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Metal Alkoxides—Models for Metal Oxides. 10.[1] Synthesis and Properties of Alkyl Alkoxides of Formula 1,2-$Mo_2R_2(OR')_4$ and $Mo_2R(OR')_5(M{\equiv}M)$

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Addition of alcohols to 1,2-$Mo_2R_2(NMe_2)_4$ compounds in hydrocarbon solvents leads to the kinetic preference for OR′ substitution of NMe_2 ligands, but protolysis of the M–C(R) bond is also possible. The kinetic products where R = a β-hydrogen-stabilized alkyl ligand are 1,2-$Mo_2R_2(OR')_4$ compounds [R = Me, R′ = *t*-Bu; R = CH_2Ph and $CH_2C_6H_4$-4-Me, R′ = *i*-Pr; R = CH_2CMe_3, R′ = *i*-Pr, CH_2CMe_3, and Et; R = CH_2SiMe_3, R′ = *t*-Bu]. Depending upon the combined steric properties of R and R′ these compounds may be coordinatively unsaturated and can be isolated as Lewis base adducts, e.g., $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$. The combined steric properties of R and R′ are crucial in assuring that protolysis of the Mo–C(alkyl) bond does not occur rapidly, e.g., while it is possible to prepare $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$, less sterically demanding alkoxy ligands such as *i*-PrO and Me_3CCH_2O gave $M_2(OR)_6$ compounds with liberation of CH_4 (2 equiv), but with the bulky alkyl ligand Me_3CCH_2, it is possible to isolate $Mo_2R_2(OR')_4$ compounds for R′ = *i*-Pr, CH_2CMe_3, and Et. The intermediate compound in these reactions $Mo_2R_2(NMe_2)_2(OR')_2$ was also detectable for bulky combinations of R and R′. By contrast reactions employing β-hydrogen-containing alkyl ligands proceed under similar conditions to generate $Mo_2R(OR')_5$ compounds with liberation of 1 equiv of alkane in addition to $HNMe_2$ (4 equiv). Though protolysis of the remaining Mo–C(alkyl) bond is thermodynamically favorable leading to $Mo_2(OR')_6$ compounds and a further equivalent of alkane, this reaction can be slowed sufficiently to allow the isolation of $Mo_2R(OR')_5$ compounds providing the groups R and R′ are sufficiently bulky: R = Bu, R′ = *t*-Bu; R = Et and Pr, R′ = *t*-Bu and *i*-Pr. Labeling studies show that the alkane liberated in the formation of $Mo_2R(OR')_5$ compounds contains the β-hydrogen/deuterium from its formerly neighboring alkyl ligand. Moreover, the alkyl ligand present in $Mo_2R(OR')_5$ compounds is generated from the hydrogen/deuterium of the hydroxyl group of the alcohol and the alkene formed in the initial liberation of alkane. This dictates that the reaction sequence involves both a reductive elimination from and an oxidative addition to the dinuclear center. The reaction between $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ and *i*-PrOH generates $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4(M\overset{4}{-}M)$ together with *i*-BuH and $Me_2C{=}CH_2$. However, when the reaction is carried out in the presence of ethylene, $Mo_2Et(O\text{-}i\text{-}Pr)_5$ is formed. Reactions employing $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ and *i*-PrOH yield initially $Mo_2(i\text{-}Pr)(O\text{-}i\text{-}Pr)_5$ which in the presence of a Lewis base isomerizes to $Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$. Possible origins for this unusual kinetic behavior in the formation and isomerization of the alkyl ligand are discussed. The physicochemical properties of the new compounds are reported, together with observations of rotations about the M≡M bond.

Introduction

Both historically and commercially, σ-alkyl complexes have played a prominent role in the development of mononuclear organo-transition-metal chemistry.[2-4] Presumably alkyl to metal bonds also play a critical role in a number of heterogeneous reactions involving either metal or metal oxide/chalcogenide surfaces. In our attempts to model metal oxide environments involving reduced molybdenum and tungsten,[5,6] we have designed routes to the preparation of di-, tri- and tetranuclear alkyl–alkoxide clusters. In this paper we describe our studies of the alcoholyses of 1,2-$Mo_2R_2(NMe_2)_4$ compounds and in the following paper we describe work relating to the ditungsten analogues.[7,8] Subsequently we shall present our results on the tri and tetranuclear systems along with studies aimed at examining the reactivity of the M–C(alkyl) bond in these "nonclassical" organometallic environments.

Results and Discussion

Syntheses. Alkane solutions of $Mo_2R_2(NMe_2)_4$ compounds react with alcohols, R′OH, to give compounds of formula 1,2-$Mo_2R_2(OR')_4$, $Mo_2R(OR')_5$, or $Mo_2(OR')_4(HOR')_4$ depending upon the nature of R and R′ as summarized in eq 1–3.

$$\text{1,2-}Mo_2R_2(NMe_2)_4 + 4R'OH\ (\geq 4\ \text{equiv}) \rightarrow Mo_2R_2(OR')_4 + 4HNMe_2 \quad (1)$$

R = Me, R′ = *t*-Bu; R = CH_2CMe_3,
R′ = Et, Me_3CCH_2, *i*-Pr, and *t*-Bu;
R = CH_2Ph and $CH_2C_6H_4$-4-Me, R′ = *i*-Pr

$$\text{1,2-}Mo_2R_2(NMe_2)_4 + R'OH\ (>5\ \text{equiv}) \rightarrow Mo_2R''(OR')_5 + RH + 4HNMe_2 \quad (2)$$

R = Et, Pr, Bu; R′ = *t*-Bu and *i*-Pr,
R″ = Et, *i*-Pr, and *sec*-Bu

$$\text{1,2-}Mo_2(i\text{-}Bu)_2(NMe_2)_4 + i\text{-}PrOH\ (>5\ \text{equiv}) \rightarrow Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4 + i\text{-}BuH + Me_2C{=}CH_2 + 4HNMe_2 \quad (3)$$

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[1] For part 9 in the series see: Chisholm, M. H.; Huffman, J. C.; Smith, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 222.

[2] Parshall, G. W. In *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley-Interscience: New York, 1980.

[3] Kochi, J. K. In *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

[4] Heck, R. F. In *Organotransition Metal Chemistry. A Mechanistic Approach*; Academic Press: New York, 1984.

[5] Chisholm, M. H. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series *211*; American Chemical Society: Washington, DC, 1983; p 243.

[6] Chisholm, M. H. *J. Solid State Chem.* **1985**, *57*, 120.

[7] A preliminary report of some aspects of this work has appeared including the crystal and molecular structure of $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$ which is not discussed in this text: Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075. The complete details of the structure are available in microfiche form only from the Indiana University Library at a cost of $2.50 per copy. Request MSC Report No. 82097.

[8] Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Tatz, R. J. *Organometallics*, following paper in this issue.

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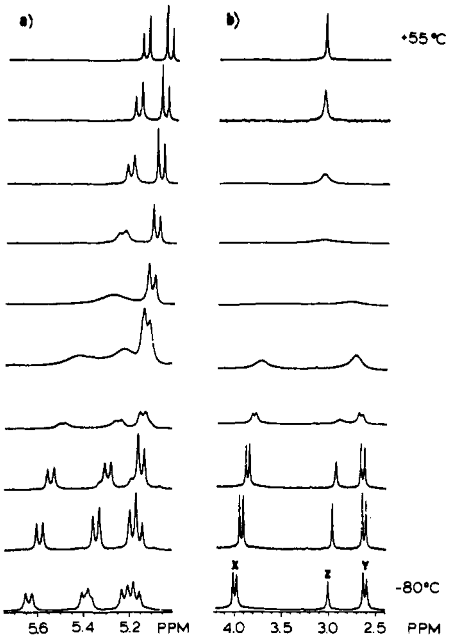

Figure 1. Variable-temperature ^{1}H NMR spectra of $Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$ in toluene-d_8 at 360 MHz recorded as a function of temperature (°C), from −80 to +55 °C in integrals of 15 °C. The temperature-dependent spectra of the OCH_2CMe_3 protons are shown on the left hand side (5.0–5.6 ppm) and those of the CH_2CMe_3 ligand on the right-hand side (2.5–4.0 ppm).

Kinetically the replacement of NMe_2 groups by OR groups is favored, though protolysis of the resulting M–C(alkyl) group and elimination of alkane with concomitant formation of $Mo_2(OR')_6$ compounds does occur in the presence of excess alcohol. The latter reaction is highly dependent upon steric crowding at the metal; bulky combinations of R and R′ suppress protolysis of the M–C(alkyl) bond. Thus for R = CH_2CMe_3, even the sterically undemanding ethoxide is accessible, but not the methoxide. Aside from the steric limitations of R and R′ on the synthesis of $Mo_2R_2(OR')_4$ compounds, the latter are favored by slow addition of 4 equiv of alcohol and by carrying out the reactions at ca. 0 °C.

