

Polynuclear metal hydrido alkoxides. Preparation and characterization of $\text{Mo}_4(\mu\text{-H})_3(\text{OBu}^t)_7(\text{HNMe}_2)$ and $[\text{K}(18\text{-crown-6})][\text{Mo}_4(\mu_4\text{-H})(\text{OR})_{12}]$ ($\text{R} = \text{Pr}^i$ or CH_2Bu^t)[†]

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The compounds $\text{Mo}_2(\text{OR})_6$ and KH [or $\text{KHB}(\text{Bu}^s)_3$] react in tetrahydrofuran in the presence of 18-crown-6 to yield the charge separated clusters, $[\text{Mo}_4(\mu\text{-H})(\text{OR})_{12}]^-$ ($\text{R} = \text{Pr}^i$ or CH_2Bu^t) supported by the potassium ions $[\text{K}^+(\eta^6\text{-18-crown-6})\cdot 2\text{THF}]$. The cluster anions contain a Mo_4 butterfly, $\text{Mo}\text{-Mo}$ 2.50 Å (average) supported by a hydride ligand that bridges the wingtip Mo atoms. Each edge of the Mo_4 butterfly is bridged by an OR group and the two faces are capped by $\mu_3\text{-OR}$ ligands. The backbone Mo atoms have one terminal bridge and the wingtip Mo atoms have two. Hydrogenation of the mixture of compounds formed in the reaction between 1,2- $\text{Mo}_2(\text{tol})_2(\text{NMe}_2)_4$ ($\text{tol} = p\text{-tolyl}$) and Bu^tOH (3.5 equivalents) in hydrocarbon solvents yields $\text{Mo}_4(\mu\text{-H})_3(\text{OBu}^t)_7(\text{HNMe}_2)$ which contains a Mo_4 butterfly asymmetrically supported by alkoxide and hydride ligands. The hydride ligands are proposed to be located on one triangle of Mo atoms, one capping the face and the other two bridging between the wingtip and backbone Mo atoms. The $\text{Mo}\text{-Mo}$ distances associated with the hydride bridges are notably shorter (2.38 Å) than those having OR bridges (2.50 Å, average). The ^1H NMR spectra of $[\text{Mo}_4(\mu\text{-H})(\text{OR})_{12}]^-$ and $\text{Mo}_4(\mu\text{-H})_3(\text{OBu}^t)_7(\text{HNMe}_2)$ reveal the presence of the hydride ligands and furthermore that these clusters are static on the NMR timescale. These results are compared with the synthesis of related tungsten hydrido alkoxides.

Transition metal complexes containing hydride ligands have played a significant role in the development of organometallic chemistry due to their involvement in numerous stoichiometric and catalytic reactions.¹ Since the initial discovery of $\text{HCo}(\text{CO})_4$ and $\text{H}_2\text{Fe}(\text{CO})_4$ in the 1930s² the chemistry of metal hydrides and metal polyhydrides³ has been developed with the ligands that are now classical and ubiquitous in organometallic chemistry, namely carbon monoxide, tertiary phosphines, cyclopentadienes and related soft π -acceptor ligands. We and others have been developing an organometallic chemistry with ancillary hard π -donor oxygen ligands (OR , OAr and OSiR_3).⁴ In this paper we report on our preparation of two types of Mo_4 cluster hydrido alkoxides formed by two different routes: (i) the addition of a hydride source to $\text{Mo}_2(\text{OR})_6$ and (ii) the hydrogenation of a mixed alkyl/alkoxide of dimolybdenum. Preliminary accounts of this work have appeared.⁵

Results and Discussion

Syntheses

$\text{K}[\text{Mo}_4(\text{H})(\text{OR})_{12}]$. When a solution of $\text{Mo}_2(\text{OR})_6$ in tetrahydrofuran is allowed to react with a suspension of KH or $\text{KHB}(\text{Bu}^s)_3$ in the presence of 18-crown-6 the cluster anion $[\text{Mo}_4(\text{H})(\text{OR})_{12}]^-$ is formed when $\text{R} = \text{Pr}^i$ or CH_2Bu^t . No such reaction is observed for $\text{R} = \text{Bu}^t$, perhaps because of the greater steric bulk of the ancillary ligands. The anions can be crystallized as salts with $\text{K}^+(18\text{-crown-6})$ counter cations. The reactions are very sensitive to the presence of trace amounts

of water. Potassium hydride and $\text{KHB}(\text{Bu}^s)_3$ react with H_2O to give H_2 and KOH or $\text{KB}(\text{Bu}^s)_3\text{OH}$, respectively. The latter and $\text{Mo}_2(\text{OR})_6$ react to give the green oxo cluster complex^{6a} $\text{K}^+[\text{Mo}_4(\text{OR})_{11}\text{O}]^-$ and ROH . Potassium hydride or $\text{KHB}(\text{Bu}^s)_3$ react with ROH generated above to give KOR and H_2 , and KOR and $\text{Mo}_2(\text{OR})_6$ react to form purple $\text{K}^+[\text{M}_2(\text{OR})_7]^-$.^{6b}

These reactions may be viewed as the sum of two half reactions. (1) The association of H^- with the weakly Lewis acidic $\text{Mo}_2(\text{OR})_6$ complex to give $[\text{Mo}_2(\text{OR})_6\text{H}]^-$. (2) The association of the anion with the neutral complex to form the cluster $[\text{Mo}_4(\text{H})(\text{OR})_{12}]^-$. Given the simplicity of this scheme it seems that other hydrido metal complexes could be made the same way or at least by a similar methodology. While we have not investigated this possibility extensively we have found that the reaction does not proceed straightforwardly for related $\text{W}_2(\text{OR})_6$ complexes, probably because the anions $[\text{W}_2(\text{H})(\text{OR})_6]^-$ are kinetically more labile to alkoxide decomposition as are the related $[\text{M}_2(\text{OR})_7]^-$ anions for $\text{M} = \text{W}$ relative to $\text{M} = \text{Mo}$.^{6a}

