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FULL PAPER

The preparation of $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-PE})]$ (E = As or Sb), the first complexes with naked heterodiatomic Group 15 ligands, and of their adducts with $W(CO)_5$

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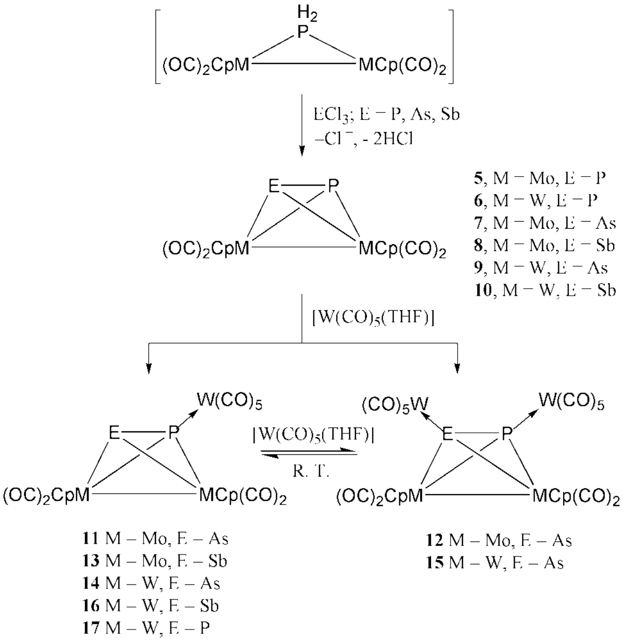
Addition of one equivalent of the Group 15 trichlorides ECl_3 (E = P, As, or Sb) to the phosphido-bridged dimetallic anions $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (M = Mo or W) afforded moderate yields of the complexes $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-PE})]$, which feature a pseudo-tetrahedral M_2PE core. Treatment of the new complexes with $[W(CO)_5(THF)]$ led to preferential co-ordination of this Lewis acid to the phosphorus atom. The additional co-ordination of a $W(CO)_5$ fragment to the As atom in $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-PAs})]$ to give a 2 : 1 adduct is reversible at room temperature on dissolution in solvents such as CH_2Cl_2 and THF; similar co-ordination to the Sb atom in $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-PSb})]$ is not observed. The crystal structures of the 1 : 1 adducts and of one 2 : 1 adduct have been determined. The P–As distances in $[W_2Cp_2(CO)_4\{\mu\text{-}\eta^2\text{-AsPW(CO)}_5\}]$ (2.217(5) Å) and that in $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-AsP}\{W(CO)_5\}_2)]$, in which the As and P atoms are disordered (2.223(3) Å), are intermediate between the P–P and As–As distances in homodiatomic E_2 complexes. Similarly, the P–Sb distances in the two crystallographically independent molecules of $[Mo_2Cp_2(CO)_4\{\mu\text{-}\eta^2\text{-SbPW(CO)}_5\}]$ (2.401(2), 2.410(2) Å) are intermediate in length between the P–P and Sb-Sb distances in related homodiatomic E_2 complexes.

Introduction

The synthesis of transition metal complexes with so-called “naked” Group 15 ligands has been the subject of intense research activity for a number of years, and a wide range of ligand types and modes of co-ordination have been reported.[1] Within this seemingly bewildering array of complexes the tetrahedrane complexes $[\{ML_n\}_xE_{(4-x)}]$ (x = 1–3, E = P, As or Sb; ML_n = transition metal fragment), formally obtained by the stepwise replacement of the corners of an E_4 tetrahedron by ML_n fragments, are among the more prevalent structural types. These complexes have been obtained by a variety of methods but none of the methods is applicable to the synthesis of complexes containing naked heteroatomic Group 15 ligands. Having synthesized and studied the reactivity of a number of new complexes containing P_2 and As_2 ligands[2] it seemed of interest to attempt the preparation of analogous complexes featuring heterodiatomic ligands, since heterodiatomic species, on account of the inherent bond polarity, often exhibit properties different from homodiatomics. Herein we report the first complexes containing the heterodiatomic Group 15 ligands PAs and PSb, synthesized by treatment of the anionic PH_2 complexes $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (M = Mo or W) with ECl_3 (E = As or Sb), and show that these complexes react with $[W(CO)_5(THF)]$ preferentially at the phosphorus atom of the diatomic ligand. The synthesis of the new heterodiatomic complexes has been facilitated by the recently reported high-yield synthesis of $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (M = Mo or W) *via* the treatment of $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)]$ with alkali metal hydroxides.[2b] This method of synthesis of the anions avoids the inconvenience and hazards associated with the use of PH_3 gas previously required for the synthesis of such complexes. Part of the work now described has been the subject of a preliminary communication.[3]

Results and discussion

The reaction of the monoanionic complexes $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (M = Mo **3** or W **4**) with the Group 15 trichlorides ECl_3 (E = P, As or Sb) leads to the formation of the tetrahedrane complexes $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-PE})]$, containing the P_2 (E = P, M = Mo **5** or W **6**) or the previously unknown PE (E = As, M = Mo **7** or W **9**; E = Sb, M = Mo **8** or W **10**) ligand, together with a small quantity of $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)(\mu\text{-}H)]$ (M = Mo **1** or W **2**) (Scheme 1). These reactions presumably proceed with elimination of LiCl and two equivalents of HCl. Generation of the latter might, in part, account for the low yields obtained, but it should be noted that when similar reactions were run in the presence of an excess of DBU



Scheme 1 Reactions leading to formation of complexes **7**–**17**.

