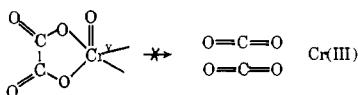


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- (59) J. Roček and F. H. Westheimer, *J. Am. Chem. Soc.*, **84**, 2241 (1962).  
 (60) The photochemical decomposition of the compound has not yet been investigated.

(61) The stability of the oxalatochromium(V) complex<sup>30</sup> is particularly striking



since this complex would be expected to undergo a very facile decomposition into carbon dioxide and chromium(III).

- (62) These values are the greater of the two estimates of the standard deviation calculated from the e.d.s. of the individual values averaged or from their deviations from that average.  
 (63) See, for example, J. Trotter, Ed., "Structure Reports", Vol. 38A and 39A, published for the International Union of Crystallography by Oosthoek, Scheltema, and Holkema, Utrecht, 1974 and 1975.  
 (64) R. Stomberg et al., *Ark. Kemi*, **22**, 29 (1964); **24**, 111 (1965); *Acta Chem. Scand.*, **22**, 1439 (1968).  
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## The Molybdenum–Molybdenum Triple Bond. 3. A Triple Bond between Two Four-Coordinated Molybdenum(III) Atoms. Structural Characterization of the Bis(dimethylamine) Adduct of Dimolybdenum Hexatrimethylsiloxide

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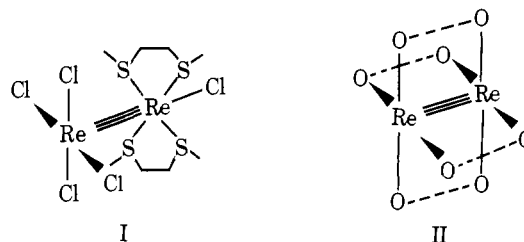
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**Abstract:** The crystal and molecular structures of the compound  $\text{Mo}_2(\text{OSiMe}_3)_6 \cdot 2\text{NHMe}_2$  are reported. The molecule has a nonbridged structure,  $(\text{Me}_3\text{SiO})_3(\text{Me}_2\text{HN})\text{MoMo}(\text{Me}_2\text{HN})(\text{OSiMe}_3)_3$ , with an Mo–Mo distance of 2.242 (1) Å, a mean Mo–O distance (average of six) of  $1.95 \pm 0.02$  Å, and a mean Mo–N distance (average of two) of  $2.282 \pm 0.004$  Å. The rotational conformation is intermediate between eclipsed and staggered, but closer to the latter. The compound crystallizes in the space group  $C2/c$  with unit cell dimensions of  $a = 40.016$  (5),  $b = 11.497$  (1),  $c = 18.829$  (2) Å,  $\beta = 98.65$  (1)°, and  $V = 8564$  (2) Å<sup>3</sup>. The structure was solved and refined to  $R_1 = 0.056$  and  $R_2 = 0.085$  using 3529 independent reflections having  $I > 3\sigma(I)$ . This compound is thus shown to provide the first proven example of a molecule containing two four-coordinate metal atoms triply bonded to each other, without any bridging groups, that is obtained by the reversible addition of two ligands to a triply bonded  $\text{M}_2\text{X}_6$  molecule. The Mo–Mo distance is only slightly longer than that in the alkoxide  $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$ , 2.222 Å, but considerably longer than typical Mo–Mo quadruple bonds, 2.09–2.15 Å.

### Introduction

In the now well-established chemistry of transition metal compounds containing multiple bonds between metal atoms,<sup>2</sup> especially triple and quadruple bonds, the most common structural pattern<sup>3</sup> is such that with quadruple bonds each metal atom is four coordinated while with triple bonds, the metal atoms are three coordinated. Thus, in the former case, the most typical sorts of species have been  $\text{X}_4\text{M}-\text{MX}_4^{n-}$ ,  $\text{M}_2(\text{O}_2\text{CR})_4$ ,  $\text{M}_2(\text{SO}_4)_4^{n-}$ , or  $\text{M}_2(\text{O}_2\text{CR})_4\text{L}_2$ , while in the case of triple bonds the predominant structure type has been  $\text{L}_3\text{M}-\text{ML}_3$ . There are, of course, exceptions to the above generalizations. Those pertinent to this discussion are cases in which a triple bond exists between metal atoms each bonded to four ligand atoms.

