spectively, of Figure 5. The principal effect of the hydrogen is stabilization of the $3a_1$ orbital and withdrawal of charge from the aluminum. The charge withdrawal has two effects. First, it stabilizes the 3s Al orbitals by increasing the positive charge on Al, thus allowing them to participate more fully in bonding. Secondly, it greatly reduces the electron–electron repulsion between the $2a_1$ and the $3a_1$ orbitals. Both effects will tend to reduce the Al—C bond length. A shorter bond length also increases the Al $3p_x$—C $2p_x$ overlap leading to additional stabilization of the $1b_1$ orbital. We note, however, that the relative Mulliken population of the $1b_1$ orbital on the Al is only 28% (11% in $AlCH_2$) and thus remains highly polarized.

(10) As suggested by a reviewer, a thermodynamic measure of the degree of XC double bonding in these compounds as well as $AlCH_2$ and BCH_2 might be obtained by considering isodesmic reactions of the form

$$HXCH_2 + XH_n \rightarrow XCH_2 + XH_{n+1} \quad (1)$$

$$XH_2 + XH_n \rightarrow XH + XH_{n+1} \quad X = B, Al;\ n = 0, 1, 2 \quad (2)$$

In the table below we give heats of reaction for these two reactions with the same basis set employed throughout our study.

ΔE_m, kcal/mol	reaction 1		reaction 2	
n	X = Al	X = B	X = Al	X = B
0	−66.0	+29.7	−142.5	−48.1
1	+76.5	+77.8	0.0	0.0
2	−177.3	−87.3	−253.8	−165.1

It is clear from the energies for the second reaction that bonding to either Al or B is very sensitive to the value of n. This variability makes it difficult to evaluate changes in the XC bonding from reaction 1. Although the trends are interesting and worthy of future study, the differences in spin multiplicity and coordination number make a detailed analysis at the minimal basis set level impractical.

Note Added in Proof. We have implicitly assumed the BC double bonded species, $B{=}CH_2$ and $HB{=}CH_2$, to be the expected and normally occurring reference compounds. However, BC double bonds have not, in fact, been observed (Onak, Thomas "Organoborane Chemistry"; Academic Press: New York, 1975; p 4). This fact undoubtedly derives from the relative stability of isomers with BC single bonds and therefore does not invalidate the BC double bonds we have calculated. It may actually enhance the value of our computational results because they elucidate the nature of a bond which has proved difficult to isolate experimentally.

Acknowledgment. We wish to thank the NIH (Grant GM 26462) for financial support.

Registry No. $AlCH_2$, 76392-50-2; BCH_2, 79435-75-9; $HAlCH_2$, 79435-76-0; $HBCH_2$, 56125-75-8.

The Molybdenum–Molybdenum Triple Bond. 11.[1] 1,1- and 1,2-Disubstituted Dimolybdenum Compounds of Formula $Mo_2X_2(CH_2SiMe_3)_4$ (M≡M). Observation of Rotation about the Triple Bond

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Received August 3, 1981

The preparation and characterization of a series of compounds of general formula $Mo_2X_2R_4$ (M≡M), where X = Br, Me, O-*i*-Pr, O-*t*-Bu, and NMe_2 and R = CH_2SiMe_3, are reported. The pattern of substitution may be 1,1-, $X_2RMo{\equiv}MoR_3$, or 1,2-, $XR_2Mo{\equiv}MoR_2X$, depending upon the nature of X and the preparative route. The 1,1- and 1,2-$Mo_2X_2R_4$ compounds do not isomerize, demonstrating the existence of a high kinetic barrier to R and X group transfer between molybdenum atoms. Alkyl group transfer may occur during the substitution reaction: 1,2-$Mo_2Br_2R_4$ and $LiNMe_2$ (2 equiv) yield 1,1-$Mo_2(NMe_2)_2R_4$, whereas 1,2-$Mo_2Br_2R_4$ and $HNMe_2$ yield 1,2-$Mo_2(NMe_2)_2R_4$. The formation of one isomer of $Mo_2(NMe_2)_2R_4$ must occur by kinetic control. Variable-temperature ^1H NMR spectra for 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ compounds provide the first observation of rotation about the Mo≡Mo bond. The energy barriers to rotation are reconcilable with steric restraints. By contrast, the barriers to rotations about Mo—N bonds in the 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ compounds are ΔG^* (kcal mol^{-1}) = 11.5 ± 0.5 and 15.0 ± 0.5, respectively, and the difference is correlated with electronic factors. The structure of 1,2-Mo_2(O-*t*-Bu)$_2R_4$, determined by a single-crystal X-ray diffraction study, revealed a staggered ethane-like (C_{2h}) *anti*-$Mo_2O_2C_4$ central skeleton with Mo—Mo = 2.209 (2) Å, Mo—O = 1.865 (8) Å, and Mo—C = 2.13 (1) and 2.14 (1) Å and internal angles Mo—Mo—O = 110.7 (3)° and Mo—Mo—C = 100.1 (5)° (averaged). Crystal data at −163 °C were a = 10.025 (3) Å, b = 18.473 (9) Å, c = 9.975 (5) Å, β = 102.03 (3)°, Z = 2, and d_{calcd} = 1.263 g cm^{-1} with space group $P2_1/n$. These new observations are discussed in the light of previous work.

Introduction

In the first paper of this series, the preparation and detailed characterization of $Mo_2(NMe_2)_6$ (M≡M) was reported.[2] This compound has since been the parent of an extensive family of others and affords an easy entry into the rich chemistry associated with the Mo≡Mo bond in Mo_2^{6+}-containing compounds.[3,4] Two views of the Mo_2-

(1) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *Inorg. Chem.* 1981, *20*, 2215.

(2) Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem. Soc.* 1976, *98*, 4469.

(3) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* 1978, *11*, 356.

(4) Chisholm, M. H. *Symp. Faraday Soc.* 1980, *No. 14*, 194.

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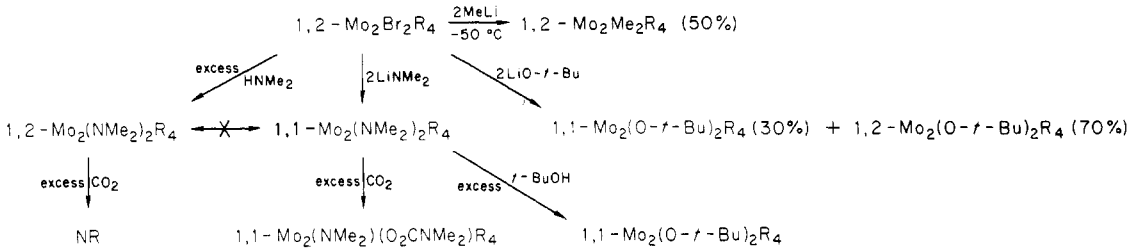
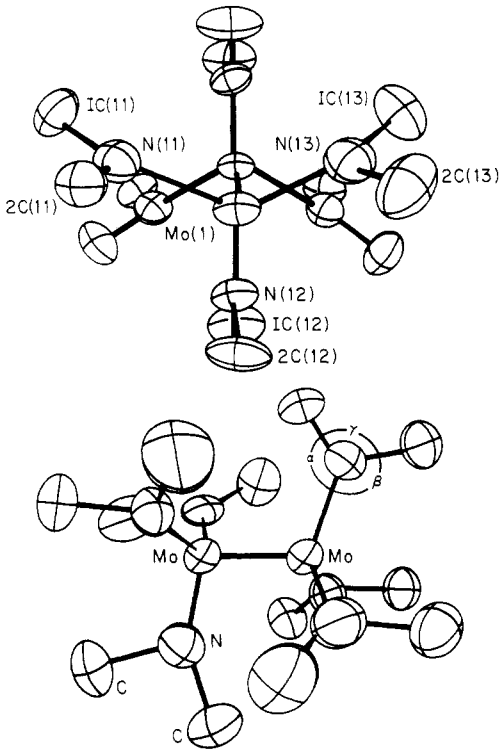
Scheme I



$1,1\text{-}Mo_2X_2R_4 = MoX_2R{\equiv}MoR_3$; $1,2\text{-}Mo_2X_2R_4 = MoXR_2{\equiv}MoXR_2$

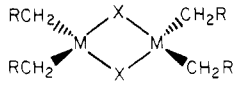
$(NMe_2)_6$ molecule are shown from which it can be seen that there are six proximal and six distal methyl groups.