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Table 1 Spectroscopic data for complexes **5**–**17**

		δ			Microanalysis[a] (%)		
Complex	IR ($\tilde{\nu}_{CO}$/cm^{-1})	^{1}H NMR	^{31}P NMR	FAB MS, *m/z*	C	H	P
5[5]	1965s, 1913s	5.20, s	−49.6, s				
6[2d]	1957s, 1904s	5.22, s	−160, s				
7	1959s, 1908s	5.17, s	28.5, s	540 (M$^+$), 484, 457, 428	30.96 (31.05)	1.76 (1.85)	
8	1949s, 1900s	5.14, s	88.4, s	588 (M$^+$), 532, 504	28.45 (28.65)	1.64 (1.72)	5.31 (5.28)
9	1952s, 1899s	5.14, s	−95.8, s	716 (M$^+$), 660, 632	23.46 (23.46)	1.33 (1.40)	
10	1940s, 1894s	5.16, s	−53.4, s	762 (M$^+$), 706, 678	22.11 (22.03)	1.31 (1.31)	3.99 (4.06)
11	2071m, 1979s, 1945s, 1936sh, 1921m	5.27, s	−9.0, s	864 (M$^+$), 838, 810, 780, 724, 696, 640, 612	26.55 (26.39)	1.05 (1.16)	
12	2079s, 2068s, 2000s, 1991m, 1964m, 1946s, 1927s	[b]	[b]	1188 (M$^+$), 1104, 1076, 1048, 1020	24.33 (24.24)	0.85 (0.84)	
13	2068s, 1969s, 1943s, 1905s	5.23, s	45.1, s	916 (M$^+$), 884, 855, 827, 799, 772, 744, 714, 686, 657	25.03 (25.06)	1.07 (1.11)	3.23 (3.40)
14	2070m, 1974s, 1943s, 1913m	5.29, s	−108.6, s	1040 (M$^+$), 1012, 984, 956, 928, 900, 872, 844, 816, 788	21.95 (21.95)	1.06 (0.96)	
15	2079m, 2068m, 1997s, 1986s, 1960s, 1944s, 1937s	[b]	[b]	1364 (M$^+$)	21.09 (21.11)	0.68 (0.73)	
16	2068s, 1976sh, 1963s, 1940s, 1899m	5.26, s	−67.5, s	1086 (M$^+$), 1058, 1031, 1004, 974	21.02 (20.98)	0.97 (0.92)	2.50 (2.85)
17	2070m, 1979s, 1943vs, 1922sh	5.33, s	−185.03 (RT); −142, s(vbr), −224.3, d, J = 587 Hz (−65 °C)	997 (M$^+$), 969, 941, 913, 885, 857, 829, 801, 773	21.23 (22.89)	1.02 (1.00)	5.96 (6.21)

[a] Calculated values in parentheses. The method of analysis for phosphorus did not allow analysis for P to be performed for As-containing complexes. [b] Dissociates in solution.

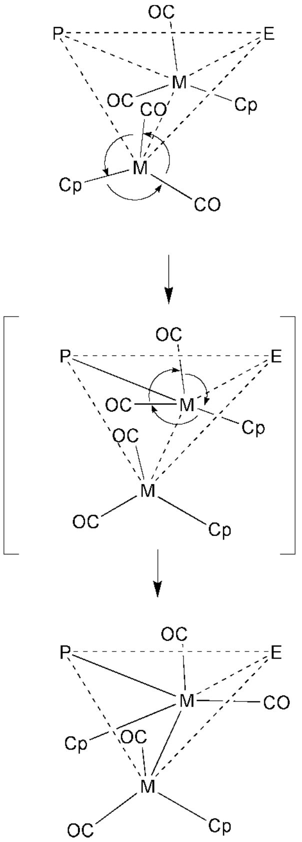
(1,8-diazabicyclo[5.4.0]undec-1-ene) as scavenger little difference in yield was noticed. Unfortunately all attempts to prepare the bismuth analogues by reaction with $BiCl_3$ led only to decomposition. We have investigated the reactivity of the new heterodiatomic μ-η^2-PE ligand towards [$W(CO)_5(THF)$], and have obtained 1 : 1 adducts of formula [$M_2Cp_2(CO)_4\{\mu$-η^2-$EPW(CO)_5\}$] (E = As, M = Mo **11** or W **14**; E = Sb, M = Mo **13** or W **16**). These results are in accord with the greater Lewis basicity of the phosphorus based lone pair compared to the arsenic or antimony based lone pairs which, as expected, leads to preferential co-ordination of the sixteen electron $W(CO)_5$ fragment at the phosphorus centre. We have also shown that the co-ordination of a $W(CO)_5$ fragment to **6** yields [$W_2Cp_2(CO)_4\{\mu$-η^2-$PPW(CO)_5\}$] **17**. The μ-η^2-PAs complexes **11** and **14** react with a further $W(CO)_5$ fragment which bonds to the arsenic atom to give the 2 : 1 adducts [$M_2Cp_2(CO)_4(\mu$-η^2-$P\{W(CO)_5\}As\{W(CO)_5\})$] (M = Mo **12** or W **15**).