When the alkyl ligand R contains β-hydrogen atoms, the products are not $Mo_2R_2(OR')_4$ compounds but $Mo_2R''(OR')_5$ compounds as shown in eq 2. Again the choice of R and R′ must allow for steric suppression of a subsequent protolysis to give $Mo_2(OR')_6$ compounds with the further elimination of alkane. There are two exceptions that we have noted to the generalized reaction shown in eq 2 for R = β-hydrogen-containing alkyl ligands. (i) The reaction between $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ leads to $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$($M\overset{4}{-}M$) with the liberation of i-BuH and $Me_2C{=}CH_2$ along with $HNMe_2$ (4 equiv). (ii) The reaction between $Mo_2(t\text{-}Bu)_2(NMe_2)_4$ and i-PrOH gives $Mo_2(t\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$. It should be noted that in the preparation of $Mo_2R''(OR')_5$ compounds (eq 2), the resulting alkyl ligand R″ may be an isomer of the original alkyl ligand R. We shall defer a discussion of the mechanistic aspects associated with these syntheses until later in the paper.

Physicochemical Properties of the Alkyl Alkoxides of Formula $Mo_2R_2(OR')_4$ and $Mo_2R(OR')_5$. The synthesis of the new alkyl alkoxides of dimolybdenum according to eq 1 and 2 gives, upon removal of the solvent and other volatile materials, waxy solids which range in color from yellow to red. Purification is possible by either vacuum sublimation or recrystallization from hexane or pentane. Analytical data and other characterization data are presented in Table I for representative samples.

It should be noted that though many of the compounds are thermally stable toward sublimation in the temperature range 70–110 °C, others are not. The thermal instability seems to arise when the combination of R and R′ leaves the dimetal center coordinatively unsaturated, e.g., $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$ which forms an adduct with pyridine $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$, does not sublime without decomposition. This is responsible for the poor elemental analyses obtained for this compound. Similar problems were associated with the compounds $Mo_2Et(O\text{-}i\text{-}Pr)_5$, $Mo_2Pr(O\text{-}i\text{-}Pr)_5$, and $Mo_2(CH_2CMe_3)_2(OEt)_4$, all of which decompose upon heating. The products obtained by thermolysis remain to be investigated.

The new compounds are air-sensitive and must be handled in dry and oxygen-free atmospheres (N_2) and solvents. They are all soluble in common aliphatic and aromatic hydrocarbons. Their stability toward common chlorinated solvents $CHCl_3$, CH_2Cl_2, etc. was not investigated. The compounds are diamagnetic and give molecular ions in the mass spectrometer. On the basis of these properties and the NMR data presented below, there is no doubt that these are members of the now quite large and well established class of compounds containing unbridged triple bonds between molybdenum atoms.[9,10]

NMR Spectroscopic Studies. ^{1}H NMR and ^{13}C NMR data are recorded in Table II. For compounds of formula $Mo_2R(OR')_5$ there are two types of OR′ ligands in the ratio 3:2 corresponding to the $(R'O)_3M$ and $R(R'O)_2M$ "halves" of the molecule. For the $R(R'O)_2M$ groups, whenever diastereotopism was expected, it was observed. These general statements are independent of temperature in the range −60 to +80 °C in toluene-d_8. From this we deduce (i) that alkoxy migration across the $M{\equiv}M$ bond is slow on the NMR time scale but rotation is rapid and (ii) the $R(R'O)_2M$ end of the molecule does not undergo rapid (NMR time scale) inversion.

The ^{1}H NMR spectra of $Mo_2R_2(OR)_4$ compounds are indicative of the 1,2-Mo_2R_2 substitution pattern and in general at room-temperature anti $\rightleftharpoons$ gauche isomerization is rapid.[10] However, for bulky R and R′ combinations restricted rotations about the $Mo{\equiv}Mo$ bond do occur as a function of temperature and it is possible in some instances to freeze out low-temperature limiting spectra of anti and gauche isomers. For example, at −80 °C, 1,2-$Mo_2(CH_2CMe_3)_2(OCH_2\text{-}t\text{-}Bu)_4$ exists in a mixture of anti and gauche isomers in a ca. 1:5 concentration ratio, respectively. Upon raising the temperature anti–gauche isomerization becomes faster until at +55 °C, the spectrum reveals only one time-averaged isomer having a mirror plane of symmetry, i.e., like that of the anti isomer. The temperature-dependent changes of the methylene protons associated with the CH_2CMe_3 and OCH_2CMe_3 ligands are shown in Figure 1. Though there are clearly some chemical shift changes with temperature, probably arising from population differences of various rotamers associated with Mo–C–C and Mo–O–C moieties, a reasonable estimate for the barrier to rotation about the $Mo{\equiv}Mo$ bond may be placed at 12 ± 0.5 kcal mol^{-1} in $Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$.[10] It is also evident that the energy of activation for gauche $\rightleftharpoons$ gauche isomerization cannot be less or, at least, cannot be significantly less than that for gauche $\rightleftharpoons$ anti isomerization, since the two types of OR′ ligands

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[9] Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

[10] For compounds of formula 1,2-$Mo_2X_2(CH_2SiMe_3)_4$ where X = Cl, Br, O-i-Pr, and O-t-Bu see: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 251. Estimates of rotational barriers were made from coalescence temperatures by using the Gutowsky–Holm equation: Pople, J. A.; Schneider, W. G.; Burnstein, H. J. *High Resolution NMR Spectroscopy*; McGraw-Hill: New York, 1959; p 223.

Table I. Analytical and Other Characterization Data for Alkyl Alkoxides of Formulas $Mo_2R_2(OR')_4$ and $Mo_2R(OR')_5$

compd	color and form	sublim *T*, °C (10^{-3} torr)	C calcd	C found	H calcd	H found	N calcd	N found
$Mo_2Me_2(O\text{-}t\text{-}Bu)_4$	purple solid	80 °C dec	42.03	39.36	8.23	7.69	0.0	0.24
$Mo_2Me_2(O\text{-}t\text{-}Bu)_4py_2$	brown crystals	loses py at room temp	50.00	49.78	7.79	7.65	4.16	4.30
$Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Bu)_4$	red crystalline solid	70–80	43.76	43.51	8.87	8.91	0.0	0.14
$Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$	yellow solid	70–90	46.32	46.15	8.83	8.69	0.0	0.18
$Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$	yellow-orange crystalline solid	120–130	52.78	52.74	9.74	9.59	0.0	<0.02
$Mo_2(CH_2CMe_3)_2(OEt)_4$	yellow crystalline solid	70–80	42.03	41.93	8.23	8.09	0.0	<0.02
$Mo_2(Et)(O\text{-}t\text{-}Bu)_5$	red solid	60–70	45.05	44.87	8.59	8.44	0.0	0.11
$Mo_2(Pr)(O\text{-}t\text{-}Bu)_5$	red solid	60–70	46.00	45.68	8.73	8.51	0.0	0.22
$Mo_2(Bu)(O\text{-}t\text{-}Bu)_5$	red solid	60–70	46.91	46.69	8.86	8.71	0.0	<0.03
$Mo_2(Et)(O\text{-}i\text{-}Pr)_5$	yellow solid	decomp						
$Mo_2(Pr)(O\text{-}i\text{-}Pr)_5$	yellow solid	decomp						
$Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$	orange solid		51.15	50.93	6.94	6.78	0.0	<0.03
$Mo_2(CH_2Ph\text{-}p\text{-}Me)_2(O\text{-}i\text{-}Pr)_4$	orange solid		52.67	52.47	7.26	7.11	0.0	<0.03

present in the gauche rotamers do not coalesce prior to involvement of the signals due to the anti rotamer.

Mechanistic Aspects of the Alcoholysis Reactions. As indicated in the section entitled "Syntheses", the combined steric properties of R and R′ are very important in controlling (i) the rate of alkoxide for NMe_2 replacement and (ii) the susceptibility of the M–C(alkyl) bond toward protolysis. Since it is well acknowledged that for early transition elements, including the group 6 elements, the bond strengths are in the order M–OR > M–NMe_2 > M–R and that these differences are greater than those associated with R–H, N–H, and O–H bonds, as shown in Table III, it seems most likely that the preferential replacement of NMe_2 groups relative to R (alkyl) ligands is a kinetic factor resulting from the relative ease of hydrogen atom transfer between a coordinated oxygen atom of a ligated alcohol molecule and the nitrogen atom of an amide ligand vs. the same hydrogen atom transfer to the carbon atom of an alkyl ligand. The former has some characteristics of the facile protonation of a lone pair of electrons while the latter involves protolysis of a metal–carbon σ-bond.