The first such case,  $\text{Re}_2\text{Cl}_5(\text{MeSCH}_2\text{CH}_2\text{SMe})_2$  (I), was reported as long ago as 1966<sup>4</sup> (and actually constitutes the first reported example of *any* triple bond between transition metal atoms). The rotational configuration here is staggered, as expected when there is no  $\delta$  bond to favor the eclipsed configuration. Very recently the situation represented schematically in II has been found to occur<sup>5</sup> in the compound  $\text{La}_4(\text{Re}_2)\text{O}_{10}$ ; in this case the configuration is eclipsed (overall symmetry  $D_{4h}$ ) because this arrangement is imposed by the crystal



structure in its entirety. In both of these cases, the Re–Re bonds are triple bonds in the simplest sense of that term, namely, in having three pairs of electrons involved primarily in metal–metal interaction and an electron configuration we can represent as  $\sigma^2\pi^4$ .

For tetrakis(2,6-dimethoxyphenyl)divanadium<sup>6</sup> a structure in which each of the two vanadium atoms, which are triply bonded to each other, is coordinated by two carbon atoms and two oxygen atoms has been suggested.<sup>6</sup> However, it has been found that this structure, though plausible, is incorrect. In fact, there is a V–V triple bond ( $d_{V-V} = 2.198$  Å) but the arrangement of the ligands is more complicated.<sup>7</sup>

There are also the molecules of the type  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ <sup>8,9</sup> for which an SCF– $X\alpha$ –SW calculation<sup>10</sup> indicates a  $\sigma^2\pi^4\delta^2\delta^*2$

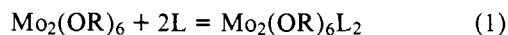
**Table I.** Positional and Thermal Parameters and Their Estimated Standard Deviations<sup>a</sup>

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mo1	0.153 35 (2)	0.157 36 (8)	0.035 37 (4)	0.000 40 (1)	0.004 75 (7)	0.001 89 (2)	-0.000 08 (4)	0.000 17 (2)	-0.000 03 (8)
Mo2	0.096 73 (2)	0.159 70 (8)	0.011 46 (4)	0.000 41 (1)	0.004 77 (7)	0.001 76 (2)	-0.000 04 (4)	0.000 19 (2)	-0.000 06 (8)
Si1	0.168 42 (8)	0.4137 (3)	-0.0514 (2)	0.000 69 (2)	0.0064 (3)	0.0036 (1)	-0.0008 (1)	0.00070 (9)	0.0016 (3)
Si2	0.195 46 (8)	0.2824 (3)	0.1788 (2)	0.000 63 (2)	0.0096 (3)	0.0025 (1)	-0.0006 (2)	-0.000 01 (8)	-0.0022 (3)
Si3	0.176 92 (9)	-0.1212 (3)	0.1099 (2)	0.000 77 (3)	0.0059 (3)	0.0041 (1)	0.0010 (1)	0.000 06 (10)	0.0022 (3)
Si4	0.068 80 (8)	0.3731 (3)	0.1240 (2)	0.000 70 (2)	0.0074 (3)	0.0030 (1)	0.0008 (1)	0.000 83 (8)	-0.0016 (3)
Si5	0.057 25 (8)	0.2976 (3)	-0.1304 (2)	0.000 58 (2)	0.0101 (3)	0.0026 (1)	0.0007 (2)	-0.000 08 (8)	0.0025 (3)
Si6	0.073 99 (8)	-0.1064 (3)	-0.0808 (2)	0.000 73 (3)	0.0063 (3)	0.0034 (1)	-0.0013 (1)	0.000 44 (9)	-0.0027 (3)
O1	0.1676 (2)	0.2836 (6)	-0.0202 (3)	3.6 (1)					
O2	0.1617 (2)	0.2374 (6)	0.1276 (3)	3.8 (1)					
O3	0.1616 (2)	-0.0013 (6)	0.0744 (3)	3.7 (1)					
O4	0.0822 (2)	0.2729 (6)	0.0757 (3)	3.7 (1)					
O5	0.0893 (2)	0.2554 (6)	-0.0743 (3)	3.5 (1)					
O6	0.0870 (2)	0.0100 (6)	-0.0395 (3)	3.8 (1)					
N1	0.1614 (2)	0.0544 (7)	-0.0644 (4)	3.4 (2)					
N2	0.0902 (2)	0.0377 (7)	0.1037 (4)	3.3 (2)					
C1	0.1387 (3)	0.505 (1)	-0.0090 (7)	7.0 (3)					
C2	0.2124 (3)	0.471 (1)	-0.0287 (7)	6.4 (3)					
C3	0.1570 (3)	0.414 (1)	-0.1535 (7)	6.6 (3)					
C4	0.2348 (3)	0.224 (1)	0.1485 (7)	7.0 (3)					
C5	0.1935 (3)	0.231 (1)	0.2745 (7)	7.3 (4)					
C6	0.1967 (4)	0.446 (1)	0.1808 (7)	7.0 (3)					
C7	0.1425 (4)	-0.217 (1)	0.1352 (8)	9.0 (4)					
C8	0.1988 (4)	-0.210 (1)	0.0466 (7)	7.9 (4)					
C9	0.2064 (4)	-0.089 (1)	0.1945 (8)	9.2 (4)					
C10	0.0345 (4)	0.317 (1)	0.1711 (8)	7.8 (4)					
C11	0.1045 (4)	0.425 (1)	0.1939 (8)	8.6 (4)					
C12	0.0500 (4)	0.493 (2)	0.680 (8)	9.8 (5)					
C13	0.0551 (3)	0.462 (1)	-0.1360 (7)	6.8 (3)					
C14	0.0167 (4)	0.242 (1)	-0.1015 (7)	7.2 (4)					
C15	0.0600 (3)	0.241 (1)	-0.2222 (7)	6.7 (3)					
C16	0.0412 (3)	-0.068 (1)	-0.1616 (7)	7.3 (4)					
C17	0.1083 (3)	-0.183 (1)	-0.1177 (7)	6.5 (3)					
C18	0.0563 (4)	-0.210 (1)	-0.0232 (7)	8.0 (4)					
C19	0.1452 (3)	0.098 (1)	-0.1398 (6)	4.8 (3)					
C20	0.1992 (3)	0.046 (1)	-0.0644 (6)	5.3 (3)					
C21	0.1065 (3)	0.068 (1)	0.1803 (6)	4.4 (2)					
C22	0.0533 (3)	0.014 (1)	0.1023 (6)	5.4 (3)					

