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Tetranuclear Phosphinidine, Phosphide, Arsenide, and Oxide Anionic Clusters of Molybdenum and Tungsten Supported by Neopentoxide Ligands: Na(18-crown-6)[$M_4(\mu_3\text{-PSiMe}_3)(\text{OCH}_2{}^t\text{Bu})_{11}$], K(18-crown-6)[$M_4(\mu_3\text{-E})(\text{OCH}_2{}^t\text{Bu})_{10}$] (E = P, As), K(18-crown-6)$_2$[$\text{Mo}_4(\mu_3\text{-O})(\text{OCH}_2{}^t\text{Bu})_{11}$][‡]

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From the reactions between $M_2(\text{OCH}_2{}^t\text{Bu})_6$ (2 equiv) and $\text{NaP(SiMe}_3)_2$ (1 equiv) in benzene and 18-crown-6 the phosphinidine clusters $[M_4(\mu_3\text{-PSiMe}_3)(\text{OCH}_2{}^t\text{Bu})_{11}]^-$, compounds **1** (M = Mo) and **2** (M = W) are formed and are reactive intermediates in the formation of $[M_4(\mu_3\text{-P})(\text{OCH}_2{}^t\text{Bu})_{10}]^-$ cluster anions, compounds **3** (M = Mo) and **4** (M = W), respectively, which have been isolated and characterized as their Na(18-crown-6)$^+$ salts. Crystals of Na(18-crown-6)$^+[\text{Mo}_4(\mu_3\text{-P})(\text{OCH}_2{}^t\text{Bu})_{10}]^-\cdot\text{C}_6\text{H}_6$ were examined by single crystal X-ray crystallography at −110 °C in the space group *Pn* with $a = 13.000(2)$ Å, $b = 17.501(3)$ Å, $c = 18.703(2)$ Å, and $\beta = 93.11(1)°$ with $Z = 2$ and at −173 °C in the space group *Cc* with $a = 22.118(4)$ Å, $b = 17.480(3)$ Å, $c = 23.250(4)$ Å, and $\beta = 110.82(1)°$ with $Z = 4$. At the lower temperature, there is higher symmetry and no disorder of the 18-crown-6 molecule. The cluster anion has a Mo_4 butterfly with a μ_3-P ligand and virtual mirror symmetry. One wing-tip Mo atom is five-coordinate and bonded to the μ_3-P atom and shows longer Mo-to-Mo distances (2.68(1) and 2.71(1) Å) relative to its counterpart (2.48(1) and 2.50(1) Å); the backbone Mo−Mo distance is 2.53(1) Å. The cluster anion in **3** but not **4** is also accessible from the reaction between $\text{Mo}_2(\text{OCH}_2{}^t\text{Bu})_6$ (2 equiv), PH_3, and $\text{KOCH}_2{}^t\text{Bu}$ (1 equiv) in THF/18-crown-6 (THF = tetrahydrofuran). A similar approach involving AsH_3, $\text{Mo}_2(\text{OCH}_2{}^t\text{Bu})_6$, and $\text{KOCH}_2{}^t\text{Bu}$ gave the μ_3-arsenide cluster complex K(18-crown-6)$^+[\text{Mo}_4(\mu_3\text{-As})(\text{OCH}_2{}^t\text{Bu})_{10}]^-$, compound **5**, which by NMR spectroscopy is analogous in structure to **3**. The reaction between $\text{Mo}_2(\text{OCH}_2{}^t\text{Bu})_6$ (2 equiv) and KOH in THF/18-crown-6 gave K(18-crown-6)$_2{}^+[\text{Mo}_4(\mu_3\text{-O})(\text{OCH}_2{}^t\text{Bu})_{11}]^-$, compound **6**, which is proposed to be isostructural with the phosphinidine complexes **1** and **2** on the basis of NMR data. Crystal data for $\text{K}(\eta^6\text{-C}_{12}\text{H}_{24}\text{O}_6)(\eta^2\text{-C}_{12}\text{H}_{24}\text{O}_6)^+[\text{Mo}_4(\mu_3\text{-O})(\text{OCH}_2{}^t\text{Bu})_{11}]^-$ at −165 °C: $a = 17.595(2)$ Å, $b = 28.044(3)$ Å, $c = 20.443(2)$ Å, $\beta = 97.61(1)°$ with $Z = 4$, and space group $P2_1/n$. The cluster anion in **6** contains a 12-electron Mo_4 butterfly with 12 M−M bonding electrons, as in **3**, but the shortest Mo−Mo distance 2.42(1) Å involves the backbone metal atoms. The Mo−Mo distances involving the oxo-capped triangle (2.61(1) and 2.62(1) Å) are notably longer than those in the other triangle (2.48(1) Å).

Introduction

Previous work in this laboratory has established the existence of the isolobally related series of compounds $(\eta^3\text{-P}_3)\text{W}(\text{OCH}_2{}^t\text{Bu})_3(\text{HNMe}_2)$,[1] $\text{W}_2(\text{O}^i\text{Pr})_6(\mu,\eta^2\text{-P}_2)(\text{py})$,[2] and $\text{W}_3(\mu_3\text{-P})(\text{OCH}_2{}^t\text{Bu})_9$.[3] The former and the latter compounds were derived from the reactions involving $\text{W}_2(\text{OCH}_2{}^t\text{Bu})_6$ and P_4. We have speculated that the latter may arise from the conproportionation of $\text{W}_2(\text{OCH}_2{}^t\text{Bu})_6$ and a reactive $({}^t\text{BuCH}_2\text{O})_3\text{W}{\equiv}\text{P}$ fragment in an analogous manner to the established formation of alkylidyne,[4] oxo,[5] and imido[6] capped trinuclear clusters of molybdenum and tungsten supported by alkoxide ligands. No terminal phosphide ligand complex is known at this time but a Fenske−Hall calculation on a hypothetical $[(\text{HO})_3\text{W}{\equiv}\text{P}]$ molecule with W−P = 2.20 Å suggested that the W≡P bond was similar in nature to a W≡S bond as in $({}^t\text{BuO})_4\text{W}{\equiv}\text{S}$.[7]

The compound $\text{W}_2(\text{O}^i\text{Pr})_6(\mu\text{-P}_2)(\text{py})$ is interesting in that it may be considered as the product of the equilibrium shown in eq 1, and in this regard it should be remembered that related

$$2[({}^i\text{PrO})_3\text{W}{\equiv}\text{P}] + \text{py} \rightleftharpoons \text{W}_2(\text{O}^i\text{Pr})_6(\mu\text{-P}_2)(\text{py}) \qquad (1)$$

equilibria involving $(\text{RO})_3\text{W}{\equiv}\text{CR}'$ compounds and $\text{W}_2(\text{OR})_6(\mu\text{-C}_2\text{R}_2{}')(\text{py})$ have been established.[8]

In the studies of the equilibrium of eq 2, it was shown that steric factors associated with R were important in favoring the alkylidyne species relative to the μ-alkyne adduct.

[‡] Dedicated to Prof. Dr. H. Roesky on the occasion of his 60th birthday.

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$$W_2(OR)_6(\mu\text{-}C_2R_2')(py) \rightleftharpoons 2[(RO)_3W{\equiv}CR'] + py \qquad (2)$$

Thus, our inability to isolate a $(RO)_3W{\equiv}P$ complex may well represent a lack of adequate steric protection of a reactive $W{\equiv}P$ functionality. This concept certainly finds support from the recent independent syntheses of $Mo{\equiv}P$ and $W{\equiv}P$ containing complexes by Cummins[9] and Schrock,[10] respectively, and in our trapping of a $(^tBuO)_3W{\equiv}P$ moiety by η^1-coordination to an electrophilic $M(CO)_5$ fragment where M = Cr and W.[11] Herein we describe further work aimed at the production of naked heteroatom clusters of molybdenum and tungsten supported by alkoxide ligands.