On the ^1H NMR time scale, these interconvert slowly at low temperature (<−60 °C) and rapidly at high temperature (>+60 °C), and the observation of this phenomenon is heightened by the large diamagnetic anisotropy exerted by the Mo≡Mo bond. We attributed[2] this proximal ⇌ distal methyl exchange to rotations about the Mo—N bonds. Subsequently, the characterization of the related compounds $1,2\text{-}W_2Cl_2(NEt_2)_4$[5] and $1,2\text{-}W_2(Me)_2(NEt_2)_4$[6] supported this mechanism over seemingly all reasonable alternate mechanisms. Two questions which were raised in the discovery of $Mo_2(NMe_2)_6$ have, however, remained unanswered. (1) Is there rotation about the Mo≡Mo bond and what factors influence the barrier to rotation?[7] (2) Do NMe_2 groups pass between the directly bonded molybdenum atoms? This type of scrambling, which is so common in dinuclear and polynuclear carbonyl chemistry,[8] might seem eminently reasonable for $Mo_2(NMe_2)_6$, since bridging dialkylamido ligands are known, e.g., as in $Cr_2(O_2CNEt_2)_4(\mu\text{-}NEt_2)_2$.[9]

Further work led to the isolation and characterization of $1,2\text{-}M_2R_2(NR'_2)_4$ compounds, where R = alkyl, R′ = Me or Et, and M = Mo and W.[10] These compounds exist in solution as mixtures of anti and gauche rotamers and show activation barriers to anti ⇌ gauche isomerization in the range 21–25 kcal mol^{-1}, depending on the nature of R and R′.[11] The mechanism of this isomerization either could involve a direct rotation about the M≡M bond or could be achieved by an indirect route in which NR_2 groups were scrambled across the Mo≡Mo bond.

Being afflicted with this uncertainty, we resolved to synthesize related molecules for which these two processes would be distinguishable. Since the cogging effect of the interlocking NC_2 units in $M_2R_2(NMe_2)_4$ compounds could be responsible for hindering rotation about the Mo≡Mo bond, we set out to prepare related $Mo_2X_2(CH_2SiMe_3)_4$ compounds which would be less sterically encumbered and would have methylene protons placed as stereochemical probes adjacent to the central Mo≡Mo bond. For an ethane-like molecule, these methylene protons would have to be diastereotopic, but a fluxional process involving passage through an intermediate or transition state of the type shown below would cause the methylene protons to be equivalent.



We report work which was prompted by these considerations. Preliminary reports of some of this work have appeared.[12,13]

Results and Discussion

Preparation of $Mo_2X_2R_4$ Compounds (R = CH_2SiMe_3). The careful addition of anhydrous HBr (2 equiv) to a saturated solution of $Mo_2(CH_2SiMe_3)_6$[14] in hexane at −78 °C leads to the precipitation of crude $1,2\text{-}Mo_2Br_2R_4$ and the formation of Me_4Si. The analytically pure compound $1,2\text{-}Mo_2Br_2R_4$ can be obtained by room-

(5) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Millar, M.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4486.

(6) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2244.

(7) For a nonlinear molecule having a triple bond consisting of a σ bond and two equivalent π bonds, which is therefore cyclindrical; there should be no electrical barrier to rotation. For a detailed discussion of the Mo≡Mo bond in these molecules, see: Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.

(8) Adams, R. D.; Cotton, F. A. In "Dynamic Nuclear Resonance Spectroscopy", Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 489.

(9) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* **1978**, *17*, 3536.

(10) Chisholm, M. H.; Haitko, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 6784. Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *Ibid.* **1981**, *103*, 4046.

(11) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1976**, *98*, 6393.

(12) Chisholm, M. H.; Rothwell, I. P. *J. Am. Chem. Soc.* **1980**, *102*, 5950.

(13) Chisholm, M. H.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1980**, 985.

(14) Huq, F.; Mowat, W.; Shortland, A.; Shapski, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1071.

Table I. Analytical and Other Characterization Data for Compounds $Mo_2X_2(CH_2SiMe_3)_4$ [a]

compd	appearance	elemental analyses C found	C calcd	H found	H calcd	X found	X calcd
1,2-$Mo_2Br_2R_4$	orange needles	27.8	27.7	6.42	6.36	23.14 [b]	23.3
1,2-$Mo_2Me_2R_4$	brown crystals	37.9	37.7	8.83	9.01		
1,1-$Mo_2(NMe_2)_2R_4$	yellow liquid	38.2	37.9	8.98	8.42	4.46 [c]	4.57
1,2-$Mo_2(NMe_2)_2R_4$	yellow liquid	38.2	36.2	8.98	8.43	4.46 [c]	4.71
1,1′-$Mo_2(NMe_2)(O_2CNMe_2)R_4$	brown liquid	37.5	36.9	8.39	8.76	4.76 [c]	4.91
1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$	red crystals	40.9	39.8	9.08	8.94		

[a] All compounds, including 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ and 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2R_4$, for which elemental analyses were not obtained, gave molecular ions, $M_2X_2R_4^+$, in the mass spectrometer. [b] X = Br. [c] X = N.

temperature hexane extraction of this precipitate, followed by condensation of the solution and low-temperature crystallization. 1,2-$Mo_2Br_2R_4$ is only very sparingly soluble in hexane at low temperatures but is much more soluble in benzene and toluene. In the above procedure, any unreacted $Mo_2(CH_2SiMe_3)_6$ and the monobromo compound Mo_2BrR_5 (discussed later) remain in the mother liquid: only $Mo_2Br_2R_4$ and further bromo-substituted products are precipitated from the cold hexane solution and only 1,2-$Mo_2Br_2R_4$ dissolves in hexane at room temperature. We have not isolated any product of formula $Mo_2Br_xR_{6-x}$, where $x > 2$ as a hydrocarbon-soluble species. Related reactions involving anhydrous HCl (2 equiv) did not yield 1,2-$Mo_2Cl_2R_4$: only hexane-insoluble products and unreacted $Mo_2(CH_2SiMe_3)_6$ were recovered.

The bromide ligands in 1,2-$Mo_2Br_2R_4$ are labile to a number of metathetic reactions involving organolithium reagents, and some of these reactions and their products are summarized in Scheme I. Analytical data and other characteristics of the $Mo_2X_2R_4$ compounds are given in Table I. All the new compounds are air-sensitive and must be handled under dry and oxygen-free conditions. They are all soluble in hydrocarbon solvents and show molecular ions in the mass spectrometer. The calculated m/e distribution for the $Mo_2(NMe_2)_2R_4^+$ ion is shown in Figure 1. An identical m/e pattern was seen for both 1,1 and 1,2 isomers.