As noted previously the hydrogenolysis of 1,2- $\text{W}_2\text{R}_2(\text{OR}')_4$ compounds is problematic. For $\text{R} = \text{CH}_2\text{CMe}_3$ and 1–3 atm H_2 at 22 °C there is little or no reaction; for $\text{R} = \text{aryl}$, there is a relatively slow reaction in hydrocarbon solutions and hydrido-aryl intermediates have been detected.⁷ For $\text{R} = \text{Bu}^t$, the addition of H_2 facilitates a sequence of reactions that involve α - and β -CH activation and elimination of isobutane.⁸ Because of the more facile nature of β -CH activation for molybdenum compounds and their propensity toward reductive elimination, attempts to prepare 1,2- $\text{Mo}_2(\text{Bu}^t)_2(\text{OR})_4$ result in M^4M containing complexes of formula $\text{Mo}_2(\text{OR})_4\text{L}_4$, e.g. $\text{R} = \text{Pr}^i$, $\text{L} = \text{HOPr}$, py or PMe_3 .⁹ We thus attempted hydrogenolysis of compounds of formula 1,2- $\text{Mo}_2(\text{CH}_2\text{CMe}_3)_2(\text{OPr})_4$ and 1,2- $\text{Mo}_2(\text{aryl})_2(\text{OBu}^t)_4$.¹⁰ Under mild conditions (hydrocarbon solutions, 1–3 atm H_2 , 22 °C) the former was unreactive while

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† Dedicated to Professor B. F. G. Johnson on the occasion of his 60th birthday.

Non-SI units employed: 1 atm = 101 325 Pa; eV \approx 1.602 \times 10⁻¹⁹ J.

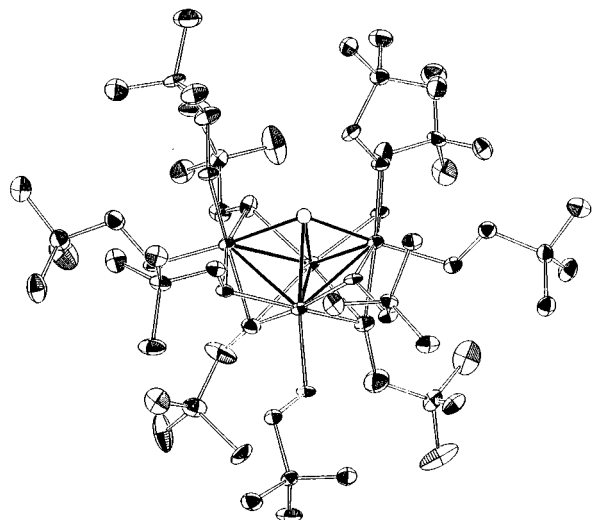
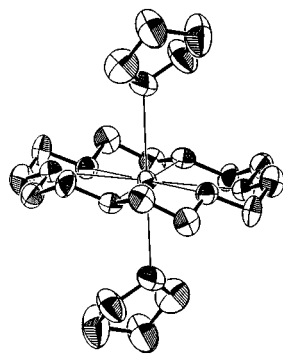
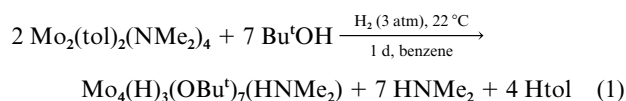


Fig. 1 An ORTEP¹² drawing of the $[\text{Mo}_4(\mu_4\text{-H})(\text{OCH}_2\text{Bu})_{12}]^-$ anion and its counter anion $[\text{K}^+(18\text{-crown-6})]\cdot 2\text{THF}$. The hydride is represented by an open circle in the drawing above



the latter gave intractable products probably as a result of the involvement of OBu^t ligand activation. However, in one reaction a product $\text{Mo}_4(\text{H})_3(\text{OBu}^t)_7(\text{HNMe}_2)$ was isolated in *ca.* 40% yield by crystallization from the mother-liquor according to the reaction shown in equation (1) (*tol* = *p*-tolyl).



In the alcoholysis reaction shown in equation (1) $1,2\text{-Mo}_2(\text{tol})_2(\text{OBu}^t)_4$ and $1,2\text{-Mo}_2(\text{tol})_2(\text{OBu}^t)_3(\text{NMe}_2)$ should be formed in a 1:1 ratio prior to hydrogenolysis. For $1,2\text{-Mo}_2(\text{tol})_2(\text{OBu}^t)_4$ we would expect facile rotation about the Mo–Mo triple bond leading to equivalent tolyl groups and one type of OBu^t group.¹⁰ However, for $1,2\text{-Mo}_2(\text{tol})_2(\text{OBu}^t)_3(\text{NMe}_2)$ the two Mo atoms would be different and, thus, even with rapid rotation about the Mo–Mo bond there would be two types of *p*-tolyl groups.¹⁰ The ¹H NMR spectrum of the alcoholysis mixture did indeed show three tolyl-*Me* signals, all singlets at δ 2.24, 2.20 (of relative intensity 2) and 2.12 as well as two broad singlets at δ 4.12 and 2.55. The latter are assignable to proximal and distal *NMe* groups given the common occurrence of restricted rotation about the Mo–*NMe*₂ bond due to *Me*₂N *p*_π to Mo *d*_π donation involving the *d*_{xy} or *d*_{*x*²–*y*²} orbitals but not the Mo *d*_{*xz*} or *d*_{*yz*} orbitals which are involved in Mo–Mo π bonding.¹¹ Thus, in terms of synthesis, we conclude that **2** is formed by the hydrogenation of a mixture of $1,2\text{-Mo}_2(\text{tol})_2(\text{OBu}^t)_4$ and $1,2\text{-Mo}_2(\text{tol})_2(\text{OBu}^t)_3(\text{NMe}_2)$. We shall return to speculate further upon mechanistic matters pertaining to its formation after presenting the characterization data.