Results and Discussion

Synthesis. The well-known lability of $P(SiMe_3)_2^-$ ligands[12] toward attack by OR^- led us to investigate the reactions between $M_2(OCH_2{}^tBu)_6$ compounds and $NaP(SiMe_3)_2$.

$$2[M_2(OCH_2{}^tBu)_6] + NaP(SiMe_3)_2 \xrightarrow[C_6H_6]{23\ ^\circ C,\ 18\text{-crown-6}} Na(18\text{-crown-6})^+[M_4(\mu_3\text{-}PSiMe_3)(OCH_2{}^tBu)_{11}]^- + Me_3SiOCH_2{}^tBu \qquad (3)$$

The compounds $Na(18\text{-crown-6})^+[M_4(\mu_3\text{-}PSiMe_3)(OCH_2{}^tBu)_{11}]^-$ **1** (M = Mo) and **2** (M = W) were formed according to eq **3** but proved difficult to isolate in pure form because of the further elimination of $Me_3SiOCH_2{}^tBu$ and the formation of the μ_3-phosphide clusters $Na(18\text{-crown-6})^+[M_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$ **3** (M = Mo) and **4** (M = W), according to eq 4.

$$Na(18\text{-crown-6})^+[M_4(\mu_3\text{-}PSiMe_3)(OCH_2{}^tBu)_{11}]^- \xrightarrow[C_6H_6]{\geq 23\ ^\circ C} Na(18\text{-crown-6})^+[M_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^- + Me_3SiOCH_2{}^tBu \qquad (4)$$

The conversion of **1** to **3** (M = Mo) was notably faster than that of **2** to **4**, where M = W, with the former proceeding at room temperature over a few hours and the latter requiring heating to 70 °C to effect a similar process. This may reflect the fact that OR groups bound to tungsten are less nucleophilic than those bound to molybdenum as a result of enhanced RO p_π to M d_π bonding. This, of course, assumes that the rate of phosphinidine to phosphide conversion is dependent upon nucleophilic attack of the $SiMe_3$ silicon by either an inter- or intramolecular process. [We have not followed the rate of the reaction as a function of the concentration of the cluster to distinguish between these possibilities.]

An independent synthesis of the phosphide capped cluster has been achieved from the reaction between $Mo_2(OCH_2{}^tBu)_6$ compounds and phosphine, PH_3, in the presence of $KOCH_2{}^tBu$ in THF/18-crown-6, eq 5. Rather interestingly no related reaction occurs for $W_2(OCH_2{}^tBu)_6$.

$$2[Mo_2(OCH_2{}^tBu)_6] + PH_3 + KOCH_2{}^tBu \xrightarrow[THF/18\text{-crown-6}]{22\ ^\circ C} K(18\text{-crown-6})_2{}^+[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^- + 3{}^tBuCH_2OH \qquad (5)$$

Table 1. Bond Distances (Å) for the Anion $[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$

Mo(1)−Mo(3)	2.7103(7)	Mo(2)−O(42)	1.948(4)
Mo(1)−Mo(4)	2.6786(7)	Mo(2)−O(48)	1.897(4)
Mo(1)−P(5)	2.3128(15)	Mo(3)−Mo(4)	2.5349(7)
Mo(1)−O(6)	2.113(4)	Mo(3)−P(5)	2.4154(16)
Mo(1)−O(12)	2.111(4)	Mo(3)−O(6)	2.004(4)
Mo(1)−O(30)	1.946(4)	Mo(3)−O(18)	2.186(4)
Mo(1)−O(36)	1.934(4)	Mo(3)−O(54)	1.983(4)
Mo(2)−Mo(3)	2.4871(7)	Mo(4)−P(5)	2.4002(15)
Mo(2)−Mo(4)	2.4938(7)	Mo(4)−O(12)	2.013(4)
Mo(2)−O(18)	2.065(4)	Mo(4)−O(24)	2.160(4)
Mo(2)−O(24)	2.057(4)	Mo(4)−O(60)	1.975(4)

With the discovery of reaction 5 we determined to examine the related reactivity of arsine and found that this gives a μ_3-arsenide cluster, **5**, for molybdenum but not for tungsten, eq 6.

$$2[Mo_2(OCH_2{}^tBu)_6] + AsH_3 + KOCH_2{}^tBu \xrightarrow[THF/18\text{-crown-6}]{22\ ^\circ C} K(18\text{-crown-6})_2{}^+[Mo_4(\mu_3\text{-}As)(OCH_2{}^tBu)_{10}]^- + 3{}^tBuCH_2OH \qquad (6)$$

A somewhat related reaction involving KOH was also carried out, leading to an oxo-capped tetranuclear cluster, compound **6**, eq 7, which is believed to be structurally related to the phosphinidine capped clusters, *vide infra*.

$$2[Mo_2(OCH_2{}^tBu)_6] + KOH \xrightarrow[THF/18\text{-crown-6}]{22\ ^\circ C} K(18\text{-crown-6})_2{}^+[Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{11}]^- + {}^tBuCH_2OH \qquad (7)$$

Finally we note that the reaction between Na_3P and $Mo_2(OCH_2{}^tBu)_6$ (2 equiv) in THF also yields compound **3** but only in *ca*. 20% yield on the basis of the stoichiometric reaction shown in eq 8. The reaction between $(RO)_3WCl_3$ and Na_3P in THF was also attempted, but no well-characterized products were obtained where R = Me and Aryl.

$$2[Mo_2(OCH_2{}^tBu)_6] + Na_3P \xrightarrow[THF/18\text{-crown-6}]{22\ ^\circ C} Na(18\text{-crown-6})^+[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^- \qquad (8)$$

Single Crystal and Molecular Structures. The $[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$ anion was characterized as its sodium salt and crystallized with the stoichiometry $Na(18\text{-crown-6})[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-\cdot C_6H_6$ where the benzene was merely contained within the lattice. Selected bond distances and bond angles are given in Tables 1 and 2, respectively. A summary of the crystal data collection parameters is given in Table 3. The Na^+ ion is encapsulated by the 18-crown-6 ether, η^6-O_6−Na^+, and neither the Na^+ ion nor the benzene molecule is associated with the cluster anion. The central $Mo_4(\mu_3\text{-}P)(\mu\text{-}O)_4O_6$ unit of the cluster anion is shown in Figure 1.

The Mo_4 butterfly contains wing-tip metal atoms that are five coordinate, Mo(1), and four-coordinate, Mo(2), excluding M−M bonding interactions. Within this description the geometry about Mo(1) is distinctly square-pyramidal with the P atom occupying the axial site. The $O_4Mo(2)$ moiety may be viewed as an ML_4 fragment derived from a trigonal-bypyramid, where O(18) and O(24) are axial sites and O(42) and O(48) equatorial. The frontier orbitals of this ML_4 fragment are thus directed toward the hinge or backbone Mo atoms, Mo(3) and Mo(4).

In looking at the $Mo_4(\mu_3\text{-}P)(\mu\text{-}O)_4O_6$ skeleton it is also interesting to note that two of the μ-O groups lie in a Mo_3 plane, namely, O(24) and O(18), whereas O(12) and O(16) are on the

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Table 2. Selected Bond Angles (deg) for the $[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$ Anion