^{1}H NMR Studies. The substitution pattern 1,1- or 1,2- in $Mo_2X_2R_4$ compounds is readily deduced by ^{1}H NMR spectroscopy.[15] The compounds 1,2-$Mo_2X_2R_4$, where X = Me, O-*i*-Pr, O-*t*-Bu, and Br, show only one type of X group and one $SiMe_3$ resonance; the methylene protons which are diastereotopic appear as either an AB or AX spectrum. The chemical shift separation between the H_aH_b resonances increases in the order Me < O-*i*-Pr ~ O-*t*-Bu < Br, with the latter being ca. 4 ppm. The spectra are essentially temperature invariant in the range −50 to +90 °C at 220 MHz. These observations are interpretable in terms of either the existence of (i) only the anti rotamer, (ii) a rapidly (NMR time scale) interconverting mixture of anti and gauche rotamers, or (iii) a frozen out mixture of anti and gauche rotamers in which the methylene protons of the three R groups are accidentally magnetically degenerate. We are inclined to discount the last, since the shielding effects of the Mo≡Mo bond and the X group are so pronounced in all the other cases. By analogy with the $Mo_2X_2(NMe_2)_4$ compounds,[10] it is likely that in hydrocarbon solvents 1,2-$Mo_2X_2R_4$ compounds exist in the anti rotamer for X = Br ($\mu = 0$), while for X = Me, O-*i*-Pr, and O-*t*-Bu, a mixture of rapidly interconverting anti and gauche rotamers is present. By studies of the vibrational spectra and dipole moments, this point could have been

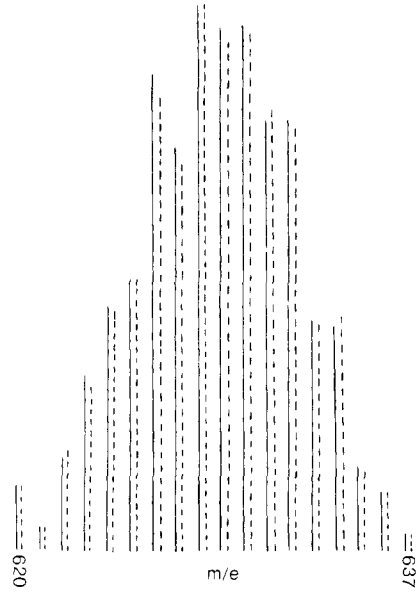


Figure 1. Observed (solid) vs. calculated (dotted) m/e distribution for the ion $Mo_2(NMe_2)_2(CH_2SiMe_3)_4^+$.

established, but, as is shown below, it was not a necessary step in establishing the dynamic properties of the class as a whole.

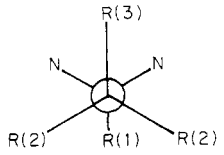
At −45 °C, 220 MHz in toluene-d_8, 1,2-$Mo_2(NMe_2)_4R_4$ shows two types of R groups in the integral ratio 1:1, each having diastereotopic methylene protons. There is only one type of NMe_2 group, though this gives rise to two singlets (1:1) assignable to proximal and distal methyl groups. Upon raising the temperature in toluene, the *N*-methyl resonances initially broaden, collapse into the base line, and sharpen to a singlet as rotations about the Mo—N bonds become fast on the NMR time scale. The resonances of the CH_2SiMe_3 groups show interesting changes with temperature, and at +95 °C, there is a single $SiMe_3$ resonance and an AB quartet for the methylene proton signals. The low-temperature spectrum is consistent with the presence of only the *gauche*-1,2-MoX_2R_2 isomer, while at high temperatures, rapid rotation about the Mo≡Mo bond leads to a time averaged spectrum akin to that expected for the *anti*-1,2-$Mo_2X_2R_4$ isomer. The threshold mechanism for rotation about the Mo≡Mo bond could be either gauche ⇌ gauche′ (enantiomerization) or gauche ⇌ anti ⇌ gauche. By analogy with R_2HSi—$SiHR_2$ molecules, the latter would seem more likely.[16] In any event, it is evident that a pairwise exchange of NMe_2 groups between the two molybdenum atoms of the type described in the Introduction is not occurring since this

(15) ^{1}H NMR spectra for 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$, 1,2-$Mo_2Br_2R_4$, and 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)R_4$ have been shown in ref 13 and 14.

(16) Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795 and references cited therein.

would generate a plane of molecular symmetry and cause the methylene protons to collapse to a single resonance.

The low-temperature ^{1}H NMR spectrum for 1,1-$Mo_2(NMe_2)_2R_4$ in toluene-d_8 at 220 MHz shows three $SiMe_3$ signals in the integral ratio 1:1:2. The methylene proton resonances appear as an AB quartet, [4 H], and two singlets, [2 H] and [2 H]. There are also two signals in the integral ratio 1:1 assignable to proximal and distal *N*-methyl groups. This is entirely in accord with the predictions based on a consideration of the Newman projection shown below for a 1,1-disubstituted ethane-like diamer.



The methylene carbons associated with R(1) and R(3) are contained in the plane of symmetry of the molecule, and thus, with free rotation about Mo—C and C—Si bonds (fast on the NMR time scale), the methylene protons of each group are equivalent but, of course, different from each other (R(1) ≠ R(2)). The methylene protons associated with R(2), on the other hand, are diastereotopic: irrespective of rotations about Mo—C and C—Si bonds, they are never equivalent.

Upon raising the temperature, the proximal and distal *N*-methyl resonances initially broaden, then collapse into the base line, and finally (>60 °C), reform to a sharp singlet as proximal ⇌ distal exchange becomes rapid due to rotation about the Mo—N bonds. With increasing temperature, one of the singlets of the methylene groups and the AB quartet broaden, collapse, and reform as a singlet. The high-temperature limiting spectrum at 100 °C, 220 MHz, thus shows one *N*-methyl resonance, [12 H], two singlets, [2 H]:[6 H], for the methylene protons, and two singlets for the $SiMe_3$ protons, [9 H]:[27 H]. These observations are *only* interpretable in terms of a temperature-dependent rate of rotation about the Mo≡Mo bond. At +100 °C, R(2) and R(3) are rapidly interconverting, but not exchanging with R(1). Indeed, the fact that 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ compounds do not isomerize to an equilibrium mixture indicates that alkyl group transfer across the Mo≡Mo bond does not occur to any significant extent below 100 °C. Thus, formation of bridged intermediates or transition states for $Mo_2(NMe_2)_2R_4$ compounds must have a high energy of activation.

A similar conclusion can be made for 1,1- and 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ compounds. The 1,1 compound is obtained by addition of *t*-BuOH to 1,1-$Mo_2(NMe_2)_2R_4$, while the 1,2 isomer can be obtained by crystallization of the 1,1 (30%) and 1,2 (70%) mixture of isomers obtained from the reaction between 1,2-$Mo_2Br_2R_4$ and LiO-*t*-Bu (2 equiv) in hexane. The ^{1}H NMR spectra of both of these isomers are consistent with rapid rotation about Mo≡Mo bonds.

It is thus evident that $Mo_2X_2R_4$ compounds, once formed, are kinetically inert to alkyl group transfer but that the mechanism of substitution at the dimetal center may proceed with kinetic control and induce alkyl group transfer, though we do not know which of the isomers is the thermodynamically more stable one.

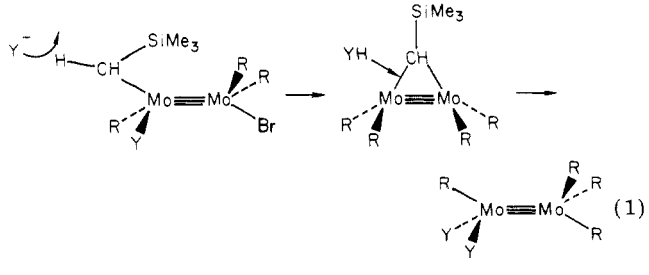
Partial Substitution Reactions. Addition of HBr (1 equiv) to $Mo_2(CH_2SiMe_3)_6$ leads to an essentially statistical mixture (1:2:1) of 1,2-$Mo_2Br_2R_4$, Mo_2BrR_5, and Mo_2R_6. The solubility of the monobromo product is so simlar to that of $Mo_2(CH_2SiMe_3)_6$ that we have been unable to separate the two. The ^{1}H NMR spectrum of the mixture leaves little doubt concerning the authenticity of Mo_2BrR_5 (see Experimental Section).

