_3$ and $SbPh_3$ molecules are more symmetric with structures not greatly distorted from a C_3 propeller.[22,23] It may be that intermolecular interactions are more important in the case of the EPh_3 molecules since PPh_3, $AsPh_3$ and $SbPh_3$ are not isostructural.

Comparisons with other [$M(CO)_5L$] *Complexes.*—Bond lengths of [$M(CO)_5(EPh_3)$] are compared in Table 6 with analogous parameters for other [$M(CO)_5L$] complexes drawn from crystal structures in the literature. Most studied have been chromium complexes with phosphorus-donor ligands and for this reason the present discussion on M–L bond lengths is concentrated on M–P.

Significant variations are seen in the Cr–P bond distances in Table 6, a consequence of the different steric and electronic properties of the ligands L. An approximately regular plot is found for the PH_3, $P(CH_2CH_2CN)_3$, PMe_3, PPh_3 and $P(C_6H_4Me\text{-}o)_3$ complexes such that the Cr–P bond distance enlarges with increase of the Tolman cone angle[35] for the phosphorus ligand L (Fig. 3). It is seen that the complexes with highly electron-withdrawing OPh, Cl or Br substituents on phosphorus lie beneath this plot and have distinctly shorter Cr–P bonds. The bond lengths increase in the order $PCl_3 \approx PBr_3 < P(OPh)_3 < PH_3 \approx P(CH_2CH_2CN)_3 \approx PMe_3 < PPh_3 < P(C_6H_4Me\text{-}o)_3$. The longer Cr–P bonds found for the triarylphosphine ligands relative to that of PMe_3 most likely arise from the greater steric demands of the aryl substituents. Indicative of this is the observation that the carbonyl infrared frequencies, considered to be a good indicator of the electronic character of L, are found to be closely similar for the PPh_3 and PMe_3 complexes.* The bond dimensions for [$Cr(CO)_5(PCl_3)$] and [$Cr(CO)_5(PBr_3)$] are consistent with the much held view that these ligands are better π acceptors than are both PPh_3 and PMe_3. Pertinent to this is recent theoretical work by Pacchioni and Bagus[36] which shows that the σ basicities of ligands as disparate as PMe_3, PH_3, $P(OMe)_3$ and PF_3 are closely similar. For [$Cr(CO)_5(PCl_3)$] the shorter Cr–P bond relative to that in [$Cr(CO)_5(PMe_3)$] evidently results primarily from electronic factors since the cone angle for PCl_3 (124°) is greater than of PMe_3 (118°).[35] On similar grounds [$Cr(CO)_5\{P(OPh)_3\}$] has a shorter Cr–P bond than expected from the cone-angle approach due to the electron-withdrawing ability of the oxygen atoms, though possibly a degree of alleviation of the steric requirement of $P(OPh)_3$ may result from the conformational flexibility of the OPh groups.[24,35,37–42]

In the case of the molybdenum complexes the Mo–P bond distance increases in the order $PF_3 < P(OCH_2)_3CMe < P(CH_2)_6N_3 = P_4S_3 < P(CH_2CH_2CN)_3 \approx PMe_3 < PPh_3$.Trefonas and co-workers[32] have pointed out that the Mo–P bond in the P_4S_3 complex is abnormally long since infrared spectral evidence indicates that this ligand is strongly π-accepting; they rule out, however, distortions due to crystal packing. The overall trend is similar to that of the chromium complexes. The plot in Fig. 3 for the molybdenum complexes is near linear apart from the PF_3 and $P(OCH_2)_3CMe$ complexes which have low Mo–P bond lengths. For the [$W(CO)_5L$] complexes the W–P bonds increase in length in the order $PMe_3 < PPh_3 < PBu^t_3$, *i.e.* with increasing steric bulk of the

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* This is also found for the analogous PPh_3 and PMe_3 complexes of Mo and W.[5]

Table 6 Selected bond lengths (Å) for $[M(CO)_5L]$[a]