Mo(3)−Mo(1)−Mo(4)	56.114(19)	Mo(1)−Mo(3)−O(54)	136.05(12)
Mo(3)−Mo(1)−P(5)	56.82(4)	Mo(2)−Mo(3)−Mo(4)	59.539(19)
Mo(3)−Mo(1)−O(6)	47.12(10)	Mo(2)−Mo(3)−P(5)	114.15(4)
Mo(3)−Mo(1)−O(12)	89.02(11)	Mo(2)−Mo(3)−O(6)	103.85(12)
Mo(3)−Mo(1)−O(30)	99.01(11)	Mo(2)−Mo(3)−O(18)	51.98(10)
Mo(3)−Mo(1)−O(36)	150.31(12)	Mo(2)−Mo(3)−O(54)	110.00(12)
Mo(4)−Mo(1)−P(5)	56.92(4)	Mo(4)−Mo(3)−P(5)	57.95(4)
Mo(4)−Mo(1)−O(6)	90.12(10)	Mo(4)−Mo(3)−O(6)	96.90(11)
Mo(4)−Mo(1)−O(12)	47.92(10)	Mo(4)−Mo(3)−O(18)	111.00(10)
Mo(4)−Mo(1)−O(30)	147.15(12)	Mo(4)−Mo(3)−O(54)	127.60(12)
Mo(4)−Mo(1)−O(36)	101.67(12)	P(5)−Mo(3)−O(6)	101.94(12)
P(5)−Mo(1)−O(6)	102.06(11)	P(5)−Mo(3)−O(18)	163.18(10)
P(5)−Mo(1)−O(12)	103.60(11)	P(5)−Mo(3)−O(54)	92.55(13)
P(5)−Mo(1)−O(30)	92.37(12)	O(6)−Mo(3)−O(18)	91.62(15)
P(5)−Mo(1)−O(36)	95.39(12)	O(6)−Mo(3)−O(54)	133.41(16)
O(6)−Mo(1)−O(12)	90.49(16)	O(18)−Mo(3)−O(54)	85.10(15)
O(6)−Mo(1)−O(30)	85.02(16)	Mo(1)−Mo(4)−Mo(2)	110.094(24)
O(6)−Mo(1)−O(36)	162.36(16)	Mo(1)−Mo(4)−Mo(3)	62.574(18)
O(12)−Mo(1)−O(30)	163.99(16)	Mo(1)−Mo(4)−P(5)	53.84(4)
O(12)−Mo(1)−O(36)	87.86(16)	Mo(1)−Mo(4)−O(12)	51.10(11)
O(30)−Mo(1)−O(36)	91.78(17)	Mo(1)−Mo(4)−O(24)	139.81(11)
Mo(3)−Mo(2)−Mo(4)	61.184(20)	Mo(1)−Mo(4)−O(60)	135.91(12)
Mo(3)−Mo(2)−O(18)	56.47(11)	Mo(2)−Mo(4)−Mo(3)	59.278(18)
Mo(3)−Mo(2)−O(24)	116.76(11)	Mo(2)−Mo(4)−P(5)	114.45(4)
Mo(3)−Mo(2)−O(42)	115.89(13)	Mo(2)−Mo(4)−O(12)	101.52(12)
Mo(3)−Mo(2)−O(48)	101.92(13)	Mo(2)−Mo(4)−O(24)	51.86(10)
Mo(4)−Mo(2)−O(18)	117.07(11)	Mo(2)−Mo(4)−O(60)	108.35(12)
Mo(4)−Mo(2)−O(24)	55.67(11)	Mo(3)−Mo(4)−P(5)	58.53(4)
Mo(4)−Mo(2)−O(42)	112.78(12)	Mo(3)−Mo(4)−O(12)	96.34(10)
Mo(4)−Mo(2)−O(48)	104.44(13)	Mo(3)−Mo(4)−O(24)	111.05(10)
O(18)−Mo(2)−O(24)	167.30(14)	Mo(3)−Mo(4)−O(60)	124.65(12)
O(18)−Mo(2)−O(42)	87.72(16)	P(5)−Mo(4)−O(12)	103.69(12)
O(18)−Mo(2)−O(48)	95.73(15)	P(5)−Mo(4)−O(24)	160.26(11)
O(24)−Mo(2)−O(42)	86.38(16)	P(5)−Mo(4)−O(60)	90.77(13)
O(24)−Mo(2)−O(48)	96.33(16)	O(12)−Mo(4)−O(24)	93.81(16)
O(42)−Mo(2)−O(48)	136.05(18)	O(12)−Mo(4)−O(60)	137.56(16)
Mo(1)−Mo(3)−Mo(2)	109.287(23)	O(24)−Mo(4)−O(60)	82.16(16)
Mo(1)−Mo(3)−Mo(4)	61.312(16)	Mo(1)−P(5)−Mo(3)	69.91(4)
Mo(1)−Mo(3)−P(5)	53.27(4)	Mo(1)−P(5)−Mo(4)	69.24(4)
Mo(1)−Mo(3)−O(6)	50.57(11)	Mo(3)−P(5)−Mo(4)	63.52(4)
Mo(1)−Mo(3)−O(18)	135.80(10)	Mo(1)−O(6)−Mo(3)	82.31(14)

Table 3. Summary of Crystal Data for Compounds **3** and **6**

	3	**6**
empirical formula	$C_{62}H_{134}Mo_4NaO_{16}P\cdot C_6H_6$	$C_{55}H_{121}Mo_4O_{12}{}^-K^+\cdot 2C_{12}H_{24}O_6$
space group	*Cc*	$P2_1/n$
temp (°C)	−173	−165
cell dimens		
a (Å)	22.118(4)	17.595(2)
b (Å)	17.480(3)	28.044(3)
c (Å)	23.250(40	20.443(2)
β (deg)	110.82(1)	97.61(1)
Z (molecules/cell)	4	4
vol (Å^3)	8402.13	9997.94
calcd dens	1.306	1.280
wavelength (Å^3)	0.710 69	0.710 69
$R(F)^a$	0.0427	0.0512
$R_w(F)^b$	0.0449	0.0496
GOF^c for the last cycle	1.115	1.225
max Δ/σ for last cycle	0.001	0.01

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2\}^{1/2}$. [c] Goodness of fit (GOF) $= \{\sum w(|F_o| - |F_c|)^2/N_{obs} - N_{variables}\}^{1/2}$.

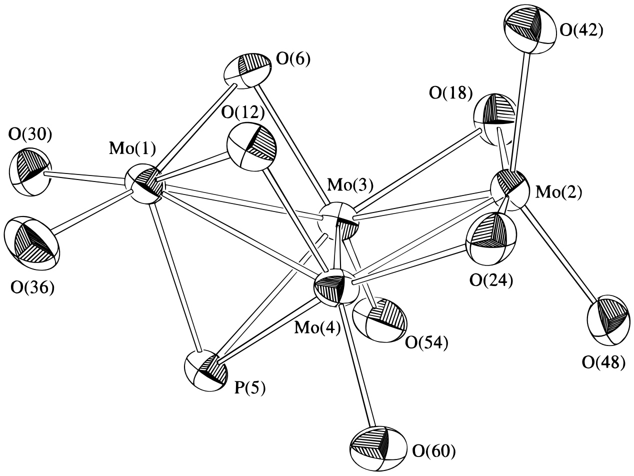

Figure 1. Central $Mo_4(\mu_3\text{-}P)(\mu\text{-}O)_4O_6$ core in the anion $[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$.

Table 4. Selected Bond Distances (Å) for the $[Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{11}]^-$ Anion

Mo(1)−Mo(2)	2.422(8)	Mo(2)−O(36)	1.955(4)
Mo(1)−Mo(3)	2.6079(8)	Mo(3)−O(5)	2.046(4)
Mo(1)−Mo(4)	2.4841(8)	Mo(3)−O(6)	2.099(4)
Mo(1)−O(5)	2.040(4)	Mo(3)−O(12)	2.112(4)
Mo(1)−O(6)	2.001(4)	Mo(3)−O(42)	1.950(4)
Mo(1)−O(24)	2.150(4)	Mo(3)−O(48)	2.030(4)
Mo(1)−O(30)	1.962(4)	Mo(3)−O(54)	1.938(4)
Mo(2)−Mo(3)	2.6213(8)	Mo(4)−O(18)	2.061(4)
Mo(2)−Mo(4)	2.4831(7)	Mo(4)−O(24)	2.101(4)
Mo(2)−O(5)	2.029(4)	Mo(4)−O(60)	1.909(4)
Mo(2)−O(12)	2.010(4)	Mo(4)−O(66)	1.916(4)
Mo(2)−O(18)	2.158(4)		

opposite face to the μ_3-P capping ligand. Mo(1) can be viewed as an ML_5 fragment of an octahedron, and in this way the cluster can be seen to be closely related to $Mo_4(OCH_2{}^cBu)_{12}(HO^cBu)$[13] and $Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{10}(py)$[14] that contain a butterfly arrangement of the metal atoms with one octahedrally coordinated wing-tip atom. In each of the three clusters there appears to be a valence disproportionation in the sense that metal−ligand bonding is maximized at one wing-tip metal atom and this leads to quite different M−M distances within the two triangles that comprise the butterfly. In the present instance the Mo(1) to Mo(3)/Mo(4) distances are 2.69(1) Å, whereas the Mo(2) to Mo(3)/Mo(4) distances are 2.49(1) Å.

The Mo−O terminal and bridging distances follow the anticipated order, namely, terminal are shorter than bridging but are not otherwise exceptional.[15] However, the P−Mo distances clearly fall into two types with Mo(1)−P = 2.31(1) and Mo(3)/Mo(4)−P = 2.41(1) Å. Finally it is worth mentioning that the cluster anion has a virtual mirror plane of symmetry. This is relevant to NMR data discussed later.

The oxo cluster anion **6** was obtained as a crystalline complex with formula $K(18\text{-crown-}6)_2{}^+[Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{11}]^-$. Selected bond distances and bond angles are presented in Tables 4 and 5. A summary of crystallographic data is given in Table 3.

