Isolation of a Homoleptic Non-oxo Mo(V) Alkoxide Complex: Synthesis, Structure, and Electronic Properties of Penta-tert-Butoxymolybdenum

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ABSTRACT: Treatment of [MoCl₄(THF)₂] with MOtBu (M = Na, Li) does not result in simple metathetic ligand exchange but entails disproportionation with formation of the well-known dinuclear complex [(tBuO)₃Mo≡Mo-(OtBu)₃] and a new paramagnetic compound, [Mo(OtBu)₅]. This particular five-coordinate species is the first monomeric, homoleptic, all-oxygen-ligated but non-oxo 4d¹ Mo(V) complex known to date; as such, it proves that the dominance of the Mo≡O group over (high-valent) molybdenum chemistry can be challenged. [Mo(OtBu)₅] was characterized in detail by a combined experimental/computational approach using X-ray diffraction; UV/vis, MCD, IR, EPR, and NMR spectroscopy; and quantum chemistry. The recorded data confirm a Jahn–Teller distortion of the structure, as befitting a d¹ species, and show that the complex undergoes Berry pseudorotation. The alkoxide ligands render the disproportionation reaction, leading the formation of [Mo(OtBu)₅] to be particularly facile, even though the parent complex [MoCl₄(THF)₂] itself was also found to be intrinsically unstable; remarkably, this substrate converts into a crystalline material, in which the newly formed Mo(III) and Mo(V) products cohabitate the same unit cell.

INTRODUCTION

Any systematic exploration of the prodigiously rich (bio-)inorganic, organometallic, organic, catalysis, and material chemistry of molybdenum has to cope with a surprising dearth of practical entry points. MoCl₅ is one of them, because this compound is available in bulk quantities at fairly low cost. In solid form, MoCl₅ is manageable, despite the rather aggressive chemical character that it draws from the combination of strong Lewis acidity, exceptional oxophilicity, and a pronounced oxidizing power; moreover, MoCl₅ is an effective chloride and/or chlorine source. Actually, only few of the commonly used solvents are inert toward MoCl₅: benzene and related aromatic hydrocarbons succumb to oligomerization and/or chlorination; etheral solvents face rapid cleavage with concomitant formation of oxo-molybdenum species such as 2 (THF, dioxanes, hexamethyldisiloxane) (Scheme 1) and/or serve as single electron reducing agents, entailing the release of Cl₂ (Me₂O, DME)]; acetonitrile also leads to reduction with formation of [MoCl₅(MeCN)₂] and chlorinated acetonitrile byproducts. These examples highlight the vigorous reactivity of MoCl₅, which can be intentionally used for synthetic purposes, such as the oxidative coupling of (electron-rich) arenes or the formation of esters by catalytic acylative ether cleavage.

Ordinary alcohols do not withstand this powerful oxidant and strong Lewis acid either: even primary alcohols R–OH are readily converted into the corresponding alkyl chlorides R–Cl.
results from a symmetry-lowering Jahn–Teller distortion of the nuclear framework, be it monomeric or oligomeric. Several independent entries into this privileged class of organometallic catalysts have been developed over the years.

Preparation and Crystallographic Characterization. For their high activity and excellent functional group tolerance, molybdenum alkylidyne complexes of the general type \([\text{R}^{3}\text{O}]_{3}\text{Mo}^{\text{II}}\) arguably define the state-of-the-art in alkylene metathesis. Several independent entries into this privileged class of organometallic catalysts have been developed over the years. One of them employs \(\text{Mo}^\text{II}[\text{t-Bu}][\text{Ar}]\) derived from \([\text{MoCl}_3(\text{THF})_2]_2\), which in turn is formed by stepwise reduction of \(\text{MoCl}_5\) with \(\text{MeCN}\) to give \([\text{MoCl}_4(\text{MeCN})_2]\), followed by ligand exchange and further reduction of the resulting complex \([\text{MoCl}_4(\text{THF})_2]\) with coarse tin. During a reinvestigation of this somewhat tedious prelude to the actual catalyst formation, we made the serendipitous discovery that treatment of \([\text{MoCl}_4(\text{THF})_2]\) with \(\text{MoBu}_4\) (\(\text{M} = \text{Na, Li}\); 3 equiv) in toluene at \(-35^\circ\text{C}\) delivers a mixture of the well-known diamagnetic dinuclear \(\text{Mo}^{\text{III}}\) complex \([\text{Bu}_2\text{O}]_2\text{Mo}^{\text{II}}\text{Mo}(\text{O}^\text{Bu})_3\) (8) and a new, green, highly air-sensitive and paramagnetic species, which was isolated by taking advantage of its high solubility in pentane; purification of the crude product by sublimation in high vacuum (23 °C, 10⁻⁷ mbar) furnished complex 1 in 30% yield (Scheme 1). It is emphasized that formation of 1 in appreciable amounts was observed only under the specified conditions: changing the stoichiometry of the reagents and/or the solvent (THF, n-pentane) resulted in lower yields (see the Supporting Information).

Compound 1 is well-soluble in n-pentane, benzene, and \(\text{CH}_3\text{Cl}_2\) but rapidly decomposes in MeCN at room temperature; it also degrades in \([\text{D}_8]\)toluene when the solution is warmed to \(\geq 50^\circ\text{C}\). Although the high sensitivity rendered elemental analysis challenging, the obtained data matched those calculated for \([\text{Mo}(\text{O}^\text{Bu})_3]\) reasonably well (Anal. Calcd for \(\text{C}_{20}\text{H}_{45}\text{O}_{5}\text{Mo}: \) C 52.05, H 9.83, Mo 20.79. Found: C 52.05, H 9.83, Mo 20.79. Found: C 52.33, H 10.01, Mo 20.58). The NMR spectroscopic fingerprint of this paramagnetic species (broad signals in \(\text{C}_2\text{D}_6\) at \(\delta_\text{H} = 7.43\) ppm and \(\delta_\text{C} = 54.9, 30.3\) ppm) is also in accord with the proposed homoleptic structure. This assignment was confirmed when single crystals suitable for X-ray diffraction were obtained from a saturated solution in n-pentane at \(-35^\circ\text{C}\).

The unit cell contains two independent molecules, which differ from each other only in conformational detail (for details, see the Supporting Information). As can be seen from Figure 1, the coordination geometry about the Mo center can be described as approximately trigonal bipyramidal, although notable deviations from the idealized structure are on record: specifically, the O2–Mo1–O2′ angle is only 169.1(5)° rather than 180°, and the angles between the O atoms forming the equatorial plane are uneven and irregular [O1–Mo1–O3, 122.7(5)°; O1–Mo1–O3′, 112.3(5)°; O3–Mo1–O3′, 124.5(5)°]. The O1–O2 distance [1.924(5) Å] is distinctly longer than the Mo–O bonds in the equatorial plane [Mo1–O1, 1.875(11) Å; Mo1–O3, 1.857(1) Å]. As will be discussed in detail below, the overall distorted structure of 1 results from a symmetry-lowering Jahn–Teller distortion of the nuclear framework, befitting this d⁶ complex (see below).