Co-ordination of $M(CO)_5$ (M = Cr, Mo or W) to arsenic centres has previously been reported to give unstable 1 : 1 and 1 : 2 adducts in the case of the As_2 ligand.[4] In the case of the PAs ligand, co-ordination of $W(CO)_5$ to the arsenic atom in the 1 : 2 adducts is reversible simply by dissolution of the adducts in common organic solvents such as CH_2Cl_2 or THF at room temperature. This ease of dissociation prevented ^{31}P NMR spectra being obtained for complexes **12** and **15** even at −65 °C. We were unable to isolate any complex in which the antimony atom of the PSb ligand was additionally complexed by $W(CO)_5$.

The spectroscopic properties of the tetrahedrane complexes **5**–**17** (Table 1) are in accord with the proposed structures. Complexes **5** and **6** were identified by comparison of their ^{31}P NMR and IR spectra to those of authentic samples.[2d,5] Complexes **7**–**17** were identified by ^{1}H, ^{31}P NMR and IR spectroscopy, mass spectrometry and microanalysis with the exception of **12** and **15** for which no NMR data were collected due to the ease of dissociation in solution. In addition, **12**, **13**, **14** and **17** have been characterised by single-crystal X-ray diffraction studies. The structures of **7** and **8** have been described previously.[3]

The ^{1}H NMR spectra of complexes **7**–**11**, **13**, **14**, and **16** each show only one singlet. An inspection of the crystal structures determined in this paper (Figs. 1–4) shows that the Cp rings adopt a transoid geometry with respect to the metal–metal bond. If this geometry were to be retained in solution two distinct environments would exist for the Cp protons and thus two peaks would be expected. Two alternative possibilities which would account for the solution NMR data are as follows: either the Cp sites are collinear with the metal–metal bond vector so that they are in equivalent positions, or the complexes are fluxional so that the Cp sites become equivalent in solution on the NMR timescale. The first possibility seems the less likely because all other documented examples of such tetrahedrane complexes show a *trans* arrangement of the Cp groups.[2,4,5] It is only when the co-ligands are very sterically demanding that a collinear arrangement is taken up.[6] A possible fluxional process which accounts for the equivalence of the two Cp sites in solution is that the Cp/2CO ligands associated with each metal centre interchange positions *via* a twist mechanism.[7] However, in no case the variable temperature ^{1}H NMR spectra of **7**, **8** or **11** revealed any broadening of the Cp signal even at −65 °C. This suggests that the fluxional process is of low energy and that interconversion is rapid on the NMR timescale. A possible mechanism leading to interconversion of the Cp groups is shown below (Scheme 2). Such a low energy fluxional process involving the Cp and CO groups has previously been reported by Chisholm *et al.* for the structurally analogous alkyne-bridged complexes [$Mo_2Cp_2(CO)_4(\mu$-η^2-$RC_2R')$] (R = H, R′ = Ph; R = H,R′ = Me).[7] The solid state structures of these complexes contain two inequivalent Cp groups, but in solution the Cp sites interconvert rapidly even at −100 °C so that only one Cp signal is observed in both the ^{1}H and ^{13}C NMR spectra.

The ^{31}P NMR spectra of complex **7**–**11**, **13**, **14** and **16** all show a sharp singlet peak, whereas **17** shows a broad singlet. No satellite peaks due to coupling of phosphorus to ^{183}W (I = 1/2, 14.4%) present in the $W(CO)_5$ fragment or in the W atoms of the tetrahedrane core were observed. It remains unclear why no coupling occurs to the ^{183}W atoms of the tetrahedrane core, although it should be noted that no ^{183}W–^{31}P coupling was observed in the parent complex [$W_2Cp_2(CO)_4(\mu$-η^2-$P_2)$] **6**.[2] It is somewhat easier to explain why no coupling was observed to the $W(CO)_5$ fragment in the 1 : 1 adducts **11**, **13**, **14** and **16**. The NMR data for the related complex [$W_2Cp_2(CO)_4\{\mu$-η^2-



Scheme 2 Possible mechanism for interconversion of Cp groups in complexes **7**–**17**.