Studies of the reaction between $Mo_2(CH_2CMe_3)_2(NMe_2)_4$ and the alcohols *i*-PrOH or Me_3CCH_2OH reveal the formation of the intermediate $(Me_3CCH_2)(R'O)(Me_2N)Mo{\equiv}Mo(NMe_2)(OR')(CH_2CMe_3)$ which has frozen out NMe groups (proximal and distal) on the NMR time scale at room temperature.[9]

If the compound $Mo_2R_2(OR')_4$ is coordinatively unsaturated, then in the presence of excess R′OH protolysis will slowly occur to give $Mo_2(OR')_6$ compounds by way of $Mo_2R(OR')_5$ in the case of R = Me, CH_2Ph, etc. (eq 1). For the compound $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$, which is coordinatively unsaturated as evidenced by its ability to pick up pyridine ligands yielding $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$, in the presence of excess *t*-BuOH, exchange between free and coordinated *t*-BuO groups is rapid on the NMR time scale. Thus, the degenerate exchange process Mo–O-*t*-Bu + *t*-Bu′OH → Mo–O-*t*-Bu′ + *t*-BuOH with $\Delta G = 0$ is kinetically more facile than protolysis of the Mo–CH_3 bond to give methane and $Mo_2Me(O\text{-}t\text{-}Bu)_5$. With each replacement of Mo–Me bonds by Mo–O-*t*-Bu bonds, steric crowding at the metal is increased and the compound $Mo_2(O\text{-}t\text{-}Bu)_6$ does not undergo rapid (NMR time scale) exchange with free *t*-BuOH.

We thus feel confident in stating that all reactions between $Mo_2R_2(NMe_2)_4$ compounds and alcohols proceed to give $Mo_2R_2(OR')_4$ compounds and that the reactivity of the latter are dependent upon both R and R′. When R contains β-hydrogen atoms, a subsequent β-hydrogen atom transfer reaction generally occurs, but in at least one instance, namely, for $Mo_2(t\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$, this is not so. As we shall show later, steric factors appear particularly important in determining the activity of β-hydrogen transfer reactions and presumably the compound $Mo_2(t\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ is kinetically isolable. The data on this compound are not very extensive since it does decompose slowly even in the solid state. However, its ^1H NMR spectrum leaves little doubt concerning its existence and we show in the following paper[8] that the related compound $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ can be formed and here we can even obtain proof from single-crystal X-ray studies.

In the presence of the liberated Me_2NH and/or R′OH, the coordinatively unsaturated $Mo_2R_2(OR')_4$ compounds where R contains β-hydrogen atoms are prone to facile β-hydrogen atom transfer to the α-carbon of the neighboring alkyl ligand. Though this most probably involves β-hydrogen atom transfer to the metal, we have not been able to establish this because the transfer occurs without any scrambling. For example, starting with the labeled compounds $Mo_2(CH_2CD_3)_2(NMe_2)_4$ and $Mo_2(CH(CD_3)_2)_2(NMe_2)_4$ the liberated alkanes were CH_2DCD_3 and CD_3CHDCD_3, respectively. This determination was made by ^2H NMR spectroscopy.[11]

Reductive elimination of alkane from $Mo_2R_2(OR')_4$ generates formally a Mo_2^{4+} center, and by use of appropriate R and OR′ groups it has proved possible to trap the reduced species as $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$ or $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4$.[12] It seems likely that related species are formed in all reactions of type 2. The alkene is undoubtedly lost from the Mo_2^{4+} center since reactions employing $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ and *t*-BuOH in the presence of C_2H_4 (10-fold excess) lead to $Mo_2Et(O\text{-}t\text{-}Bu)_5$. No reaction is observed between $Mo_2(n/i\text{-}Pr)(O\text{-}t\text{-}Bu)_5$ and C_2H_4.

Following reductive elimination, the alkyl ligand formed in eq 2 owes its origin to the hydroxyl hydrogen atoms of an alcohol and the liberated alkene. Reactions employing *t*-BuOD or *i*-PrOD and $Mo_2(CH_2CH_3)_2(NMe_2)_4$ reveal incorporation of D into the ethyl ligand in $Mo_2(C_2H_4D)(OR')_5$ compounds. At short reactions times, and, in particular for R′ = *t*-Bu, the initial position of D incorporation is the β-carbon atom. With time and particularly for R′ = *i*-Pr, scrambling over the α- and β-positions occurs.

It is also interesting to note that the alkyl ligand kinetically formed in reaction 2 is the most hindered alkyl

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(11) The ethane CH_2DCD_3 has been previously characterized by ^2H NMR spectroscopy and is formed in the dinuclear reductive elimination reaction $1,2\text{-}Mo_2(CH_2CD_3)_2(NMe_2)_4 + CO_2 \rightarrow Mo_2(O_2CNMe_2)_4 + CH_2{=}CD_2 + CH_2DCD_3$, which has many parallels with the present work when R contains β-hydrogen atoms: Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138.

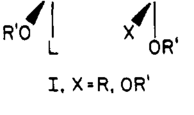
(12) Structural characterization of these and related $Mo_2(OR)_4L_4$ compounds (R = *i*-Pr, L = py; R = CH_2CMe_3, L = PMe_3) have been reported in preliminary form: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 1153.

ligand that can be generated by insertion of the liberated olefin and a metal hydride, the latter being presumably derived from R'O–H oxidative addition to the dinuclear center. Thus reactions between $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ and *i*-PrOH yield, at short reaction times, mostly $Mo_2(i\text{-}Pr)(O\text{-}i\text{-}Pr)_5$ which in the absence of a donor ligand is stable with respect to conversion to $Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$. The product mixture formed in the reaction between $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ and *i*-PrOH (>5 equiv) in hexane at 0 °C is ca. 70% $Mo_2(i\text{-}Pr)(O\text{-}i\text{-}Pr)_5$ and 30% $Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$ as determined by ^1H NMR spectroscopy. This mixture, once formed, is not isomerized in the absence of $HNMe_2$, pyridine, or PMe_3. However, addition of any of the latter causes isomerization to $Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$, with the rate of isomerization being in the order py ≈ PMe_3 (5 min, 22 °C) > $HNMe_2$ (60 min, 22 °C), correlating roughly with the affinity of the base for the dimetal center. In the case of the alcoholysis reaction involving $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ with *t*-BuOH, the kinetically formed product is $Mo_2(i\text{-}Pr)(O\text{-}t\text{-}Bu)_5$ which is present ca. 10:1 over the $Mo_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$ compound. Isomerization in the latter case is much slower in the presence of added bases ($HNMe_2$, py, PMe_3), reflecting the poorer binding of Lewis bases when the bulky O-*t*-Bu ligands are present relative to O-*i*-Pr ligands.

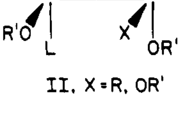
Speculation about Reaction Pathways. Having presented the facts, it is worthwhile spending a few moments to speculate about some of the possible reaction pathways that may be involved in reactions which proceed according to eq 2. First let us review the facts: 1. Alcoholysis leads to $Mo_2R_2(OR')_4$ compounds. 2. In the presence of $HNMe_2$ and/or excess R'OH, $Mo_2R_2(OR')_4$ compounds reductively eliminate both alkane and alkene by a β-hydrogen atom process. 3. In some instances, the reduced Mo_2^{4+}-containing species can be isolated (eq 3), but in most instances a further sequence of reactions is set into motion whereby a new alkyl ligand is generated, R'OH + alkene + "$Mo_2(OR')_4$" → $Mo_2R''(OR')_5$, and the Mo_2^{4+} center is converted back to Mo_2^{6+}. 4. The sterically encumbered alkyl ligand is kinetically generated in 3 above (*t*-Bu > *i*-Bu; *i*-Pr > *n*-Pr; *sec*-Bu > *n*-Bu) (No C–C skeletal rearrangements are involved.) Addition of a Lewis base promotes alkyl isomerization [$Mo_2(i\text{-}Pr) \rightarrow Mo_2(n\text{-}Pr)$], and the rate of this isomerization correlates roughly with the ability of the Lewis base to bind to the dimetal center. These are the facts; now to the speculations.