The fairly clean formation of 1 by disproportionation of \([\text{MoCl}_4(\text{THF})_2]\) in the presence of NaOtfBu at low temperature was unexpected in view of two earlier literature reports. Specifically, it had been reported that treatment of \([\text{MoCl}_4(\text{THF})_2]\) with LiOtfBu in THF/hexane entails simple ligand exchange; a workup with \(\text{CH}_3\text{Cl}_2\) followed by recrystallization from cold n-pentane supposedly gave \([\text{Mo}(\text{O}^\text{Bu})_4]\) in 25% yield. This assignment, however, had been (Scheme 1). The reaction is thought to proceed by partial ligand exchange with formation of transient Mo(V) alkoxides (e.g., 3) followed by rupture of a MoO–R bond; the resulting oxo-molybdenum complexes of type \([\text{O}==\text{MoCl}_2]\) (4) dimerize and can lead to adducts such as 5 or even complex polynuclear arrays. The ease of formation of the \([\text{Mo}==\text{O}]\) group manifest in these examples is a hallmark of (high-valent) molybdenum chemistry, this prevalent functionality dominates the field and plays a pivotal role in biological and industrial catalysis alike. Only highly fluorinated alcohols were found to subject to such degradation: trifluoroethanol, for example, on treatment with \(\text{MoCl}_4\) affords the stable heteroleptic complex 6. The fact that even the electron-poor O atom of trifluoroethoxide serves as a bridging ligand highlights the very strong bias for dimerization, which is yet another characteristic trait of the coordination chemistry of molybdenum. A closely related binuclear molybdenum(V) alkoxide 7 was prepared by salt metathesis between \(\text{MoCl}_4\) and NaOme, but complete ligand exchange could not be accomplished either. Analogous reactions with electron-rich alkoxides are unlikely in view of the ease of reduction of \(\text{MoCl}_4\) even by much milder agents; in any case, no follow-up investigation describing the preparation of analogues of 7 has been published.

It is against this backdrop that the isolation and full characterization of \([\text{Mo}(\text{O}^\text{Bu})_3]\) (1) must be seen: even oxo-free alkoxides of Mo(V) with a mixed ligand sphere, such as 6 and 7, are exceedingly rare chemical entities, but homoleptic alkoxides of Mo(V) are elusive and may perhaps even be deemed inaccessible. It is therefore perplexing that complex 1 as the first incarnation of this previously unknown class of compounds carries tertiary alkyl residues on all oxygen atoms: a priori, these ligands are particularly prone to \([\text{Mo}==\text{O}]\) formation, independent of whether the actual O–C bond cleavage proceeds in a heterolytic or homolytic manner with release of a stabilized tertiary carbocation or tertiary radical, respectively; most notably, the clean and efficient radical breakdown of tert-butoxide at a Mo(V) center has been explicitly mentioned in the literature. The fact that 1 is monomeric even in the solid state is equally striking if one considers that a d⁶ electron count is potentially conducive to metal–metal bonding. Moreover, the sheer size of a \(\text{tBuO}\) group certainly does not exempt it from serving as a bridging ligand; in general, the formation of \(\mu\)-bridged dimers (oligomers) is so favorable that even very poorly donating fluorinated alkoxides do not get away (cf. 6). Finally, the synthesis of 1 by disproportionation tells fundamental lessons about the meta-stability of low-valent molybdenum complexes in general and, in doing so, casts doubts on previous reports claiming the isolation of putative tetra-valent \([\text{Mo}(\text{O}^\text{Bu})_4]\).

Results and Discussion

Preparation and Crystallographic Characterization. For their high activity and excellent functional group tolerance, molybdenum alkylidyne complexes of the general type \([\text{R}^{3}\text{O}]_{3}\text{Mo}^{\text{II}}\) arguably define the state-of-the-art in alkylene metathesis. Several independent entries into this privileged class of organometallic catalysts have been developed over the years.

The fairly clean formation of 1 by disproportionation of \([\text{MoCl}_4(\text{THF})_2]\) in the presence of NaOtfBu at low temperature was unexpected in view of two earlier literature reports. Specifically, it had been reported that treatment of \([\text{MoCl}_4(\text{THF})_2]\) with LiOtfBu in THF/hexane entails simple ligand exchange; a workup with \(\text{CH}_3\text{Cl}_2\) followed by recrystallization from cold n-pentane supposedly gave \([\text{Mo}(\text{O}^\text{Bu})_4]\) in 25% yield. This assignment, however, had been (Scheme 1). The reaction is thought to proceed by partial ligand exchange with formation of transient Mo(V) alkoxides (e.g., 3) followed by rupture of a MoO–R bond; the resulting oxo-molybdenum complexes of type \([\text{O}==\text{MoCl}_2]\) (4) dimerize and can lead to adducts such as 5 or even complex polynuclear arrays. The ease of formation of the \([\text{Mo}==\text{O}]\) group manifest in these examples is a hallmark of (high-valent) molybdenum chemistry, this prevalent functionality dominates the field and plays a pivotal role in biological and industrial catalysis alike.
based on a rather rudimentary characterization by elemental analysis and the fact that a single resonance in the $^1$H NMR spectra was observed; the compound was reported to be EPR-silent. In our hands, treatment of [MoCl$_4$(THF)$_2$] with either NaOtBu or LiOtBu invariably resulted in disproportionation with formation of 8 and 1; the latter is EPR-active (see below). Unfortunately, the paucity of data reported for [Mo(OtBu)$_4$] precludes a detailed comparison with 1 and an accurate assessment. We cannot exclude that [Mo(OtBu)$_4$] had previously been formed by ligand exchange, yet we are also unable to confirm it, despite considerable experimentation.

A second report describes [Mo(OtBu)$_4$] as a thermally unstable green-brown solid material formed on reaction of [Mo(NMe$_2$)$_4$], with tBuOH. Its characterization was based upon elemental analysis, IR, and mass spectrometry: it is stunning, however, that the peak in the reported mass spectrum with the highest $m/z$ 461 actually fits to [Mo-(OtBu)$_5$]$^+$, although the observed base-peak at $m/z$ 388 matches the mass of [Mo(OtBu)$_4$]$^+$. The reported IR data have not been analyzed in any detail and therefore do not allow one to make a final judgment; we note that the reported bands are close to those observed for 1 (see below). In consideration thereof, we tried to reproduce this literature route (Scheme 3). Although it cannot be rigorously excluded that [Mo(OtBu)$_4$] is present in the crude mixture, the only complexes that we were able to isolate in pure form in several independent runs were, once again, [Mo(OtBu)$_4$] (1) and the new dinuclear species 9. From the structure in the solid state it is apparent that 9 contains a bridging amide and a bridging oxo-ligand; moreover, a molecule of Me$_2$NH released upon reaction of [Mo(NMe$_2$)$_4$] with tBuOH now serves as a donor ligand to one the Mo centers (Figure 2). The short Mo1–Mo2 distance [2.486(3) Å] speaks for a metal–metal bonding interaction within the core of this paramagnetic species. The question as to how this peculiar product is formed has to remain open at this point. The fact that the μ-oxo atom can only derive from a tBuO precursor ligand could imply an oxidative cleavage mechanism, which might transform a transient dinuclear Mo(III) precursor as the expected low-valent product of the actual disproportionation reaction into the ultimately isolated complex 9.