A ca. 1:2:1 mixture of 1,2-$Mo_2Br_2R_4$, $MoBrR_5$, and Mo_2R_6 was obtained from the reaction between 1,2-$Mo_2Br_2R_4$ and $LiCH_2SiMe_3$ (1 equiv) in hexane. However, 1,2-$Mo_2Br_2R_4$ and Mo_2R_6 do not react in toluene-d_8 (6 months at room temperature): no Mo_2BrR_5 was detected by ^{1}H NMR spectroscopy. Evidently, intermolecular alkyl-for-bromo group transfer does not occur, and in each of the reactions, (i) Mo_2R_6 + 2HBr and (ii) 1,2-$Mo_2Br_2R_4$ + 2LiR, the rates of the first and second substitutions are comparable.

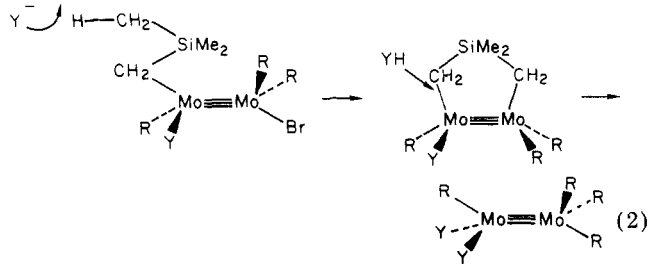
Similar observations were made in studies of the reaction between 1,2-$Mo_2Br_2R_4$ and MeLi (1 equiv). The compound 1,2-$Mo_2(Br)(Me)R_4$ was not separated from 1,2-$Mo_2Me_2R_4$ because of their similar solubilities, but ^{1}H NMR data leave little doubt concerning the existence of this compound.

In the reaction between 1,2-$Mo_2Br_2R_4$ and $LiNMe_2$ (2 equiv), which yields 1,1- (95%) and 1,2-$Mo_2(NMe_2)_2R_4$ (5%), alkyl transfer could occur with the first or second substitution. Attempts to follow the course of the reaction when only 1 equiv of $LiNMe_2$ was used were not very informative. Many species were present and this reaction could be complicated by the presence of trace quantities of free $HNMe_2$ (arising from unavoidable hydrolysis) which would catalyze Mo—Br and Mo—NMe_2 group scrambling. Consequently, we followed in detail the course of the reaction between 1,2-$Mo_2Br_2R_4$ and LiO-*t*-Bu which leads ultimately to mixture of 1,1- (30%) and 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ (70%).

The reaction between 1,2-$Mo_2Br_2R_4$ and LiO-*t*-Bu (1 equiv) proceeds slowly at room temperature in hexane or toluene to give 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)R_4$ which appears spectroscopically pure (see Figure 2). Evidently, an alkyl group transfer does not accompany the first O-*t*-Bu-for-Br substitution. Furthermore, the second substitution of Br by O-*t*-Bu must be significantly slower than the first: 1,2-$Mo_2Br_2R_4$ + LiO-*t*-Bu $\xrightarrow{k_1}$ 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)R_4$; 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)R_4$ + LiO-*t*-Bu $\xrightarrow{k_2}$ 1,1- + 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$; where $k_1 \gg k_2$. It is tempting to suggest that the difference in rates reflects steric congestion [$Mo_2Br(O\text{-}t\text{-}Bu)R_4$ > $Mo_2Br_2R_4$] and that as crowding increases, the organolithium reagent (LiO-*t*-Bu or $LiNMe_2$) acts as a base and promotes a net alkyl transfer by a reversible deprotonation of the CH_2SiMe_3 ligand. This could occur at either the α- or γ-carbon with the formation of either a bridging carbene or dimetallacycle intermediate as shown below in eq 1 and 2.[17]



(1)



(2)

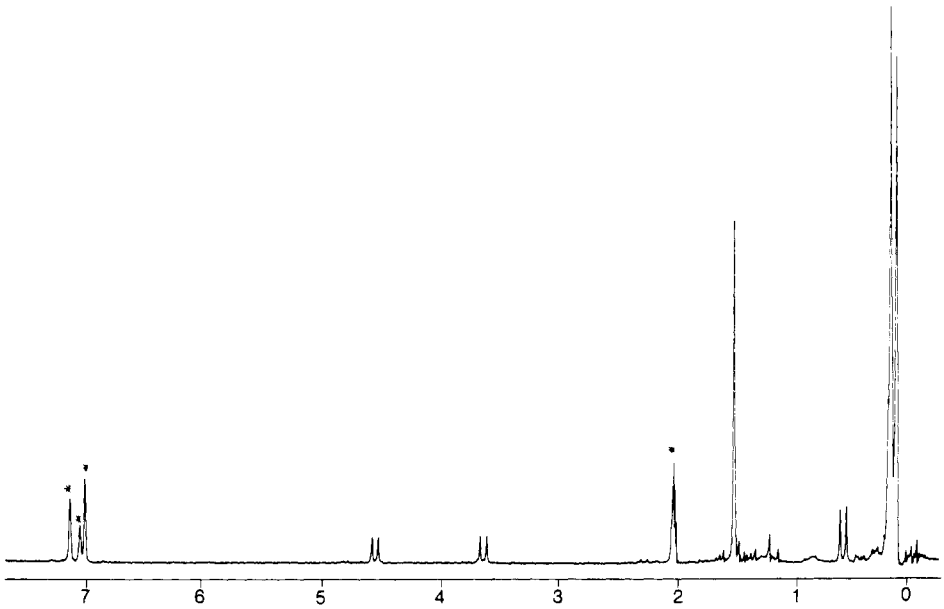


Figure 2. ^1H NMR spectrum of the crude hexane-soluble product from the reaction between 1,2-$Mo_2Br_2R_4$ and LiO-*t*-Bu (1 equiv) recorded at 220 MHz, 16 °C, in toluene-d_8 solvent. The methylene protons of the CH_2SiMe_3 groups appear as two AX spectra with the high-field doublets overlapping. The methyl signals of the O-*t*-Bu and CH_2SiMe_3 ligands appear as three singlets in the integral ratio 1:2:2 as expected for 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)(CH_2SiMe_3)_4$. The signals arising from protio impurities in the solvent are denoted by asterisks.

Table II. Rotational Barriers about M≡M and M—N Bonds[a]

compd (R = CH_2SiMe_3)	$\Delta G^{\ddagger}$, kcal mol^{-1} M≡M	$\Delta G^{\ddagger}$, kcal mol^{-1} M—N	ref
$Mo_2(NMe_2)_6$	not measurable	11.5 ± 0.5	*b*
$W_2(NMe_2)_6$	not measurable	11.2 ± 0.5	*c*
$Mo_2(NEt_2)_6$	not measurable	13.6 ± 0.5	*b*
anti-1,2-$Mo_2Cl_2(NMe_2)_4$	not observed, > 16 kcal mol	14.0 ± 0.5	*d*
1,2-$W_2Me_2(NEt_2)_4$	anti ⇌ gauche, 21 ± 1	(11-14)	*e*
1,2-$W_2R_2(NEt_2)_4$	anti ⇌ gauche, 24 ± 1	(11-14)	*f*
1,1-$Mo_2(NMe_2)_2R_4$	14.0 ± 1	10.3 ± 0.5	this work
1,2-$Mo_2(NMe_2)_2R_4$	15.6 ± 1	15.0 ± 0.5	this work
1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$	not observed, < 8		this work

[a] Estimates from coalescence temperature 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. [b] Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem Soc.* **1976**, *96*, 4469. [c] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Ibid.* **1976**, *96*, 4477. [d] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407. [e] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Millar, M.; Stults, B. R. *Ibid.* **1976**, *15*, 2244. [f] Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1976**, *98*, 6393.

However, neither of these mechanisms could account for the alkyl migration observed in the reaction between 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)R_4$ and *t*-BuOH, which leads to a mixture 1,1- and 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$.