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

electronic configuration. In these cases, though five electron pairs are concerned in the M-M interaction, the bond is effectively a triple one because the  $\delta$  contribution is nullified by the presence of a pair of electrons in the  $\delta^*$  orbital. The rotational configuration remains eclipsed for steric reasons.<sup>9</sup>

To this short list of examples of the  $L_4M-ML_4$  triple bond type of compound, we now add another. We think that this one may be of special significance because of the simple and potentially general manner in which it can be prepared. We have previously reported<sup>11</sup> that for  $R = Me_3Si$  and  $Me_3CCH_2$  and  $L = NH_3$ ,  $MeNH_2$ ,  $Me_2NH$ ,  $Me_3N$ , and  $Me_2PhP$  the following equilibrium lies well to the right:



In each of the two cases where  $L = Me_2NH$  and  $R$  is one of those mentioned, the adducts were isolated as red or purple crystalline solids, and their H and <sup>13</sup>C NMR spectra were recorded at both high and low temperatures. However, it was not possible to infer the molecular structures from such data, nor even to make the critical choice between bridged or nonbridged types of structure. We have therefore conducted an x-ray crystallographic study of the purple compound  $Mo_2(OSiMe_3)_6(Me_2NH)_2$ , the results of which are reported here. The tungsten analogue of this compound is also known.<sup>12</sup> As implied by the introductory discussion, this compound has been found to have an  $(RO)_3LM-ML(OR)_3$  triple bond type of structure.

## Experimental Section

The compound was prepared as previously described.<sup>11</sup> A crystal that appeared bluish-black in color and measured about  $0.2 \times 0.3 \times 0.6$  mm was used to collect data. Since the compound is very sensitive to air and moisture, and its decomposition, once begun, appears to be autocatalytic, all crystals examined were promptly wedged into thin-walled glass capillaries and sealed under nitrogen. Several of these underwent decomposition before the one used was reached. This one was shown to be of good quality by  $\omega$  scans of several intense low-angle reflections which had peak widths at half heights of ca.  $0.2^\circ$ .