Collectively, these results suggest that alkoxide ligands favor the disproportionation of Mo(IV), even though a discrete and well-characterized homoleptic Mo(IV) enolate complex is known that has been made from [MoCl$_4$(THF)$_2$], by ligand exchange with the corresponding bulky alkali-metal enolate. [MoCl$_4$(THF)$_2$] itself also shows the propensity to disproportionate, although more latently. This complex had previously been recognized as unstable under nitrogen atmosphere, but the decomposition products had not been identified. When a solution of [MoCl$_4$(THF)$_2$] in dichloromethane was kept at ambient temperature for ≥4 d, a solid material started to precipitate that is composed of a 1:1 mixture of the oxo-species 10, crystallized with one THF and one adventitious water ligand, and the known dinuclear complex 11 (Scheme 4).

The coexistence of these Mo(V) and Mo(III) complexes in a single unit cell is unprecedented (Figure 3); it provides compelling evidence for the notion that Mo(IV) is inherently

Scheme 3. Literature-Inspired Control Experiment

Figure 1. Structure of [Mo(OtBu)$_4$] (1) in the solid state; only one of the two independent molecules in the unit cell is depicted, and H atoms are omitted for clarity.

Figure 2. Structure of complex 9 in the solid state; hydrogen atoms (except for the NH atom) and the disorder of one of the tert-butyl groups over two positions are not shown for clarity.
A comparison between the crystal structure and the optimized geometry based on the crystal structure shows a good agreement (Table 1). The axial direction of the trigonal bipyramid is given by the O2–Mo and/or Mo–O2' direction (O2–Mo–O2' = 160.6°). The low symmetry of the molecule also leads to an inequivalence of the x and y directions. This geometrical aspect is indeed reflected, for example, in the observation of a rhombic EPR spectra (see below).

In addition, in an effort to explore the potential energy surface in more depth, additional geometry optimizations were performed with modified starting structures, by rotating the tBu groups about the Mo–O direction in various permutations. While some calculations ended up converging to identical minima, a range of stable, slightly different conformations have indeed been found, indicative of a potential energy surface with multiple close-lying minima.

Figure 3. Structure of cocrystallized 10 and 11; hydrogen atoms are omitted except for those of the adventitious water molecule completing the ligand sphere of the oxo-complex 10.

Table 1. Selected Bond Distances (Å) and angles (deg) of Complex 1 Compared to Model 1a

| bond       | distance | angle     |
|------------|----------|-----------|
| Mo–O1      | 1.875    | 169.1     |
| Mo–O2      | 1.932    | 112.7     |
| Mo–O2'     | 1.923    | 112.3     |
| Mo–O3      | 1.857    | 124.5     |
| Mo–O3'     | 1.857    | 124.5     |

structure (see the Supporting Information for computational details) is intermediate between square pyramidal and trigonal bipyramidal, thus rendering all O atoms inequivalent. The distortion from trigonal bipyramidal and square pyramidal can be quantified by a Berry pseudorotation, where the O3–Mo–O1 angle has decreased from 180° (square pyramidal limit) to 135.7°. Since the complex is homoleptic, multiple minima likely exist on the potential energy surface, such as, the system is Jahn–Teller-active.

Figure 4. Structures of the three lowest minima on the potential energy surface, found by geometry optimizations from different starting structures. Structure 1a was found by geometry-optimizing the crystal structure; this structure is closest to an idealized square pyramid. Structures 1b and 1c show a more trigonal bipyramidal structure of the MoO5 core. The structures additionally differ in the relative orientations of the tBu groups. All three structures are within 3 kcal/mol of each other, with 1b being lowest in energy. Cartesian coordinates are provided in the Supporting Information.

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5a), the pattern of a second batch in Figure 5c shows a splitting of the band at 5.5°. Moreover, this sample also seems to contain some dimer, \([\text{Mo}_2(\text{OtBu})_6]\]. While the powder pattern confirms the presence of two discrete conformers, the measured data does not contain enough information to allow a confident identification of the second structure of the monomer.

**Electronic Structure.** In spite of the significant Berry rotation of the optimized crystal structure 1a, the computed d-orbital scheme of 1a shown in Figure 6 closely resembles that of the theoretical d-orbital scheme of 1a obtained by single-crystal data. Figure 6a shows a splitting of the band at 5.5°. Moreover, this sample also seems to contain some dimer, [Mo_2(OtBu)_6]. While the powder pattern confirms the presence of two discrete conformers, the measured data does not contain enough information to allow a confident identification of the second structure of the monomer.

![Figure 6](image-url)

**Figure 6.** Molecular orbital scheme (quasi-restricted orbitals) for the 4d manifold of [Mo(OtBu)_5] represented by the geometry-optimized crystal structure 1a. Also included are four representative oxygen-based doubly occupied orbitals (at about -6.8 eV). Since the orbital structure largely corresponds to that of a square pyramid, the molecular z-axis is chosen as parallel to the Mo–O3’ direction and the x-axis as along the O2–O2’ direction. Symmetry labels under approximate C_2v symmetry were added accordingly for the orbitals and for the transitions; the 2Bu groups are omitted for clarity. Upon consideration of the ligand character, the low-lying y-polarized 2B_2 and x-polarized 2B_1 d-d transitions (blue) are expected to gain oscillator strength owing to an overlap of the ligand part of the donor orbital with the metal part of the acceptor orbital, leading to a symmetry-allowed, nonzero transition dipole moment upon admixture of ligand character into the orbital. Electronic excitations from the oxygen-centered doubly occupied orbitals with approximate C_2v symmetry labels are included in the dashed boxes.
Figure 7. UV/vis ($T = 296$ K, left) and MCD ($T = 2$ K, $B = 10$ T, right) spectra of 1 (black) and their simulations (red) and Gaussian deconvolution (blue). The UV/vis sample was a pentane solution, whereas MCD was obtained from a mull. The bottom panels show in addition calculated UV/vis spectra (bottom) as obtained for the structural models a, b, and c with sticks representing the number of possible transitions. Also included are the natural transition orbitals for the lowest two calculated d→d transitions and the difference densities (red, positive) for bands 7→10, structure 1a.