We know that addition of Lewis bases, at least PMe_3, to $1,2\text{-}Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ promotes a rapid and reversible, 1,2-benzyl migration giving an isolable adduct, $(i\text{-}PrO)_3Mo{\equiv}Mo(CH_2Ph)_2(O\text{-}i\text{-}Pr)(PMe_3)$.[13] If such a reaction also occurs in the presence of $HNMe_2$ (or excess R'OH) for $Mo_2R_2(OR')_4$ compounds, where R contains β-hydrogen atoms, then a coordinatively unsaturated center, $\equiv MoR_2(OR')$, will be formed and should be prone to β-hydrogen elimination since at least one of the in-plane $d_{x^2-y^2}$ or d_{xy} orbitals is no longer involved in metal–OR π-bonding.[14] Thus the initial β-hydrogen atom abstraction and reductive elimination of alkane could occur from one metal center rather than by a route involving transference of the β-H atom across the Mo–Mo bond.[15] At the point of reductive elimination we would have generated an asymmetric Mo_2^{4+} unit having the elements $(R'O)_3Mo$ and Mo(OR), i.e., a quadruple bond between a Mo(3+), d^3 center and a Mo(1+), d^5 center. There is precedent for such a compound, namely, the isolation by Wilkinson and co-workers[16] of $(Me_3SiCH_2)_2Mo(CH_2SiMe_2CH_2)Mo(PR_3)_3$ which has a Mo–Mo quadruple bond, Mo–Mo = 2.16 Å between molybdenum atoms in differing oxidation states, Mo(3+) and Mo(1+), and different coordination numbers, 3 and 4, respectively. In the present work, donor molecules such as $HNMe_2$, R'OH, and alkene are available for coordination and reaction with the coordinatively unsaturated species $(R'O)_3Mo\overset{4}{—}Mo(OR')$ and oxidative addition of R'OH would generate a molecule containing the elements $Mo_2(H)(OR')_5$. Whether or not in the presence of $HNMe_2$ and R'OH such a species would contain an unbridged or bridged d^3-d^3 structure is a matter for speculation. Coordination of an alkene will be favored such that its C–C vector is aligned along the Mo–Mo vector in this way allowing for Mo d_{xz}/d_{yz} to olefin π* back-bonding. (The *z* axis is taken to be coincident with the M–M axis.) Substituents on the alkene will be directed in a distal manner based on steric factors.

If the olefin and the hydride react across the M–M bond to generate the alkyl, it will be the most sterically encumbered alkyl that will be formed kinetically. However, if β-hydrogen atom abstraction is possible, as is rotation about the metal–alkene bond, then occasionally reaction of an alkene with its substituent(s) proximal to the M_2 center will occur to generate the least sterically encumbered alkyl ligand. It is thus possible to envisage that intermediates of types I and II are involved in both the reductive elimination step, X = R, and the insertion step, X = OR', and that the role of the Lewis base L is to promote β-hydrogen atom transfer across the M–M bond. Conversely dissociation of L will promote olefin–hydride coupling to regenerate the three-coordinate $X_3M{\equiv}MX_3$-type compound, and by I we see that a propene molecule will generate $Mo_2(i\text{-}Pr)(OR')_5$ while II will yield $Mo_2(n\text{-}Pr)(OR)_5$. It should be recognized that if intermediates of types I and II are involved, then we do not have to invoke alkyl migration from one metal center to the other. The preferred conformations of I and II will be determined largely by steric factors as is seen in compounds of formula $M_2(OR)_6L_2$ where M = Mo or W and L = Lewis base.[17]



I, X = R, OR'



II, X = R, OR'

Concluding Remarks

Alcoholysis reactions involving $1,2\text{-}Mo_2R_2(NMe_2)_4$ compounds have allowed the isolation of new mixed alkyl alkoxides of formula $1,2\text{-}Mo_2R_2(OR')_4$ or $Mo_2R(OR')_5$ for β-hydrogen-stabilized and β-hydrogen atom containing alkyl groups R. The scope of such compounds is limited by the combined steric properties of R and R'. The generation of the monoalkyl complexes $Mo_2R(OR')_5$ where R contains β-hydrogen atoms involves a circuitous route

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[13] Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 5385.

[14] For a discussion of the bonding and kinetic stability of $1,2\text{-}M_2R_2(NMe_2)_4$ compounds, where R contains β-hydrogen atoms, see: Chisholm, M. H.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4245.

[15] Trinquier, G.; Hoffman, R. *Organometallics* **1984**, *3*, 370.

[16] Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

[17] Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

Table II. ^{1}H and ^{13}C NMR Data for Alkyl–Alkoxy Compounds of Formulas $Mo_2R_2(OR')_4$ and $Mo_2R(OR')_5(M{\equiv}M)$

compd	^{1}H chem shift (rel int, multiplicity; J, Hz)[a,b]				^{13}C chem shift (rel int)[a,c]			
	alkyl		alkoxide		alkyl		alkoxide	
$Mo_2Me_2(O\text{-}t\text{-}Bu)_4$	α	2.00 (1, s)	β	1.47 (6, s)	α	29.81 (1)	α	79.41 (2)
$Mo_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$	α	2.66 (2, s)	β	1.54 (18, s)		NR[e]	β	33.40 (6)
	γ	0.90 (9, s)						
$Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$[d]	α	3.10 (2, s)	α	5.95 (2, sept; 6.0)		NR		
	γ	0.98 (9, s)	β	1.53 (6, d; 6.0)				
				1.52 (6, d; 6.0)				
$Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$	α	3.11 (2, s)	α	5.25 (2, d; 10)	α	71.47 (1)	α	88.76 (2)
	γ	1.00 (9, s)		5.10 (2, d; 10)	β	33.11 (1)	β	34.74 (2)
			γ	1.07 (18, s)	γ	33.75 (3)	γ	26.72 (6)
$Mo_2(CH_2CMe_3)_2(OEt)_4$[d]	α	3.08 (2, s)	α	5.51 (2, dq; 10.4, 6.8)		NR		
	γ	0.96 (9, s)		5.33 (2, dq; 10.4, 6.8)				
			β	1.49 (6, t; 6.8)				
$Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Bu)_4$	α	2.47 (2, s)	β	1.50 (18, s)		NR		
	γ	0.25 (9, s)						
$Mo_2(CH_2SiMe_3)_2(O\text{-}i\text{-}Pr)_4$	α	2.11 (2, s)	α	5.78 (2, sept; 6.0)		NR		
	γ	0.11 (9, s)	β	1.47 (6, d; 6.0)				
				1.44 (6, d; 6.0)				
$Mo_2(CH_2SiMe_3)_2(OCH_2CMe_3)_4$	α	2.10 (2, s)	α	5.09 (2, d; 10)	α	42.21 (1)	α	89.02 (2)
	γ	0.09 (9, s)		5.00 (2, d; 10)	γ	1.82 (3)	β	34.66 (2)
			γ	1.04 (18, s)			γ	26.67 (6)
$Mo_2(CH_2SiMe_3)_2(OEt)_4$[d]	α	2.09 (2, s)	α	5.44 (2, dq; 10.4, 6.8)		NR		
	β	0.09 (9, s)		5.27 (2, dq; 10.4, 6.8)				
			β	1.47 (6, t; 6.8)				
$Mo_2Et(O\text{-}t\text{-}Bu)_5$[d]	α	2.98 (2, q; 7.7)	β	1.59 (18, s)	α	47.58 (1)	α	79.53 (2)
	β	1.78 (3, t; 7.7)	β'	1.50 (27, s)	β	16.24 (1)	β	33.27 (6)
							α'	79.01 (3)
							β'	33.21 (9)
$Mo_2(i\text{-}Pr)(O\text{-}t\text{-}Bu)_5$	α	3.52 (1, sept; 7.6)	β	1.52 (18, s)	α	60.34 (1)	α	79.82 (2)
	β	1.85 (6, d; 7.6)	β'	1.45 (27, s)	β	26.60 (2)	β	33.22 (6)
							α'	78.75 (3)
							β'	33.27 (9)
$Mo_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$	α	2.95 (2, t; 7.6)	β	1.50 (18, s)	α	57.77 (1)	α	79.58 (2)
	β	1.88 (2, sext; 7.6)	β'	1.47 (27, s)	β	24.99 (1)	β	33.27 (6)
	γ	1.68 (3, q; 7.6)			γ	19.52 (1)	α'	78.95 (3)
							β'	33.27 (9)
$Mo_2(t\text{-}Bu)(O\text{-}t\text{-}Bu)_5$	β	1.86 (1, s)	β	1.55 (2, s)	α	69.86 (1)	α	79.99 (2)
			β	1.45 (3, s)	β	34.99 (3)	β	33.31 (6)
							α'	78.76 (3)
							β'	33.57 (9)
$Mo_2(i\text{-}Bu)(O\text{-}t\text{-}Bu)_5$	α	2.98 (2, d; 7.6)	β	1.54 (18, s)	α	66.10 (1)	α	79.99 (2)
	β	2.18 (1, t-sept; 7.6)	β'	1.48 (27, s)	β	30.35 (1)	β	33.31 (6)
	γ	1.16 (6, d; 7.6)			γ	27.42 (2)	α'	78.76 (3)
							β'	33.57 (9)