Apparently the larger K^+ ion favors the coordination of two 18-crown-6 ether molecules, and in so doing an η^6-,η^2-bonding mode is achieved, as shown in Figure 2. Again the coordination of the K^+ ion does not involve the $Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{11}{}^-$ anion whose central Mo_4O_{12} skeleton is shown in Figure 3. A Mo_4 butterfly is supported by an oxo group that caps one triangle, four μ-OR groups, and seven terminal OR ligands. One wing-tip Mo atom is now seen to be octahedrally coordinated, and the other three have only four Mo−O bonds. In this regard the cluster again resembles that seen for $Mo_4(\mu_3\text{-}O)(OCH_2{}^cBu)_{12}\cdot(HOCH_2{}^cBu)$ and $Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{10}(py)$, and as in $[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$ the Mo−Mo distances of the two edge-shared triangles seem to indicate a valence disproportion-

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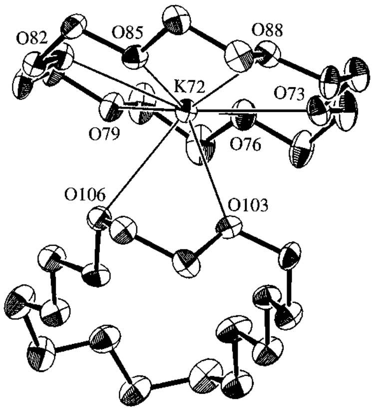


Figure 2. Coordination geometry of the K(η^6-18-crown-6)(η^2-18-crown-6)$^+$ ion in K(18-crown-6)$_2{}^+$[Mo$_4$(μ_3-O)(OCH$_2{}^t$Bu)$_{11}$]$^-$.

Table 5. Selected Bond Angles (deg) for the [Mo$_4$(μ_3-O)(OCH$_2{}^t$Bu)$_{11}$]$^-$

Mo(2)−Mo(1)−Mo(3)	62.688(22)	Mo(1)−Mo(3)−O(12)	89.34(11)
Mo(2)−Mo(1)−Mo(4)	60.793(22)	Mo(1)−Mo(3)−O(42)	93.78(12)
Mo(2)−Mo(1)−O(5)	53.27(11)	Mo(1)−Mo(3)−O(48)	134.91(12)
Mo(2)−Mo(1)−O(6)	99.40(11)	Mo(1)−Mo(3)−O(54)	136.92(12)
Mo(2)−Mo(1)−O(24)	114.01(11)	Mo(2)−Mo(3)−O(5)	49.69(11)
Mo(2)−Mo(1)−O(30)	119.77(12)	Mo(2)−Mo(3)−O(6)	90.93(11)
Mo(3)−Mo(1)−Mo(4)	110.413(25)	Mo(2)−Mo(3)−O(12)	48.83(11)
Mo(3)−Mo(1)−O(5)	50.44(11)	Mo(2)−Mo(3)−O(42)	135.76(12)
Mo(3)−Mo(1)−O(6)	52.18(11)	Mo(2)−Mo(3)−O(48)	137.69(12)
Mo(3)−Mo(1)−O(24)	138.45(11)	Mo(2)−Mo(3)−O(54)	91.61(12)
Mo(3)−Mo(1)−O(30)	132.00(12)	O(5)−Mo(3)−O(6)	98.26(15)
Mo(4)−Mo(1)−O(5)	112.16(11)	O(5)−Mo(3)−O(12)	97.95(15)
Mo(4)−Mo(1)−O(6)	102.65(12)	O(5)−Mo(3)−O(42)	86.66(16)
Mo(4)−Mo(1)−O(24)	53.35(11)	O(5)−Mo(3)−O(48)	171.70(16)
Mo(4)−Mo(1)−O(30)	109.95(12)	O(5)−Mo(3)−O(54)	88.07(16)
O(5)−Mo(1)−O(6)	101.74(16)	O(6)−Mo(3)−O(12)	90.97(15)
O(5)−Mo(1)−O(24)	162.97(15)	O(6)−Mo(3)−O(42)	88.53(16)
O(5)−Mo(1)−O(30)	90.48(16)	O(6)−Mo(3)−O(48)	86.12(16)
O(6)−Mo(1)−O(24)	91.14(15)	O(6)−Mo(3)−O(54)	173.34(16)
O(6)−Mo(1)−O(30)	137.62(17)	O(12)−Mo(3)−O(42)	175.39(16)
O(25)−Mo(1)−O(30)	87.33(16)	O(12)−Mo(3)−O(48)	88.98(16)
Mo(1)−Mo(2)−Mo(3)	62.125(22)	O(12)−Mo(3)−O(54)	86.07(16)
Mo(1)−Mo(2)−Mo(4)	60.836(22)	O(42)−Mo(3)−O(48)	86.41(17)
Mo(1)−Mo(2)−O(5)	53.66(11)	O(42)−Mo(3)−O(54)	93.93(17)
Mo(1)−Mo(2)−O(12)	97.22(11)	O(48)−Mo(3)−O(54)	87.86(16)
Mo(1)−Mo(2)−O(18)	112.98(10)	Mo(1)−Mo(4)−Mo(2)	58.371(20)
Mo(1)−Mo(2)−O(36)	119.11(12)	Mo(1)−Mo(4)−O(18)	114.14(11)
Mo(3)−Mo(2)−Mo(4)	110.008(25)	Mo(1)−Mo(4)−O(24)	55.15(11)
Mo(3)−Mo(2)−O(5)	50.25(11)	Mo(1)−Mo(4)−O(60)	101.97(12)
Mo(3)−Mo(2)−O(12)	52.24(11)	Mo(1)−Mo(4)−O(66)	111.81(13)
Mo(3)−Mo(2)−O(18)	140.89(10)	Mo(2)−Mo(4)−O(18)	55.78(11)
Mo(3)−Mo(2)−O(36)	133.56(12)	Mo(2)−Mo(4)−O(24)	113.39(11)
Mo(4)−Mo(2)−O(5)	112.58(11)	Mo(2)−Mo(4)−O(60)	104.43(12)
Mo(4)−Mo(2)−O(12)	100.07(11)	Mo(2)−Mo(4)−O(66)	111.49(12)
Mo(4)−Mo(2)−O(18)	52.15(10)	O(18)−Mo(4)−O(24)	168.39(16)
Mo(4)−Mo(2)−O(36)	108.22(12)	O(18)−Mo(4)−O(60)	94.49(16)
O(5)−Mo(2)−O(12)	101.89(16)	O(18)−Mo(4)−O(66)	91.14(16)
O(5)−Mo(2)−O(18)	160.63(15)	O(24)−Mo(4)−O(60)	92.49(16)
O(5)−Mo(2)−O(36)	90.96(16)	O(24)−Mo(4)−O(66)	89.49(16)
O(12)−Mo(2)−O(18)	93.34(15)	O(60)−Mo(4)−O(66)	139.78(17)
O(12)−Mo(2)−O(36)	141.50(16)	Mo(1)−O(5)−Mo(2)	73.07(13)
O(18)−Mo(2)−O(36)	84.31(16)	Mo(1)−O(5)−Mo(3)	79.33(14)
Mo(1)−Mo(3)−Mo(2)	55.187(19)	Mo(2)−O(5)−Mo(3)	80.06(14)
Mo(1)−Mo(3)−O(5)	50.22(11)	Mo(1)−O(6)−Mo(3)	78.95(14)
Mo(1)−Mo(3)−O(6)	48.87(11)		

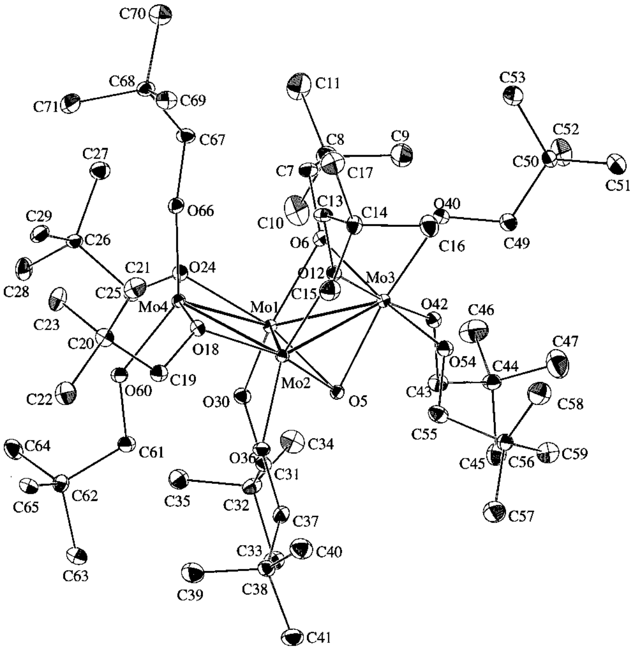
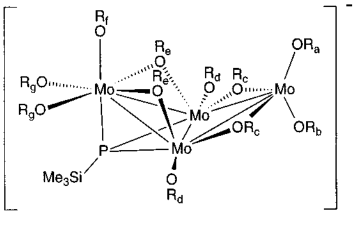


Figure 3. ORTEP drawing of the [Mo$_4$(μ_3-O)(μ-OCH$_2{}^t$Bu)$_4$(OCH$_2{}^t$Bu)$_7$]$^-$ anion giving the atom numbering scheme.