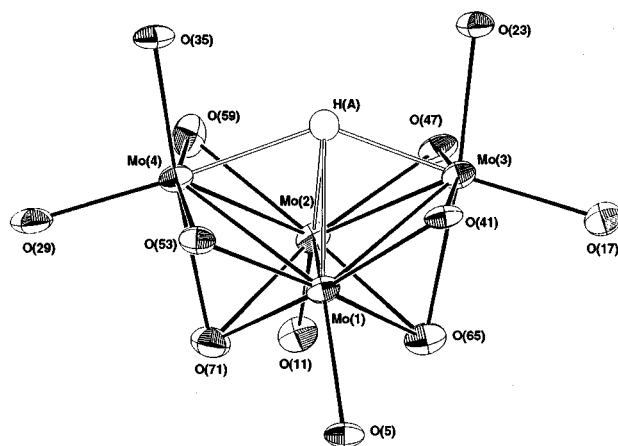


Fig. 2 The central $\text{Mo}_4(\mu_4\text{-H})(\text{O})_{12}$ skeleton of the $[\text{Mo}_4(\mu_4\text{-H})(\text{OCH}_2\text{Bu})_{12}]^-$ anion giving the atom number scheme in the tables

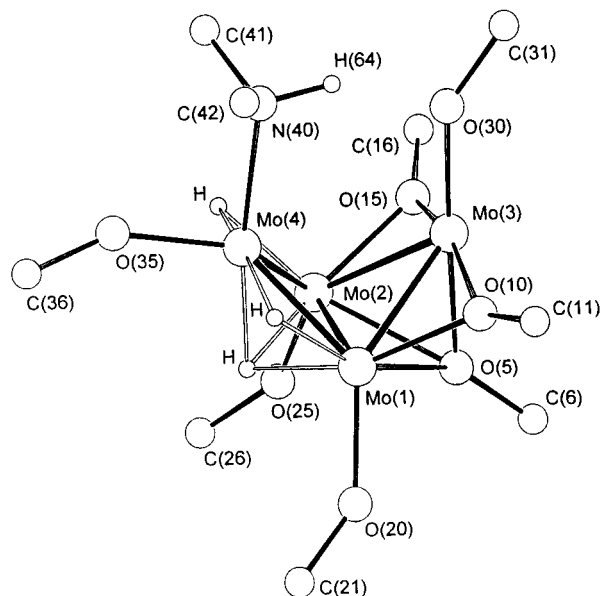


Fig. 3 The central $\text{Mo}_4(\text{H})_3(\text{OC}_7)(\text{HNMe}_2)$ skeleton of the $\text{Mo}_4(\text{H})_3(\text{OBu}^t)_7(\text{HNMe}_2)$ molecule. The hydride ligands are shown as open circles in proposed locations. The H(64) of the *Me*₂NH ligand is hydrogen bonded to O(30)

Solid-state and molecular structures

An ORTEP¹² drawing of $[\text{K}(18\text{-crown-6})][\text{Mo}_4(\mu_4\text{-H})(\text{OCH}_2\text{Bu})_{12}]$ **1** is given in Fig. 1 showing both the anion and cation. An ORTEP drawing of the central $\text{Mo}_4(\mu_4\text{-H})(\text{O})_{12}$ moiety of the anion is given in Fig. 2. The structure of the anion bears a close resemblance to that of the $\text{Mo}_4\text{Br}_4(\text{OPr}^t)_8$ butterfly which has terminal Mo–Br bonds that are radial to the cluster unit.¹³ The metrical parameters of the Mo_4O_{12} units are very similar as are the Mo–Mo distances consistent with the 12-electron cluster bonding description previously reported. Selected bond distances and bond angles for **1** are given in Table 1. The position of the hydride ligand which was not located crystallographically is placed (as shown in Fig. 2) bridging between the two wingtip Mo atoms. The evidence for this location is two-fold. (1) The wingtip to wingtip Mo–Mo distance in **1** is 3.74 Å, notably longer than that in $\text{Mo}_4\text{Br}_4(\text{OPr}^t)_8$, 3.28 Å. (2) Calculations show that this position is favored relative to the only other conceivable position, namely that bridging the two backbone Mo atoms, as is described later.

A ball-and-stick drawing of the central portion of the $\text{Mo}_4(\text{H})_3(\text{OBu}^t)_7(\text{HNMe}_2)$ **2** molecule is given in Fig. 3 where the hydride ligands are shown in their proposed positions.

Table 1 Selected bond distances (Å) and angles (°) for the $[\text{Mo}_4(\mu_4\text{-H})(\text{OCH}_2\text{Bu}^t)_{12}]^-$ anion