Figure 8. (Left) Continuous wave Q-band EPR spectrum of [Mo(OtBu)$_5$] in n-pentane and a simulation. Experimental conditions: $T = 20$ K, microwave frequency 34.053 GHz, microwave power 0.1 mW, modulation amplitude 0.78 mT. The g-values extracted from the simulation amount to 1.818, 1.903, and 1.936. The fitted Mo(V) hyperfine coupling constants amount to 145, 10, and 61 MHz. (Right) Temperature cycle from 30 to 100 K back to 30 K and to 4.2 K of one sample, recorded at the X-band. Conditions: microwave frequency 9.635 GHz, microwave power 2 mW.
expected for a square pyramidal coordination geometry. The unpaired electron is located in the nonbonding \( d_{xz} \) orbital. The other orbitals are destabilized owing to the metal–ligand interactions: specifically, the SOMO is followed by the \( d_{yz}/d_{x^2-y^2} \) pair, the degeneracy of which has been lifted by the Jahn–Teller distortion. Next comes the \( d_{z^2} \) orbital and finally, as the most destabilized orbital, \( d_{xy} \). The symmetry labels of the orbitals under approximate \( C_{2v} \) symmetry (vide infra) are included in Figure 6. Inspection of the doubly occupied orbital structure reveals a plethora of “nonbonding” linear combinations of oxygen-centered orbitals (the first four are included in Figure 6) that do not directly overlap with the Mo 4d orbitals owing to symmetry. This set of orbitals occurs at about 3.5 eV (28 000 cm\(^{-1}\)) in energy below the SOMO. The first oxygen-based orbital with bonding character to Mo occurs even lower, at \(-8.50 \text{ eV}\), in which the oxygen orbitals are \( \pi \)-bonding to the 4d\(_y\) orbital (not shown in the figure). While it is in principle possible to induce a 2p-polarized \( ^1A_1 \) charge-transfer transition from this orbital into the SOMO, this electronic transition is expected at an energy above 40 000 cm\(^{-1}\), where it would be difficult to detect. A comparison of the electronic differences in terms of ligand field splittings of complexes 1a–1c is given in the Supporting Information.

**UV/Vis and MCD Spectroscopy.** The UV/vis spectrum displays a broad and relatively featureless absorption in the blue part of the spectrum (Figure 7, left). It could be well-deconvoluted with four Gaussians of width 6400 cm\(^{-1}\), centered at 29 950, 34 030, 40 035, and 46 850 cm\(^{-1}\). In order to investigate whether \( d \rightarrow d \) transitions are present in the infrared region, we recorded an MCD spectrum on a concentrated sample, which is surprisingly rich in structure and displays a multitude of bands in the infrared region (Figure 7, right). A particularly strong band is present at about 6000 cm\(^{-1}\), indicating the presence of multiple \( d \rightarrow d \) transitions that are not observed in the UV/vis spectrum. The MCD spectrum has been fitted with six Gaussians centered at 5935, 8616, 11 100, 12 808, 16 804, and 22 499 cm\(^{-1}\). The observation of six transitions in the MCD spectrum below 23 000 cm\(^{-1}\) is already remarkable for a 4d\(^{1}\) system in itself, since only a maximum of four \( d \rightarrow d \) transitions can occur; on the basis of our calculations, we do not expect more than three \( d \rightarrow d \) transitions below 20 000 cm\(^{-1}\) [cf. Figure S9 (SI) and vide infra]. Thus, this observation provides additional evidence for the coexistence of several conformers under the experimental conditions. Attempts to address the structural heterogeneity by additional MCD experiments of deposited and smeared-out monocristalline material were not successful due to scattering, as were experiments with frozen solutions, since \( \nu \)-pentane and toluene or mixtures thereof produced a poor glass at low temperature. The calculations shown in Figure 7 will be discussed in the Theoretical Spectroscopy section.

**EPR Spectroscopy.** The Q-band continuous wave (cw) EPR spectrum (Figure 8) has been well-fitted by using a minimalistic spin Hamiltonian that included the three g-values and the Mo hyperfine coupling constants, as well as three line width parameters. The fitted g-values amount to 1.818, 1.903, and 1.936. The observed rhombicity of the g-tensor provides direct confirmation of the symmetry-lowering of \([\text{Mo}(\text{O} \cdot \text{Bu})_3]^\text{2-}\) (1) as compared to the structure of this complex in the solid state. It is worth noting that the \( g \)-values of the EPR spectrum shows a splitting in two poorly resolved bands. A comparison of spectra recorded at the X-band and Q-band (Supporting Information) indicates that the two bands are not caused by hyperfine splitting and must stem from slightly different conformers present in frozen solution, with possibly slightly altered orientation of the tBu groups and thereby slightly changed Mo–O covalencies and thus \( g \)-values.

Being aware of possible structural heterogeneity, we investigated the EPR spectrum as a function of temperature. The temperature dependence in Figure 8 (right) measured at the X-band displays a drastic change of the spectrum upon raising the temperature from 30 to 100 K, in the form of the disappearance of the intense signal at 360 mT and the merging together of the \( g \)-feature at 380 mT. The change is completely reversible, as subsequent cooling of the sample back to 30 K recovered the original signal. The spectrum at 4.2 K is essentially identical to the one at 30 K. The change in shape of the signal with temperature and, in particular, the presence of a split \( g \)-signal at low temperature provide a rather strong experimental indication of the presence of two conformers corresponding to local minima of the potential energy surface of the Jahn–Teller-active molecule, the thermal populations of which change.

**Theoretical Spectroscopy.** In order to interpret the recorded spectra, a detailed comparison with quantum chemical calculations is necessary. A particular problem occurs in interpreting the six bands in the MCD spectrum (Figure 7). First, the AILFT calculation (Figure S9, SI) that included the five 4d-orbitals and one electron features only three \( d \rightarrow d \) transitions below 20 000 cm\(^{-1}\). The natural transition orbitals for the lowest two transitions are included in Figure 7. These are the 1\( ^2 \)-B\(_1\) and 1\( ^2 \)-B\(_2\) transitions featuring the \( d_{xy} \) orbital as the donor orbital and the \( d_{yz}/d_{x^2-y^2} \) pair as the acceptor orbitals. Out of all four \( d \rightarrow d \) transitions these two are expected to have the largest oscillator strength. The oxygen-centered non-bonding orbitals were not included in the CAS calculation, because they are located more than 3.5 eV below the SOMO.