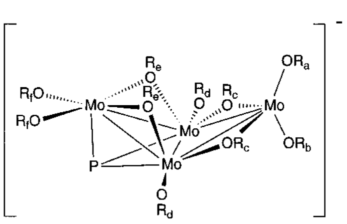
ation within the cluster. Thus, the distances to the wing-tip Mo(3) that is octahedrally coordinated are 2.61(1) and 2.62(1) Å as compared to the four-coordinate wing-tip Mo(4) that are 2.48(1) Å. Finally we mention that the oxo anion structure for **6** is presented in this work because it is isoelectronic and believed to be structurally related to the phosphinidine anion clusters [M$_4$(μ_3-PSiMe$_3$)(OCH$_2{}^t$Bu)$_{11}$]$^-$ that are intermediates in the formation of the phosphide clusters.

NMR and Solution Behavior. Na(18-crown-6)$^+$[M$_4$(μ_3-PSiMe$_3$)(OCH$_2{}^t$Bu)$_{11}$]$^-$ complexes **1** (M = Mo) and **2** (M = W) show eight doublets of equal intensity (J = 11 Hz) and three singlets in the ^{1}H NMR spectrum assignable to the methylene protons of the OCH$_2{}^t$Bu ligands. This is reconcilable with the static (NMR time-scale) structure depicted by **A**. The phosphinidine signal occurs at δ 294 for **1** (M = Mo) and at δ 170 for **2** (M = W). The latter signal is flanked by two sets of satellites due to coupling to ^{183}W, I = $^1/_2$, 14.5% natural abundance, as shown in Figure 4. The satellite spectrum is consistent with a stronger interaction with the one wing-tip W atom than the 2 equiv W backbone atoms.



A

The phosphide cluster anions, **3** and **4**, also display NMR data consistent with the butterfly structure observed in the solid state for **3**. Again the methylene protons of the symmetry related pairs of OR ligands that lie off the virtual mirror plane of symmetry, namely, c, d, e, and f in **B**, appear as doublets because they are diastereotopic and the most downfield resonance reveals evidence of a further small coupling at *ca.* 3 Hz to ^{31}P to one of the CH$_2$ methylene protons, as shown in Figure 5. The methylene protons that lie on the mirror plane, namely, those associatedwith OR groups a and b in structure **B**, appear as singlets.



B

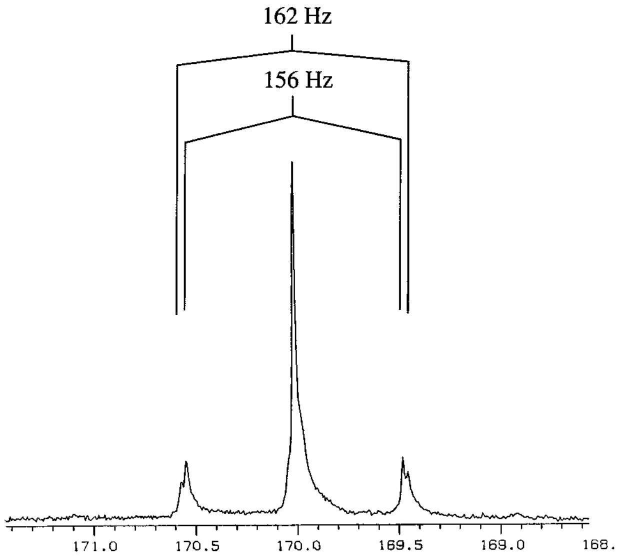


Figure 4. ^{31}P signal of the μ_3-P ligand in the $[W_4(\mu_3\text{-PSiMe}_3)(\mu\text{-OCH}_2{}^t\text{Bu})_4(\text{OCH}_2{}^t\text{Bu})_7]^-$ anion in C_5D_5N at 23 °C (SF = 146 MHz), showing the two sets of couplings to ^{183}W: $I = {}^1/_2$, 14.5% natural abundance.

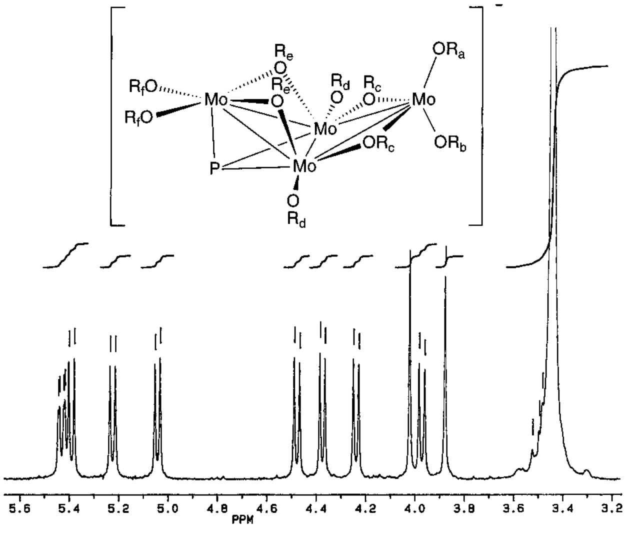


Figure 5. Methylene region of the ^{1}H NMR spectrum of the $[Mo_4(\mu_3\text{-P})(\mu\text{-CH}_2{}^t\text{Bu})_4(\text{OCH}_2{}^t\text{Bu})_6]^-$ anion. The signal at ~3.4 is due to 18-crown-6.

The ^{31}P signal assignable to the μ_3-phosphide ligand in **3** occurs as a singlet at δ 854.3 (40 °C, py-d_5) and in **4** at δ 504.8 with the latter showing coupling to two inequivalent groups of W atoms, as shown in Figure 6. Again the larger coupling constant is associated with the satellites of integral intensity 7%, consistent with the stronger (and in the solid-state shorter) W$-$P bond relative to those of the backbone W atoms. Of particular note in comparing the spectra shown in Figures 4 and 6 is that the magnitude of the $^{1}J_{^{183}\text{W}-^{31}\text{P}}$ coupling constants differ markedly in the phosphide and phosphinidine complexes, with the latter being roughly 5 times greater than that in the phosphide. This is perhaps counterintuitive in the sense that phosphorus is four-coordinate in **2**, whereas it is three-coordinate in **4**, and it is well-known in the chemistry of carbon that the magnitude of $^{1}J_{^{13}\text{C}-\text{X}}$ depends upon the coordination number of carbon, *c.f.* $^{1}J_{^{13}\text{C}-\text{H}} = 250$ Hz in ethyne, 175 Hz in ethene, and 125 Hz in methane.[16] However, the real reason for the latter is that the s contribution in the C$-$H bond is changing, C_{sp} vs C_{sp^2} vs C_{sp^3}, and herein most probably lies the reason for the relative magnitudes of $^{1}J_{^{183}\text{W}-^{31}\text{P}}$ in **2** and **4**. In the phosphide anion **4** phosphorus probably uses predominantly its 3p atomic orbitals to bond to the three W atoms with the phosphorus 3s atomic orbital accommodating the lone pair, whereas in **2** phosphorus is formally sp^3 hybridized and thus the phosphorus 3s to W bonding is greater in the phosphinidine than in the phosphide. A similar argument can be advanced to explain why the magnitude of $^{1}J_{^{31}\text{P}-^{1}\text{H}}$ increases upon the complexation of PH_3 to a metal.[17]

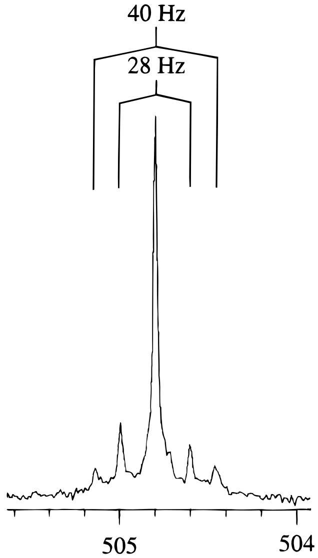


Figure 6. ^{31}P signal of the μ_3-P ligand in the anion $[W_4(\mu_3\text{-P})(\mu\text{-OCH}_2{}^t\text{Bu})_4(\text{OCH}_2{}^t\text{Bu})_6]^-$ in C_5D_5N at 60 °C (SF = 146 MHz), showing the two distinct couplings to different ^{183}W nuclei.

The ^{1}H NMR spectrum of the arsenide complex anion $[Mo_4(\mu_3\text{-As})(\text{OCH}_2{}^t\text{Bu})_{10}]^-$ is akin to that of the related phosphide complex **2**, and that of the oxo anion $[Mo_4(\mu_3\text{-O})(\text{OCH}_2{}^t\text{Bu})_{11}]^-$ is akin to that of the phosphinidine complex **1** described before. Since the oxo anion was structurally characterized in **6**, it is this close relationship of the NMR spectra that leads us to propose that the phosphinidine has the structure shown in **A**.