Lattice constants and the orientation matrix used for data collection were obtained from the least-squares refinement of diffractometer settings for 15 intense reflections having  $24^\circ < 2\theta(\text{Mo K}\alpha) < 35^\circ$ . The unit cell dimensions are  $a = 40.016$  (5),  $b = 11.497$  (1),  $c = 18.829$  (2) Å,  $\beta = 98.65$  (1)°, and  $V = 8564$  (2) Å<sup>3</sup>. From the lattice constants and axial photographs it was concluded that the crystal belongs to the monoclinic system.

Data were collected at  $22 \pm 2^\circ\text{C}$  using a Syntex P1 autodiffractometer, with graphite monochromatized Mo K $\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique. Variable scan rates of 6-24°/min were used to collect a shell of data having  $0^\circ < 2\theta(\text{Mo K}\alpha) < 25^\circ$ . The crystal diffracted quite well and since we were concerned lest the crystal decompose during data collection, higher angle data,  $25^\circ \leq 2\theta(\text{Mo K}\alpha) < 45^\circ$ , were collected at a constant scan speed of 8°/min. The scan ranges were from Mo K $\alpha_1 - 1.0^\circ$  to Mo K $\alpha_2 + 1.0^\circ$ . The systematic absences, namely,  $hkl$  ( $h + k = 2n + 1$ ) and  $h0l$  ( $l = 2n + 1$ ), indicated the space group to be either  $Cc$  (no. 9) or  $C2/c$  (no. 15).

A total of 6036 reflections having  $2\theta(\text{Mo K}\alpha) < 45.00^\circ$  were collected. The intensities of three standard reflections were monitored

**Table II.** Bond Distances (Å)<sup>a</sup> in  $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$ 

Atoms	Distance	Atoms	Distance
Mo(1)–Mo(2)	2.242 (1)	Si(3)–C(7)	1.88 (1)
–O(1)	1.925 (5)	–C(8)	1.88 (1)
–O(2)	1.949 (5)	–C(9)	1.87 (1)
–O(3)	1.976 (5)	Si(4)–O(4)	1.608 (5)
–N(1)	2.285 (6)	–C(10)	1.86 (1)
Mo(2)–O(4)	1.926 (5)	–C(11)	1.89 (1)
–O(5)	1.940 (5)	–C(12)	1.83 (1)
–O(6)	1.981 (5)	Si(5)–O(5)	1.609 (5)
–N(2)	2.278 (6)	–C(13)	1.90 (1)
Si(1)–O(1)	1.610 (5)	–C(14)	1.90 (1)
–C(1)	1.86 (1)	–C(15)	1.86 (1)
–C(2)	1.87 (1)	Si(6)–O(6)	1.595 (5)
–C(3)	1.91 (1)	–C(16)	1.91 (1)
Si(2)–O(2)	1.623 (5)	–C(17)	1.85 (1)
–C(4)	1.88 (1)	–C(18)	1.82 (1)
–C(5)	1.91 (1)	N(1)–C(19)	1.55 (1)
–C(6)	1.88 (1)	–C(20)	1.52 (1)
Si(3)–O(3)	1.612 (5)	N(2)–C(21)	1.53 (1)
		–C(22)	1.50 (1)

<sup>a</sup> Figures in parentheses are the estimated standard deviations in the least significant digits. Atoms are labeled as in Figure 1.

frequently and showed an essentially linear decrease. The extent of decomposition at the end of data collection was 25%. The data were reduced<sup>13</sup> to a set of relative  $|F|^2$  values. After corrections were made for crystal decay, weak and systematically absent reflections and non-unique data were rejected. The 3529 reflections having  $I > 3\sigma(I)$  were used in subsequent structure solution and least-squares refinement.

**Structure Solution and Refinement.**<sup>13</sup> The three-dimensional Patterson function was consistent with the space group  $C2/c$  and yielded the positions of the two crystallographically distinct molybdenum atoms. The successful solution and refinement of the entire structure verifies the above choice of space group. The remaining 36 nonhydrogen atoms were located by the usual succession of least-squares refinement and difference Fourier maps. Least-squares refinement of the positional and isotropic thermal parameters yielded discrepancy indices of

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.072$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.106$$

The function minimized during least-squares refinement was  $\Sigma w(|F_o| - |F_c|)^2$  where  $w$  was the weighting factor. A value of 0.07 was used for the  $p$  in the calculation of the weights.<sup>13</sup>