Mo(1)–Mo(2)	2.522(3)	Mo(1)–O(71)	2.146(8)	Mo(2)–O(65)	2.154(8)	Mo(3)–O(65)	2.170(8)
Mo(1)–Mo(3)	2.545(3)	Mo(2)–Mo(3)	2.505(2)	Mo(2)–O(71)	2.135(8)	Mo(4)–O(29)	1.933(7)
Mo(1)–Mo(4)	2.503(3)	Mo(2)–Mo(4)	2.538(3)	Mo(3)–O(17)	1.939(7)	Mo(4)–O(35)	1.993(8)
Mo(1)–O(5)	2.032(7)	Mo(2)–O(11)	2.005(8)	Mo(3)–O(23)	1.996(9)	Mo(4)–O(53)	2.138(7)
Mo(1)–O(41)	2.092(8)	Mo(2)–O(47)	2.146(8)	Mo(3)–O(41)	2.145(7)	Mo(4)–O(59)	2.138(8)
Mo(1)–O(53)	2.135(8)	Mo(2)–O(59)	2.100(8)	Mo(3)–O(47)	2.172(8)	Mo(4)–O(71)	2.181(8)
Mo(1)–O(65)	2.158(9)						
Mo(2)–Mo(1)–Mo(3)	59.26(8)	Mo(3)–Mo(2)–Mo(4)	95.79(9)	O(17)–Mo(3)–O(23)	98.4(3)	Mo(2)–O(11)–C(12)	126.5(8)
Mo(2)–Mo(1)–Mo(4)	60.67(5)	Mo(3)–Mo(2)–O(11)	126.5(3)	O(17)–Mo(3)–O(41)	90.8(3)	Mo(3)–O(17)–C(18)	135.1(8)
Mo(2)–Mo(1)–O(5)	129.9(2)	Mo(3)–Mo(2)–O(47)	55.02(2)	O(17)–Mo(3)–O(47)	97.9(3)	Mo(3)–O(23)–C(24)	116.9(7)
Mo(2)–Mo(1)–O(41)	113.2(2)	Mo(3)–Mo(2)–O(59)	127.1(2)	O(17)–Mo(3)–O(65)	172.2(3)	Mo(4)–O(29)–C(30)	133.0(7)
Mo(2)–Mo(1)–O(53)	114.6(2)	Mo(3)–Mo(2)–O(65)	54.90(2)	O(23)–Mo(3)–O(41)	97.2(3)	Mo(4)–O(35)–C(36)	118.4(7)
Mo(2)–Mo(1)–O(65)	54.2(2)	Mo(3)–Mo(2)–O(71)	114.8(2)	O(23)–Mo(3)–O(47)	92.4(3)	Mo(1)–O(41)–Mo(3)	73.83(2)
Mo(2)–Mo(1)–O(71)	53.7(2)	Mo(4)–Mo(2)–O(11)	136(2)	O(23)–Mo(3)–O(65)	85.2(3)	Mo(1)–O(41)–C(42)	126.4(7)
Mo(3)–Mo(1)–Mo(4)	95.66(9)	Mo(4)–Mo(2)–O(47)	122.5(2)	O(41)–Mo(3)–O(47)	166.0(3)	Mo(3)–O(41)–C(42)	127.2(6)
Mo(3)–Mo(1)–O(5)	137.5(2)	Mo(4)–Mo(2)–O(59)	53.91(2)	O(41)–Mo(3)–O(65)	81.9(3)	Mo(2)–O(47)–Mo(3)	70.93(3)
Mo(3)–Mo(1)–O(41)	54.04(2)	Mo(4)–Mo(2)–O(65)	113.5(3)	O(47)–Mo(3)–O(65)	88.8(3)	Mo(2)–O(47)–C(48)	122.8(8)
Mo(3)–Mo(1)–O(53)	120.8(2)	Mo(4)–Mo(2)–O(71)	54.8(2)	Mo(1)–Mo(4)–Mo(2)	60.03(8)	Mo(3)–O(47)–C(48)	125.4(8)
Mo(3)–Mo(1)–O(65)	54.21(2)	O(11)–Mo(2)–O(47)	94.8(3)	Mo(1)–Mo(4)–O(29)	126.4(2)	Mo(1)–O(53)–Mo(4)	71.72(2)
Mo(3)–Mo(1)–O(71)	127.5(2)	O(11)–Mo(2)–O(59)	99.5(3)	Mo(1)–Mo(4)–O(35)	122.9(2)	Mo(1)–O(53)–C(54)	123.8(6)
Mo(4)–Mo(1)–O(53)	54.2(2)	O(11)–Mo(2)–O(65)	86.4(3)	Mo(1)–Mo(4)–O(53)	54.1(2)	Mo(4)–O(53)–C(54)	124.0(7)
Mo(4)–Mo(1)–O(65)	114.7(2)	O(11)–Mo(2)–O(71)	92.1(3)	Mo(1)–Mo(4)–O(59)	112.5(2)	Mo(2)–O(59)–Mo(4)	73.57(2)
Mo(4)–Mo(1)–O(71)	55.33(2)	O(47)–Mo(2)–O(59)	102.0(3)	Mo(1)–Mo(4)–O(71)	54.00(2)	Mo(2)–O(59)–C(60)	127.7(7)
O(5)–Mo(1)–O(41)	98.7(3)	O(47)–Mo(2)–O(65)	89.9(3)	Mo(2)–Mo(4)–O(29)	118.5(2)	Mo(4)–O(59)–C(60)	125.8(7)
O(5)–Mo(1)–O(53)	94.2(3)	O(47)–Mo(2)–O(71)	169.8(3)	Mo(2)–Mo(4)–O(35)	128.5(2)	Mo(1)–O(65)–Mo(2)	71.56(3)
O(5)–Mo(1)–O(65)	95.1(3)	O(59)–Mo(2)–O(65)	166.1(3)	Mo(2)–Mo(4)–O(53)	113.8(2)	Mo(1)–O(65)–Mo(3)	72.01(3)
O(5)–Mo(1)–O(71)	87.7(3)	O(59)–Mo(2)–O(71)	84.1(3)	Mo(2)–Mo(4)–O(59)	52.5(2)	Mo(1)–O(65)–C(66)	166.5(2)
O(41)–Mo(1)–O(53)	101.6(3)	O(65)–Mo(2)–O(71)	83.2(3)	Mo(2)–Mo(4)–O(71)	53.16(2)	Mo(1)–O(65)–C(66')	118.0(1)
O(41)–Mo(1)–O(65)	83.4(3)	Mo(1)–Mo(3)–Mo(2)	59.91(7)	O(29)–Mo(4)–O(35)	99.4(3)	Mo(2)–O(65)–Mo(3)	70.79(2)
O(41)–Mo(1)–O(71)	165.3(3)	Mo(1)–Mo(3)–O(17)	119.3(2)	O(29)–Mo(4)–O(53)	96.6(3)	Mo(2)–O(65)–C(66)	115.1(1)
O(53)–Mo(1)–O(65)	168.7(3)	Mo(1)–Mo(3)–O(23)	128.3(2)	O(29)–Mo(4)–O(59)	90.2(3)	Mo(2)–O(65)–C(66')	125.7(1)
O(53)–Mo(1)–O(71)	91.1(3)	Mo(1)–Mo(3)–O(41)	52.1(2)	O(29)–Mo(4)–O(71)	171.3(3)	Mo(3)–O(65)–C(66)	120.9(2)
O(65)–Mo(1)–O(71)	82.8(3)	Mo(1)–Mo(3)–O(47)	113.9(2)	O(35)–Mo(4)–O(53)	93.1(3)	Mo(3)–O(65)–C(66')	161.9(2)
Mo(1)–Mo(2)–Mo(3)	60.83(5)	Mo(1)–Mo(3)–O(65)	53.78(2)	O(35)–Mo(4)–O(59)	97.5(3)	Mo(1)–O(71)–Mo(2)	72.17(3)
Mo(1)–Mo(2)–Mo(4)	59.30(8)	Mo(2)–Mo(3)–O(17)	127.3(3)	O(35)–Mo(4)–O(71)	85.9(3)	Mo(1)–O(71)–Mo(4)	70.67(3)
Mo(1)–Mo(2)–O(11)	127.5(2)	Mo(2)–Mo(3)–O(23)	123.2(2)	O(53)–Mo(4)–O(59)	166.3(3)	Mo(1)–O(71)–C(72)	123.0(8)
Mo(1)–Mo(2)–O(47)	115.7(2)	Mo(2)–Mo(3)–O(41)	112.0(2)	O(53)–Mo(4)–O(71)	90.1(3)	Mo(2)–O(71)–Mo(4)	72.00(3)
Mo(1)–Mo(2)–O(59)	113.1(2)	Mo(2)–Mo(3)–O(47)	54.1(2)	O(59)–Mo(4)–O(71)	82.1(3)	Mo(2)–O(71)–C(72)	123.0(8)
Mo(1)–Mo(2)–O(65)	54.29(2)	Mo(2)–Mo(3)–O(65)	54.3(2)	Mo(1)–O(5)–C(6)	123.9(7)	Mo(4)–O(71)–C(72)	160.9(9)
Mo(1)–Mo(2)–O(71)	54.10(2)						