$PPW(CO)_5\}]$ **17** (Table 1) may be explained in terms of a rapid dissociation of the $W(CO)_5$ fragment from the phosphorus atom from which it is bound followed by reco-ordination to either phosphorus atom. The two phosphorus centres then become equivalent on the NMR timescale and a broad singlet is observed in the room temperature ^{31}P NMR spectrum at δ −185.03. Cooling of the sample to −65 °C leads to a partial resolution of the two phosphorus centres such that the ^{31}P NMR spectrum consists of a very broad singlet at δ −142 and a broad doublet at δ −224.3. The broadness of these peaks shows that at this temperature dissociation and reco-ordination is not rapid enough to render the two phosphorus centres equivalent. It is reasonable to assume that a rapid conversion between the $W(CO)_5$ adduct and the unco-ordinated species occurs in complexes **11**, **13**, **14** and **16** and is responsible for the single ^{31}P resonance at room temperature which has no observable ^{183}W satellites. A VT ^{31}P NMR study of **11** showed that the room temperature and −65 °C spectra were identical, indicating that the dissociation and co-ordination of the $W(CO)_5$ fragment is a low energy process.

Mass spectroscopy revealed a peak assigned to the molecular ion in each case, in addition to fragmentation peaks due to the loss of carbonyl ligands. Microanalytical data are in accord with the proposed structures.

Crystal structure determinations

In view of the fact that the complexes reported herein represent the first examples of complexes containing naked heterodiatomic Group 15 ligands, the crystal structures of **12**, **13**, **14** and **17** have been determined by single-crystal X-ray diffraction studies. Those of **7** and **8** were reported in a preliminary communication.[3] For **12**, **13**, **14** and **17**, suitable crystals were prepared in each case by diffusion of hexane into a concentrated dichloromethane solution at 0 °C under an inert atmosphere. The molecular structures are shown in Figs. 1–4 respectively. Selected bond lengths and angles are given in Tables 2–5 respectively. Whilst **14** and **17** are isomorphous, **13** crystallises in space group $P\bar{1}$ with two molecules in the asymmetric unit.

Table 2 Selected bond lengths (Å) and angles (°) for complex **12**

Mo(1)–Mo(1A)	3.059(2)	E(1)–E(1A)	2.223(3)
E(1)–Mo(1)	2.496(2)	Mo(1)–E(1A)	2.616(2)
E(1)–Mo(1)–E(1A)	51.49(6)	E(1)–Mo(1)–Mo(1A)	55.06(4)
E(1A)–Mo(1)–Mo(1A)	51.47(4)	E(1A)–E(1)–Mo(1)	67.03(5)
E(1A)–E(1)–W(2)	135.36(4)	Mo(1)–E(1)–W(2)	145.96(6)
Mo(1)–E(1)–Mo(1A)	73.47(5)	W(2)–E(1)–Mo(1A)	136.45(6)

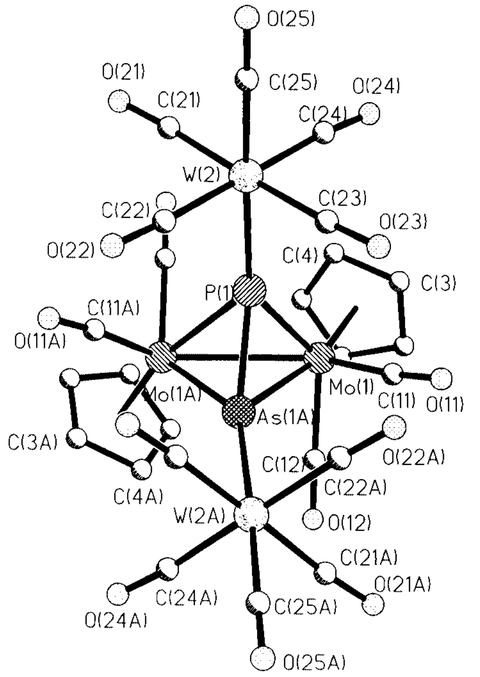


Fig. 1 Molecular structure of complex **12** showing the atom numbering scheme.

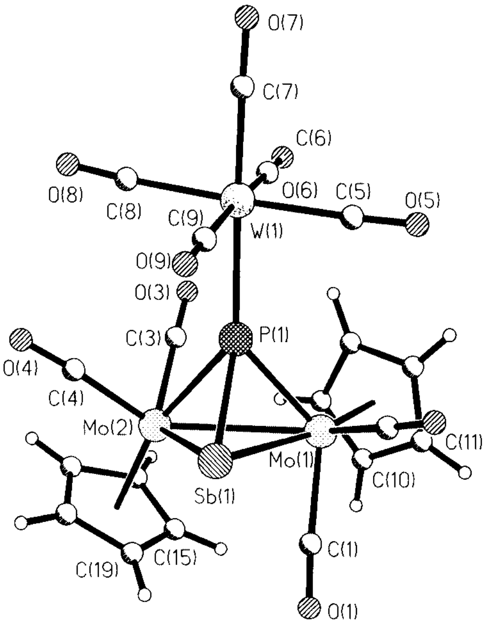


Fig. 2 Molecular structure of complex **13** showing the atom numbering scheme.