The seemingly doubled number of bands in the MCD spectrum, in addition to the observed splitting of the \( g \)-feature in the EPR spectrum (Figure 8) and the splitting observed at 5.5° for one of the batches in the powder diffraction pattern (Figure 5c), is compatible with the presence of two conformers with perhaps slightly changed orientations of the Otbu groups and, concomitantly, slightly changed Mo–O covalencies. This is additionally confirmed by the calculations of the electronic spectrum, where structures 1a, 1b, and 1c each display two bands in the near-infrared region at different positions (Figure 7, bottom, right), which is a direct consequence of the slightly changed ligand field splitting of the conformers (Figure S9, SI). While a definite assignment of the bands in the MCD spectrum seems presently not feasible owing to the Jahn–Teller-induced heterogeneity, the mere observation of these bands in the near-IR region shows unambiguously that the molecular species does not feature an oxo-ligand. An oxo-ligand, in turn, would lead to an MCD spectrum where the lowest \( d \rightarrow d \) transition would be significantly higher in energy, \( e.g. \), 20 000 cm\(^{-1}\) in \([\text{Mo(O)}\text{Cl}_3\cdot(\text{dppe})]\)\(^{56}\) or larger than 23 000 cm\(^{-1}\) in a derived in silico \([\text{MoO(O} \cdot \text{Bu})_2]\)\(^-\) complex contained in the Supporting Information (Figure S7).

Analysis of the \( g \)-values in terms of ligand field theory (see the Supporting Information) yielded good agreement with experiment. However, a confident, detailed assignment of all low-energy MCD bands could not be achieved. The calculated \( g \)-values for structure 1a amount to 1.87, 1.94, and 1.95, in reasonable agreement with experiment, whereby in particular the middle \( g \)-shift is calculated slightly too low. The
calculated Löwdin spin population at Mo amounted to 85%, and the calculation was largely spin-uncontaminated ($S^2 = 0.754$). The more-trigonal geometries 1b and 1c found on the potential energy surface gave rise to slightly different g-values, typically changed by about 0.02 (Table S7, SI).

It is instructive to investigate the observed splitting of the least-shifted g-value, $g_σ$. In perturbation theory, the $g_σ$ shift in structure 1a arises from the matrix elements of spin–orbit coupling and the orbit–Zeeman interaction between the $(xy)^1$ ground state and the $(x^2−y^2)^1$ excited state $[3a_g, ΔE(xy, x^2−y^2) = 34 540 \text{ cm}^{-1}]$. In structures 1b and 1c, the least-shifted g-value occurs between the $(xz)^1$ ground state and contributions of both the $(z^2)^1$ (1a$'$) and the $(x^2−y^2)^1$ (1e$''$) excited states. The excitation energy of the 1e$''$ contribution changes from 17 667 to 19 883 cm$^{-1}$ upon going from 1b to 1c (cf. Figure S9, SI), i.e., a change of 12.5%, which would lead to a change of the g-values of up to 0.008, compatible with experiments and thus providing yet another confirmation of the Jahn–Teller heterogeneity between the $C_{3v}$ and $C_{3h}$ structures.

Subsequently, a TDDFT calculation has been performed in order to assign bands 7–10 in the UV/vis spectrum shown in Figure 7. The agreement between experiment and theory is good for structure 1a, providing additional confidence that the chosen model accurately mimics the actual structure of [Mo(OBu)$_3$] (1). Structures 1b and 1c, although essentially equal in energy to structure 1a, seem to provide a less accurate description of the UV/vis spectrum. The plethora of individual transitions (depicted as sticks) included in the diagram gives information that a large number of transitions contribute to the Gaussians used in the deconvolution. As already noted, the large number of transitions originates from the presence of a large number of ligand-centered orbitals, mainly with oxygen character, that are located about 3.5 eV below the SOMO. Difference densities for representative sticks are included in Figure 7. Although the relative phases of the oxygen orbitals inhibit admixture of Mo(4d) character, all of these orbitals principally contribute to the rich manifold of excited states that are all formally of oxygen-to-molybdenum charge-transfer character. The more intense transitions involve the $B_2$ and $B_1$ transitions of the 1a$_g$, 1b$_g$, 1a$_u$, and 1b$_u$ orbitals as donor orbitals (cf. Figure 6).

Most convincingly, the calculated IR spectra for all three model structures included in Figure S11 (SI) reproduce virtually all bands observed in the experimental spectrum very nicely and hence allows for their assignment (see the Supporting Information).

Overall, we conclude that despite the observed complications owing to temperature-dependent structural heterogeneity, generally excellent agreement between experiment and theory is found for all spectroscopic methods employed in this study. This provides confidence in the model structures used in the calculations. The calculated geometric and electronic structure therefore accurately represents the so far unique homoleptic Mo(V) alkoxide [Mo(OBu)$_3$] (1), including the symmetry-lowering as a result of Berry rotation.

## CONCLUSION

The chemistry of Mo(V) is dominated by oxo-complexes, which are readily formed by formal oxygen atom abstraction even from substrates as stable as ethers, phosphine oxides, sulfoxides, and, most commonly, alcohols. Due to the proclivity to form and maintain [Mo═O] groups, Mo(V)-alkoxides devoid of at least one additional oxo-ligand in general are exceedingly rare, and homoleptic representatives were entirely unknown prior to the present study. It is now shown that disproportionation of Mo(IV) provides access to this previously elusive class of compounds under notably mild conditions. The first embodiment is [Mo(OBu)$_3$] (1). This compound is a monomeric entity with a Jahn–Teller-distorted trigonal bipyramidal structure in the solid state but is subject to facile symmetry-lowering Berry pseudorotation in solution. The geometric and electronic structures of this unique complex are accurately described by DFT, which was calibrated against experimental spectra (IR, UV/vis, MCD, EPR).57

Indirect evidence suggests that alkoxide ligands render the disproportionation reaction of Mo(IV), leading to the formation of [Mo(OBu)$_3$], remarkably facile, even though [MoCl$_4$(THF)$_2$] was also found to be intrinsically unstable toward decay into Mo(III) and Mo(V) in CH$_2$Cl$_2$ solution at ambient temperature. The question whether the increased reaction rate in the presence of tert-butoxide has to do with the formation of the dinuclear complex [[(BuO)$_3$MoMo(OBu)$_3$]] as a particularly favorable low-valent product of the disproportionation process or if stabilization of [Mo(OBu)$_3$] itself by dispersive forces within the ligand sphere plays any significant role will be the subject of future studies.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/DOI/10.1021/jacs.0c07073.