Ligand L	M–L	M–C_{ax}	M–C_{eq}	C–O_{ax}	C–O_{eq}
M = Cr					
PPh_3[15,16]	2.422(1)	1.845(4)	1.880(4)	1.154(5)	1.147(6)
PMe_3[24]	2.3664(5)	1.850(2)	1.893(5)	1.153(2)	1.134(3)
$P(OPh)_3$[16]	2.309(1)	1.861(4)	1.896(4)	1.136(6)	1.131(6)
PH_3[25]	2.351	1.884	1.889	1.145	1.18
PCl_3[26]	2.245(1)	1.900(4)	1.905(4)	1.141(5)	1.130(4)
PBr_3[26]	2.250(2)	1.896(9)	1.902(9)	1.133(11)	1.134(11)
$P(CH_2CH_2CN)_3$[18]	2.364(1)	1.876(4)	1.891(4)	1.136(4)	1.138(4)
$P(C_6H_4Me\text{-}o)_3$[27]	2.469(2)	1.85(1)	1.91(1)	—	—
Quinuclidine[2]	2.249(5)	1.824(9)	1.893(6)	1.156(5)[b]	1.142(7)
Pyridine[28]	2.156(6)	1.851(6)	1.901(10)	1.148(6)	1.140(6)
Piperidine[28,29]	2.204(5)	1.824(5)	1.901(7)	1.162(5)	1.136(6)
$AsPh_3$[17]	2.4972(5)	1.859(3)	1.897	1.147(4)	1.139
$SbPh_3$[17]	2.6170(3)	1.865(3)	1.899	1.136(4)	1.140
M = Mo					
PPh_3[18]	2.560(1)	1.995(3)	2.046(4)	1.142(4)	1.134(4)
PMe_3[26]	2.5082(7)	1.984(3)	2.036(4)	1.152(3)	1.134(3)
$P(OCH_2)_3CMe$[4]	2.417(1)	2.026(6)	2.043(8)	1.137(10)	1.132(8)
$P(CH_2CH_2CN)_3$[18]	2.506(1)	2.008(4)	2.044(5)	1.145(5)	1.134(5)
PF_3[30]	2.37(1)	2.063(6)	2.063(6)	1.154(5)	1.154(5)
P_4S_3[31]	2.477(6)	2.06(2)	2.05(2)	1.14(4)	1.14(4)
$P(CH_2)_6N_3$[32]	2.479(5)	2.034(5)	2.01(2)	1.12(2)	1.16(2)
$AsPh_3$	2.612(0)	1.975(3)	2.039(3)	1.129(3)	1.135(3)
$SbPh_3$	2.756(0)	1.989(4)	2.040(4)	1.142(4)	1.136(3)
M = W					
PPh_3	2.545(1)	2.006(5)	2.033(5)	1.125(6)	1.135(6)
PMe_3[33]	2.516(2)	2.00(1)	2.01(2)	1.15(1)	1.15(4)
PBu^t_3[34]	2.686(4)	1.98(2)	2.01(2)	1.13(3)	1.15(3)
PCl_3[26]	2.378(4)	2.02(2)	2.033(12)	1.17(2)	1.15(2)
PBr_3[26]	2.382(2)	2.037(11)	2.048(12)	1.139(13)	1.131(13)
$AsPh_3$	2.617(0)	1.961(7)	2.031(10)	1.164(9)	1.128(9)
$SbPh_3$	2.753(0)	1.993(7)	2.035(8)	1.147(8)	1.135(9)

[a] All data were obtained from crystal structure analyses except for $[Mo(CO)_5(PF_3)]$ for which bond dimensions were determined by gas-phase electron diffraction.[30] [b] Incorrectly reported as 1.115 Å in an earlier paper.[2]

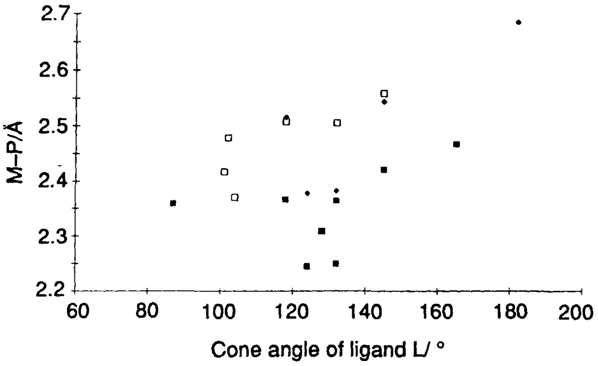

Fig. 3 Plot of the M–P bond length with cone angle of the phosphorus-donor ligand L in $[M(CO)_5L]$ [M = Cr (■), Mo (□) or W (◆)]

phosphorus ligand; the W–P bonds of the PCl_3 and PBr_3 compounds are shorter.