Mo≡Mo and Mo—N Roational Barriers. Rotational barriers, calculated from the variable-temperature dependence of the ^1H NMR spectra, are given in Table II for the 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ compounds. For a nonlinear molecule having a cylindrical triple bond ($\sigma^2 + \pi^4$), there should be no electronic or quantum mechanical barrier to rotation. It is of significance, therefore, that of the $Mo_2X_2R_4$ compounds studied, only when X = NMe_2, have we observed a barrier to rotation in the range which is observable by NMR spectroscopy ($\Delta G^{\ddagger} > 8$ kcal mol^{-1}) and it is reasonable to assign the origin of the barrier to steric factors. The NC_2 units which are aligned along the axis introduce cogging between the two ends of the molecule. This is more pronounced for gauche 1,2-$Mo_2(NMe_2)_2R_4$ than for the 1,1 isomer, since the two NC_2 blades cannot allow a facile gauche–gauche′ (enantiomerization) rotation without a twisting or simultaneous rotation about Mo—N bonds. It is quite likely that this causes the slighlty higher activation to rotation about the Mo≡Mo bond in the 1,2 isomer.

Proximal ⇌ distal methyl exchange is quite significantly slower for the 1,2-$Mo_2(NMe_2)_2R_4$ isomer. One might initially be tempted to believe that this also correlates with the greater contact of the NC_2 units in the *gauche*-1,2-$Mo_2(NMe_2)_2R_4$ molecule. However, this idea falls into trouble when one recognizes that in $Mo_2(NMe_2)_6$, a molecule which has all six NC_2 blades meshed, the energy of activation is only 11 kcal mol^{-1}—as is found for the 1,1-$Mo_2(NMe_2)_2R_4$ isomer. Consequently, we believe that electronic factors must be responsible for the higher activation energy for the 1,2 isomer. As a result of forming three σ bonds and the Mo≡Mo bond, each molybdenum atom achieves only a 12 valence shell of electrons in $X_3Mo{\equiv}MoX_3$ compounds. This number falls short of satisfying the EAN rule and π donation from X is possible when X = NR_2 or OR, but not R. This ligand to metal π donation is favored when the NC_2 units are aligned along

(17) The compound $(Me_3SiCH_2)_2Mo(CH_2SiMe_2CH_2)Mo(PMe_3)_3$ (M≡M) has been isolated from the reaction between $Mo_2(OAc)_4$, Me_3SiCH_2MgCl, and PMe_3: Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

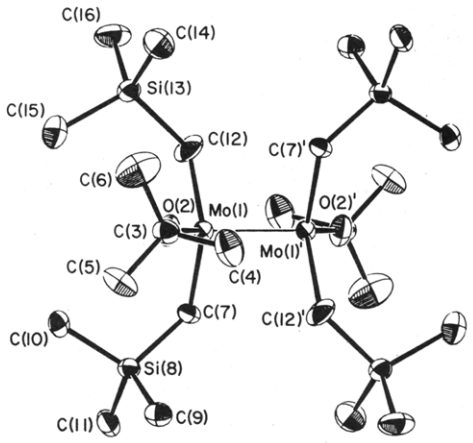


Figure 3. An ORTEP view of 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ molecule showing the atom numbering scheme used in the tables.

the Mo—Mo axis (defined as the z axis): the d_{xz} and d_{yz} atomic orbitals are used in forming the Mo—Mo π bonds, while one set of in-plane atomic orbitals (p_x, p_y) or ($d_{x^2-y^2}$, d_{xy}) is avaiable for receiving ligand π electrons. In this way in 1,1-$Mo_2(NMe_2)_2R_4$, one molybdenum atom attains a 16 valence shell of electrons, but in the 1,2 isomer, a 14 valence shell is all that is possible. Thus, ligand to metal π bonding is expected to be more important in each Mo—N bond in the 1,2 isomer than in the 1,1 isomer. This in turn yields a higher Mo—N rotational barrier for the 1,2 isomer. Within this line of reasoning, it should be noted that the Mo—O bond distances in 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ (see below) are shorter than in the related compounds $Mo_2(OCH_2CMe_3)_6$,[18] $Mo_2(OSiMe_3)_6(HNMe_2)_2$[19] and $Mo(O\text{-}t\text{-}Bu)_2(py)_2(CO)_2$, which have decreasing degrees of oxygen-to-molybdenum π bonding.

Solid-State Structure of 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$. An ORTEP view of the molecule giving the atom numbering scheme is shown in Figure 3 and a view of the molecule looking down the Mo—Mo axis, which clearly emphasizes the disposition of alkyl ligands, is shown in Figure 4. Final atomic coordinates and thermal parameters are given in Table III and IV, respectively. Complete listings of bond distances and angles are given in Table V and VI, respectively.

In the solid state, 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_2$ exists in the anti rotameric form and has a crystallographically imposed center of inversion. The Mo—Mo distance is 2.209 (2) Å, which is longer than in $Mo_2(CH_2SiMe_3)_6$ (2.169 (?) Å)[14] but shorter than that in $Mo_2(OCH_2CMe_3)_6$ (2.222 (2) Å).[18] The Mo—O distance, 1.865 (8) Å, is slighlty shorter than those in $Mo_2(OCH_2CMe_3)_6$[18] and $Mo_2(OSiMe_3)_6(HNMe_2)_2$[19] which, together with the obtuse Mo—O—C angle, 158.4 (7)°, is indicative of strong oxygen-to-molybdenum π bonding. The internal angles for the $Mo_2O_2C_4$ unit are similar to those in other ethane-like Mo_2^{6+}-containing compounds. The Mo—Mo—O angle (110.7 (3)°) and the Mo—Mo—C angles (100.0 (3)° and 100.2 (4)°) probably reflect the packing of the *tert*-butyl and trimethylsilyl groups which are proximal and distal to the Mo≡Mo bond, respectively.

Concluding Remarks. Rotation about the Mo≡Mo bond has been observed and rotational barriers appear very low (<8 kcal mol^{-1}) in the absence of dialkylamide ligands, consistent with the view that the origin of the barrier is steric and not electronic.

1,1- and 1,2-$Mo_2X_2R_4$ compounds do not isomerize readily which implies a high barrier to alkyl group migration across the Mo≡Mo bond. Bridged $Mo_2X_2R_4$ compounds must be relatively high-energy species, probably because the required rehybridization of metal atomic orbitals would involve a significant disruption of the Mo≡Mo bond. The threshold mechanism for anti ⇌ gauche isomerization in 1,2-$Mo_2X_2(NMe_2)_4$ compounds is, by inference, one of Mo≡Mo rotation.

The formation of 1,1-$Mo_2X_2R_4$ compounds from 1,2-$Mo_2X'_2R_4$ starting materials, and vice versa, which is seen

Table III. Fractional Coordinates for the 1,2-$Mo_2(C\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ Molecule[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	5311 (1)	359.8 (5)	895 (1)	15
O(2)	6903 (9)	860 (5)	790 (8)	30
C(3)	8049 (12)	1098 (6)	228 (13)	25
C(4)	7875 (16)	871 (8)	−1257 (16)	43
C(5)	8110 (14)	1925 (7)	278 (16)	37
C(6)	9327 (15)	833 (11)	1204 (18)	53
C(7)	3525 (11)	1012 (6)	691 (11)	19
Si(8)	3730 (3)	1998 (2)	884 (3)	19
C(9)	4094 (12)	2394 (6)	−708 (12)	24
C(10)	5145 (12)	2196 (6)	2364 (11)	22
C(11)	2121 (13)	2418 (6)	1199 (13)	27
C(12)	5477 (13)	−409 (7)	2520 (14)	34
Si(13)	7070 (3)	−386 (2)	391 (3)	22
C(14)	8584 (14)	−791 (8)	3331 (15)	35
C(15)	7453 (14)	572 (8)	4540 (14)	35
C(16)	6768 (15)	−939 (8)	5355 (14)	39

atom	10^3x	10^3y	10^3z	$10B_{iso}$, Å^2
H(1)	706	108	−178	53
H(2)	863	103	−161	53
H(3)	782	36	−132	53
H(4)	823	208	120	47
H(5)	885	209	−10	47
H(6)	728	212	−24	47
H(7)	930	32	128	63
H(8)	1011	97	86	63
H(9)	938	104	208	63
H(10)	299	92	−20	29
H(11)	305	85	136	29
H(12)	490	218	−89	34
H(13)	335	230	−145	34
H(14)	421	290	−60	34
H(15)	494	200	317	32
H(16)	597	199	221	32
H(17)	525	271	247	32
H(18)	224	293	129	37
H(19)	139	231	45	37
H(20)	192	223	202	37
H(21)	472	−34	294	44
H(22)	542	−88	212	44
H(23)	840	−128	309	45
H(24)	874	−53	256	45
H(25)	937	−76	405	45
H(26)	825	58	524	45
H(27)	759	87	380	45
H(28)	671	76	489	45
H(29)	602	−75	569	50
H(30)	657	−142	505	50
H(31)	756	−93	607	50

[a] The isotropic thermal parameter listed for those atoms refined anisotropically are the isotropic equivalent. Numbers in parentheses in this and all following tables refer to the error in the least significant digits. Estimated standard deviations greater than 29 are not statistically significant but are left "unrounded", since the tables are all produced automatically by the X-TEL interactive programs.