In the structures of complexes **13**, **14** and **17** a $W(CO)_5$ fragment is co-ordinated to the phosphorus atom of the PSb, PAs and P_2 ligands respectively. The PE ligands in these complexes show no crystallographic disorder similar to that observed in the parent PE complexes **7** and **8**.[3] The PAs bond length of

Table 3 Selected bond lengths (Å) and angles (°) for the two crystallographically independent molecules of complex **13**

Mo(1)–Mo(2)	3.0588(12), 3.061(2)	Mo(1)–P(1)	2.448(2), 2.432(2)
Mo(2)–P(1)	2.524(2), 2.524(2)	Mo(1)–Sb(1)	2.8532(13), 2.865(2)
Mo(2)–Sb(1)	2.762(2), 2.7665(11)	P(1)–Sb(1)	2.401(2), 2.410(2)
P(1)–W(1)	2.528(2), 2.518(2)		
P(1)–Sb(1)–Mo(1)	54.73(5), 54.08(5)	P(1)–Sb(1)–Mo(2)	58.03(5), 57.87(5)
Mo(2)–Sb(1)–Mo(1)	65.99(3), 65.82(3)	P(1)–Mo(1)–Sb(1)	53.19(5), 53.36(5)
P(1)–Mo(1)–Mo(2)	53.16(5), 53.22(5)	Sb(1)–Mo(1)–Mo(2)	55.57(3), 55.54(3)
P(1)–Mo(2)–Sb(1)	53.79(5), 53.96(5)	P(1)–Mo(2)–Mo(1)	50.93(5), 50.52(5)
Sb(1)–P(1)–Mo(1)	72.08(6), 72.56(5)	Mo(1)–P(1)–Mo(2)	75.91(2), 76.26(6)
Mo(1)–P(1)–W(1)	139.46(8), 136.89(8)	Sb(1)–Mo(2)–Mo(1)	58.44(3), 58.64(4)
Sb(1)–P(1)–Mo(2)	68.17(6), 68.17(5)	Sb(1)–P(1)–W(1)	130.01(8), 131.97(8)
Mo(2)–P(1)–W(1)	140.08(8), 140.94(8)		

Table 4 Selected bond lengths (Å) and angles (°) for complex **14**

W(1)–P(1)	2.537(4)	W(1)–As(1)	2.591(2)
W(1)–W(2)	3.0388(11)	W(2)–P(1)	2.433(4)
W(2)–As(1)	2.694(2)	W(3)–P(1)	2.524(4)
As(1)–P(1)	2.217(5)		
			50.77(10)
P(1)–W(1)–As(1)	51.22(11)	P(1)–W(1)–W(2)	50.93(11)
As(1)–W(1)–W(2)	56.51(5)	P(1)–W(2)–As(1)	53.88(10)
As(1)–W(2)–W(1)	53.32(5)	P(1)–W(2)–W(1)	58.43(12)
P(1)–As(1)–W(1)	63.15(12)	P(1)–As(1)–W(2)	70.64(14)
W(1)–As(1)–W(2)	70.17(5)	As(1)–P(1)–W(2)	140.3(2)
As(1)–P(1)–W(3)	130.3(2)	W(2)–P(1)–W(3)	75.35(13)
As(1)–P(1)–W(1)	65.63(12)	W(2)–P(1)–W(1)	
W(3)–P(1)–W(1)	141.1(2)		

Table 5 Selected bond lengths (Å) and angles (°) for complex **17**

W(1)–P(1)	2.590(4)	W(1)–P(2)	2.427(4)
W(1)–W(2)	3.0242(10)	W(2)–P(1)	2.488(4)
W(2)–P(2)	2.519(4)	W(3)–P(2)	2.517(4)
P(2)–P(1)	2.096(6)		
P(1)–W(1)–P(2)	49.25(14)	P(1)–W(1)–W(2)	51.92(10)
P(2)–W(1)–W(2)	53.69(10)	P(1)–W(2)–P(2)	49.48(14)
P(2)–W(2)–W(1)	50.95(9)	P(1)–W(2)–W(1)	55.01(10)
P(1)–P(2)–W(1)	69.4(2)	P(1)–P(2)–W(2)	64.5(2)
W(1)–P(2)–W(2)	75.35(10)	P(2)–P(1)–W(2)	66.0(2)
P(1)–P(2)–W(3)	132.2(2)	W(2)–P(2)–W(3)	141.3(2)
P(2)–P(1)–W(1)	61.33(15)	W(2)–P(1)–W(1)	73.06(12)
W(3)–P(1)–W(1)	139.8(2)		