Reference to columns 3 and 4 of Table 6 shows that the metal–carbonyl bond lengths vary with the ligand L. Generally, complexes with longer M–P bonds tend to have shorter M–C, especially those *trans* to L, though there are exceptions to this. This could be due to hybridisation changes in P with different substituents[17] or, in the case of M–C_{eq} bonds, to steric buttressing by the bulkier ligands L.

Comparisons are made of the M–C bond lengths for a given metal M. Where M = Cr, M–C_{ax} decreases in the order $PCl_3 \approx PBr_3 > PH_3 > P(CH_2CH_2CN)_3 > SbPh_3 \approx P(OPh)_3 \approx AsPh_3 > PMe_3 \approx P(C_6H_4Me\text{-}o)_3 \approx PPh_3 \approx$ pyridine > quinuclidine ≈ piperidine. The average M–C_{eq} distances are similar across this series with that of the PPh_3 complex marginally lower than the others. The M–C_{ax} is shielded from the steric effects of L by the equatorial $M(CO)_4$ grouping so variations in the M–C_{ax} bond distances mainly reflect the electronic nature of the M–L interaction. The longest Cr–C_{ax} bonds in the $[Cr(CO)_5L]$ complexes are those for the PCl_3 and PBr_3 ligands which are considered to be strong π acceptors, whereas the shortest Cr–C_{ax} bonds are those of the aliphatic amines which are σ bonded to the metal. The complex with pyridine has a longer Cr–C_{ax} and slightly shorter Cr–N than those of the aliphatic amines, in accord with the observation that bonds to sp^2 N tend to be shorter than those to sp^3 N and consistent with a π-acceptor capacity for pyridine as found in ref. 2. The general trend, however, does not completely follow the usually accepted sequence of π-acid behaviour, and it may be that the donor ability of L also has some effect on the M–C bonding. Studies by Atwood and coworkers[43] have shown appreciable bond shortening *trans* to ligands with high σ-donor ability.

For the complexes $[M(CO)_5L]$ (M = Mo or W), the steric effect of L would be less important than for the chromium complexes and comparisons of bond dimensions are a better indicator of the electronic factors in the metal–ligand bonding. In the $[Mo(CO)_5L]$ series the Mo–C_{ax} bonds decrease in length in the order $PF_3 \approx P_4S_3 > P(CH_2)_6N_3 \geqslant P(OCH_2)_3CMe > P(CH_2CH_2CN)_3 > PPh_3 \approx SbPh_3 \approx PMe_3 > AsPh_3$, *i.e.* generally in accord with expected π-acceptor character of L. The Mo–C_{eq} average distance shows little variation within the series (2.05 ± 0.01 Å) apart from an unusually short value of 2.01 Å reported for the constrained phosphorus ligand $P(CH_2)_6N_3$.[32]

In the $[W(CO)_5L]$ complexes the W–C_{ax} bond distances are very similar for L = PPh_3, PMe_3, PBu^t_3 and $SbPh_3$ and slightly lower in the case of $AsPh_3$. The near constancy in M–C_{ax}