Selected bond distances and angles are given in Table 2. There are several points worthy of mention with respect to this cluster. (1) The formal oxidation state of the Mo atoms is +2.5 since the Mo_4 unit bears an overall +10 charge if the hydride and alkoxide ligands are counted as uninegative ligands. (2) In the absence of the hydride ligands the co-ordination geometry is very asymmetric: six of the OR ligands are associated with the Mo(1)–Mo(2)–Mo(3) triangle. (3) The Mo(4) to Mo(1) and Mo(2) distances are 2.38 Å (average), significantly shorter than those of the other three Mo–Mo distances which span the range 2.49 to 2.59 Å. (4) The evidence for the Me_2NH ligand comes from the long Mo–N distance, 2.22 Å, the pyramidal geometry at nitrogen and the N(40) to O(30) distance of 3.0 Å is consistent with the presence of a $\text{NH}\cdots\text{O}$ hydrogen bond. (5) Although not crystallographically located the 3H ligands are observed by ^1H NMR spectroscopy (see later) which indicates a 2H:1H ratio. The positions proposed in Fig. 3 complement the co-ordination geometry of the other triangle and are acceptable to the hydride locating program XHYDEX.¹⁴

^1H NMR and IR spectroscopic studies

The complexes $[\text{Mo}_4(\mu_4\text{-H})(\text{OR})_{12}]^-$ ($\text{R} = \text{Pr}^i$ and CH_2Bu^t) reveal by ^1H NMR spectroscopy that the anion has C_{2v} symmetry. The twelve OR groups fall into five groups of integral ratio 2:2:2:2:4. The terminal OR ligands and the μ_3 -OR ligands lie on mirror planes of symmetry but the four symmetry equivalent μ -OR groups do not. Thus the methylene protons where $\text{R} = \text{CH}_2\text{Bu}^t$ and methyl groups for $\text{R} = \text{Pr}^i$ are diastereotopic. The hydride signal appears as a singlet at δ ca. –12

to –15 *upfield* of Me_4Si in contrast to signals of all other polynuclear hydrido tungsten clusters characterized thus far.^{8,15}

We have not been able to obtain evidence for the $\mu_4\text{-H}$ (or $\mu_4\text{-D}$) ligand in **1** in the infrared spectrum. It may be either too weak or in a frequency region below 1500 cm^{-1} where IR bands from the OR ligands obscure it. However, for **2**, bands present in the protio compound $\text{Mo}_4(\text{H})_3(\text{OBU}^t)_7(\text{HNMe}_2)$ at 1609 and 1561 cm^{-1} are not present in $\text{Mo}_4(\text{D})_3(\text{OBU}^t)_7(\text{DNMe}_2)$ and they are tentatively assigned to the $\mu\text{-H}$ ligands in **2**.

The ^1H NMR spectrum of **2** in $[\text{H}_8]\text{toluene}$ indicates that the molecule has a virtual mirror plane of symmetry, as seen in the structure (see Fig. 3). [The virtual mirror plane contains Mo(3), Mo(4), O(5), O(30), O(35) and N(40) as well as the $\mu_4\text{-H}$ atom.] The OBU^t resonances are in the ratio 1:1:1:2:2 and the hydride signals appear at δ 1.99 (1 H) as a triplet and δ 3.55 (2 H) as a doublet with $J_{\text{HH}} \approx 2.0$ Hz. The NH proton appears at δ 5.32 as a septet ($J_{\text{HH}} \approx 5.7$ Hz) and the NMe_2 signal as a doublet at δ 1.84 ($J_{\text{HH}} \approx 5.7$ Hz). The spectral data are thus in full agreement with the proposed composition and structure determined by the single crystal study and the elemental analysis.

Comments on the mechanism of the formation of **1** and **2**

The $\text{Mo}_2(\text{OR})_6$ compounds are known to be weakly Lewis acidic¹⁶ and react reversibly with bases such as py and PMe_3 to form adducts of the type $\text{Mo}_2(\text{OR})_6\text{L}_2$ and with $\text{L} = \text{PBU}^t_3$, or OR^- to form $\text{Mo}_2(\text{OR})_6\text{L}$ complexes.¹⁷ It seems likely that H^- , as provided by KH in 18-crown-6/THF or $\text{K}^+\text{HB}(\text{Bu}^s)_3^-$ in THF/18-crown-6, forms a related complex anion $[\text{Mo}_2\text{H}(\text{OR})_7]^-$ and

Table 2 Selected bond distances (Å) and angles (°) for Mo₄(H)₃(OBu^t)₇(HNMe₂)