Comments on Reactivity. In the addition of $NaP(SiMe_3)_2$ to $M_2(OCH_2{}^tBu)_6$ the formation of a transient (reactive intermediate) dinuclear anion can be considered to be the nucleophile toward another $M_2(OCH_2{}^tBu)_6$ molecule. In this regard there is a similarity with our earlier finding that KH and $Mo_2(OCH_2{}^tBu)_6$ react in THF/18-crown-6 to give the potassium salt of the hydrido cluster $[Mo_4(\mu\text{-H})(\text{OCH}_2{}^t\text{Bu})_{12}]^-$.[18] In the present work the cluster building reaction occurs with the stepwise elimination of $Me_3SiOCH_2{}^tBu$. The fact that the conversion of **2** to **4** is notably slower than the conversion of **1** to **3** may well reflect that OR bonds bound to W are more covalent and less nucleophilic than those bound to Mo.

The reactions involving PH_3 and AsH_3 fail for tungsten. From preliminary NMR studies it seems that oxidative addition occurs in reactions involving PH_3 and this may well reflect the now well-accepted fact that W$-$W bonds are more reactive in this manner than their Mo$-$Mo counterparts.[19] Finally it is worth noting that although $M_4(OCH_2R)_{12}$ compounds are known for M = Mo and W, where R = ^{c}Bu, ^{c}Pen, and ^{i}Pr;[13] none of these compounds were reactive with $NaP(SiMe_3)_2$ to give the phosphide clusters **3** and **4** and RCH_2OSiMe_3. Evidently the

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dinuclear compounds $M_2(OCH_2{}^tBu)_6$ are kinetically more labile than their tetranuclear clusters, and this has been seen before in a comparison of their reactivities with nitriles and alkynes.[20]

Concluding Remarks

The present work extends the cluster building reactions of $M_2(OR)_6$ to include phosphinidine, phosphide, and arsenide ligands. The cluster anions described in this work share a common structural motif of an unsymmetrical M_4 butterfly, wherein one M_3 triangle is capped by a P, As, or oxo group. The M−M distances and the local coordination geometries suggest that an intracluster valence disproportionation has occurred such that in one triangle M−M bonding is maximized, while at the wing-tip metal atom of the other M_3 triangle metal−ligand bonding is maximized. This type of bonding has been seen before,[13,14] and in the present case none of the clusters is fluxional, which indicates a significant barrier to intramolecular ligand scrambling that might otherwise cause an equivalence of the two triangles within the butterfly.

Experimental Section

All synthetic procedures were performed under an inert atmosphere utilizing standard procedures in conjunction with a Vacuum Atmospheres Corp. DriLab. The solvents used were dried by standard procedures and stored over 4 Å sieves. Benzene-d_6, toluene-d_8, and pyridine-d_5 were obtained commercially but were degassed and stored over 4 Å molecular sieves prior to use. The metal alkoxides were prepared as described in the literature[21] and were recrystallized from cold hexanes and dried *in vacuo* prior to use. $KOCH_2{}^tBu$, $NaOCH_2{}^tBu$, and $KOCH_2{}^iPr$ were prepared by reacting the appropriate dry alcohol and the corresponding alkali metal in THF at room temperature and were dried *in vacuo* (0.01 Torr, 75 °C) prior to use. Na_3P and $NaP(SiMe_3)_2$ were prepared by following previously published procedures.[22] The crown ether (18-crown-6) was purchased commercially (Aldrich) and sublimed twice (0.01 Torr, 100 °C) prior to use. PH_3 (Scott specialty gases) and AsH_3 (MG Industries) were used as supplied from commercial sources. NMR spectra were recorded on Varian XL-300 (300.1 MHz for ^1H operation), Bruker AM-500 (500.0 MHz), and Nicolet NT-360 (360.0 MHz) spectrometers and were referenced to residual protio impurities of the deuterated solvents. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. UV−visible spectra were recorded in THF on a Hewlett-Packard 8452A diode array spectrophotometer.

$[Na(18\text{-crown-}6)]^+[Mo_4(\mu_3\text{-}PSiMe_3)(OCH_2{}^tBu)_{11}]^-$, 1. Solid $NaP(SiMe_3)_2$ (28 mg, 0.14 mmol), 18-crown-6 (74 mg, 0.28 mmol), and $Mo_2(OCH_2{}^tBu)_6$ (200 mg, 0.28 mmol) were weighed into a Schlenk flask in the glovebox. C_6H_6 (∼10 mL) was then added outside the box by cannula under nitrogen and the mixture heated briefly so that all of the solids dissolved. The reaction was then allowed to stand for 2 days, whereupon large green crystals deposited. These were filtered, washed with additional benzene, and analyzed by NMR spectroscopy, which showed them to consist of an approximately 60:40 mixture of the phophinidene, **1**, and the phosphide, **3**. All attempts to obtain **1** in pure form (free from **3**) failed, apparently due to the greater solubility of the former. When the reaction was performed under similar conditions in an NMR tube in C_6D_6 (without the initial heating) and monitored by ^1H NMR spectroscopy, the formation of the cluster anion **1** with concomitant formation of $^tBuCH_2OSiMe_3$ (whose identity was verified by comparison with an authentic sample prepared from $KOCH_2{}^tBu$ and Me_3SiCl, see below) and formation of **3** with liberation of another equivalent of $^tBuCH_2OSiMe_3$ could be clearly discerned. At no point did the spectroscopic yield of **1** exceed 70%. An intermediate adduct of formula $[Na(18\text{-crown-}6)][Mo_2(OCH_2{}^tBu)_6(P(SiMe_3)_2]$ was not detected. For **1**: ^1H NMR (500 MHz, benzene-d_6, 23 °C): $-CH_2-$ region, δ 5.21, 4.92, 4.83, 4.58, 4.42, 4.17, 4.14, 3.68 (d, 2H each, $J = 11$ Hz), 4.32, 4.01, 3.58 (s, 2H each); $-OCH_2CH_2-$, region 3.20 (s, 24H); $-C(CH_3)_3$ region, δ 1.39 (s, 9H), 1.38 (s, 18H), 1.35 (s, 18H), 1.28 (s, 18H), 1.20 (s, 18H), 1.19 (s, 9H), 1.18 (s, 9H); $-PSi(CH_3)_3$ region, δ 0.98 (d, 9H, $J_{P-H} = 2$ Hz). $^{31}P\{^1H\}$ (146 MHz, benzene-d_6, 23 °C): δ 294 (s).

$[Na(18\text{-crown-}6)]^+[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-$, 3. An identical procedure was used to that described above except that the reaction was heated at 75 °C overnight. Upon cooling to room temperature, green crystals deposited. These were filtered, washed with additional benzene (2 × 2 mL), and found to be pure **3**. Yield: 120 mg, 54.5%. For **3**: ^1H NMR (500 MHz, pyridine-d_5, 23 °C) $-CH_2-$ region, δ 5.42 (dd, $J_{P-H} = 3$ Hz, $J_{H-H} = 11$ Hz), 5.38, 5.22, 5.03, 4.87, 4.37, 4.23, and 3.96 (d, 2H each, $J = 11$ Hz), 4.02 and 3.87 (s, 2H each); $-OCH_2CH_2-$ region, δ 3.44 (s, 24 H); $-C(CH_3)_3$ region, δ 1.47, 1.30, 1.23, 1.17, 1.06, 1.05 (s, 18:18:9:18:9:18). $^{13}C\{^1H\}$ (125 MHz, pyridine-d_5, 23 °C): $-CH_2-$ region 99.49 (d, 2C, $J = 19$ Hz), 91.11 (d, 2C, $J = 16$ Hz), 87.75 (s, 1C), 87.14 (s, 1C), 86.23 (s, 2C), 84.31 (s, 2C), 70.12 (s, $-CH_2CH_2O-$), 35.96, 35.44, 35.42, 34.96, 34.74, 34.56 (s, 1:2:1:2:2:2 for $-C(CH_3)_3$), 28.65, 28.52, 28.14, 28.09, 27.95, 27.34 (s, 2:2:1:2:1:2 for $-CH_3$). $^{31}P\{^1H\}$ (146 MHz, pyridine-d_5, 40 °C): δ 854 (s). Anal. Calcd (found) for $C_{62}H_{134}O_{16}NaPMo_4$: C, 47.33 (47.75); H, 8.58 (8.69).