Table 7 Fractional atomic coordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) [W(CO)$_5$(PPh$_3$)]							
W	0.2697(1)	0.2220(1)	0.0506(1)	C(14)	−0.0511(4)	0.2748(4)	0.3621(3)
P	0.1526(1)	0.1408(1)	0.2426(1)	C(15)	−0.1837(5)	0.3461(5)	0.3755(4)
C(1)	0.1211(4)	−0.0497(4)	0.2766(3)	C(16)	−0.2847(4)	0.3690(5)	0.2908(5)
C(2)	−0.0106(4)	−0.0983(4)	0.3028(4)	C(17)	−0.2552(4)	0.3252(5)	0.1952(4)
C(3)	−0.0285(5)	−0.2424(5)	0.3232(4)	C(18)	−0.1241(4)	0.2587(4)	0.1810(3)
C(4)	0.0842(5)	−0.3412(5)	0.3186(4)	C(19)	0.3290(4)	0.4056(4)	0.0789(3)
C(5)	0.2169(5)	−0.2961(4)	0.2937(4)	C(20)	0.0929(5)	0.3396(5)	−0.0323(4)
C(6)	0.2350(5)	−0.1512(4)	0.2727(4)	C(21)	0.2062(5)	0.0424(5)	0.0149(4)
C(7)	0.2544(3)	0.1513(4)	0.3659(3)	C(22)	0.4509(4)	0.1126(4)	0.1247(4)
C(8)	0.2720(4)	0.0391(5)	0.4628(3)	C(23)	0.3723(4)	0.2659(4)	−0.0974(3)
C(9)	0.3402(4)	0.0532(5)	0.5571(4)	O(1)	0.3646(4)	0.5101(4)	0.0898(3)
C(10)	0.3943(4)	0.1810(6)	0.5544(4)	O(2)	−0.0006(4)	0.4061(4)	−0.0841(3)
C(11)	0.3777(5)	0.2941(6)	0.4586(4)	O(3)	0.1713(5)	−0.0551(5)	−0.0074(4)
C(12)	0.3101(5)	0.2784(5)	0.3643(4)	O(4)	0.5557(4)	0.0523(4)	0.1638(3)
C(13)	−0.0205(3)	0.2316(3)	0.2642(3)	O(5)	0.4314(4)	0.2864(4)	−0.1797(3)
(*b*) [Mo(CO)$_5$(AsPh$_3$)]							
Mo	0.2313(1)	0.2238(1)	0.4547(1)	C(14)	0.6368(3)	0.2661(3)	0.3184(2)
As	0.3502(1)	0.1424(1)	0.2608(1)	C(15)	0.7674(3)	0.3331(3)	0.3034(3)
C(1)	0.3830(3)	−0.0596(2)	0.2226(2)	C(16)	0.7937(3)	0.3697(3)	0.2057(3)
C(2)	0.2718(3)	−0.1580(3)	0.2297(2)	C(17)	0.6910(3)	0.3380(3)	0.1219(3)
C(3)	0.2895(3)	−0.3026(3)	0.2058(3)	C(18)	0.5604(3)	0.2697(3)	0.1355(2)
C(4)	0.4203(4)	−0.3481(3)	0.1765(3)	C(19)	0.2965(3)	0.0465(3)	0.4919(2)
C(5)	0.5303(3)	−0.2517(3)	0.1693(3)	O(1)	0.3329(3)	−0.0507(3)	0.5137(2)
C(6)	0.5131(3)	−0.1060(3)	0.1926(2)	C(20)	0.0495(3)	0.1125(3)	0.3800(2)
C(7)	0.2427(2)	0.1531(3)	0.1295(2)	O(2)	−0.0537(2)	0.0517(2)	0.3403(2)
C(8)	0.1881(3)	0.2802(3)	0.1297(2)	C(21)	0.1707(3)	0.4049(3)	0.4229(2)
C(9)	0.1185(3)	0.2942(4)	0.0349(3)	O(3)	0.1349(2)	0.5079(2)	0.4093(2)
C(10)	0.1020(3)	0.1816(4)	−0.0591(3)	C(22)	0.4091(3)	0.3404(3)	0.5369(2)
C(11)	0.1549(3)	0.0555(4)	−0.0593(2)	O(4)	0.5041(2)	0.4069(3)	0.5865(2)
C(12)	0.2252(3)	0.0398(3)	0.0345(2)	C(23)	0.1311(3)	0.2674(3)	0.5977(2)