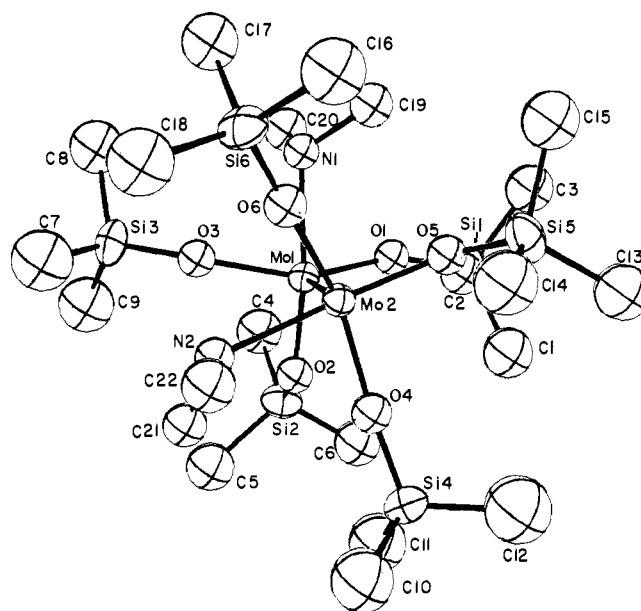
The structure was then refined to convergence using anisotropic thermal parameters for the tungsten and silicon atoms while retaining isotropic thermal parameters for the remaining atoms. The final discrepancy indices were  $R_1 = 0.056$  and  $R_2 = 0.085$  and the estimated standard deviation of an observation of unit weight was 1.830. During the final refinement cycle no parameter shifted by more than  $0.05\sigma$ . A final difference Fourier map yielded no peaks of chemical significance.

A listing of the observed and the final calculated structure factors is available as supplementary material.

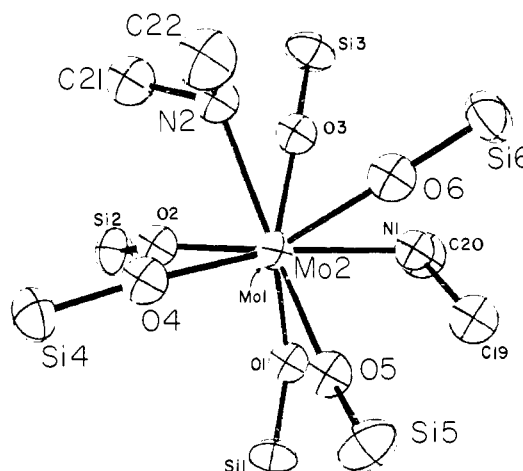
## Results

The final positional and thermal parameters are listed in Table I. The entire structure is depicted in Figure 1, where the atom numbering scheme is defined. Figure 2 is a view of only the more central atoms looking straight down the Mo–Mo axis. The bond distances and bond angles are listed in Tables II and III, respectively.

The dimensions of ligands are all reasonable and require little comment. For example, the mean Si–C distance is  $1.88 \pm 0.02$  Å and the mean Si–O distance is  $1.61 \pm 0.01$  Å, both of which are entirely typical values.<sup>14</sup> There is an interesting pattern in the Mo–O–Si bond angles, although its significance is not evident. For the two siloxy ligands that are trans to



**Figure 1.** An ORTEP projection of the entire  $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$  structure. Each atom is represented by its ellipsoid of thermal vibration, and the atom numbering scheme is defined.



**Figure 2.** An ORTEP view of the  $\text{Mo}_2(\text{OSi})_6(\text{NC}_2)_2$  portion of  $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$  looking directly down the Mo–Mo bond with Mo(1) eclipsed by Mo(2). Atoms labeled in smaller print are bonded to Mo(1). All atoms are represented by 50% probability ellipsoids.

Mo–N bonds the angles are  $135 \pm 1^\circ$  whereas for the other four the angles are much greater, ranging from  $157^\circ$  to  $176^\circ$ . There is, however, no corresponding pattern in the Mo–O distances.

Although the molecular structure does not possess any crystallographically imposed symmetry, the two halves of the molecule are very similar and are approximately related by a twofold rotation axis perpendicularly bisecting the Mo–Mo bond. This is particularly evident in Figure 2, where the axis would bisect the angle between the projection of the Mo–N bonds. It is also clear that the orientations of the  $\text{NC}_2$  groups, which are essentially equivalent, make C(20) and C(22) distinctly distal and C(19) and C(21) proximal with respect to the Mo–Mo bond.