An experimental part including procedures; characterization data; supporting crystallographic information; EPR experiments in X, Q$_g$, and W-bands; NMR spectroscopy; infrared spectroscopy; a computational part including methodological details and a comparison of the ligand field splitting of structures 1a–1c and comparison to an in silico Mo$^+$-oxy model (PDF)

X-ray crystallographic data for penta-(tert-butoxy)-molybdenum(V) in CIF format (CIF)

X-ray crystallographic data for tris(µ$_2$-chloro)-trichloro-tris(tetrahydrofuran)-di-molybdenum trichloro-oxy-tetrahydrofuran-aqua-molybdenum in CIF format (CIF)

X-ray crystallographic data for (µ$_2$-dimethylamido)-(dimethylamine)-(µ$_2$-oxy)-penta(tert-butoxy)-di-molybdenum in CIF format (CIF)

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**REFERENCES**

(1) The empirical formula "MoCl₅" is used throughout this paper for convenience. Note that MoCl₅ is dimeric in the solid state but (largely) monomeric in the gas phase; solvent-dependent equilibria between dimer and monomer seem to exist in solution. (a) Schafer, H.; Schiessl, H.-G.; Völlin, F.; Wohle, H.; Baumann, H. Neue Untersuchungen über die Chloride des Molybdän. Z. Anorg. Allg. Chem. 1967, 353, 281–310. (b) Beck, J.; Wolf, F. Three New Polymeric Forms of Molybdenum Pentachloride. Acta Crystallogr., Sect. B: Struct. Sci. 1997, 53, 895–903. (c) McGuire, M. A.; Pandey, T.; Mu, S.; Parker, D. S. Ferromagnetic Spin-1/2 Dimers with Strong Anisotropy in MoCl₅. Chem. Mater. 2019, 31, 2982–2989.

(2) Black-crystalline MoCl₅ is moisture sensitive and should be kept under inert atmosphere; because hydrolysis, which leads to the appearance of a greenish color, is rather slow, the compound can be manipulated in air for short periods of time.

(3) (a) Kovacic, P.; Lange, R. M. Polymerization of Benzeno to p-Polyphenyl by Molybdenum Pentachloride. J. Org. Chem. 1963, 28, 968–972. (b) Kovacic, P.; Lange, R. M. Reactions of Molybdenum Pentachloride and Vanadium Tetrachloride with Alkyl- and Halobenzens. J. Org. Chem. 1965, 30, 4251–4254.

(4) (a) Marchetti, F.; Pampaloni, G.; Zacchini, S. The reactivity of molybdenum pentachloride with ethers: routes to the synthesis of Mo₅Cl₈ adducts, Mo₅Cl₈(v) chloro-alkoxydes and Mo₅Cl₈ oxychlo. Dalton Trans. 2013, 42, 15226–15234. (b) Hey-Hawkins, E.; von Schnering, K. H. Synthese und Kristallstruktur von MoCl₅(DME)-15-Krone-5 und MoCl₅(DME) (DME = 1,2-Dimethoxyethan). Z. Naturforsch., B: J. Chem. Sci. 1991, 46, 307–314.

(5) (a) Dolci, S.; Marchetti, F.; Pampaloni, G.; Zacchini, S. A systematic study on the activation of simple polyethers by MoCl₅ and WCl₅. Dalton Trans. 2010, 39, 5367–5376. (b) Gibson, V. C.; Kee, T. Inorganic Synthesis, 2298.

(6) For the cleavage of THF and the characterization of the resulting molybdenum complex [MoOCl₄(THF)]₂, see the following: (a) Feenan, K.; Fowles, G. W. A. Reactions of Molybdenum(V) Chloride and Molybdenum(V) Oxotrichloride with Some Oxygen and Sulfur Donor Molecules. Inorg. Chem. 1965, 4, 310–313. (b) Zittlhuber, C.; Robinson, F.; Pfitzner, A. Structural characterization of MoOCl₄(THF)₂, the pre-reactant for Kauffmann olefination reactions. Monatsh. Chem. 2017, 148, 629–633.

(7) In the present context, it is particularly relevant to note that it is the Bu₂O–O bond of Bu₂OCl which is selectively cleaved by MoCl₅; see the following: (a) Guo, Q.; Miyaji, T.; Gao, G.; Hara, R.; Takahashi, T. Catalytic C-O bond cleavage of ethers using group 5 or 6 metal halide/acid chloride systems. Chem. Commun. 2001, 1018–1019. (b) Guo, Q.; Miyaji, T.; Hara, R.; Shen, B.; Takahashi, T. Group 5 and group 6 metal halides as very efficient catalysts for acylative cleavage of ethers. Tetrahedron 2002, 58, 7327–7334.

(8) (a) Dilworth, J. R.; Zubieta, J.; et al. Trichlorotris-(tetrahydrofuranyl)-Molybdenum(III). Inorg. Synth. 2007, 24, 193–194. (b) Dilworth, J. R.; Richards, R. L.; et al. The Synthesis of Molybdenum and Tungsten Dinitrogen Complexes. Inorg. Synth. 2007, 42, 33.

(9) (a) Schubert, M.; Waldvogel, S. R. MoV Reagents in Organic Synthesis. Eur. J. Org. Chem. 2016, 2016, 2191–2196. (b) Waldvogel, S. R.; Trosien, S. Oxidative transformations of aryls using molybdenum pentachloride. Chem. Commun. 2012, 48, 9109–9119.

(10) (a) Garner, C. D.; Charnock, J. M. Molybdenum(III) (IV) and (V). In Comprehensive Coordination Chemistry; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Peragon: Oxford, 1987; Vol. 3, pp 1329–1374. (b) Young, C. G. Molybdenum. In Comprehensive Coordination Chemistry II; McCleverty, J. A., Meyer, T. J., Eds.; Peragon: Oxford, 2003; Vol. 4, pp 415–527.

(11) (a) Limberg, C.; Parsons, S.; Downs, A. J.; Watkin, D. J. Isolation and Crystal Structure of a Dimeric OXOMolybdenum(V) Complex containing Two Ethoxy Bridges and one Ethanol Bridge. J. Chem. Soc., Dalton Trans. 1994, 1169–1174. (b) Limberg, C.; Downs, A. J.; Blake, A. J.; Parsons, S. Modeling the Formation of Molybdenum Oxides from Alkoxides: Crystal Structures of [MoO₅(OMe)], [MoO₄(OMe)₂(H₂O)], [MoO₃(OEt)₂], and [MoO₂(OEt)₃]. Inorg. Chem. 1996, 35, 4439–4448. (c) Limberg, C.; Boese, R.; Schiemenz, B. Intermediates and products of the reaction of MoCl₅ with ethanol: crystal structures of [MoOCl₃(EtOH)] and [H₂MoOCl₄] EtOH. J. Chem. Soc., Dalton Trans. 1997, 1633–1637. (d) Marchetti, F.; Pampaloni, G.; Zacchini, S. The reactivity of MoCl₅ with molecules containing the alcohol functionality. Polyhedron 2015, 85, 369–375.

(12) Rillem, D. P.; Brubaker, C. H. Complexes of Molybdenum(V) and Tungsten(V). Far-Infrared Spectra and Some Other Properties. Inorg. Chem. 1969, 8, 1645–1649.