C(13)	0.5328(2)	0.2341(2)	0.2346(2)	O(5)	0.0721(3)	0.2887(2)	0.6787(2)
(*c*) [W(CO)$_5$(AsPh$_3$)]							
W	0.2311(1)	0.2250(1)	0.4564(1)	C(14)	0.6360(7)	0.2609(7)	0.3191(6)
As	0.3498(1)	0.1421(1)	0.2621(1)	C(15)	0.7673(7)	0.3301(8)	0.3036(8)
C(1)	0.3822(6)	−0.0595(6)	0.2224(5)	C(16)	0.7924(8)	0.3658(9)	0.2066(8)
C(2)	0.2702(7)	−0.1588(7)	0.2314(6)	C(17)	0.6894(8)	0.3368(8)	0.1209(8)
C(3)	0.2912(9)	−0.3012(7)	0.2058(8)	C(18)	0.5617(7)	0.2696(7)	0.1372(6)
C(4)	0.4173(9)	−0.3491(8)	0.1758(7)	C(19)	0.2974(8)	0.0495(8)	0.4942(6)
C(5)	0.5283(9)	−0.2512(9)	0.1693(8)	O(1)	0.3347(8)	−0.0450(7)	0.5159(6)
C(6)	0.5122(7)	−0.1076(7)	0.1915(6)	C(20)	0.0508(7)	0.1142(7)	0.3817(6)
C(7)	0.2422(6)	0.1534(6)	0.1302(5)	O(2)	−0.0525(6)	0.0507(7)	0.3419(6)
C(8)	0.1894(8)	0.2793(8)	0.1301(6)	C(21)	0.1691(6)	0.4044(7)	0.4234(5)
C(9)	0.1220(9)	0.2923(10)	0.0341(7)	O(3)	0.1342(7)	0.5046(6)	0.4087(5)
C(10)	0.1053(8)	0.1793(11)	−0.0591(7)	C(22)	0.4065(8)	0.3445(8)	0.5387(6)
C(11)	0.1550(8)	0.0547(9)	−0.0591(6)	O(4)	0.5029(6)	0.4111(7)	0.5876(5)
C(12)	0.2231(7)	0.0388(7)	0.0336(6)	C(23)	0.1309(8)	0.2675(8)	0.5980(6)
C(13)	0.5337(6)	0.2326(6)	0.2354(5)	O(5)	0.0718(7)	0.2900(6)	0.6823(5)
(*d*) [Mo(CO)$_5$(SbPh$_3$)]							
Mo	0.2345(1)	0.2270(1)	0.4659(1)	C(14)	0.6584(4)	0.2784(4)	0.3201(3)
Sb	0.3554(1)	0.1419(1)	0.2682(1)	C(15)	0.7840(4)	0.3419(4)	0.3009(4)
C(1)	0.3905(3)	−0.0768(3)	0.2230(3)	C(16)	0.8045(4)	0.3666(4)	0.2009(4)
C(2)	0.5160(4)	−0.1248(4)	0.1855(3)	C(17)	0.7002(4)	0.3251(4)	0.1172(4)
C(3)	0.5325(5)	−0.2684(5)	0.1584(4)	C(18)	0.5735(4)	0.2602(4)	0.1354(3)
C(4)	0.4256(6)	−0.3627(4)	0.1685(4)	C(19)	0.3045(4)	0.0537(4)	0.5065(3)
C(5)	0.3017(5)	−0.3163(4)	0.2058(4)	C(20)	0.0543(4)	0.1138(4)	0.3907(3)
C(6)	0.2822(4)	−0.1732(4)	0.2339(3)	C(21)	0.1717(3)	0.4036(4)	0.4274(3)
C(7)	0.2370(3)	0.1535(3)	0.1228(3)	C(22)	0.4146(4)	0.3439(4)	0.5446(3)
C(8)	0.1820(4)	0.2790(5)	0.1195(3)	C(23)	0.1362(4)	0.2717(4)	0.6046(3)
C(9)	0.1127(5)	0.2916(6)	0.0229(4)	O(1)	0.3442(4)	−0.0427(4)	0.5292(3)
C(10)	0.0975(5)	0.1770(6)	−0.0677(4)	O(2)	−0.0468(3)	0.0502(3)	0.3501(3)
C(11)	0.1506(5)	0.0541(5)	−0.0646(3)	O(3)	0.1367(3)	0.5040(3)	0.4081(2)
C(12)	0.2206(4)	0.0415(4)	0.0304(3)	O(4)	0.5120(3)	0.4108(3)	0.5888(3)
C(13)	0.5520(3)	0.2356(3)	0.2365(3)	O(5)	0.0770(4)	0.2941(3)	0.6829(2)