Preparation of $^tBuCH_2OSi(CH_3)_3$. $KOCH_2{}^tBu$ was prepared by the reaction of metallic potassium with a slight excess of $HOCH_2{}^tBu$ in THF and dried *in vacuo* (0.01 Torr, 100 °C). (TMS)Cl (76 mg, 86 μL, 0.70 mmol) was syringed into a well-stirred slurry of the potassium alkoxide (88 mg, 0.70 mmol) in Et_2O (∼5 mL). The reaction was stirred for 10 min and filtered, and the filtrate solvent was evaporated *in vacuo* (0.01 Torr ≤ 0 °C). The clear liquid residue was analyzed by ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 3.16 (s, 2H), 0.95 (s, 9H), 0.09 (s, 9H). These signals were in an identical location and relative intensity to those attributed to $^tBuCH_2OSi(CH_3)_3$ formed in the crude reaction mixtures during the preparation of **1**−**4**.

Alternative Preparation of 3 From Na_3P. Solids Na_3P (14 mg, 0.14 mmol), 18-crown-6 (100 mg, 0.38 mmol), and $Mo_2(OCH_2{}^tBu)_6$ (200 mg, 0.28 mmol) were weighed into a Schlenk flask equipped with a magnetic stir bar. THF (∼10 mL) was then added by cannula under nitrogen and the mixture stirred for 3 h. Originally the solution is yellow-green with a black precipitate (Na_3P is black), but at the conclusion of the reaction it is dark brown with a black precipitate. The slurry was then filtered, the solids were washed with a little THF, and the solvent was evaporated from the filtrate *in vacuo* (0.01 Torr, 23 °C). The brown gooey residue was then treated with ∼10 mL of benzene and allowed to stand. Green crystalline **3** formed and was filtered, washed with 2 × ∼5 mL of benzene, and shown to be pure (>95%) by NMR spectroscopy. Yield: 40 mg, 18%.

Preparation of $[K(18\text{-crown-}6)][Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]$, 3, from PH_3. Solid $Mo_2(OCH_2{}^tBu)_6$ (280 mg, 0.391 mmol), $KOCH_2{}^tBu$ (25 mg, 0.198 mmol), and 18-crown-6 (60 mg, 0.227 mmol) were dissolved in ∼10 mL of 1:1 C_6H_6/THF in a Schlenk flask equipped with a magnetic stirring bar. PH_3 was then added (50 Torr × 70 mL = 0.188 mmol) via a calibrated gas handling manifold at −196 °C. Upon thawing and warming, the purple solution turns green. The reaction was stirred for 1 h at room temperature and filtered, and the solvent was evaporated from the filtrate *in vacuo* (0.01 Torr, 23 °C). The green residue was treated with ∼10 mL C_6H_6, whereupon green crystalline **3** formed which was isolated by filtration and washed with additional C_6H_6. The material was shown to be spectroscopically pure. Yield: 160 mg, 53.5%.

$[Na(18\text{-crown-}6)][W_4(\mu_3\text{-}PSiMe_3)(OCH_2{}^tBu)_{11}]$, 2. Solid $W_2(OCH_2{}^tBu)_6$ (250 mg, 0.281 mmol), 18-crown-6 (60 mg, 0.227 mmol), and $NaP(SiMe_3)_2$ (28 mg, 0.140 mmol) were weighed into a Schlenk flask equipped with a magnetic stirring bar. C_6H_6 was added by cannula under nitrogen and the reaction heated to 60 °C overnight. Upon cooling, green crystals were deposited which were isolated by decanting the solvent and washing with additional C_6H_6 and drying *in vacuo*. Spectroscopic analysis confirmed the identity of the material as the

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phosphinidene complex **2**, which was contaminated with a small amount (~5%) of phosphide complex **4**. Yield: 79 mg, 27%. For **2**: ^{1}H (pyridine-d_5, 300 MHz, 23 °C) $-CH_2$ region δ 5.35, 5.01, 4.87, 4.81, 4.52, 4.21, 3.84, and 3.76 (d, 2H each, $J = 11$ Hz), 4.67, 3.80, and 3.50 (s, 2H each); 3.38 (s, 24H for $-CH_2CH_2O$); 1.46, 1.41, 1.40, 1.31, 1.25, 1.14, and 0.99 (s, 18:9:18:18:18:9:9 for $-CH_3$); 1.19 (d, 9H, $J_{P-H} = 4$ Hz for $PSi(CH_3)_3$). $^{13}C\{^1H\}$ (pyridine-d_5, 125 MHz, 23 °C): δ 100.36 (d, 2C, $J_{P-C} = 12.5$ Hz), 95.35 (d, 2C, $J_{P-C} = 6$ Hz), 93.56 (s, 1C), 87.83 (s, 1C), 82.44 (s, 2C), 82.35 (s, 2C), 79.69 (s, 1C) for $-CH_2$; 69.94 ($-CH_2CH_2O-$), 36.94, 36.10, 35.62, 35.57, 34.94, 34.72, 34.61 (2:2:1:1:1:2:2 relative ratio for $-CH_2CMe_3$); 29.75, 28.87, 28.77, 28.49, 28.06, 27.93, 27.70 (1:2:2:2:1:1:2 relative ratio for $-CH_2C(CH_3)_3$; 10.00 (d, $J_{P-C} = 9$ Hz, $PSi(CH_3)_3$). $^{31}P\{^1H\}$ (pyridine-d_5, 146 MHz, 23 °C): δ 170.0 ($J_{W-P} = 156$, 162 Hz (13, 7%, respectively)). It is important to note that the above reaction fails in donor solvents such as C_6H_5N or if the source of the tungsten is a base stabilized adduct such as $W_2(OCH_2{}^tBu)_6(py)_2$.

[Na(18-crown-6)][$W_4(\mu_3$-P)$(OCH_2{}^tBu)_{10}$], 4. Solid $W_2(OCH_2{}^tBu)_6$ (250 mg, 0.281 mmol), 18-crown-6 (60 mg, 0.227 mmol), and $NaP(SiMe_3)_2$ (28 mg, 0.140 mmol) were weighed into a Schlenk flask equipped with a magnetic stirring bar. C_6H_6 was added by cannula under nitrogen and the reaction heated to 70 °C for 3 days. Upon cooling, green crystals were deposited which were isolated by decanting the solvent and washing with additional C_6H_6 and drying *in vacuo*. Yield: 60 mg, 22%. For **4**: ^{1}H (pyridine-d_5, 300 MHz, 23 °C): $-CH_2$ region δ 5.47 (dd, 2H, $J_{P-H} = 3$ Hz, $J_{H-H} = 11$ Hz), 5.36, 5.17, 4.80, 4.43, 4.31, 3.96, and 3.94 (d, 2H each, $J = 11$ Hz), 3.76 and 3.62 (s, 2H each), 3.40 (s, 24H for $-CH_2DH_2O-$), 1.51, 1.31, 1.18, 1.17, 1.05, and 1.04 (s, 18:18:18:9:18:9 for $-CH_3$). $^{13}C\{^1H\}$ (pyridine-d_5, 125 MHz, 23 °C): δ 99.93 (d, 2C, $J_{P-C} = 19$ Hz), 93.21 (d, 2C, $J_{P-C} = 17$ Hz), 88.75 (s, 2C), 88.60 (s, 1C), 86.76 (s, 1C), 83.13 (s, 2C) for $-CH_2$; 69.97 ($-CH_2CH_2O-$), 36.51, 35.83, 35.44, 35.19, 34.82, 34.45 (2:2:1:1:2:2 relative ratio for $-CH_2CMe$); 28.81, 28.69, 28.07, 27.99, 27.95, 27.39 (2:2:2:1:1:2 relative ratio for $-CH_2C(CH_3)_3$. $^{31}P\{^1H\}$ (pyridine-d_5, 146 MHz, 40 °C) δ 506.4 ($J_{W-P} = 40$, 28 Hz (7, 13%, respectively)). This compound, like **1**−**3**, is highly colored, and the color depends on the solvent in which it is dissolved: hot C_6H_6 = green, pyridine = red, THF = purple. UV−vis (THF, 23 °C, λ_{max} (ϵ, M^{-1} cm^{-1})): 206 (50 000), 258 sh (16 000), 324 sh (6000), 452 br (2900), 566 (4000). UV−vis (pyridine, 23 °C, λ_{max} (ϵ)): 260 (60 000), 310 sh (9000), 340 (7000), 430 (3700), 584 (6300). Anal. Calcd (found) for $C_{62}H_{134}O_{16}NaPW_4$: C, 38.68 (38.24); H, 7.02 (6.95).

