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$Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$: A Novel Hydrido Cluster of Molybdenum

Malcolm H. Chisholm,* John C. Huffman,
Keith S. Kramer, and William E. Streib

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

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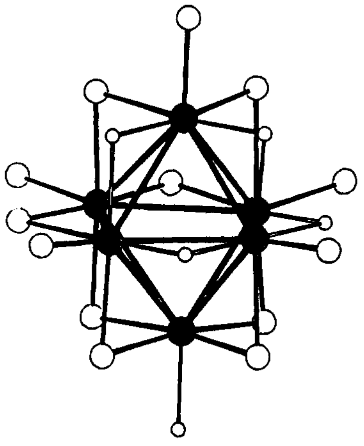
Metal hydrides have played an important role in the development of organometallic chemistry and are involved in numerous catalytic processes, e.g., the hydrogenation, hydrosilation, hydrocyanation, and the hydroformylation of olefins, as well as being important functional groups in numerous stoichiometric transformations.[1] Recently, niobium and tantalum hydrides supported by aryloxide ligands were shown to be catalytically active in the all *cis*-hydrogenation of fused aromatic rings,[2] and the dinuclear compound $[(silox)_2Ta(H)_2]_2$ is reactive toward reduction of carbon monoxide in a remarkable sequence of stoichiometric reactions.[3] We have been pursuing the chemistry of polynuclear hydrido alkoxides of tungsten and, in particular, the chemistry of the compounds $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$,[4] $W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_8\cdot Na(diglyme)$,[5] $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_{11})_7L$ (where L = $HNMe_2$ and PMe_3)[6] and $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$.[7] The latter compound is truly remarkable in being the first polynuclear polyhydride of a transition metal supported exclusively by alkoxide (or O-donor) ligands and was found to exist in one stereoisomer. (In the crystal both enantiomers were present.) The $W_6O_{13}H_5$ moiety is shown in A below.



A

The formation of $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$ occurred in the reaction between $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ and molecular hydrogen in a hydrocarbon solvent at room temperature and represents the major W-containing species present in solution.[7]

We report here on our initial studies aimed at preparing polynuclear polyhydrides of molybdenum supported by alkoxide ligands. In initial reactions between $1,2\text{-}Mo_2(O\text{-}t\text{-}Bu)_4(p\text{-}tolyl)_2$ and H_2, only intractable molybdenum-containing products were formed. We were, however, able to isolate a hydrido alkoxide molybdenum cluster, namely, $Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$ from the reaction shown in eq 1.

$$2[1,2\text{-}Mo_2(p\text{-}tolyl)_2(NMe_2)_4] + 7Bu^tOH + H_2(excess) \xrightarrow[\text{hexane}]{22\,°C} Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2) + 7HNMe_2 + 4toluene \quad (1)$$

The dark brown crystalline compound $Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$ (**1**) is air sensitive and hydrocarbon soluble and is obtained by crystallization of the concentrated mother liquor generated in reaction **1** upon cooling to −20 °C. It can be isolated in *ca.* 40% yield based on preparations involving 0.5–1.0 g of $Mo_2(p\text{-}tolyl)_2(NMe_2)_4$.

Reaction **1** can be carried out in two steps. First, the alcoholysis, involving Bu^tOH (3.5 equiv) and $1,2\text{-}Mo_2(p\text{-}tolyl)_2(NMe_2)_4$, yields a mixture of $Mo_2(p\text{-}tolyl)_2(O\text{-}t\text{-}Bu)_4$ and $Mo_2(p\text{-}tolyl)_2(O\text{-}t\text{-}Bu)_3(NMe_2)$. The former compound has been isolated as a pure compound.[9] The latter is presumed present on the basis of the ^1H NMR spectrum that clearly reveals the presence of a NMe_2 ligand.[10] This mixture may have its solvents removed and may be dried thoroughly in vacuum. The sample so generated lacks any *t*-BuOH or $HNMe_2$. Second, this sample is redissolved in hexane and D_2 gas is added, and the compound $Mo_4(D)_3(O\text{-}t\text{-}Bu)_7(Me_2ND)$ is formed. The source of the Me_2NH ligand is thus traced to hydrogenolysis, most probably of a Me_2N ligand, though it is possible that Bu^tOH is initially formed and that this then reacts with the NMe_2 ligand. Suffice it to say that **1** is formed from the coupling of two coordinatively unsaturated Mo_2 species, and in all likelihood one of these is reduced from its Mo_2^{6+}-containing precursor.