Table 7 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*e*) [W(CO)$_5$(SbPh$_3$)]							
W	0.2343(1)	0.2279(1)	0.4674(1)	C(14)	0.5738(7)	0.2600(8)	0.1354(6)
Sb	0.3554(1)	0.1413(1)	0.2687(1)	C(15)	0.7010(9)	0.3271(9)	0.1170(8)
C(1)	0.3896(7)	−0.0776(7)	0.2238(5)	C(16)	0.8056(9)	0.3655(10)	0.2013(8)
C(2)	0.2814(9)	−0.1726(8)	0.2360(7)	C(17)	0.7840(8)	0.3413(9)	0.3021(8)
C(3)	0.2987(11)	−0.3169(9)	0.2066(8)	C(18)	0.6589(7)	0.2773(8)	0.3228(7)
C(4)	0.4239(11)	−0.3650(9)	0.1660(8)	C(19)	0.1713(7)	0.4013(7)	0.4269(6)
C(5)	0.5311(10)	−0.2697(9)	0.1577(8)	C(20)	0.4137(8)	0.3460(9)	0.5441(6)
C(6)	0.5158(8)	−0.1237(8)	0.1874(7)	C(21)	0.3076(8)	0.0563(9)	0.5094(7)
C(7)	0.2361(6)	0.1527(7)	0.1222(5)	C(22)	0.0559(8)	0.1135(7)	0.3916(6)
C(8)	0.2208(7)	0.0408(8)	0.0294(6)	C(23)	0.1352(8)	0.2712(8)	0.6072(6)
C(9)	*0.1501(10)*	*0.0515(12)*	*−0.0646(7)*	O(1)	0.1362(6)	0.5020(6)	0.4074(6)
C(10)	0.0960(10)	0.1771(14)	−0.0687(8)	O(2)	0.5119(7)	0.4134(7)	0.5890(6)
C(11)	0.1108(11)	0.2897(13)	0.0220(9)	O(3)	0.3454(8)	−0.0395(8)	0.5309(7)
C(12)	0.1836(9)	0.2788(9)	0.1197(7)	O(4)	−0.0449(6)	0.0488(7)	0.3524(6)
C(13)	0.5523(6)	0.2353(6)	0.2371(5)	O(5)	0.0785(8)	0.2928(7)	0.6877(5)