It may also be seen in Figure 2 that the rotational conformation is far from eclipsed as in quadruply bonded species (e.g.,  $\text{Mo}_2\text{Cl}_8^{4-}$  or  $\text{Mo}_2\text{Me}_8^{4-}$ ) but at the same time not fully staggered. Doubtless there is a complex interplay of many nonbonded repulsions (and perhaps attractions) and, of course,

**Table III.** Bond Angles (deg)<sup>a</sup> in Mo<sub>2</sub>(OSiMe<sub>3</sub>)<sub>6</sub>(HNMe<sub>2</sub>)<sub>2</sub>

Atoms	Angle	Atoms	Angle
Mo(2)-Mo(1)-O(1)	104.8 (2)	O(1)-Si(1)-C(3)	110.8 (4)
-O(2)	101.9 (2)	C(1)-Si(1)-C(2)	110.2 (5)
-O(3)	101.1 (1)	-C(3)	111.1 (5)
-N(1)	96.0 (2)	C(2)-Si(1)-C(3)	107.8 (4)
Mo(1)-Mo(2)-O(4)	105.9 (2)	O(2)-Si(2)-C(4)	111.6 (4)
-O(5)	101.4 (2)	-C(5)	108.3 (4)
-O(6)	101.9 (2)	-C(6)	110.4 (4)
-N(2)	93.9 (2)	C(4)-Si(2)-C(5)	109.5 (5)
O(1)-Mo(1)-O(2)	95.9 (2)	-C(6)	109.9 (5)
-O(3)	148.4 (2)	C(5)-Si(2)-C(6)	107.2 (5)
-N(1)	81.6 (2)	O(3)-Si(3)-C(7)	111.0 (5)
O(2)-Mo(1)-O(3)	96.2 (2)	-C(8)	112.7 (4)
-N(1)	162.0 (2)	-C(9)	109.5 (4)
O(3)-Mo(1)-N(1)	78.0 (2)	C(7)-Si(3)-C(8)	105.9 (5)
O(4)-Mo(2)-O(5)	96.7 (2)	-C(9)	107.0 (6)
-O(6)	146.7 (2)	C(8)-Si(3)-C(9)	110.6 (5)
-N(2)	81.8 (2)	O(4)-Si(4)-C(10)	110.7 (4)
O(5)-Mo(2)-O(6)	95.5 (2)	-C(11)	109.8 (4)
-N(2)	164.4 (2)	-C(12)	110.9 (4)
O(6)-Mo(2)-N(2)	78.3 (2)	C(10)-Si(4)-C(11)	108.2 (5)
Mo(1)-O(1)-Si(1)	157.4 (3)	-C(12)	105.6 (6)
Mo(1)-O(2)-Si(2)	134.1 (3)	C(11)-Si(4)-C(12)	111.5 (6)
Mo(1)-O(3)-Si(3)	167.3 (3)	O(5)-Si(5)-C(13)	111.3 (4)
Mo(2)-O(4)-Si(4)	175.6 (3)	-C(14)	110.0 (4)
Mo(2)-O(5)-Si(5)	136.4 (3)	-C(15)	110.5 (4)
Mo(2)-O(6)-Si(6)	172.5 (3)	C(13)-Si(5)-C(14)	108.5 (5)
Mo(1)-N(1)-C(19)	119.7 (5)	-C(15)	107.7 (5)
-C(20)	107.4 (5)	C(14)-Si(5)-C(15)	108.7 (5)
C(19)-N(1)-C(20)	107.5 (6)	O(6)-Si(6)-C(16)	109.3 (4)
Mo(2)-N(2)-C(21)	119.9 (5)	-C(17)	112.1 (4)
-C(22)	108.9 (5)	-C(18)	112.5 (4)
C(21)-N(2)-C(22)	109.7 (6)	C(16)-Si(6)-C(17)	105.7 (5)
O(1)-Si(1)-C(1)	108.6 (4)	-C(18)	110.1 (5)
-C(2)	108.3 (4)	C(17)-Si(6)-C(18)	106.9 (5)

<sup>a</sup> Figures in parentheses are estimated standard deviations in the least significant digits. Atoms are labeled as in Figure 1.

in the crystalline substance intermolecular forces may also have an influence. The fact that the O-Mo-O angles are larger (mean 96.1°) than the O-Mo-N angles (80.0°) means that no entirely objective definition of staggered is possible without some arbitrariness. The important point, however, is that the conformation is decidedly not eclipsed.