(13) A similar mechanism might be operative in the deoxygenation of Ph₂P=O or DMSO; see the following: Horner, S. M.; Tyree, S. Y. The Reaction of Some Oxygen Donors with Molybdenum Pentachloride: Coordination Cyclodimers of Molybdenum(V) Oxychloride and Molybdenum(VI) Dioxidochloride. Inorg. Chem. 1962, 1, 122–127.

(14) (a) Cotten, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. Advanced Inorganic Chemistry, 6th ed.; Wiley: New York, 1999.

(15) A few homolecotic Mo(VI) alkoxides are known; see the following: (a) Jacob, E. Metallohexamethoxides. Angew. Chem. 1982, 94, 146–147. (b) Seidenbaeva, G. A.; Kloo, L.; Wernrup, P.; Kessler, V. G. Electrochemical Synthesis, X-ray Single Crystal, IR Spectroscopic and Quantum Chemical Investigation of Molybdenum and Tungsten Hexamethoxides. Inorg. Chem. 2001, 40, 3815–3818. (c) Buth, S.; Wocadlo, S.; Neumüller, B.; Weller, F.; deHrinick, K. Synthese und Kristallstrukturen von Tris(glycolato) molybdän(VI) und Tris (pinakolato)molybdän(VI). Z. Naturforsch., B: J. Chem. Sci. 1992, 47B, 706–712.

(16) See the following for leading references and literature cited therein: (a) Mitchell, P. C. H. Oxo-species of molybdenum(V) and (VI). Q. Rev., Chem. Soc. 1966, 20, 103–118. (b) Braithwaite, E. R.; Haber, J., Eds. Molybdenum: An Outline of its Chemistry and Uses. Studies in Inorganic Chemistry; Elsevier: Amsterdam, 1994; Vol. 19. (c) Souza, S. A. C.; Cabrita, I.; Fernandes, A. C. High-valent oxo-molybdenoxo- and oxo-xenium complexes as efficient catalysts for X=H (X = Si, B, P or H) bond activation and for organic reductions. Chem. Soc. Rev. 2012, 41, 5641–5653. (d) Arzumanian, H. Molybdenum-Vloxo and Peroxo Complexes in Oxygen Atom Transfer Processes with O₂ as the Primary Oxidant. Curr. Inorg. Chem. 2011, 1, 140–145. (e) Karanadasa, H. I.; Chang, C. J.; Long, J. R. A molecular molybdenum-oxo catalyst for generating hydrogen from water. Nature 2010, 464, 1329–1333.

(17) (a) Coughlan, M. P., Ed. Molybdenum and Molybdenum-Containing Enzymes; Peragon Press: Oxford, 1980. (b) Hille, R.; Rétyé, J.; Bartlewski-Hof, U.; Reichenbecher, W.; Schink, B.
Mechanistic aspects of molybdenum containing enzymes. FEMS Microbiol. Rev. 1998, 22, 459–501. (c) Grosyman, S.; Holm, R. H. Biomimetic Chemistry of Iron, Nickel, Molybdenum and Tungsten in Sulfur-Ligated Protein Sites. Biochemistry 2009, 48, 2310–2320. (d) Hille, R.; Hall, J.; Basu, P. The Mononuclear Molybdenum Enzymes. Chem. Rev. 2014, 114, 3963–4038.

(18) Schubert, M.; Leppin, J.; Wehming, K.; Schollmeyer, D.; Heinze, K.; Waldvogel, S. R. Powerful Fluorooalkoxy Molybdenum(V) Reagent for Selective Oxidative Arene Coupling Reaction. Angew. Chem., Int. Ed. 2014, 53, 2494–2497.

(19) Complex 6 dissociates partly in CH 2Cl 2 and fully in trifluoroethanol (cf. ref 18); in the solid state, it is diamagnetic and shows a short Mo–Mo distance (2.832 Å), which suggests metal–metal bonding/antiferromagnetic spin coupling, although this aspect has not been addressed in the original publication. A single bond featuring a similar Mo–Mo distance has not been addressed in the original publication. A single bond of molybdenum is representative; see the following: Bazhenova, M. H.; Huffman, J. C.; Kramer, K. S.; Streib, W. E. Mo(II)-(H 2 Bu)(HNNMe 2): A Novel Hydrido Cluster of Molybdenum. J. Am. Chem. Soc. 1993, 115, 9866–9867. (b) Chisholm, M. H.; Huffman, D. M.; McCandless Northius, J.; Huffman, J. C. Further studies of the reactions involving ethylene and Mo(OBu) 2, where M = Mo and W. Polycyclotetraene formation versus formation of ethylene adducts and C–C coupled products. Polyhedron 1997, 16, 839–847.

(20) Bardina, N. V.; Bazhenova, T. A.; Lyssenko, K. A.; Antipin, M. Yu.; Shulga, Y. M.; Filina, T. A.; Shestakov, A. F. Unusual binuclear alkoxoalkylmolybdenum(V) complex free of oxo groups: synthesis, structure and spectral properties. Mendeleev Commun. 2006, 16, 307–308.

(21) The plethora of complexes formed on treatment of MoCl 6 with methanol/methoxide is representative; see the following: Bazhenova, T. A.; Lyssenko, K. A.; Kuznetsov, D. A.; Kovaleva, N. V.; Manakin, Y. V.; Savinykh, T. A.; Shestakov, A. F. Methanolysis of MoCl 6 in the Presence of Different Alkaline Agents; Molecular Structures of the Polynuclear Molybdenum(V) Methoxides and Electron Charge Density Distribution from X-ray Diffraction Study of the New K-Mo Cluster. Polyhedron 2014, 76, 108–116.

(22) In addition to various ethers, benzene, and MeCN, simple olefins (norbornene, allyltrimethylsilane, tetrachloroethane) were employed to prepare lower-valent molybdenum species; of course, silanes, Zn, Sn, Al, SnCl 2, organolithium, and organozinc reagents can also be used as reducing agents. For an overview, see ref 5 and the following reference, including the literature cited therein: Persson, C. C.; Andersson, C. Reduction of tungsten(IV) and molybdenum(V) by allyltrimethylsilane and cyclopentene. Simple high yield syntheses of MoCl 5 (OET) 2, MoCl 5 (dme), WCl 5 (thf) 2, WCl 5 (dme) and WOCl 5 (thf) 2. Inorg. Chm. Acta 1993, 203, 235–238.