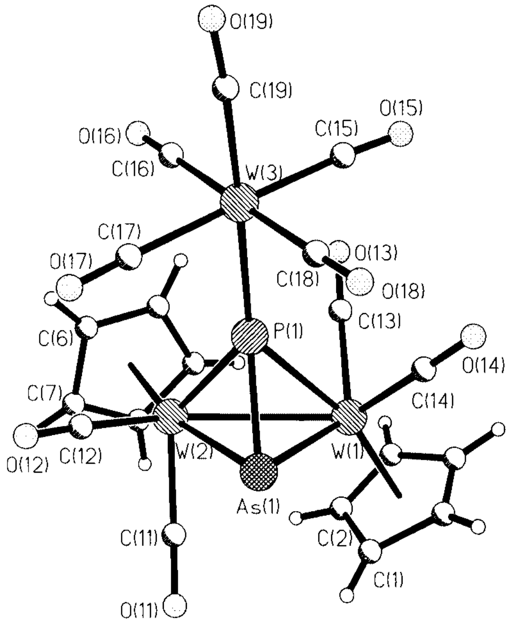


Fig. 3 Molecular structure of complex **14** showing the atom numbering scheme.

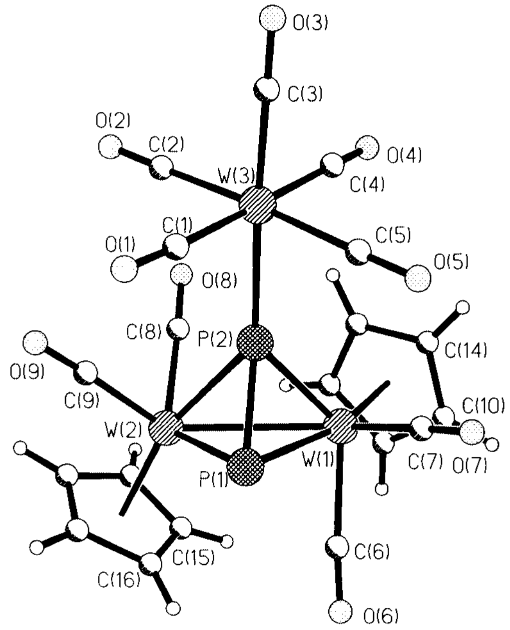


Fig. 4 Molecular structure of complex **17** showing the atom numbering scheme.

2.217(5) Å in **14** falls between the P–P separation in **1**[7] and **17** and the As–As separation in $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-}As_2)]$.[8] Similarly, the P–Sb bond length in **13**, averaged over the two independent molecules, is observed to be 2.406 Å, intermediate between the E–E bond lengths observed in **1**[7] and in $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-}Sb_2)]$.[9] The M–M bond distances correspond to single bonds, as required by simple electron counting schemes. The M–E distances reveal a considerable distortion of the pseudo-tetrahedral core from C_2 symmetry. Thus in **17** the M–P bonds involving P(2), the atom bonded to the $W(CO)_5$ unit, are significantly shorter (2.427(4), 2.519(4) Å) than the bonds involving the naked P(1) atom (2.488(4), 2.590(4) Å)). The W–P(1) bonds in **14** are only slightly longer than the W–P[$W(CO)_5$] distances in **17** taking into account the experimental error of 3σ (2.433(4), 2.537(4) Å), similarly the Mo–P distances in **13** are comparable with the corresponding distances in **1**. This means that the larger the heteroatom E the greater is the distortion of the M_2PE core from its idealised tetrahedral geometry. In **13** and **14**, M–As and M–Sb distances are correspondingly greater than the M–P(1) distances in **17** as expected. The E–P–$W(CO)_5$ angles of 132.2(2) (E = P, **17**), 130.01(8), 131.97(8) (E = Sb **13**) and 130.3(2)° (E = As **14**) are in good agreement with the corresponding angles in related complexes.[1] There are no statistically significant differences in the W–P σ bond distances to the $W(CO)_5$ fragment in complexes **13**, **14** and **17**, all these distances being in the range 2.517(4)–2.528(2) Å.

By contrast, the phosphorus and arsenic atoms are not distinguishable in the structure of complex **12**, a 50 : 50 disorder of

Table 6 Crystallographic data for complexes **12**, **13**, **14** and **17**[a]

	12	**13**	**14**	**17**
Formula	$C_{24}H_{10}AsMo_2O_{14}PW_2$	$C_{19}H_{10}Mo_2O_9PSbW$	$C_{19}H_{10}AsO_9PW_3$	$C_{19}H_{10}O_9P_2W_3$
Formula weight	1187.79	910.72	1039.71	995.76
T/K	290(2)	150(2)	294(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a/Å	18.677(5)	15.974(5)	19.306(3)	19.255
b/Å	10.799(5)	16.236(8)	8.103(2)	8.095
c/Å	16.916(5)	10.623(2)	32.374(2)	31.957
α/°		97.85(3)		
β/°	110.220(10)	96.34(2)	107.987(7)	106.510
γ/°		118.86(2)		
V/Å^3	3202(2)	2340.4(14)	4817.1(14)	4775.7(25)
Z	4	4	8	8
μ/mm^{-1}	9.066	7.203	15.768	14.597
Reflections collected	3014	8554	4392	4356
Independent reflections	3014 ($R_{int} = 0.0321$)	8232 ($R_{int} = 0.0301$)	3961 ($R_{int} = 0.1009$)	4223 ($R_{int} = 0.0500$)
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0409, 0.0702	0.0350, 0.0896	0.0440, 0.1150	0.0444, 0.0891
(all data)	0.0786, 0.0820	0.0389, 0.0922	0.1051, 0.1730	0.1189, 0.2240