Mo(1)–Mo(2)	2.593(2)	Mo(1)–O(20)	1.93(1)	Mo(2)–O(25)	1.95(1)	Mo(3)–O(15)	2.037(9)
Mo(1)–Mo(3)	2.500(2)	Mo(2)–Mo(3)	2.493(2)	Mo(3)–Mo(4)	3.072(2)	Mo(3)–O(30)	1.942(9)
Mo(1)–Mo(4)	2.377(2)	Mo(2)–Mo(4)	2.379(2)	Mo(3)–O(5)	2.081(8)	Mo(4)–O(35)	1.94(1)
Mo(1)–O(5)	2.326(9)	Mo(2)–O(5)	2.35(1)	Mo(3)–O(10)	2.047(9)	Mo(4)–N(40)	2.22(11)
Mo(1)–O(10)	2.03(10)	Mo(2)–O(15)	2.05(1)				
Mo(2)–Mo(1)–Mo(3)	58.56(6)	Mo(3)–Mo(2)–Mo(4)	78.16(6)	Mo(2)–Mo(3)–O(30)	121.0(3)	O(35)–Mo(4)–N(40)	85.2(5)
Mo(2)–Mo(1)–Mo(4)	56.98(6)	Mo(3)–Mo(2)–O(5)	50.85(2)	Mo(4)–Mo(3)–O(5)	95.0(2)	Mo(1)–O(5)–Mo(2)	67.5(2)
Mo(2)–Mo(1)–O(5)	56.63(3)	Mo(3)–Mo(2)–O(15)	52.19(3)	Mo(4)–Mo(3)–O(10)	89.0(3)	Mo(1)–O(5)–Mo(3)	68.9(3)
Mo(2)–Mo(1)–O(10)	110.6(3)	Mo(3)–Mo(2)–O(25)	143.4(3)	Mo(4)–Mo(3)–O(15)	89.6(3)	Mo(1)–O(5)–C(6)	144.6(1)
Mo(2)–Mo(1)–O(20)	119.2(4)	Mo(4)–Mo(2)–O(5)	109.6(3)	Mo(4)–Mo(3)–O(30)	87.0(3)	Mo(2)–O(5)–Mo(3)	68.2(3)
Mo(3)–Mo(1)–Mo(4)	78.04(6)	Mo(4)–Mo(2)–O(15)	112.0(3)	O(5)–Mo(3)–O(10)	79.5(4)	Mo(2)–O(5)–C(6)	141.7(1)
Mo(3)–Mo(1)–O(5)	50.94(2)	Mo(4)–Mo(2)–O(25)	132.5(3)	O(5)–Mo(3)–O(15)	81.4(4)	Mo(3)–O(5)–C(6)	131.9(8)
Mo(3)–Mo(1)–O(10)	52.50(2)	O(5)–Mo(2)–O(15)	75.0(3)	O(5)–Mo(3)–O(30)	117.9(4)	Mo(1)–O(10)–Mo(3)	75.6(3)
Mo(3)–Mo(1)–O(20)	143.1(3)	O(5)–Mo(2)–O(25)	94.7(4)	O(10)–Mo(3)–O(15)	160.7(4)	Mo(1)–O(10)–C(11)	135.8(9)
Mo(4)–Mo(1)–O(5)	110.3(3)	O(15)–Mo(2)–O(25)	113.6(4)	O(10)–Mo(3)–O(30)	100.1(5)	Mo(3)–O(10)–C(11)	146.4(1)
Mo(4)–Mo(1)–O(10)	112.2(3)	Mo(1)–Mo(3)–Mo(2)	72.58(5)	O(15)–Mo(3)–O(30)	99.1(5)	Mo(2)–O(15)–Mo(3)	75.1(3)
Mo(4)–Mo(1)–O(20)	134.7(3)	Mo(1)–Mo(3)–Mo(4)	49.20(5)	Mo(1)–Mo(4)–Mo(2)	66.1(6)	Mo(2)–O(15)–C(16)	133.1(1)
O(5)–Mo(1)–O(10)	74.3(4)	Mo(1)–Mo(3)–O(5)	60.2(3)	Mo(1)–Mo(4)–Mo(3)	52.8(5)	Mo(3)–O(15)–C(16)	149.1(1)
O(5)–Mo(1)–O(20)	95.2(4)	Mo(1)–Mo(3)–O(10)	51.9(3)	Mo(1)–Mo(4)–O(35)	135.5(5)	Mo(1)–O(20)–C(21)	144.1(1)
O(10)–Mo(1)–O(20)	110.4(4)	Mo(1)–Mo(3)–O(15)	114.8(3)	Mo(1)–Mo(4)–N(40)	121.2(3)	Mo(2)–O(25)–C(26)	143.2(1)
Mo(1)–Mo(2)–Mo(3)	58.85(6)	Mo(1)–Mo(3)–O(30)	121.2(3)	Mo(2)–Mo(4)–Mo(3)	52.6(5)	Mo(3)–O(30)–C(31)	144.4(9)
Mo(1)–Mo(2)–Mo(4)	56.93(6)	Mo(2)–Mo(3)–Mo(4)	49.27(5)	Mo(2)–Mo(4)–O(35)	131.7(5)	Mo(4)–O(35)–C(36)	150.1(1)
Mo(1)–Mo(2)–O(5)	55.92(3)	Mo(2)–Mo(3)–O(5)	60.9(3)	Mo(2)–Mo(4)–N(40)	123.1(4)	Mo(4)–N(40)–C(41)	112.5(1)
Mo(1)–Mo(2)–O(15)	110.6(3)	Mo(2)–Mo(3)–O(10)	113.9(3)	Mo(3)–Mo(4)–O(35)	170.6(4)	Mo(4)–N(40)–C(42)	113.4(1)
Mo(1)–Mo(2)–O(25)	116.0(4)	Mo(2)–Mo(3)–O(15)	52.7(3)	Mo(3)–Mo(4)–N(40)	85.8(3)		

that this, once formed, reacts with the Mo₂(OR)₆ in a bimolecular manner to form the anion [Mo₄(μ₄-H)(OR)₁₂][−]. There are steric constraints involved in these reactions and when R = Bu^t no reaction is observed. Note, we cannot determine whether or not H[−] adds reversibly to Mo₂(OR)₆ and is trapped in its subsequent reaction with Mo₂(OR)₆ or merely that the formation of [Mo₂H(OR)₆][−] is slow relative to the second bimolecular reaction which gives the [Mo₄(H)(OR)₁₂][−] anion irreversibly. The cluster anion, however, once formed is inert to reaction with both PMe₃ and py and may be viewed as saturated since each metal atom is six-co-ordinate. The hydride ligand (or μ₄-D ligand if prepared from KD) is not labile to exchange with either ROD (or ROH) or molecular H₂ in [²H₈]toluene at room temperature.