$Mo_2(s\text{-}Bu)(O\text{-}t\text{-}Bu)_5$	α	3.54 (1, tq; 7.6)	β	1.56 (9, s)	α	67.92 (1)	α	79.92 (2)
	β	2.56 (2, dt; 7.6)		1.55 (9, s)	β	32.19 (1)	β	33.26 (6)
	γ	1.63 (3, t; 7.6)	β	1.45 (27, s)	γ	14.58 (1)	α′	78.66 (3)
	β′	1.86 (3, d; 7.6)			β′	21.91 (1)	β′	33.26 (9)
$Mo_2(n\text{-}Bu)(O\text{-}t\text{-}Bu)_5$	α	3.03 (2, t; 7.6)	β	1.51 (18, s)		NR		
	β	1.82 (2, tt; 7.6)	β	1.50 (27, s)				
	γ	1.2 (2, tq; 7.6)						
	δ	1.02 (3, t; 7.6)						
$Mo_2Et(O\text{-}i\text{-}Pr)_5$	α	2.85 (2, q; 7.6)	α	5.30 (5, br)		NR		
	β	1.52 (3, t; 7.6)	β	1.39 (30, br d)				
$Mo_2(i\text{-}Pr)(O\text{-}i\text{-}Pr)_5{}^d$	α	3.44 (1, sept; 7.6)	α	5.93 (2, sept; 6.0)		NR		
	β	1.71 (6, d; 7.6)	β	1.55 (6, d; 6.0)				
				1.54 (6, d; 6.0)				
			α′	5.29 (3, sept; 6.0)				
			β′	1.39 (18, d; 6.0)				
$Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5{}^d$	α	2.83 (2, t; 7.6)	α	6.11 (2, sept; 6.0)		NR		
	β	1.74 (2, sext; 7.6)	β	1.65 (6, d; 6.0)				
	γ	0.95 (3, t; 7.6)		1.56 (6, d; 6.0)				
			α′	5.45 (3, sept; 6.0)				
			β′	1.40 (18, d; 6.0)				
$Mo_2(t\text{-}Bu)(O\text{-}i\text{-}Pr)_5$	β	1.79 (9, s)	α	5.90 (2, sept; 6.0)		NR		
			β	1.60 (6, d; 6.0)				
				1.49 (6, d; 6.0)				
			α′	5.03 (3, sept; 6.0)				
			β	1.33 (18, d; 6.0)				
$Mo_2(i\text{-}Bu)(O\text{-}i\text{-}Pr)_5$	α	2.95 (2, d; 7.6)	α	6.17 (2, sept; 6.0)		NR		
	β	2.16 (1, t-sept; 7.6)	β	1.75 (6, d; 6.0)				
	γ	1.20 (6, d; 7.6)		1.57 (6, d; 6.0)				
			α′	5.44 (3, sept; 6.0)				
			β′	1.39 (18, d; 6.0)				
$Mo_2(t\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$	β	1.84 (9, s)	α	5.25 (2, sept; 6.0)		NR		
			β	1.42 (6, d; 6.0)				
				1.38 (6, d; 6.0)				
$Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4{}^d$	α	4.10 (2, s)	α	5.48 (2, sept; 6.0)	α	56.12	α	79.08 (2)
	o	7.00 (2, d; 6.8)	β	1.37 (6, d; 6.0)	β	143.52	β	26.85 (6)
	m	6.98 (2, tt; 6.8)		1.34 (6, d; 6.0)	o	128.82		26.48 (6)
	p	6.79 (1, t; 6.8)			m	128.57		
					p	124.16		
$Mo_2(CH_2Ph\text{-}p\text{-}Me)_2(O\text{-}i\text{-}Pr)_4{}^d$	α	4.14 (2, s)	α	5.53 (2, sept; 6.0)		NR		
	o	6.96 (2, d; 7.9)	β	1.40 (6, d; 6.0)				
	m	6.81 (2, d; 7.9)		1.38 (6, d; 6.0)				
	p-Me	2.05 (3, s)						
$Mo_2(CH_2CMe_3)_2(NMe_2)_2(O\text{-}t\text{-}Bu)_2$	α	3.23 (1, d; 13.5)	β	1.63 (9, s)		NR		
		2.75 (1, d; 13.5)						
	γ	1.02 (9, s)	NMe_2	proximal 4.09 (3, s)				
				distal 2.56 (3, s)				
$Mo_2(CH_2CMe_3)_2(NMe_2)_2(O\text{-}i\text{-}Pr)_2$	α	2.95 (1, d; 13.5)	α	5.89 (1, sept; 6.0)		NR		
		2.82 (1, d; 13.5)	β	1.68 (3, d; 6.0)				
	γ	1.03 (9, s)		1.50 (3, d; 6.0)				
			NMe_2	proximal 4.05 (3, s)				

				distal 2.59 (3, s)	
$Mo_2(CH_2CMe_3)_2(NMe_2)_2(OCH_2CMe_3)_2$	α	3.09 (1, d; 13.5) 2.52 (1, d; 13.5)	α	5.17 (1, d; 10) 4.83 (1, d; 10)	NR
	γ	1.06 (9, s)	γ	1.13 (9, s)	
			NMe_2	proximal 4.03 (3, s) distal 2.61 (3, s)	

[a] All chemical shifts are reported in δ (ppm) relative to Me_4Si. The assignments α, β, and γ are relative to the metal for the alkyl and relative to oxygen for the alkoxides. s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, and sept = sept. [b] Spectra were recorded at room temperature in toluene-d_8 at 220 MHz unless otherwise noted. [c] Spectra were recorded at room temperature in benzene-d_6 at 90 MHz. [d] Recorded at 360 MHz. [e] NR = not recorded.

Table III. Thermochemical Data Pertaining to Alcoholyses of Molybdenum-Alkyl and -Dimethylamido Ligands

bond	D, kcal mol^{-1}	ref	bond	D, kcal mol^{-1}	ref
H_3C–H	104.0	*a*	H_3C–Mo	38.0	*d*
Me_2N–H	93.0	*b*	Me_2N–Mo	68.8	*b*
i-PrO–H	104.7	*c*	*i*-PrO–Mo	93.0	*e*

[a] Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125. [b] Connor, J. A.; Pilcher, G.; Skinner, H. A.; Chisholm, M. H.; Cotton, F. A. *J. Am. Chem. Soc.* **1978**, *100*, 7738. [c] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. [d] This value is ΔH_d(W–C) in $W(CH_3)_6$ and is taken to be a reasonable estimate for Mo–CH_3 in the present systems because of two well-recognized opposing factors: (i) bond strengths for Mo–C are weaker than W–C in related pairs of compounds and (ii) metal–ligand bond strengths for metals in lower oxidation states are greater than those in compounds involving the same metal atoms in higher oxidation states. [e] Cavell, K. J.; Conner, J. A.; Pilcher, G.; Ribeiro da Silva, M. A.; Ribeiro da Silva, M. D. M. C.; Skinner, H. A.; Yirmani, Y.; Zafarani-Moattar, M. T. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1585.

wherein reductive elimination and oxidative addition to the dinuclear center must be invoked. To our knowledge such a reaction sequence is not known in mononuclear chemistry. Addition of alcohols to alkyl–metal complexes commonly leads to alkoxide group formation with liberation of alkane by protolysis of the metal–carbon bond, though certain alkyl–metal complexes are inert to this type of reaction at ambient temperatures. The detailed nature of the β-hydrogen atom transfer reaction and the generation of the new alkyl ligand remains unknown. However, it is evident that the presence of the dinuclear center presents certain options which are not commonly encountered in mononuclear chemistry. For example, in mononuclear organometallic chemistry β-hydrogen atom transfer normally involves initial ligand (Lewis base) dissociation, thereby creating a coordinatively unsaturated center capable of accommodating the incipient hydride and olefin ligands in the four-center transition state.[18] In the present work we see that Lewis base association promotes β-hydrogen abstraction and alkyl isomerization. While many mechanistic points remain to be elucidated, the new compounds afford us the opportunity to study the chemistry of the Mo–C(alkyl) bonds supported by alkoxide ligands at a dinuclear center.

Further studies are in progress.

Experimental Section

General Procedures. Throughout the syntheses, care was taken to maintain dry and oxygen-free atmospheres (nitrogen) and solvents. Standard Schlenk procedures were coupled with the use of Vacuum Atmospheres Co. Dri-Lab Systems.

^1H and ^2H NMR spectra were recorded by using either a Varian HR-220 or a Nicolet NT-360 spectrometer. Infrared spectra were obtained from Nujol mulls between CsI plates with the use of a Perkin-Elmer 283 spectrophotometer, and data were calibrated with polystyrene. Mass spectra were obtained, courtesy of Mr. Peter Cook, by the method of direct insertion using an AEl MS902 spectrometer. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories, West Germany, using drybox sampling techniques.

Chemicals. $Mo_2R_2(NMe_2)_4$ compounds were made by the published procedure involving the reaction of $Mo_2Cl_2(NMe_2)_4$ with alkyllithium reagents.[14] The alkyllithium reagents were synthesized according to published procedures. CD_3CH_2Li was synthesized from CD_3CH_2Br which was purchased from Merck, Sharp and Dohme. $(CD_3)_2CHLi$ was synthesized from $(CD_3)_2CHCl$ prepared by route of $LiAlH_4$ reduction of acetone-d_6.