[a] Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å.

these two atoms being imposed by a crystallographic twofold axis. The distance between the average P/As positions is 2.223(3) Å, similar to that observed in **14** and almost identical to that observed in **7**; it should be noted that for **12** the atoms were constrained to fit the same positions during refinement and would not in actuality do so. The E′–E′–W angle of 135.36(4)° is slightly larger than that observed for complexes **13** and **14**. This is possibly a result of steric interference between the two bulky W(CO)$_5$ fragments. A similar widening of the P–P-Cr(CO)$_5$ angle was observed for [$Cr_2Cp_2(CO)_4$\{μ-η^2-Cr(CO)$_5$P$_2$Cr(CO)$_5$\}] as compared to that in [$Cr_2Cp_2(CO)_4$\{μ-η^2-P$_2$Cr(CO)$_5$\}].[10]

Experimental

General procedures

Unless otherwise stated, all reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were distilled over the appropriate drying agent under a nitrogen atmosphere immediately prior to use. The complexes [$Mo_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **1** and [$W_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **2** were prepared by the literature method.[2b] The monoanions [$Mo_2Cp_2(CO)_4$(μ-PH$_2$)]$^-$ **3** and [$W_2Cp_2(CO)_4$(μ-PH$_2$)]$^-$ **4** were prepared by addition of one equivalent of *tert*-butyllithium to THF solutions of **1** and **2** respectively and used immediately. Group 15 trichlorides were obtained from Aldrich and used without further purification. Complexes are reported in order of elution.

Reaction of [$M_2Cp_2(CO)_4$(μ-PH$_2$)]$^-$ (M = Mo or W) with ECl$_3$ (E = P, As, or Sb)

General method. To a solution of complex **3** or **4** (1.05 mmol) in THF (50 ml) was added ECl$_3$ (1.15 mmol) whereupon the solution immediately turned orange. The solvent was removed under reduced pressure, the residue redissolved in the minimum quantity of dichloromethane, applied to the base of TLC plates, and eluted with 3 : 2 dichloromethane–hexane.

(i) M = Mo, E = P. Elution gave orange crystalline [$Mo_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **1** (117 mg, 0.150 mmol, 24%) and orange crystalline [$Mo_2Cp_2(CO)_4$(μ-η^2-P$_2$)] **5** (177 mg, 0.378 mmol, 36%).

(ii) M = W, E = P. Elution gave orange crystalline [$W_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **2** (183 mg, 0.284 mmol, 27%) and orange crystalline [$W_2Cp_2(CO)_4$(μ-η^2-P$_2$)] **6** (183 mg, 0.273 mmol, 26%).

(iii) M = Mo, E = As. Elution gave [$Mo_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **1** (157 mg, 0.336 mmol, 32%) and orange crystalline [$Mo_2Cp_2(CO)_4$(μ-η^2-PAs)] **7** (205 mg, 0.378 mmol, 36%).

(iv) M = Mo, E = Sb. Elution gave orange crystalline [$Mo_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **1** (133 mg, 0.284 mmol, 27%) and orange-red crystalline [$Mo_2Cp_2(CO)_4$(μ-η^2-PSb)] **8** (246 mg, 0.42 mmol, 40%).

(v) M = W, E = As. Elution gave orange crystalline [$W_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **2** (190 mg, 0.294 mmol, 28%) and orange crystalline [$W_2Cp_2(CO)_4$(μ-η^2-PAs)] **9** (256 mg, 0.357 mmol, 34%).

(vi) M = W, E = Sb. Elution gave orange crystalline [$W_2Cp_2(CO)_4$(μ-PH$_2$)(μ-H)] **2** (95 mg, 0.147 mmol, 14%) and red-orange crystalline [$W_2Cp_2(CO)_4$(μ-η^2-PSb)] **10** (316 mg, 0.431 mmol, 41%).

Reaction of [$M_2Cp_2(CO)_4$(μ-η^2-PE)] (M = Mo or W; E = As or Sb) with [W(CO)$_5$ (THF)]

General method. To a solution of complex **7**–**10** (0.217 mmol) in THF (20 ml) was added a solution of [W(CO)$_5$(THF)] (excess) in THF. The solution was stirred overnight at room temperature, during which time it darkened notably. The solvent was removed under reduced pressure, the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Samples were eluted with 1 : 1 dichloromethane–hexane solutions.