As noted earlier, hydrogenolysis reactions of 1,2-Mo₂-(CH₂R)₂(OR')₄, Mo₂(R)₂(OR')₄ and Mo₄(R)₂(OR')₁₀ compounds are very sensitive to the nature of R (= alkyl or aryl) and the alkoxide. These reactions are slower than related reactions involving tungsten analogues which may reflect that H₂ oxidative-addition to the M–M triple bond initiates the hydrocarbon elimination reaction. In any event, under the mild conditions reported here only the novel compound Mo₄(H)₃(OBu^t)₇(HNMe₂) **2** has been isolated and characterized. This compound may be viewed as being formed from the coupling of two reactive fragments such as Mo₂(H)₂(OBu^t)₄ and Mo₂(H)₂(OBu^t)₃(NMe₂). This would give a 12-electron cluster having a Mo₄¹²⁺ core of formula Mo₄(H)₄(OBu^t)₇(NMe₂). That this is not the product clearly implies that reduction occurs either prior or subsequent to cluster formation, e.g. Mo₄(H)₄(OBu^t)₇(NMe₂) → Mo₄(H)₃(OBu^t)₇(HNMe₂) **2**. In the reaction involving D₂ gas the cluster Mo₄(D)₃(OBu^t)₇(DNMe₂), **2-d** is formed, which reliably traces the source of NH as being the added D₂ gas and is consistent with the proposed reduction Mo(H)(NMe₂) → Mo(HNMe₂).

EHMO calculations

Since the structural evidence for the location of the μ₄-H ligand in **1** rests largely on the opening up of the Mo₄ butterfly such that the Mo to Mo wingtip atom distance is 3.74 Å [relative to 3.24 Å in Mo₄Br₄(OPr^t)₈], we investigated with EHT calculations potential modes of H[−] bonding to a neutral Mo₄(OH)₁₂ molecule with the geometry taken from the structure of **1**.

[Note the fact that the hydrogen ligand does not exchange with D in reactions of protio **1** with ROD rules out the possibility that the hydride is not a hydride but rather a hydroxyl proton of a co-ordinated ROH ligand. It also rules out an acidic or basic hydride and one that is in equilibrium with a co-ordinated ROH ligand.] Given the symmetry of the Mo₄(OH)₁₂ fragment there are only two reasonable positions for a hydride (i) a μ₄-H ligand bridging the backbone Mo atoms or (ii) a μ₄-H ligand as shown in Fig. 2.

The EHMO calculation on the Mo₄(OH)₁₂ molecule gives a LUMO as depicted in the preliminary communication^{5a} and predicts a very small HOMO – LUMO gap for this molecule: 0.04 eV. Such a situation is indicative of a missing atom or high kinetic lability. The LUMO is the in-phase combination of the LUMO's localized on each Mo center. Note each Mo is part of an octahedral L₅M fragment with the missing site being directed toward the center wherein the μ₄-H ligand is proposed to be. The introduction of the H[−] ligand into this position creates a very stable a₁ orbital (at lower energy than the HOMO). This is both Mo–H and Mo–Mo bonding in a fully delocalized manner for the Mo₄(μ₄-H) moiety. The out of phase combination of H[−] and the LUMO appears at higher energy. The HOMO of the cluster is of different symmetry and thus not affected by this interaction. Thus the introduction of the μ₄-H ligand stabilizes the cluster and enlarges the HOMO – LUMO gap. In relation to H[−] addition to the μ₄-H site, the addition of H[−] across the backbone Mo atoms leads to a much poorer interaction (one third of the overlap compared to the μ₄-H position). Thus the simple MO picture supports the structural evidence in clear favor of the μ₄-H ligand.

Conclusion

The present report of the formation of tetranuclear hydrido-alkoxide clusters of molybdenum leads us to suggest that a general class of molybdenum hydrido-alkoxide clusters, having a variety of oxidation states for Mo, cluster electron counts and modes of hydride cluster bonding should be accessible. Although μ₄-carbides, -nitrides and -oxides are known in cluster chemistry,¹⁸ μ₄-hydrides are rare. Indeed, the compound **1** appears to be the first example, although as seen in the bonding description wherein H[−] combines with Mo₄(OH)₁₂ this is clearly

a bonding mode which can be expected under the appropriate conditions of symmetry and electron count.

Very recently μ_5 -H ligands have been observed in the cluster anion $[\text{Rh}_{13}\text{H}_2(\text{CO})_{24}]^{3-}$ by neutron diffraction study.¹⁹ The low symmetry and electron count in $\text{Mo}_4(\text{H})_3(\text{OBU}^t)_7(\text{HNMe}_2)$ is certainly quite striking. Within the Mo_4 unit we see a segregation of Mo–O bonding from M–M and M–H bonding. This seems to be a recurrent theme in a number of alkoxide clusters of Mo and W as seen, for example, in $\text{Mo}_4(\text{OCH}_2\text{Bu}^t)_{12}(\text{HOCH}_2\text{Bu}^t)$ ²⁰ and $\text{W}_6(\text{H})_5(\text{OPr}^i)_{12}(\text{CPr}^i)$.⁸ Further work directed toward the synthesis, characterization, and study of reactivity of these hydrido-alkoxide clusters of molybdenum and tungsten seems warranted.

Experimental

The compounds $\text{Mo}_2(\text{OR})_6$ ($\text{R} = \text{CH}_2\text{Bu}^t$ or Pr^i) were prepared as described previously.²¹ Potassium hydride/deuteride and $\text{KHB}(\text{Bu}^s)_3/\text{KDB}(\text{Bu}^s)_3$ in THF were purchased (Aldrich) and used as received. All solvents were dried and deoxygenated prior to use and samples were handled under a purified N_2 atmosphere. Schlenk and drybox procedures were employed for the syntheses and characterization of compounds.

Elemental analyses were performed by Oneida. Proton, ^{13}C - $\{\text{H}\}$ and ^{13}C NMR spectra were obtained on either a Varian XL-300 or a Bruker AM-500 and spectra are referenced to the ^1H impurities in $[\text{H}_2]$ toluene or $[\text{H}_6]$ benzene. Deuterium NMR spectra (Bruker AM-500) are referenced on the ^2H natural abundance in benzene. Infrared spectra were recorded as KBr pellets or as Nujol mulls using a Nicolet SLOP FT-IR spectrometer.