(23) There is evidence for both mechanisms; see the following: (a) Chisholm, M. C.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. Reactions of Metal-Metal Multiple Bonds. 10. Reactions of Mo 2(OR) 6 (a) Chisholm, M. C.; Folting, K.; Huffman, J. C.; Kramer, K. S.; Streib, W. E. Mo(II)-(H 2 Bu)(HNNMe 2): A Novel Hydrido Cluster of Molybdenum. J. Am. Chem. Soc. 1993, 115, 9866–9867. (b) Chisholm, M. H.; Hoffman, D. M.; McCandless Northius, J.; Huffman, J. C. Further studies of the reactions involving ethylene and Mo(OBu) 2, where M = Mo and W. Polycyclotetraene formation versus formation of ethylene adducts and C–C coupled products. Polyhedron 1997, 16, 839–847.

(24) Peters, J. C.; Johnson, A. R.; Odom, A. L.; Wanandi, P. W.; Davis, W. M.; Cummins, C. C. Assembly of Molybdenum/Titanium μ-Oxo Complexes via Radical Alkoxide C-O Cleavage. J. Am. Chem. Soc. 1996, 118, 10175–10188. (25) Cotton, F. A.; Murillo, C. A. Multiple Bonds Between Metal Atoms, 3rd ed.; Walton, R. A., Ed.; Springer: New York, 2005. (26) Homoelectic, low-valent, and monomeric Mo complexes are known; for classical case studies, see the following: (a) Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, E. B.; Cundari, T. R. Low Coordination, Monomeric Molybdenum and Tungsten (III) Complexes: Structure, Reactivity and Calculational Studies of (silo)x Mo and (silo)x ML (M = Mo, W; L = PMe 3, CO; silox = ‘BuSiO’). J. Am. Chem. Soc. 2008, 130, 12931–12943. (b) Schrock, R. C. Catalytic Reduction of Dinitrogen to Ammonia by a Single Molybdenum Center. Acc. Chem. Res. 2005, 38, 955–962. (c) Cummins, C. C. Reductive Cleavage and Related Reactions Leading to Molybdenum-Element Multiple Bonds: New Pathways Offered by Three-coordinate Molybdenum(III). Chem. Commun. 1998, 1777–1786.

(27) For representative examples, see the following: (a) Chisholm, M. H.; Huffman, J. C.; Kramer, K. S.; Streib, W. E. Mo(II)-(H 2 Bu)(HNNMe 2): A Novel Hydrido Cluster of Molybdenum. J. Am. Chem. Soc. 1993, 115, 9866–9867. (b) Chisholm, M. H.; Huffman, D. M.; McCandless Northius, J.; Huffman, J. C. Further studies of the reactions involving ethylene and Mo(OBu) 2, where M = Mo and W. Polycyclotetraene formation versus formation of ethylene adducts and C–C coupled products. Polyhedron 1997, 16, 839–847.
Metathesis and Efficient Nitrogen Transfer Agents. J. Am. Chem. Soc. 2009, 131, 9468–9470.

(40) (a) Cummins, C. C. Reductive cleavage and related reactions leading to molybdenum-element multiple bonds: new pathways offered by three-coordinate molybdenum(III). Chem. Commun. 1998, 1777–1786. (b) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, L. J. Dintrigene Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data. J. Am. Chem. Soc. 1996, 118, 8623–8638.

(41) The use of coarse tin facilitates product isolation; cf. the following: Poli, R.; Gordon, J. C. 1H NMR Investigation of the Tetrahydrofuran Replacement by Phosphine Ligands on MoCl5(THF). A Trans Effect. Inorg. Chem. 1991, 30, 4550–4554.

(42) Chisholm, M.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. The Molybdenum-Molybdenum Molybdenum Complexes: Preparation, Properties, and Structural Characterization of Mo2(OCH2CMe3)6. Inorg. Chem. 1977, 16, 1801–1808.

(43) Broderick, E. M.; Browne, S. C.; Johnson, M. J. A.; et al. Dimolybdenum and Ditungsten Hexa(Alkoxy) Complexes. Inorg. Synth. 2014, 36, 95–102.

(44) 95Mo NMR was used as an additional probe to confirm the formation of 8 (see the SI); the shift of δMo = 2640 ppm in [D3]toluene corresponds very well with the shift of δMo = 2645 ppm reported in the literature; see the following: Young, C. G.; Kofer, E. M.; Enemark, J. H. 95Mo and 183W NMR Studies on Triply Bonded Dinuclear M(III) and Related Mo2C (M = Mo or W) Complexes. Polyhedron 1987, 6, 255–259.

(45) A brown/black precipitate starts to form at 50°C in [D3]toluene; the decomposition becomes very fast when the temperature is further increased (see the Supporting Information); isobutene was the only detectable byproduct.

(46) The diffraction data had to be recorded at 200 K because the single crystals cracked upon further cooling.

(47) Certain analogies with monomeric MoCl5 are noteworthy. At high temperature, MoCl5 populates a trigonal bipyramidal (D3h) and a square pyramidal form (C4v) (some Mo2Cl4 might also be present). In an argon or nitrogen matrix, only the C4v geometry was observed; see the following: (a) Brunvoll, J.; Ischenko, A. A.; Spiridonov, V. P.; Strand, T. G. Composition and Molecular Structure of Gaseous Molybdenum Pentachloride by Electron Diffraction. Acta Chem. Scand. 1984, 38A, 115–120. (b) Brisdon, A. K.; Graham, J. T.; Hope, E. G.; Jenkins, D. M.; Levason, W.; Ogden, J. S. Spectroscopic Studies on Matrix-isolated Molybdenum Pentachloride. J. Chem. Soc., Dalton Trans. 1990, 1529–1532. For a discussion of the possible Jahn–Teller distortion of the structure, see the following: (c) Bader, R. F. W.; Westland, A. D. The Electronic Spectra of MoCl3 and NbCl3. Can. J. Chem. 1961, 39, 2306–2315.

(48) The reported 1H NMR signal of putative [Mo(OBu)3]2 in C6D6 at 1.55 ppm is consistently close to that of [(BuO)2Mo(OBu)]3, which resonates at 1.57 ppm in this solvent; see ref. 43. (49) Attempted formation of [Mo(OBu)3]2+ by chemical or electrochemical oxidation of 1 was unsuccessful; cyclodovolametric studies showed very broad and irreversible oxidation waves at z0.5 and ±1.1 V; see the Supporting Information.

(50) We appreciate that the Mo–Mo distance per se is no reliable indicator; therefore, we refrain from assigning a bond order. While structurally remotely related but diamagnetic Mo complexes have previously been proposed to contain Mo≡Mo bonds, the paramagnetic character of 9 renders a formal double bond unlikely.

(a) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. Structure and Bonding in Octaisopropoxydimolybdenum(IV). Inorg. Chem. 1978, 17, 2944–2946. (b) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. Reactions of M-M Triple Bonds with C-N Triple Bonds: Adduct Formation (M = Mo) and Metathesis (M = W) as Seen in the Reactions between Dimethylcynamide and Hexaalkoxydes of Dimolybdenum and Ditungsten. J. Am. Chem. Soc. 1983, 105, 6162–6163.