Preparation of [K(18-crown-6)][$Mo_4(\mu_3$-As)$(OCH_2{}^tBu)_{10}$], 5, from AsH_3. Solid $Mo_2(OCH_2{}^tBu)_6$ (280 mg, 0.391 mmol), $KOCH_2{}^tBu$ (25 mg, 0.198 mmol), and 18-crown-6 (60 mg, 0.227 mmol) were dissolved in ~10 mL of 3:1 C_6H_6/THF in a Schlenk flask equipped with a magnetic stirring bar. AsH_3 was then added (50 Torr × 70 mL = 0.188 mmol) via a calibrated gas handling manifold at −196 °C. Upon thawing and warming, the solution turned from purple to dark green, and upon standing at room temperature for 1.5 day, a large mass of green crystalline **5** had formed. The solvent was decanted, the crystals washed with additional C_6H_6, and the solid dried *in vacuo* (0.01 Torr, 23 °C). Yield: 165 mg, 53.7%. For **5**: ^{1}H (pyridine-d_5, 500 MHz, 23 °C) $-CH_2$ region δ 5.37, 5.34, 5.31, 4.99, 4.54, 4.45, 4.27, and 3.91 (d, 2H each, $J = 11$ Hz), 4.06 and 3.87 (s, 2H each), 3.46 (s, 24 H for $-CH_2CH_2O-$), 1.48, 1.31, 1.25, 1.17, 1.05, and 1.04 (s, 18:18:9:18:9:18 for $-CH_3$). $^{13}C\{^1H\}$ (pyridine-d_5, 125 MHz, 23 °C) δ 102.30, 93.66, 88.39, 87.06, 86.15, 84.11 (sw, 2:2:1:1:2:2 for $-CH_2$), 70.43 ($-CH_2CH_2O-$), 36.17, 35.66, 35.47, 35.00, 34.77, and 34.58 (2:2:1:2:2:1 relative ratio for $-CH_2CMe_3$), 28.68, 28.58, 28.21, 28.10, 27.96, and 27.41 (2:2:1:2:1:2 relative ratio for $-CH_2C(CH_3)_3$). Anal. Calcd (found) for $C_{62}H_{134}O_{16}AsKMo_4$: C, 45.59 (45.44), H, 8.27 (8.59).

Reaction of $M_4(OCH_2{}^iPr)_{12}$ Clusters with $PH_3/KOCH_2{}^iPr$. In both cases the group 6 metal alkoxide, $KOCH_2{}^iPr$, and 18-crown-6 were weighed into an NMR tube equipped with a J. Young valve in the glovebox in a 1:1:1 ratio (~0.045 mmol each). C_6D_6 (~0.6 mL) was added and the tube connected to a calibrated gas handling manifold where PH_3 (12 Torr × 70 mL = 0.045 mmol) was condensed in at −196 °C. When the mixture thawed, the formation of a black precipitate occurred rapidly in each case. Spectroscopic analysis showed that the soluble material consisted almost entirely of unreacted cluster, Pr^iCH_2OH, and 18-crown-6. On the basis of the relative proportions of these reagents (~1:1:5:1) in solution, it was assumed that the vast majority of the cluster is untouched and the black precipitate may be K_3P or a group 6 metal material which is rich in phosphorous. Heating at this point did not effect any further reaction save at long reaction times and high temperatures (>100 °C), whereupon decomposition to intractable material(s) occurs.

Reaction of $M_4(OCH_2{}^iPr)_{12}$ Clusters with $NaP(SiMe_3)_2$. The reactions were carried out as above (~0.045 mmol each of M_4 cluster, $NaP(SiMe_3)_2$, and 18-crown-6) in NMR tubes equipped with J. Young valves. At room temperature no reaction occurs for hours. At higher temperatures (>60 °C), the cluster apparently is left untouched but the signal for the crown ether is broadened and a signal at 0.32 ppm (d, $J = 4$ Hz) which may be attributable to $P(SiMe_3)_3$ is observed. No discernable reaction involving the group 6 metal cluster was observed.

Single Crystal X-ray Determinations. General Operating procedures and listings of programs have been previously given.[23] A summary of crystallographic data is given in Table 3.

$Na(18\text{-crown-}6)^+[Mo_4(\mu_3\text{-}P)(OCH_2{}^tBu)_{10}]^-\cdot C_6H_6$. A crystal of suitable size was mounted in a nitrogen atmosphere glovebag using silicone grease, and it was then transferred to a goniostat, where it was cooled to −173 °C for characterization and data collection. After about an hour of initial work, it became obvious that some of the intensities were undergoing large changes and new peaks were appearing; *i.e.*, the crystal was undergoing a slow phase transition. Fortunately the crystal survived, and a good set of data was obtained for the low-temperature phase. When the low-temperature data collection was complete, the temperature was raised to −110 °C. The crystal survived the phase transition (going from a C-centered cell to a primitive cell), and a second set of data was collected. The structure of the higher temperature phase, in which the sodium−crown ether ion is disordered, will not be described here.

When the initial transition to the low-temperature phase was complete, a selective search of a limited hemisphere of reciprocal space revealed a C-centered monoclinic cell. Following complete intensity data collection, the additional conditions $h = 2n$ and $l = 2n$ for $h0l$ limited the space group to $C2/c$ or Cc. The eventual choice of Cc was proven correct by the successful solution of the structure. Data processing produced an unique set of 9710 intensities and gave a residual of 0.028 for the averaging of 2111 of those which had been measured more than once, assuming Friedel related pairs to be redundant. Since the space group is acentric, this averaging was removed to give an unique set of 11 821 intensities prior to the final cycles of refinement below. Four standards measured every 300 data showed no significant trends. No correction was made for absorption ($\mu = 6.5$ cm^{-1}).

The structure was solved by using a combination of direct methods (SHELXS-86), least-squares refinement, and Fourier techniques. The positions of the molybdenum atoms were obtained from an initial E-map. The positions of the remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and difference Fourier calculation. Hydrogens were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the atom to which they were bonded.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters using the unaveraged data above. Data having $F < 3*\sigma(F)$ were given zero weight. The final difference map was reasonably clean, the largest peak being 1.1 and the deepest hole being −0.8 e/A^3.

An inverse refinement was not significantly different ($R(F) = 0.0427$ *vs* 0.0440 for the inverse refinement), *i.e.*, this work does not determine the absolute structure.

In addition to the anion of interest and the cation of lesser interest, the crystal structure also contains a molecule of benzene which had been used as solvent.

$K(18\text{-crown-}6)^+[Mo_4(\mu_3\text{-}O)(OCH_2{}^tBu)_{11}]^-$. A suitable crystal was selected under inert atmosphere conditions. The crystal was transferred to the goniostat where it was cooled to −165 °C for characterization and data collection.

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A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic (2/*m*) symmetry. The systematic extinction of $0k0$ for $k = 2n + 1$ and of $h0l$ for $h + 1 = 2n + 1$ uniquely identified the space group as $P2_1/n$. This choice was confirmed by the successful solution and refinement of the structure. Data collection was undertaken as detailed in Table 3 of this report. A total of 14 166 reflections (including space group extinctions and standards) was collected within the given range. Following the usual data reduction and averaging of equivalent reflections, an unique set of 13 099 reflections was obtained. The *R* for the averaging was 0.041 for 581 unique reflections observed more than once. Plots of the four standard reflections (224, 006, $\bar{4}00$, 0,-12,0) measured every 400 reflections showed no systematic trends. Unit cell dimensions were determined by a least-squares fit of the setting angles for 62 unique reflections having two θ values between 23 and 33°.

The structure was solved by the usual combination of direct methods (MULTAN 78) and Fourier techniques. The asymmetric unit was found to contain one Mo_4^- anion, one K^+ cation, and two molecules of 18-crown-6 ether. Following initial least-squares refinement almost all of the hydrogen atoms were located in a difference map. The hydrogen atoms on the Mo_4^- anion were introduced in fixed idealized positions during the final cycles of full-matrix least-squares refinement. It should be noted that almost all of the hydrogen atoms on the two crown ether molecules also were locatable, however, program limitations prevented their inclusion. All of the non-hydrogen atoms were refined using anisotropic thermal parameters, the hydrogen atoms were fixed with isotropic thermal parameters equal to 1.0 plus the isotropic equivalent of the parent atom. The final $R(F)$ was 0.051; $R_w(F)$ was 0.050.

The final difference map contained many peaks of about 1.0 e/Å^3, almost all of these peaks could be interpreted as hydrogen atoms on the crown ether molecules.

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Supporting Information Available: Tables listing isotropic thermal parameters, anisotropic coordinates, complete listings of bond distances and bond angles and a summary of crystallographic data collection and figures showing VERSORT drawings with complete atom numbering schemes (37 pages). Ordering information is given on any current masthead page.

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