Syntheses

$[\text{K}(\text{18-crown-6})][\text{Mo}_4(\mu_4\text{-H})(\text{OCH}_2\text{Bu}^t)_{12}]$ 1. A solution of $\text{KHB}(\text{Bu}^s)_3$ (0.65 mL, 1.0 M in Et_2O , 0.65 mmol) was dissolved in dry and deoxygenated tetrahydrofuran (10 mL) in the presence of 18-crown-6 (175 mg, 0.66 mmol) to generate a solution of $[\text{K}(\text{18-crown-6})]^+[\text{HB}(\text{Bu}^s)_3]^-$. This solution was cooled to -78°C and added *via* cannula dropwise to a stirred solution of $\text{Mo}_2(\text{OCH}_2\text{Bu}^t)_6$ (1.00 g, 1.40 mmol) in THF (5 mL) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for an additional 15 min. The solvent was removed *in vacuo* to afford a dark purple microcrystalline solid which was washed with benzene (3×10 mL) and collected by filtration (88% yield). X-Ray quality crystals were grown from a THF solution by hexane diffusion.

In preparations involving KH which forms a suspension in THF/18-crown-6, a substantially longer time is required (24 h) owing to the low solubility of the KH.

The $[\text{Mo}_4(\mu\text{-D})(\text{OCH}_2\text{Bu}^t)_{12}]^-$ anion was synthesized as above using commercial sources of either KD or KDB(Bu^s)₃.

^1H NMR (CD_2Cl_2 , 22°C , 500 MHz): δ 4.56 (d, $J = 11$, 4 H), 4.33 (d, $J = 11$ Hz, 4 H), 4.31 (s, 4 H), 4.04 (s, 4 H), 3.63 (s, 24 H), 3.28 (s, 4 H), 3.24 (s, 4 H), 1.22 (s, 36 H), 0.94 (s, 18 H), 0.89 (s, 18 H), 0.79 (s, 18 H), 0.65 (s, 18 H), -15.14 (s, 1 H). ^{13}C - $\{\text{H}\}$ (CD_2Cl_2 , 22°C , 125 MHz): δ 84.67, 83.88, 81.76, 81.04, 79.11 (4:2:2:2:2 for OCH_2), 70.54 ($\text{OCH}_2\text{CH}_2\text{O}$), 35.28, 34.79, 33.93, 33.34 (2:6:2:2:2 for OCH_2CMe_3), 28.90, 28.21, 28.14, 27.99, 27.49 (4:2:2:2:2 for OCH_2CMe_3). IR (KBr disc) cm^{-1} : 2946, 2903, 2861, 1477, 1455, 1387, 1353, 1285, 1250, 1214, 1110, 1070, 1049, 1017, 995, 965, 934, 838, 835, 753, 663, 623.

$[\text{K}(\text{18-crown-6})][\text{Mo}_4(\mu_4\text{-H})(\text{OPr}^i)_{12}]$ was prepared from the reaction between $\text{K}^+[\text{HB}(\text{Bu}^s)_3]^-$ and $\text{Mo}_2(\text{OPr}^i)_6$ (1 to 2 mole ratio) in THF as for **1** described above. ^1H NMR ($[\text{H}_6]$ benzene, 22°C , 500 MHz): δ 5.73 (2 H, sept, $J_{\text{HH}} = 6$), 5.41 (1 H, sept, $J_{\text{HH}} = 6$), 5.23 (1 H, sept, $J_{\text{HH}} = 6$), 4.18 (1 H, sept, $J_{\text{HH}} = 6$), 3.47 (36 H, s), 2.16 (6 H, d, $J_{\text{HH}} = 6$), 2.04 (6 H, d, $J_{\text{HH}} = 6$), 2.69 (6 H, d, $J_{\text{HH}} = 6$), 2.64 (6 H, d, $J_{\text{HH}} = 6$), 1.29 (6 H, d, $J_{\text{HH}} = 6$) and 1.16 (6 H, d, $J_{\text{HH}} = 3$ Hz), -12.50 [1 H ($\mu\text{-H}$), s].

$\text{Mo}_4(\text{H})_3(\text{OBU}^t)_7(\text{HNMe}_2)$ 2. In a Schlenk flask 1,2- $\text{Mo}_2(\text{tol})_2(\text{NMe}_2)_4$ ²² (0.450 g, 0.818 mmol) was dissolved in toluene (30 mL). Butyl alcohol (4.2 M in benzene, 0.681 mL, 2.86 mmol) was then added and the contents of the flask were stirred for 24 h. The solvent and liberated amine were removed *in vacuo*. The crude reaction mixture was then dissolved in toluene (*ca.* 20 mL) and transferred to a Kontes[®] solvent seal 30 mL flask. The contents were frozen in liquid N_2 and the flask evacuated and attached to a gas manifold/vacuum line. Dihydrogen gas was added and the flask was sealed to give *ca.* 3 atm H_2 pressure at 22°C . The flask was allowed to warm to room temperature and the solution was stirred for 24 h. The excess H_2 was then removed and the brown solution was transferred to a Schlenk flask. The volume of the solution was reduced to *ca.* 6 mL and the flask and its content were cooled in a fridge at *ca.* -20°C . Two crops of crystals were collected by filtration and dried (yield 0.171 g, 44%) [Calc. (found) for $\text{C}_{30}\text{H}_{73}\text{Mo}_4\text{NO}_7$: C, 38.31 (37.87); H, 7.80 (7.83); N, 1.48 (1.36%)]. ^1H NMR (300 MHz, 22°C , $[\text{H}_6]$ benzene): δ 1.78 (s, 18 H), 1.77 (s, 9 H), 1.70 (s, 18 H), 1.36 (s, 9 H) (OCMe_3); 1.84 (6 H, d, $J_{\text{HH}} = 5.7$) (HNMe_2); 5.32 (sept, 1 H, $J_{\text{HH}} = 5.7$); 1.99 (1 H, t, $J_{\text{HH}} = 2.0$) ($\mu_3\text{-H}$); 3.55 (2 H, d, $J_{\text{HH}} = 2.0$ Hz) ($\mu\text{-H}$). ^{13}C - $\{\text{H}\}$ (75 MHz, 22°C , $[\text{H}_6]$ benzene): δ 82.4, 82.2, 79.6, 75.2, 73.8 (OCMe_3); 35.1, 35.0, 33.9, 32.6, 31.9 (OCMe_3); 40.8 (HNMe_2). IR (KBr disc) cm^{-1} : 3100 [$\nu(\text{NH})$], 2300 [$\nu(\text{ND})$], 1609, 1561 [$\nu(\text{MoH})$], 1387, 1362, 1227, 1175, 887, 961, 900, 772, 536.

Crystallographic studies

Full information is available from the CCDC upon request as per ref. 5.

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