The molecular structure of **1**, deduced from a single-crystal X-ray study, is shown in Figure 1.[11] The hydride ligands, which were not located crystallographically, are placed in idealized positions, two μ_2-H and one μ_3-H, to complement the coordination of each fused Mo_3 triangle that makes up the observed Mo_4 butterfly. The location of the ligands in these sites was acceptable to the HYDEX program, and the location of the μ_3-H group provided a significantly lower potential energy minimum relative to the alternative solution of placing the unique hydride bridging between Mo(1) and Mo(2). The Mo–Mo distances are notably different within the two Mo_3 triangles: Mo(4) to Mo(1) and Mo(2) are 2.38 Å, whereas Mo(3) to Mo(1) and Mo(2) are 2.50 Å. Our proposal places the three hydride ligands within the Mo(4)–Mo(1)–Mo(2) triangle. The hinge angle between the two Mo_3 planes is 96.2°, and the N(40)–O(30) distance of 2.82 Å is indicative of hydrogen-bonding between the Me_2NH ligand and the O(32) of the terminal O-*t*-Bu ligand bound to Mo(3). The terminal Mo–O distances span a very small range, 1.93–1.95 Å.

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(8) ^1H NMR data (300 MHz, 22 °C, benzene-d_6): δ 1.47 (s, 36H (O-*t*-Bu)), 2.17 (s, 6H ($C_6H_5CH_3$)), 8.06, (d, 4H (0-C_6H_5), 7.14 (d, 4H (*m*-C_6H_5), J_{HH} = 7.8 Hz).

(9) A compound of formula $Mo_2(p\text{-}tolyl)_2(NMe_2)(O\text{-}t\text{-}Bu)_3$ may exist in two rotamers, and for each the *p*-tolyl ligands are on different metal atoms. By ^1H NMR spectroscopy (300 MHz, 22 °C, benzene-d_6), we see three *p*-tolyl Me resonances δ 2.24, 2.17, and 2.12 (all singlets) and proximal and distal N*Me* signals as broad resonances at δ 4.12 and 2.55, respectively.

(10) Crystal data for **1** at −84 °C: $a = 17.489(2)$ Å, $b = 21.293(3)$ Å, $c = 11.487(2)$ Å, $Z = 4$, $d_{calcd} = 1.46$ g cm^{-3}, space group $P2_12_12_1$. Of the 4498 reflections collected (Mo Kα, $6° < 2\theta < 45°$), the 3578 having $F > 3\sigma(F)$ were used in the refinement. All atoms other than H atoms were refined anisotropically. Final residuals are $R(F) = 0.058$ and $R_w(F) = 0.049$.