The alcohols were commercially available. Ethanol and 2-propanol were distilled over calcium hydride and sodium, respectively. Neopentyl alcohol was dissolved in toluene and stored over molecular sieves. *tert*-Butyl alcohol was distilled from benzene as an azeotrope and stored over molecular sieves.

Preparation of $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$. $Mo_2Me_2(NMe_2)_4$ (2.51 g, 6.3 mmol) was dissolved in 20 mL of hexane at 0 °C to give a bright yellow solution. *tert*-Butyl alcohol (benzene azeotrope, 6 mL, 25 mmol, 4 equiv) was added via microsyringe. The solution immediately turned bright red, and all volatile materials were removed in vacuo at 0 °C. The solid residue (dark red or purple) was then redissolved in hexane (10 mL), and pyridine (1 mL, 12 mmol) was added to give a dark brown solution. Brown crystals formed upon cooling to −20 °C.

Analytical data and ^1H NMR data are given in Tables I and II, respectively.

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[18] Often ligand loss is demanded by the 18-electron rule as in the reactions $CpFe(CO)(PPh_3)(alkyl) \rightarrow CpFe(CO)(PPh_3)(H)$ + alkene, see: Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789. However, even in the chemistry of square-planar platinum(II) and gold(III), which are coordinatively unsaturated 16-valence-electron metal complexes, the dissociation of a Lewis base is the initial step prior to β-hydrogen atom abstraction, see, for example: Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258. Kochi, J. K.; Tamaki, A. *J. Chem. Soc., Chem. Commun.* **1973**, 423.

Infrared data (Nujol mull, CsI plates): 425 (w), 475 (w), 570 (w), 692 (m), 720 (w), 752 (m), 765 (m), 780 (m), 940 (br), 1040 (m), 1070 (s), 1170 (s), 1230 (m), 1260 (w), 1350 (s), 1360 (s), 1600 (m) cm^{-1}. A parent ion at *m/e* 514 in the mass spectrum corresponds to $Mo_2Me_2(O\text{-}t\text{-}Bu)_4^+$ (based on ^{96}Mo).

Preparation of $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$. The above procedure was followed. Crystalline $Mo_2Me_2(O\text{-}t\text{-}Bu)_4py_2$ was pumped dry (10^{-3} torr) at room temperature for 2 h. The brown crystals fractured and turned royal purple. $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$ sublimed with some decomposition, forming both $Mo_2Me_2(O\text{-}t\text{-}Bu)_5$ and $Mo_2(O\text{-}t\text{-}Bu)_6$. Analytical data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 265 (w, br), 295 (w), 355 (w), 470 (w), 510 (w), 555 (w), 620 (w), 720 (w), 770 (m), 785 (m), 920 (s), 970 (s), 1020 (w), 1170 (s), 1230 (m), 1260 (w), 1360 (s) cm^{-1}. A parent ion at *m/e* 514 in the mass spectrum corresponds to $Mo_2Me_2(O\text{-}t\text{-}Bu)_4^+$ (based on ^{96}Mo).

Preparation of $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$. *i*-PrOH (0.30 mL, 4.0 mmol) was added via microsyringe to a solution of $Mo_2(CH_2CMe_3)_2(NMe_2)_4$ (0.503 g, 0.985 mmol) in hexane (20 mL). The solution was stripped to dryness after 4 h and the yellow solid sublimed at 70 °C to yield $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$ (0.39 g, 70%). Analytical data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 295 (w), 455 (w, br), 540 (w), 610 (m), 630 (m), 720 (w), 733 (2), 850 (s), 973 (vs), 980 (s), 1120 (s), 1160 (m), 1225 (m), 1322 (s), 1366 (s) cm^{-1}. A parent ion at *m/e* 656 in the mass spectrum corresponds to $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4^+$ (based on ^{96}Mo).

Preparation of $Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$. Similar procedure as for $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$ was used but with Me_3CCH_2OH in place of *i*-PrOH. Reaction time equaled 4 h. The residue was sublimed (120–130 °C, 10^{-3} torr) to yield yellow-orange crystalline $Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$ (80%). Analytical data and ^1H NMR data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 316 (w), 373 (w), 400 (w), 460 (w, br), 540 (w), 690 (m), 718 (w), 730 (w), 748 (w), 796 (w, br), 900 (w), 930 (w), 1000 (m), 1021 (s), 1058 (vs, br), 1215 (w), 1224 (m), 1254 (w), 1360 (s), 1390 (s) cm^{-1}.

Preparation of $Mo_2(CH_2CMe_3)_2(OEt)_4$. Similar procedure as for $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$ was used, with EtOH. Reaction time equaled 2 h. The residue liquified around 50 °C and sublimed (70–80 °C, 10^{-3} torr) to yield small yellow crystals (20%), while decomposing to give a black residue. Analytical data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 450 (w, br), 600 (m), 715 (m), 798 (w, br), 920 (s), 1052 (vs), 1090 (s), 1140 (w), 1224 (w), 1268 (w), 1300 (w, br), 1345 (m), 1360 (s) cm^{-1}.

Preparation of $Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Bu)_4$. *tert*-Butyl alcohol (2.4 mL, 10 mmol) in benzene was added by syringe to a solution of $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ (0.55 g, 1.0 mmol) in hexane (30 mL). After 2 days of stirring, the solvent was removed in vacuo and the residue was purified by sublimation (70–80 °C, 10^{-3} torr) to yield deep red crystalline $Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Bu)_4$ (0.85 g, 80%). Analytical data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 470 (w, br), 490 (w), 560 (w), 606 (m), 675 (w), 694 (m), 736 (w), 770 (s), 780 (m), 825 (m), 842 (s), 880 (m), 900 (m), 920 (s), 932 (m), 964 (vs), 1020 (w), 1162 (s, br), 1230 (m), 1239 (s), 1250 (m), 1365 (s) cm^{-1}.

A parent ion at *m/e* 666 in the mass spectrum corresponds to $Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Bu)_4$ (based on ^{96}Mo).

Preparation of $Mo_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$. $Mo_2(CH_2CMe_3)_2(NMe_2)_4$ (0.06 mmol) was dissolved in toluene-d_8 in an NMR tube. *t*-BuOH (0.25 mmol) in benzene was added. After 3 days, the solvent was removed in vacuo. The residue was redissolved in toluene-d_8, and its ^1H NMR spectrum was taken, which is reported in Table II.

Preparation of $Mo_2(CH_2SiMe_3)_2(OR)_4$ (R = *i*-Pr, CH_2CMe_3, Et). Similar procedure as above was used with $Mo_2(CH_2SiMe_3)_2(NMe_2)_4$ and alcohols ROH. Reaction times: *i*-PrOH, 4 h; Me_3CCH_2OH, 4 h; EtOH, 3 h. ^1H NMR data are reported in Table II.

Preparation of $Mo_2(CH_2CMe_3)_2(NMe_2)_2(OR')_2$ (R = *i*-Pr, CH_2CMe_3, *t*-Bu). $Mo_2(CH_2CMe_3)_2(NMe_2)_4$ (0.635 g, 1.2 mmol) was dissolved in hexane (20 mL). A solution of *i*-PrOH (180 μL, 2.4 mmol) in hexane (10 mL) was added slowly via a dropping funnel. After 1 h, the solvent was removed in vacuo, and a ^1H NMR spectrum was taken, which indicated a mixture of ca. 85% $Mo_2(CH_2CMe_3)_2(NMe_2)_2(O\text{-}i\text{-}Pr)_2$, 10% $Mo_2(CH_2CMe_3)_2(NMe_2)_4$, and 5% $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$. The mixture was sublimed (70–80 °C, 10^{-3} torr) to yield a yellow solid whose ^1H NMR spectrum suggested the same approximate mixture.

When $Mo_2(CH_2CMe_3)_2(NMe_2)_4$ was reacted with *t*-BuOH or Me_3CCH_2OH, $Mo_2(CH_2CMe_3)_2(NMe_2)_2(O\text{-}t\text{-}Bu)_2$ and $Mo_2(CH_2CMe_3)_2(NMe_2)_2(OCH_2CMe_3)_2$ can be identified by ^1H NMR spectroscopy. ^1H NMR data are reported in Table II.

Preparation of $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$. 1,2-$Mo_2(CH_2Ph)_2(NMe_2)_4$ (0.45 g, 0.86 mmol) was dissolved in hexane (20 mL) to give a bright yellow solution. *i*-PrOH (0.30 mL, 3.9 mmol) was added while stirring. The solution darkened and was stirred for 1 h. The solution was then stripped to dryness, and the orange residue was redissolved in ca. 3 mL of hexane. Cooling to −20 °C gave orange crystals in round clumps. Upon storage, the surface of the crystals may darken slightly. Analytical data and NMR data are reported in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 454 (w), 617 (w), 691 (m), 720 (m), 747 (m), 832 (w), 850 (m), 944 (m, br), 982 (s, br), 1028 (w), 1108 (s), 1161 (m), 1198 (w), 1319 (m), 1365 (s), 1485 (m), 1596 (m) cm^{-1}.