(18) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *J. Am. Chem. Soc.* **1977**, *99*, 1652; *Inorg. Chem.* **1977**, *16*, 1801.
(19) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153.
(20) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7615.

Table IV. Anisotropic Thermal Parameters for the 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ Molecule[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	22 (1)	18 (1)	18 (1)	−0.1 (4)	6.5 (4)	0.5 (4)
O(2)	46 (5)	39 (5)	28 (5)	−14 (4)	3 (4)	−4 (4)
C(3)	31 (7)	26 (6)	38 (7)	−2 (5)	6 (5)	5 (5)
C(4)	64 (10)	50 (9)	55 (9)	−1 (8)	24 (8)	−14 (8)
C(5)	49 (8)	25 (7)	71 (10)	5 (6)	24 (8)	2 (7)
C(6)	38 (8)	100 (14)	66 (11)	10 (9)	16 (8)	20 (10)
C(7)	29 (6)	20 (6)	23 (6)	5 (5)	10 (5)	3 (5)
Si(8)	28 (2)	22 (2)	23 (2)	3 (1)	5 (1)	2 (1)
C(9)	31 (6)	26 (6)	36 (7)	−2 (5)	9 (5)	6 (5)
C(10)	36 (7)	29 (6)	21 (6)	−0 (5)	13 (5)	−4 (5)
C(11)	50 (8)	24 (6)	31 (7)	0 (6)	13 (6)	−3 (5)
C(12)	31 (7)	47 (8)	42 (8)	−7 (6)	−17 (6)	5 (7)
Si(13)	31 (2)	29 (2)	23 (2)	3 (1)	5 (1)	2 (1)
C(14)	43 (8)	43 (8)	52 (9)	4 (6)	17 (7)	−1 (7)
C(15)	41 (8)	49 (8)	39 (8)	−7 (6)	2 (6)	−9 (6)
C(16)	61 (8)	48 (9)	42 (8)	19 (7)	13 (7)	20 (7)

[a] The form of the exponent is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}lc^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. All U's are $\times 10^3$.

Table V. Bond Distances for the 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ Molecule

A	B	dist
Mo(1)	Mo(1)	2.209 (2)
Mo(1)	O(2)	1.865 (8)
Mo(1)	C(7)	2.133 (11)
Mo(1)	C(12)	2.135 (14)
Si(8)	C(7)	1.838 (11)
Si(8)	C(9)	1.852 (12)
Si(8)	C(10)	1.858 (12)
Si(8)	C(11)	1.875 (13)
Si(13)	C(12)	1.891 (13)
Si(13)	C(14)	1.893 (13)
Si(13)	C(15)	1.888 (14)
Si(13)	C(16)	1.833 (13)
O(2)	C(3)	1.449 (14)
C(3)	C(4)	1.514 (19)
C(3)	C(5)	1.528 (17)
C(3)	C(6)	1.520 (19)

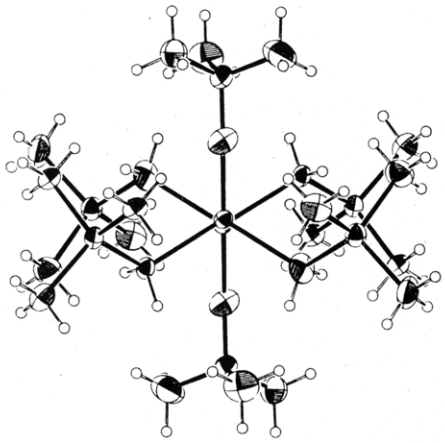


Figure 4. An ORTEP view of the 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ molecule looking down the Mo≡Mo bond.

in certain reactions, shows that alkyl transfer can occur during the substitution reaction at the dimetal center. Further studies of the substitutional behavior of these $(Mo{\equiv}Mo)^{6+}$-containing compounds are warranted and will be undertaken.

Experimental Section

General procedures[1] and the preparation of $Mo_2(CH_2SiMe_3)_6$[14] have been described.

Preparation of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$. To a solution of $Mo_2(CH_2SiMe_3)_6$ (1.95 g) in hexane (25 mL), frozen at −198 °C (1. N_2), was added anhydrous HBr (5.5 mmol, 2 equiv) by use of a calibrated vacuum manifold. Upon being slowly warmed, the initially clear yellow solution darkened and, at temperatures between −50 and −20 °C, a pale brown precipitate formed. This was collected by filtration. The toluene-soluble solids were extracted (50 mL), and the filtrate was reduced in volume to ca. 20 mL and cooled to −15 °C in the refrigerator of the Dri-Lab, yielding orange crystals. These were collected by filtration and dried in vacuo: 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$, 1.5 g (80% yield based on Mo).

Table VI. Bond Angles (Deg) for the 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ Molecule

A	B	C	angle
Mo(1)′	Mo(1)	O(2)	110.7 (3)
Mo(1)′	Mo(1)	C(7)	100.0 (3)
Mo(1)′	Mo(1)	C(12)	100.2 (4)
O(2)	Mo(1)	C(7)	115.2 (4)
O(2)	Mo(1)	C(12)	116.1 (4)
C(7)	Mo(1)	C(12)	112.3 (5)
C(7)	Si(8)	C(9)	109.8 (5)
C(7)	Si(8)	C(10)	109.2 (5)
C(7)	Si(8)	C(11)	110.3 (5)
C(9)	Si(8)	C(10)	110.4 (5)
C(9)	Si(8)	C(11)	108.1 (5)
C(10)	Si(8)	C(11)	109.1 (5)
C(12)	Si(13)	C(14)	111.7 (7)
C(12)	Si(13)	C(15)	110.2 (6)
C(12)	Si(13)	C(16)	108.3 (7)
C(14)	Si(13)	C(15)	110.5 (6)
C(14)	Si(13)	C(16)	107.2 (6)
C(15)	Si(13)	C(16)	108.8 (7)
Mo(1)	O(2)	C(3)	158.4 (7)
O(2)	C(3)	C(4)	110.8 (10)
O(2)	C(3)	C(5)	108.7 (10)
O(2)	C(3)	C(6)	106.5 (10)
C(4)	C(3)	C(5)	107.7 (11)
C(4)	C(3)	C(6)	116.6 (12)
C(5)	C(3)	C(6)	106.2 (12)
Mo(1)	C(7)	Si(8)	118.5 (6)
Mo(1)	C(12)	Si(13)	117.8 (6)

Under similar conditions, addition of 1 equiv of HBr followed by stripping the solvent and toluene extraction gave an orange solution which, based on ^1H NMR spectroscopy, was a 1:2:1 mixture of 1,2-$Mo_2Br_2R_4$, Mo_2BrR_5, and Mo_2R_6. (NMR data is given later.) By careful crystallizations of this mixture in hexane at −15 °C, 1,2-$Mo_2Br_2R_4$ was removed, but the compounds Mo_2BrR_5 and Mo_2R_6 were inseparable by crystallization.