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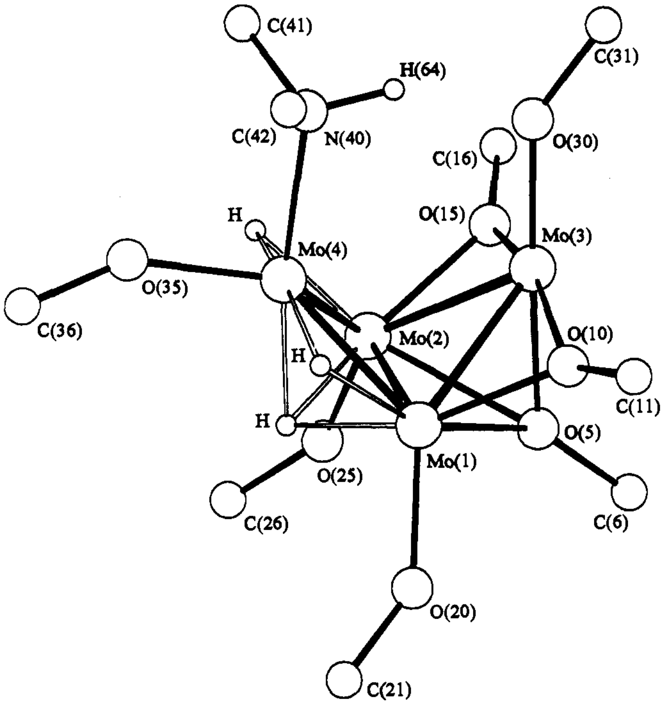

Figure 1. Ball-and-stick drawing of the $Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$ molecule. The hydride ligands are placed in proposed locations, as is the hydrogen on the Me_2NH ligand. For clarity, the O-t-Bu ligands are represented by only their respective O–C moieties. Selected distances and angles are noted in the text. Complete listings are given in the supplementary material.

The Mo–μ_2-O distances are 2.03–2.05 Å, and the Mo–μ_3-O distances are 2.08, 2.33, and 2.35 Å, with the short distance of 2.08 being Mo(3)–O(5), namely, the bond that is trans to a terminal alkoxide. The long Mo–μ_3-O distances are thus those that are trans to the Mo–H bonds, as drawn in Figure 1. This is consistent with the known high trans influence of hydride ligands.[12] The presence of the Me_2NH bond is clearly implicated by (i) the long Mo–N distance (2.22 Å), (ii) the pyramidality at the nitrogen atom, and (iii) the appearance of the N*H* proton signal in the ^1H NMR spectrum which shows coupling to the six H atoms of the two *N*-methyl groups.

The infrared spectrum also provides evidence for the NH group as a band at 3100 cm^{-1} which moves to *ca.* 2300 in the deuterated compound $Mo_4(D)_3(O\text{-}t\text{-}Bu)_7(DNMe_2)$. Tentatively we also assign bands at 1609 and 1561 to Mo–μ-H stretching vibrations that are only present in the protio sample.

The ^1H NMR spectrum reveals that the molecule has a virtual mirror plane of symmetry.[13] The O-*t*-Bu groups fall in the ratio 1:1:1:2:2, and the hydride signals were located at δ 1.99 (1H) and −3.55 (2H) as a triplet and doublet, respectively. Homonuclear decoupling showed that the hydrides were coupled to each other, $J_{HH} = 2.0$ Hz. The N*H* proton appears as a septet at δ 5.32 and the NMe_2 group as a doublet at δ 1.84 ($J_{HH} = 5.7$ Hz).

In conclusion, the elemental analysis,[14] the spectroscopic data, and the crystallographic data provide uniform confirmation that we have, indeed, prepared $Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$, the first polynuclear polyhydride of molybdenum supported by alkoxide ligands. The overall oxidation state of molybdenum has gone from +3.0 to +2.5 as a result of the reduction of an amide to an amine ligand, and the structure of the 14-electron cluster (Figure 1) is, to our knowledge, without a precedent. It is interesting to note that in both **1** and $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$, the hydride ligands reveal a propensity to group themselves on a triangular face, though in the latter molecule there are additional hydride ligands.

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Supplementary Material Available: Listings of atomic coordinates, bond distances and angles, VERSORT diagram, and stereodrawings (11 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[12] ^1H NMR data for O-*t*-Bu ligands (300 MHz, 22 °C, benzene-d_6): δ 1.79 (18H), 1.77 (9H), 1.70 (18H), 1.36 (9H), 1.12 (9H).

[13] Anal. Calcd for $Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$: C, 38.27; H, 7.60; N, 1.49. Found: C, 37.87; H, 7.83; N, 1.36.