Preparation of $Mo_2(CH_2Ph\text{-}p\text{-}Me)_2(O\text{-}i\text{-}Pr)_4$. Similar procedure as for $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ but starting with $Mo_2(CH_2Ph\text{-}p\text{-}Me)_2(NMe_2)_4$ was used. ^1H NMR data are reported in Table I.

Infrared data (Nujol mull between CsI plates): 452 (w), 460 (w), 487 (w), 530 (w), 614 (m), 629 (m), 646 (w), 718 (m), 803 (s), 848 (m), 982 (vs), 1020 (w), 1108 (s), 1160 (m), 1198 (w), 1318 (m), 1360 (s), 1500 (m), 1606 (w) cm^{-1}.

Preparation of $Mo_2Et(O\text{-}t\text{-}Bu)_5$. $Mo_2(Et)_2(NMe_2)_4$ (0.192 g, 0.45 mmol) was dissolved in hexane (10 mL) to give a bright yellow solution. Upon addition of *t*-BuOH (2.0 mL, 3.6 mmol) in benzene, the solution began to darken. After 15 min, the solution was bright red. The solvent was removed in vacuo after 30 min to give a bright red solid which sublimes (60–70 °C, 10^{-3} torr) to yield $Mo_2Et(O\text{-}t\text{-}Bu)_5$ (0.19 g, 72%). Analytical data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 470 (w, br), 560 (w, br), 605 (w), 720 (w), 772 (m), 788 (m), 820 (w), 900 (m), 925 (s), 980 (vs), 1024 (m), 1172 (s), 1232 (m), 1260 (w), 1360 (s) cm^{-1}.

A parent ion at *m/e* 570 in the mass spectrum corresponds to $Mo_2Et(O\text{-}t\text{-}Bu)_5^+$ (based on ^{96}Mo).

Preparation of $Mo_2(C_3H_7)(O\text{-}t\text{-}Bu)_5$. Similar procedure as above starting with either $Mo_2(i\text{-}Pr)_2(NMe_2)_4$ or $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ was used. Reaction time equaled 90 min. ^1H NMR spectroscopy shows a mixture of ca. 95% $Mo_2(i\text{-}Pr)(O\text{-}t\text{-}Bu)_5$ and 5% $Mo_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$. The ratio of *i*-Pr/*n*-Pr did not change upon sublimation or after 1 month in hexane or toluene. Analytical data and ^1H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 335 (m, br), 468 (w), 552 (w), 574 (m, br), 718 (w), 938 (vs), 950 (s), 1040 (m), 1118 (w), 1142 (s), 1240 (s), 1310 (w), 1360 (m), 1413 (m), 1420 (m) cm^{-1}.

Preparation of $Mo_2(C_4H_9)(O\text{-}t\text{-}Bu)_5$. Similar procedure as for $Mo_2(Et)(O\text{-}t\text{-}Bu)_5$ but starting with $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ was used. Reaction time equaled 6 h. ^1H NMR data show a mixture of $Mo_2(t\text{-}Bu)(O\text{-}t\text{-}Bu)_5$ and <5% $Mo_2(i\text{-}Bu)(O\text{-}t\text{-}Bu)_5$. ^1H NMR data for $Mo_2(t\text{-}Bu)(O\text{-}t\text{-}Bu)_5$ are reported in Table II.

Preparation of $Mo_2(C_3H_7)(O\text{-}i\text{-}Pr)_5$. *i*-PrOH (630 mL, 8.3 mmol) was added to a solution of $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ (0.74 g, 1.6 mmol) in hexane (20 mL). The solution darkened to yellow-brown, and the solvent was removed in vacuo to yield a yellow solid which was indicated by ^1H NMR spectroscopy to be a mixture of ca. 70% $Mo_2(i\text{-}Pr)(O\text{-}i\text{-}Pr)_5$ and 30% $Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$. When pyridine or PMe_3 was added to the mixture in toluene-d_8 or hexane, rapid isomerization to yield 100% $Mo_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$ occurred. Attempted sublimation (60–70 °C, 10^{-3} torr) resulted in decomposition to an unidentified black solid. ^1H NMR data are reported in Table II.

Preparation of $Mo_2Et(O\text{-}i\text{-}Pr)_5$. *i*-PrOH (5.1 equiv) was added to a solution of $Mo_2Et_2(NMe_2)_4$ in toluene-d_8 in an NMR tube. After 5 min, the solvent was removed in vacuo. The residue was redissolved in toluene-d_8, and the ^1H NMR spectrum was run, which indicated the formation of $Mo_2Et(O\text{-}i\text{-}Pr)_5$ and some $Mo_2(O\text{-}i\text{-}Pr)_6$. ^1H NMR data are reported in Table II.

Reaction of $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ with i-PrOH. i-PrOH (5.1 equiv) was added to a solution of $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ in toluene-d_8 in an NMR tube. Immediately after addition of i-PrOH, resonances due to free $HNMe_2$ and isobutane were observed in the ^1H NMR spectrum. In subsequent spectra, new resonances appeared which were assigned to free isobutene and coordinated $HNMe_2$. The major product was identified as $Mo_2(O\text{-}i\text{-}Pr)_4(HNMe_2)_4$. Addition of ethylene to the reaction mixture led to the immediate formation of $Mo_2Et(O\text{-}i\text{-}Pr)_5$.

Preparation of $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$. $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ (1.5 g, 3.1 mmol) was dissolved in hexane (5 mL). i-PrOH (20 mL) was added while stirring which caused the solution to change from yellow to deep blue-purple in ca. 10 min. After 30 min, the solution was evaporated to dryness under a dynamic vacuum to yield a dark purple solid which was redissolved in ca. 10 mL i-PrOH and 10 mL of hexane. A large mass of dark purple crystals of $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$ formed upon cooling to −20 °C. This compound must be stored at −20 °C to prevent decomposition. The elemental analyses were very poor presumably due to decomposition in transit.

Infrared data (hexane solution vs. hexane, KBr solution cells): 300 (m), 450 (m), 570 (m), 585 (m), 606 (m), 833 (s), 900 (m), 950 (s), 980 (s), 1020 (w), 1110 (s), 1154 (m), 1358 (w), 1420 (s), 3280 (m, br) cm^{-1}.

UV–vis data (hexane solutions, extinction coefficient ($M^{-1}\ cm^{-1}$) in parentheses: 558 (600), 267 nm (4800), concentration = 2.99×10^{-3} M.

The ^1H NMR spectrum revealed only one type of O-i-Pr ligand at δ 4.51 (septet, $J_{HH} = 5.8$ Hz) and 1.38 (d, $J_{HH} = 5.8$ Hz) and the hydroxyl proton at δ 13.10.

Preparation of $Mo_2(OCH_2CMe_3)_4(HNMe_2)_4$. $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ (1.0 g, 2.1 mmol) was dissolved in hexane (20 mL) in a 100-mL flask equipped with a side arm and rubber septum cap. Upon addition of Me_3CCH_2OH (5.5 mL, 8.3 mmol), the solution changed from yellow to deep red to red-purple. After 45 min, the solution was evaporated to dryness under a dynamic vacuum to give a dark purple solid which was recrystallized from hexane (3 mL) to yield $Mo_2(OCH_2CMe_3)_4(HNMe_2)_4$ (ca. 50%). Reducing the volume of the mother liquor gave additional material which was contaminated with $Mo_2(i\text{-}Bu)(OCH_2CMe_3)_5$. Anal. Calcd for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4$: C, 46.66; H, 10.07; N, 0.00. Found: C, 46.46; H, 9.90; N, <0.05.

^1H NMR data: $\delta(OCH_2)$ 3.51 (s), $\delta(OCH_2CMe_3)$ 1.05 (s), $\delta(HNMe_2)$ 7.08 (septet, J = 5.8 Hz), $\delta(HNMe_2)$ 2.64 (d, J = 5.8 Hz).

Infrared data (hexane solution vs. hexane, KBr solution cell): 380 (m), 400 (m), 7472 (m), 640 (s), 660 (s), 758 (m), 910 (s), 932 (m), 1020 (vs), 1080 (vs), 1128 (m), 1220 (m), 1260 (w), 1360 (s), 1600 (m br), 2680 (m), 3209 (m, br) cm^{-1}.

UV–vis data (hexane solutions, extinction coefficient ($M^{-1}\ cm^{-1}$) in parentheses): 585 (1200), 280 nm (7400), concentration = 2.8×10^{-3} M; 220 nm (76 000, shoulder), concentration = 2.8×10^{-4} M.