Addition of 1,2-$Mo_2Br_2R_4$ to a toluene solution of $LiCH_2SiMe_3$ (1 equiv) at −78 °C led to a hexane soluble extract which was indistinguishable by ^1H NMR spectroscopy from the 1:2:1 mixture of $Mo_2Br_2R_4$, Mo_2BrR_5, and Mo_2R_6 prepared in the above manner.

Reaction of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ with $LiNMe_2$. Addition of $Mo_2Br_2R_4$ (0.56 g) to a suspension of $LiNMe_2$ (0.1 g, >2 equiv) in hexane (25 mL) at −50 °C led to a suspension of reagents which mostly went into solution upon warming to 0 °C over 2 h. The solution was filtered to remove finely divided LiCl and unreacted

$LiNMe_2$; the filtrate was collected and the solvent was stripped to yield a yellow liquid, which by ^1H NMR spectroscopy was identified as predominantly 1,1-$Mo_2(NMe_2)_2R_4$ (95%) with an NMR detectable impurity (5%) of the 1,2-$Mo_2(NMe_2)_2R_4$ isomer.

Preparation of 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$. To a suspension of 1,2-$Mo_2Br_2R_4$ (0.517 g), in pentane (20 mL), was added $HNMe_2$ (ca. 10 equiv) by use of a calibrated vacuum manifold. This led to the rapid precipitation of $H_2NMe_2^+Br^-$ and a clear solution. Filtration, followed by stripping the solvent, gave a yellow liquid which was identified as 1,2-$Mo_2(NMe_2)_2R_4$ by ^1H NMR spectroscopy. The elemental analyses obtained on the yellow liquid are slightly high in nitrogen and low in carbon, a fact which probably reflects some contamination by $H_2NMe_2^+Br^-$. The dimolybdenum compounds are volatile, and purification by vacuum distillation would presumably be possible. However, this was not undertaken since samples prepared in the above manner appeared spectroscopically pure (^1H NMR).

Preparation of 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$. Addition of bone-dry CO_2, by use of a vacuum manifold, to a hexane solution of 1,1-$Mo_2(NMe_2)_2R_4$ (plus its ca. 5% impurity of 1,2-$Mo_2(NMe_2)_2R_4$) led to an immediate reaction with the formation of 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)R_4$ which was obtained as a yellow-brown liquid upon stripping the solvent. The ^1H NMR spectrum revealed the pattern of substitution, and furthermore, that the impurity of the 1,2-$Mo_2(NMe_2)_2R_4$ isomer remained unreacted.

These observations were confirmed in experiments carried out in NMR tubes: the 1,2-$Mo_2(NMe_2)_2R_4$ compound does not react with CO_2 (<5 atm) at temperatures below +80 °C.

Reaction of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ with LiO-*t*-Bu. (a) A mixture of 1,2-$Mo_2Br_2R_4$ (0.417 g) and LiO-*t*-Bu (0.106 g, 2.2 equiv) was placed in a round-bottomed flask. Hexane (40 mL) was added, and the suspension was stirred for 5 h to give a red solution and gray solids. The solids were removed by filtration, and the filtrate was collected. Stripping the solvent yielded red microcrystalline solids which were identified by ^1H NMR spectroscopy as 70:30 mixture of 1,2- and 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$. Crystallization of this mixture from cold pentane solutions (−15 °C) gave deep red crystals of the isomerically pure 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ compound. This compound sublimes at 80 °C (10^{-4} torr) with little decomposition and without detectable isomerization.

(b) To a suspension of 1,2-$Mo_2Br_2R_4$ (0.5 g) in hexane (40 mL) was added LiO-*t*-Bu (0.06 g, 1 equiv), and the reaction mixture was stirred for 1 h. The solvent was then stripped to give a red solid which was identified by ^1H NMR spectroscopy as 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)R_4$. Addition of a further equivalent of LiO-*t*-Bu to this solid dissolved in hexane (20 mL) gave, after 4 h, a mixture of 1,2- and 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$, indistinguishable from that in a above.

(c) Small scale reactions were carried out in sealed NMR tubes to monitor with time the reaction between LiO-*t*-Bu and 1,2-$Mo_2Br_2R_4$. These showed the initial, relatively fast, formation of 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)R_4$, followed by formation of the 70:30 mixture of 1,2- and 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$.

Reaction of 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ with *t*-BuOH. A large excess of *t*-BuOH in benzene (azeotrope) was added to a solution of 1,1-$Mo_2(NMe_2)_2R_4$ (ca. 0.4 g) in hexane (10 mL). The solution was stirred for 12 h, and then the solvent was stripped to give a red solid which was identified by ^1H NMR spectroscopy as 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ contaminated with ca. 5% of 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R$, which presumably arose from the ca. 5% impurity of the 1,2-$Mo_2(NMe_2)_2R_4$ isomer in the sample of 1,1-$Mo_2(NMe_2)_2R_4$. The red solid sublimed at 80 °C (10^{-4} torr) with little decomposition and no apparent isomerization.

Neither the 1,1-, nor the 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$ compounds reacted with CO_2 nor was isomerization observed in the presence of excess LiO-*t*-Bu or *t*-BuOH.

Reaction of 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$ with *t*-BuOH. Addition of an excess of *t*-BuOH in benzene (azeotrope) to a hexane solution of 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)R_4$ yielded a red solution within 0.5 h. Stripping the solvent yielded red solids which, by ^1H NMR spectroscopy, were determined to be an ca. 4:1 mixture of 1,2- and 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2R_4$, respectively.

^1H NMR Data. ^1H NMR data for the compounds 1,2-$Mo_2X_2(CH_2SiMe_3)_4$ recorded in toluene-d_8 at 220 MHz and 16 °C. (a) X = Br: 1.49 4.76 (d), 0.73 (d, J = 11.1 Hz); $\delta(SiMe_3)$ 0.22. (b) X = CH_3: $\delta(Mo\text{–}CH_3)$ 1.49 (s); $\delta(Mo\text{–}CH_2)$ 1.11 (d), 2.69 (d, J = 11.8 Hz); $\delta(SiMe_3)$ 0.20 (s). (c) X = O-*i*-Pr: $\delta(OCH)$ 5.36; $\delta(OCHMe_2)$ 1.45 (d, J = 6.5 Hz); $\delta(Mo\text{–}CH_2)$ 3.63 (d), 0.01 (d, J = 12.0 Hz); $\delta(SiMe_3)$ 0.21 (s). (d) X = O-*t*-Bu: $\delta(OCMe_3)$ 1.54 (s); $\delta(Mo\text{–}CH_2)$ 3.55 (d), 0.03 (d, J = 12.0 Hz); $\delta(SiMe_3)$ 0.20 (s). (e) X = NMe_2 at −35 °C: $\delta(NMe_2)$ 3.57 (s, proximal), 2.55 (s, distal); $\delta(Mo\text{–}CH_2)$ −0.25 (d), 3.45 (d, J = 11.0 Hz), 1.52 (d), 1.66 (d, J = 11.0 Hz); $\delta(SiMe_3)$ 0.17 (s), 0.23 (s).

^1H NMR data for $Mo_2Br(CH_2SiMe_3)_5$ obtained at 220 MHz, 16 °C in toluene-d_8: $(Me_3SiCH_2)_2BrMo$, $\delta(CH_2)$ 4.56 (d), 0.66 (d, J = 11.5 Hz); $\delta(SiMe_3)$ 0.34 (s); $Mo(CH_2SiMe_3)_3$, $\delta(CH_2)$ 2.00 (s); $\delta(SiMe_3)$ 0.26 (s).

^1H NMR data for 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ obtained at 220 MHz, −42 °C in toluene-d_8: δ (NMe_2) 3.07 (br s); $\delta(Mo\text{–}CH_2)$ 1.37 (s), 1.52 (s), 1.67 (d), 2.24 (d, J = 11.2 Hz); $\delta(SiMe_3)$ 0.21 (s), 0.25 (s), 0.27 (s).