(i) M = Mo, E = As. Elution gave [$Mo_2Cp_2(CO)_2$\{μ-η^2-AsPW(CO)$_5$\}] **11** (36 mg, 0.042 mmol, 19%) and red crystalline [$Mo_2Cp_2(CO)_4$\{μ-η^2-(OC)$_5$WAsPW(CO)$_5$\}] **12** (201 mg, 0.169 mmol, 78%).

(ii) M = Mo, E = Sb. Elution gave orange-red crystalline [$Mo_2Cp_2(CO)_2$\{μ-η^2-SbPW(CO)$_5$\}] **13** (176 mg, 0.193 mmol, 89%).

(iii) M = W, E = As. Elution gave orange-red crystalline [$W_2Cp_2(CO)_2$\{μ-η^2-AsPW(CO)$_5$\}] **14** (50 mg, 0.048 mmol, 21%) and red crystalline [$W_2Cp_2(CO)_4$\{μ-η^2-(OC)$_5$WAsPW(CO)$_5$\}] **15** (211 mg, 0.150 mmol, 69%).

(iv) M = W, E = Sb. Elution gave orange-red crystalline [$W_2Cp_2(CO)_4$(μ-η^2-\{SbPW(CO)$_5$\}] **16** (203 mg, 0.187 mmol, 86%).

(v) M = W, E = P. Elution gave orange-red crystalline [$W_2Cp_2(CO)_4$(μ-η^2-\{PPW(CO)$_5$\}] **17** (203 mg, 0.187 mmol, 86%).

Thermolysis of [$Mo_2Cp_2(CO)_4$\{μ-η^2-(OC)$_5$WAsPW(CO)$_5$\}] 12

Complex **12** (101 mg, 0.085 mmol) was dissolved in dichloromethane (20 ml) and stirred overnight at room temperature. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with 1 : 1 dichloromethane–hexane gave orange-red crystalline $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-}\{AsPW(CO)_5\}]$ **11** (65 mg, 0.076 mmol, 89%).

Thermolysis of $[W_2Cp_2(CO)_4\{\mu\text{-}\eta^2\text{-}(OC)_5WAsPW(CO)_5\}]$ 15

Complex **15** (214 mg, 0.157 mmol) was dissolved in dichloromethane (40 ml) and stirred overnight at room temperature. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with 1 : 1 dichloromethane–hexane gave orange-red crystalline $[W_2Cp_2(CO)_4\{\mu\text{-}\eta^2\text{-}AsPW(CO)_5\}]$ **14** (140 mg, 0.135 mmol, 86%).

Crystallography

Crystal data are given in Table 6.

CCDC reference number 186/1954.

See http://www.rsc.org/suppdata/dt/b0/b001409p/ for crystallographic files in .cif format.

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References

1 For leading reviews see: K. H. Whitmire, *Adv. Organomet. Chem.*, 1998, **42**, 2; O. J. Scherer, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 1104 and references therein.

2 (*a*) J. E. Davies, M. J. Mays, P. R. Raithby, G. P. Shields and P. K. Tompkin, *Chem. Commun.*, 1996, 2051; (*b*) J. E. Davies, M. J. Mays, P. R. Raithby, G. P. Shields and P. K. Tompkin, *Chem. Commun.*, 1997, 361; (*c*) J. E. Davies, M. J. Mays, E. J. Pook, P. R. Raithby and P. K. Tompkin, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3283; (*d*) J. E. Davies, M. C. Klunduk, M. J. Mays, P. R. Raithby, G. P. Shields and P. K. Tompkin, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 715; (*e*) J. E. Davies, M. J. Mays, E. J. Pook, P. R. Raithby and P. K. Tompkin, *Chem. Commun.*, 1997, 1997.

3 J. E. Davies, L. C. Kerr, M. J. Mays, P. R. Raithby, P. K. Tompkin and A. D. Woods, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1428.

4 M. Muller and H. Vahrenkamp, *J. Organomet. Chem.*, 1983, **252**, 95.

5 O. J. Scherer, H. Sitzmann and G. Wolmerhäuser, *J. Organomet. Chem.*, 1984, **268**, C9.

6 G. L. Geoffroy, A. L. Rheingold and J. B. Sheridan, *Organometallics*, 1986, **5**, 1514; G. L. Geoffroy, D. B. Pourreau, A. L. Rheingold and J. B. Sheridan, *Organometallics*, 1988, **7**, 289; H. Adams, N. A. Bailey, M. N. Bancroft, A. P. Bisson and M. J. Morris, *J. Organomet. Chem.*, 1997, **542**, 131.

7 W. I. Bailey, M. H. Chisholm, F. A. Cotton and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764.

8 M. L. Ziegler, K. Blechschmitt, B. Nuber and T. Zahn, *Chem. Ber.*, 1988, **121**, 159.

9 J. R. Harper and A. L. Rheingold, *J. Organomet Chem.*, 1990, **390**, C36.

10 L. Y. Goh, R. C. S. Wong and T. C. W. Mak, *J. Organomet. Chem.*, 1989, **373**, 71; *J. Organomet. Chem.*, 1995, **503**, 47.