Labeling Studies. Reaction of $Mo_2(CH(CD_3)_2)_2(NMe_2)_4$ with t-BuOH. Addition of t-BuOH (64 μL, 0.27 mmol) in benzene to a solution of $Mo_2(CH(CD_3)_2)_2(NMe_2)_4$ (0.025 g, 0.054 mmol) in toluene in an NMR tube gave a bright red solution in 3 h. Resonances in the ^2H NMR spectrum (NT 360) at 1.36 (d) and 0.932 ppm (d) (relative intensity = 1:6) were assigned to CD_3CHDCD_3. Resonances in the region 1.75 to 1.95 ppm were assigned to $Mo\text{–}C_3D_5H_2$.

Reaction of $Mo_2(CH_2CD_3)_2(NMe_2)_4$ with t-BuOH. Upon addition of t-BuOH (5.1 equiv) in benzene to a solution of $Mo_2(CH_2CD_3)_2(NMe_2)_4$ in toluene, CD_3CH_2D (identified by ^2H NMR) was formed. After 6 weeks in a sealed tube, ^2H NMR spectroscopy (NT 360) indicated that all three possible isomers of the product $Mo_2(C_2H_3D_2)(O\text{-}t\text{-}Bu)_5$ were present (CD_2CH_3, $CDHCDH_2$, and CH_2CD_2H).

Reaction of $Mo_2Et_2(NMe_2)_4$ with t-BuOD. A. t-BuOD (1.2 mL, 5.0 mmol) in benzene was added to a solution of $Mo_2Et_2(NMe_2)_4$ (0.270 g, 0.673 mmol) in hexane (20 mL). The solution turned brown initially. After 2 h, the red solution was stripped to dryness. The ^2H NMR spectrum (NT 360) exhibited one peak at 1.8 ppm, which was assigned to $Mo_2(CH_2CH_2D)(O\text{-}t\text{-}Bu)_5$.

B. t-BuOD (5.1 equiv) in benzene was added to a solution of $Mo_2Et_2(NMe_2)_4$ in toluene (0.5 mL) in an NMR tube. After 1 day, the ^2H NMR indicated $Mo_2Et(O\text{-}t\text{-}Bu)_5$ labeled with D in the β-position. After 5 weeks, the solution was stripped and fresh toluene was added. The ^2H NMR spectrum exhibited peaks at 3.08 and 1.84 ppm in a ca. 2:3 ratio, which were assigned to the α- and β-positions, respectively.

Alkene Exchange Reactions. Reaction of $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ with t-BuOH and C_2H_4. t-BuOH (0.35 mmol) in benzene was syringed into a solution of $Mo_2(n\text{-}Pr)_2(NMe_2)_4$ (0.068 mmol) in toluene-d_8 in an NMR tube, which was frozen immediately to −196 °C. Ethylene (0.11 mmol) was added by vacuum transfer from a calibrated gas line. Upon warming, the solution turned deep red. The ^1H NMR spectrum (NT 360) revealed the presence of $Mo_2Et(O\text{-}t\text{-}Bu)_5$ as the major product. When ethylene was added to a pure sample of $Mo_2(i\text{-}Pr)(O\text{-}t\text{-}Bu)_5$, no $Mo_2Et(O\text{-}t\text{-}Bu)_5$ was observed after 2 weeks.

Reaction of $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ with t-BuOH and C_2H_4. t-BuOH (0.27 mmol) in benzene was syringed into a solution of $Mo_2(i\text{-}Bu)_2(NMe_2)_4$ (0.052 mmol) in toluene-d_8 in a NMR tube, which was frozen immediately to −196 °C. Ethylene (0.13 mmol) was added by vacuum transfer from a calibrated gas line. After 1 day at room temperature, the ^1H NMR spectrum (NT 360) revealed the presence of $Mo_2Et(O\text{-}t\text{-}Bu)_5$ as the only product.

Reaction of $Mo_2Et_2(NMe_2)_4$ with t-BuOH in Hexene. $Mo_2Et_2(NMe_2)_4$ (0.134 g, 0.314 mmol) was dissolved in 1-hexene (20 mL). t-BuOH (0.40 mL, 1.7 mmol) in benzene was added via syringe. After 1 h, the solvent was removed in vacuo to yield a bright red oil. ^1H NMR spectroscopy revealed the presence of ca. 15% $Mo_2Et(O\text{-}t\text{-}Bu)_5$ and 85% $Mo_2(hexyl)(O\text{-}t\text{-}Bu)_5$.

Reactions of $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$. Reaction of $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$ with t-BuOH. t-BuOH/benzene (50 μL) was syringed into a NMR tube containing a solution of $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$ in toluene-d_8. The NMR tube was sealed under vacuum. The NMR spectrum was recorded at various time intervals. Fifteen minutes after the t-BuOH was added, a sharp singlet at 1.95 ppm and a broad peak at 1.50 ppm were observed along with a broad peak around 1.4 ppm. The singlet at 1.95 ppm is assigned to the molybdenum methyl of $Mo_2Me(O\text{-}t\text{-}Bu)_5$ while the butoxy methyl resonance is at 1.50 ppm. These two peaks continued to grow in but started to lose intensity as a sharp singlet at 1.53 ppm due to $Mo_2(O\text{-}t\text{-}Bu)_6$ gains intensity. The final spectrum showed a resonance for $Mo_2(O\text{-}t\text{-}Bu)_6$ at 1.53 ppm and t-BuOH at 1.04 ppm ($-CH_3$) and 0.68 ppm ($-OH$) along with methane at 0.18 ppm.

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Registry No. $Mo_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$, 85049-11-2; $Mo_2Me_2(O\text{-}t\text{-}Bu)_4$, 72286-49-8; $Mo_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$, 101859-82-9; $Mo_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$, 101859-81-8; $Mo_2(CH_2CMe_3)_2(OET)_4$, 85049-16-7; $Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Bu)_4$, 101859-80-7; $Mo_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$, 101859-79-4; $Mo_2(CH_2SiMe_3)_2(O\text{-}t\text{-}Pr)_4$, 101859-78-3; $Mo_2(CH_2SiMe_3)_2(OCH_2CMe_3)_4$, 101859-77-2; $Mo_2(CH_2SiMe_3)_2(OEt)_4$, 85049-17-8; $Mo_2(CH_2CMe_3)_2(NMe_2)_2(O\text{-}i\text{-}Pr)_2$, 85049-18-9; $Mo_2(CH_2CMe_3)_2(NMe_2)_2(OCH_2CMe_3)_2$, 101859-76-1; $Mo_2(CH_2CMe_3)_2(NMe_2)_2(O\text{-}t\text{-}Bu)_2$, 101859-75-0; $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$, 91443-57-1; $Mo_2(CH_2Ph\text{-}p\text{-}Me)_2(O\text{-}i\text{-}Pr)_4$, 101859-74-9; $Mo_2Et(O\text{-}t\text{-}Bu)_5$, 68046-31-1; $Mo_2(i\text{-}Pr)(O\text{-}t\text{-}Bu)_5$, 85049-23-6; $Mo_2(t\text{-}Bu)(O\text{-}t\text{-}Bu)_5$, 88589-07-5; $Mo_2(i\text{-}Pr)(O\text{-}i\text{-}Pr)_5$, 85066-77-9; $Mo_2Et(O\text{-}i\text{-}Pr)_5$, 85049-20-3; $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$, 88589-06-4; $Mo_2(O\text{-}i\text{-}Pr)_4(HNMe_2)_4$, 101859-83-0; $Mo_2(OCH_2CMe_3)_4(HNMe_2)_4$, 88589-05-3; $Mo_2Me_2(NMe_2)_4$, 67030-82-4; t-BuOH, 75-65-0; i-PrOH, 67-63-0; $Mo_2(CH_2CMe_2(NMe_2)_4$, 72286-61-4; Me_3CCH_2OH, 75-84-3; EtOH, 64-17-5; $Mo_2(CH_2SiMe_3(NMe_2)_4$, 72286-62-5; $Mo_2(CH_2Ph)(NMe_2)_4$, 82555-51-9; $Mo_2(CH_2Ph\text{-}p\text{-}Me)_2(NMe_2)_4$, 84417-29-8; $Mo_2(Et)_2(NMe_2)_4$, 68046-30-0; $Mo_2(i\text{-}Pr)_2(NMe_2)_4$, 72286-60-3; $Mo_2(n\text{-}Pr)_2(NMe_2)_4$, 85049-12-3; $Mo_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$, 85049-21-4; $Mo_2(i\text{-}Bu)_2(NMe_2)_4$, 101859-73-8; $Mo_2(i\text{-}Bu)(O\text{-}t\text{-}Bu)_5$, 101859-72-7; $Mo_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$, 85049-22-5; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $Mo_2(CH(CD_3)_2)_2(NMe_2)_4$, 101859-71-6; $Mo_2(CH_2CD_3)_2(NMe_2)_4$, 72286-58-9; $Mo_2(O\text{-}t\text{-}Bu)_6$, 51956-21-9; $Mo_2Me(O\text{-}t\text{-}Bu)_5$, 85049-14-5; Mo, 7439-98-7.