^1H NMR data for 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$ obtained at 220 MHz, 16 °C in toluene-d_8: $\delta(O\text{-}t\text{-}Bu)$ 1.39 (s); $\delta(Mo\text{–}Ch_2)$ 1.94 (s, intensity 6 H), 2.33 (s, intensity 2 H); $\delta(SiMe_3)$ 0.25 (s).

^1H NMR data for 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$ obtained at 220 MHz, 16 °C in toluene-d_8: $\delta(NMe_2)$ 3.80 (s, proximal), 2.81 (s, distal); $\delta(O_2CNMe_2)$ 2.58 (s); $\delta(Mo\text{–}CH_2)$ 2.18 (d), 1.65 (d, J = 11.0 Hz);, 1.61 (d), 1.42 (d, J = 12.1 Hz); $\delta(SiMe_3)$ 0.13 (s), 0.19 (s).

^1H NMR data for 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)(CH_2SiMe_3)_4$ obtained at 220 MHz, 16 °C in toluene-d_8: $\delta(O\text{-}t\text{-}Bu)$ 1.62 (s); $(Me_3SiCH_2)_2BrMo$, $\delta(CH_2)$ 4.60 (d), 0.75 (d, J = 11.5 Hz); $\delta(SiMe_3)$ 0.22 (s); $(Me_3SiCH_2)_2(O\text{-}t\text{-}Bu)Mo$, $\delta(CH_2)$ 3.72 (d), 0.75 (d, J = 11.5 Hz); $\delta(SiMe_3)$ 0.19 (s).

^1H NMR data for 1,2-$Mo_2MeBr(CH_2SiMe_3)_4$ obtained at 220 MHz, 16 °C in toluene-d_8: $\delta(Mo\text{–}CH_3)$ 1.49 s; $(Me_3SiCH_2)_2BrMo$, $\delta(CH_2)$ 4.22 (d), 0.91 (d, J = 11.0 Hz); $\delta(SiMe_3)$ 0.21 (s); $(Me_3SiCH_2)_2MeMo$, $\delta(CH_2)$ 2.82 (d), 1.21 (d, J = 12.0 Hz); $\delta(SiMe_3)$ 0.20 (s).

X-ray Structural Determination for 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$. General procedures were described previously.[21]

An orange crystal of dimensions 0.21 × 0.21 × 0.19 mm was selected and transferred to the cold stream of the goniostat under an atmosphere of dry nitrogen. The cell dimensions obtained from 31 reflections at −163 °C with Mo Kα (λ = 0.71069 Å) were a = 10.025 (3) Å, b = 18.473 (9) Å, c = 9.975 (5) Å, β = 102.03 (3)°, Z = 2, and d_{calcd} = 1.263 g cm^{-3} with space group P_{21}/n.

A total number of 4057 reflections were collected by using standard moving-crystal moving-detector techniques with the following values: scan speed = 3.0 deg min^{-1}; scan width = 2.0 + dispersion; single background time at extremes of scan = 4 s; aperture size = 3.0 × 4.0 mm. The limits of data collection were 6° < 2θ < 50°. Of the 4057 reflections, 3189 were unique, and the number of $F > 2.33\sigma(F)$ was 2715.

The structure was solved by a combination of direct methods and Fourier techniques. All nonhydrogen atoms were located and refined by full-matrix least-squares using anisotropic thermal parameters. The final R was 0.083 for 2620 reflections having $F > 3\sigma(F)$. The hydrogen atoms were included as fixed atoms in calculated positions, each having an isotropic B equivalent to that of the parent C atom plus 1. An isotropic extinction parameter was included in the refinement: the final value was 1.878 × 10 exp(−6). No absorption correction was performed.

The maximum peak height in the final Difference map was 2.1 e/Å^3. The peaks could not be interpreted in terms of a solvent molecule or disorder. We are unable to account for the rather high value of R. Attempts at changing the weighting scheme by changing the uncertainty factor did not improve the refinement. We did note that R was fairly independent of sin θ and dependent of the magnitude of F: R increased with decreasing values of F. The overall R for 3190 reflections was 0.093.

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Registry No. 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$, 75059-90-4; 1,2-$Mo_2Me_2(CH_2SiMe_3)_4$, 75059-91-5; 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, 75059-94-8; 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, 76599-13-8; 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$, 76716-47-7; 1,2-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$, 75059-93-7; 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2(CH_2SiMe_3)_4$, 75059-92-6; $Mo_2Br(CH_2SiMe_3)_5$, 79172-46-6; 1,1-$Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$, 75059-95-9; 1,2-$Mo_2Br(O\text{-}t\text{-}Bu)(CH_2SiMe_3)_4$, 79172-47-7; 1,2-$Mo_2MeBr(CH_2SiMe_3)_4$, 79172-75-1; $Mo_2(CH_2SiMe_3)_6$, 34439-17-3.

Supplementary Material Available: A listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 8024, is available in microfiche form only, from the Indiana University Library.

Unsaturated (π-Allyl)nickel Halide Complexes. Reactions To Produce Dienes

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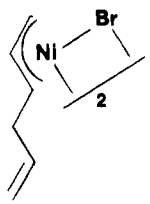
The (π-allyl)nickel halide complexes of 1-bromohexa-2,5-diene (1), 1-bromopenta-2,4-diene (2), 1-bromohexa-2,4-diene (3), and 2-(bromomethyl)-1,3-butadiene (4) were prepared from either nickel carbonyl or bis(cyclooctadiene)nickel and were characterized. The nonconjugated (π-1-(2-propenyl)allyl)nickel halide complex 1 reacted cleanly with iodobenzene, β-bromostyrene, cinnamyl bromide, iodocyclohexane, iodohexane, o-bromobenzamide, and o-bromoaniline to replace the halogen with the 1,4-hexadienyl group. The complexes from 1-bromopenta-2,4-diene (2) and 1-bromohexa-2,4-diene (3) were considerably less useful, reacting only with the very reactive substrates iodobenzene, cinnamyl bromide, and β-bromostyrene. The complex from 2-(bromomethyl)-1,3-butadiene (4) was used to synthesize myrcene, β-farnesene, and tagetol.

(π-Allyl)nickel halide complexes are easily prepared from the reaction of allylic halides with either nickel carbonyl or bis(cyclooctadiene)nickel in a nonpolar solvent such as benzene. The complexes are usually deep red crystalline, air-sensitive solids that can be stored in the absence of air for at least several years. In polar solvents such as DMF, they are generally reactive toward a wide range of organic halides, reacting to replace the halide in the substrate with the allyl group originally on nickel.[1] Under more severe conditions, some (π-allyl)nickel halide complexes react with ketones or aldehydes to produce homoallylic alcohols.[2] In relation to ongoing studies directed toward the synthesis of heterocycles by palladium-catalyzed cyclizations of amino olefins,[3-6] a number of diene-containing substrates were required. Although a number of new methods for the introduction of pentadienyl and hexadienyl groups into organic substrates have been recently reported,[7-9] none offered viable approaches to the desired substrates. Thus, we synthesized four new (π-allyl)nickel halide complexes containing an additional double bond and studied their reactions with organic halides and carbonyl compounds.

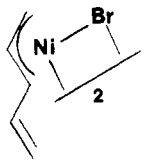
Results and Discussion

Preparation of (π-Allyl)nickel Halide Complexes

Complex 1 was prepared in 76% isolated yield on a 10-g



1



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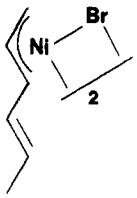

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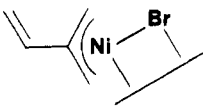

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scale by the reaction of a mixture of 1-bromo-2,5-hexadiene and 3-bromo-1,5-hexadiene with nickel carbonyl in benzene at 70 °C. This stable red crystalline solid was a typical (π-allyl)nickel halide complex in both its physical and chemical characteristics. In that regard, complex 1 is similar to other nonconjugated, unsaturated (π-allyl)nickel halide complexes such as those containing π-geranyl ligands.[10]

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