parallels the behaviour of the complexes of Cr and Mo for comparable ligands. No structures have previously been reported for complexes with phosphorus ligands bearing electronegative substituents. Data for the PCl$_3$ and PBr$_3$ complexes, recently determined,[26] are included here for comparison. The W–C$_{eq}$ bond lengths do not differ significantly in view of the stated errors. In the case of [W(CO)$_5$(PBu$^t_3$)] the four equatorial CO ligands are inclined away from the bulky phosphine, apparently to alleviate steric strain, and an elongation of the P–C bond in the PBu$^t_3$ ligand is observed (average 1.93 Å) compared with the average P–C bond lengths in the PMe$_3$ (1.815 Å)* and PPh$_3$ (1.830 Å) complexes.

In a wide ranging study of steric and σ- and π-bonding effects in metal complexes containing the ZPPh$_3$ group (Z = metal, O, halogen, *etc.*), Orpen and co-workers[44,45] found a 'strong negative correlation' between the P–C bond length and the C–P–C bond angle. The question of hybridisation of the L donor atom has also been considered. Arguments were advanced which attribute changes in the M–L bond length in [M(CO)$_5$L] complexes to the relative amounts of s and p character in the M–L bond.[17,46] For the [M(CO)$_5$L] complexes of Table 6 which have phosphorus-donor ligands L, examination of the bond angles about P shows there are significant changes to the s- and p-orbital character of the phosphorus atom from one ligand to another. The following average bond angles have been found: PBu$^t_3$ 106.7, P(C$_6$H$_4$Me-*o*)$_3$ 103.5, PMe$_3$ 102.5–102.7, PPh$_3$ 102.6–102.9, P(CH$_2$CH$_2$CN)$_3$ 102.4–102.8, P(OCH$_2$)$_3$CMe 101.9, PBr$_3$ 99.9–100.4, P(OPh)$_3$ 99.6, PCl$_3$ 99.6–100.0, PF$_3$ 99.5, P$_4$S$_3$ 99.5 and P(CH$_2$)$_6$N$_3$ 98.2°.† In a study on [Cr(CO)$_5$(EPh$_3$)] (E = P, As, Sb or Bi), Carty *et al.*[17] found that the smaller the C–E–C bond angle the greater is the s character of the E-donor orbital and in turn the larger is the M–E bond order. The same trends appear not to be followed through the present series of phosphorus-ligand complexes. For example, the C–P–C bond angles are closely similar for PPh$_3$, PMe$_3$ and P(CH$_2$CH$_2$CN)$_3$ yet the Cr–P bond length in [Cr(CO)$_5$(PPh$_3$)] is substantially greater than those of [Cr(CO)$_5$(PMe$_3$)] and [Cr(CO)$_5${P(CH$_2$CH$_2$CN)$_3$}]. Similarly in the [Mo(CO)$_5$L] complexes where L is P(CH$_2$)$_6$N$_3$, P(CH$_2$CH$_2$CN)$_3$ or P$_4$S$_3$ the Mo–P bond distances are 2.48 ± 0.02 Å yet the phosphorus bond angles vary by more than 4°. The results of the present study suggest that the length of the M–P bond in these complexes is less affected by hybridisation changes in P than by the steric and π-acceptor properties of the phosphorus-containing ligand.

Conclusion

The crystal structures of [W(CO)$_5$(PPh$_3$)], [Mo(CO)$_5$(AsPh$_3$)], [W(CO)$_5$(AsPh$_3$)], [Mo(CO)$_5$(SbPh$_3$)] and [W(CO)$_5$(SbPh$_3$)] have been determined and a comparative structural study made for the nine complexes of general formula [M(CO)$_5$(EPh$_3$)] (M = Cr, Mo or W; E = P, As or Sb). Trends in bond lengths and angles are rationalised in terms of steric and electronic interactions between the bonded M(CO)$_5$ and EPh$_3$ fragments. The results are consistent with the notion that the EPh$_3$ ligands are weaker π acceptors than is CO. The E–C$_{ar}$ bond lengths and C$_{ar}$–E–C$_{ar}$ bond angles of the solid state free EPh$_3$ are little changed on complexation with [M(CO)$_5$].

Small deviations from regular octahedral geometry about M are observed for these complexes as well as *ca.* 6° tilting of EPh$_3$ throughout. Torsion angles which define the conformational disposition of the EPh$_3$ group in relation to M(CO)$_5$ are almost invariant within the series. For all nine complexes the EPh$_3$ ligands have propeller-type geometry with relatively small distortions from the symmetric C_3 structure. The conformation of PPh$_3$ is found to be greatly changed on complexation.

The studies are extended to include other related [M(CO)$_5$L] complexes so that trends in structural parameters are obtained for a total of 29 compounds. The results are related to the steric behaviour and π-acceptor capacity of the ligands L. It is shown that M–P bond dimensions are not adequately explained in terms of hybridisation of the phosphorus-donor atom in the ligands L.

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* The average P–C bond lengths in [Cr(CO)$_5$(PMe$_3$)] and [Mo(CO)$_5$(PMe$_3$)] are 1.814 and 1.811 Å, respectively. The X-ray analyses of these compounds were carried out at −75[24] and −143 °C,[26] respectively. The average P–C bond length reported for [W(CO)$_5$(PMe$_3$)] determined at 22 °C was 1.85 Å.[30] The latter study suffered from high thermal motion of the atoms and loss of crystallinity of the low-melting compound during data collection.

† Where L occurs in more than one complex in Table 6 the range of the average bond angle per molecule is shown.

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