There is another noteworthy, though again not easily interpretable, pattern in the Mo-Mo-ligand angles. The Mo-Mo-O angles are all relatively large, being in the range 101-106° (comparable to the Mo-Mo-X angles in quadruply bonded Mo<sub>2</sub>X<sub>8</sub><sup>4-</sup> species), while the Mo-Mo-N angles here are 93.9 and 96.0°.

Finally, we have here an Mo-Mo distance that is slightly longer than any previously observed for an Mo<sub>2</sub>X<sub>6</sub> or Mo<sub>2</sub>X<sub>4</sub>Y<sub>2</sub> type compound containing an Mo-Mo triple bond. The previously reported distances are 2.167 Å in Mo<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>6</sub>,<sup>15</sup> 2.201 Å in Mo<sub>2</sub>Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>,<sup>16</sup> 2.214 Å in Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>,<sup>17</sup> and 2.222 Å in Mo<sub>2</sub>(OCH<sub>2</sub>CMe<sub>3</sub>)<sub>6</sub>.<sup>11</sup>

## Discussion

This x-ray study resolves completely the previous uncertainty concerning the structures of the adducts formed reversibly according to eq 1. Contrary to our speculative suggestion,<sup>11</sup> they do not contain bridging groups. It is to be noted that the structure we find is entirely consistent with the NMR data.<sup>11</sup> At -60 °C both the <sup>1</sup>H and <sup>13</sup>C spectra showed that there are two kinds of OSiMe<sub>3</sub> groups. While this is in accord with a bridged structure, (Me<sub>2</sub>HN)(Me<sub>3</sub>SiO)<sub>2</sub>-Mo(μ-Me<sub>3</sub>SiO)<sub>2</sub>Mo(OSiMe<sub>3</sub>)<sub>2</sub>(NHMe<sub>2</sub>), as previously noted, it is also in accord with the structure we have found in the crystal. We consider it reasonable to believe that the molecular

structure found in the crystal persists in solution, and that the two types of OSiMe<sub>3</sub> groups, present in a 2:1 ratio, are those cis and trans to the NHMe<sub>2</sub> groups. It was also observed that at 38 °C all the OSiMe<sub>3</sub> groups become equivalent. We do not know the mechanism for that process.

In view of the fact that a bridged structure is not now tenable, we are again in search of a rationale for the fact that while Mo<sub>2</sub>(OSiMe<sub>3</sub>)<sub>6</sub> readily adds amines such as NHMe<sub>2</sub> the isosteric Mo<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>6</sub> does not. It is, of course, a slight exaggeration to say that OSiMe<sub>3</sub> and CH<sub>2</sub>SiMe<sub>3</sub> are literally "isosteric" but they are sufficiently similar that one is reluctant to believe that the two compounds differ primarily for steric reasons. It seems much more likely that an electronic difference is the controlling factor. While we are not prepared to suggest a specific electronic argument, it is pertinent to note that there is a remarkably large difference in the Mo-Mo bond lengths for the two compounds. These distances, quoted above, differ by 0.055 Å. We also recall that the Mo-Mo distance in the adduct reported here is still longer than that found in the alkoxide, Mo<sub>2</sub>(OCH<sub>2</sub>CMe<sub>3</sub>)<sub>6</sub>, by 0.020 Å. Thus, if adduct formation requires some weakening of the Mo-Mo bond, then the shortest and presumably strongest of these bonds, in Mo<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>6</sub>, may offer enough resistance to this that adduct formation is precluded.

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**Supplementary Material Available:** A listing of the observed and the final calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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## Diastereotopic Groups in Silyllithium and Germyllithium Compounds. Slow Inversion about Silicon and Germanium

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**Abstract:** Diisopropylphenylsilyllithium (**1**), dibenzylphenylsilyllithium (**2**), and diisopropylphenylgermyllithium (**3**) have been prepared by the reaction of lithium with the corresponding disilane or digermane. The methyls in the isopropyl groups of **1** and **3** are diastereotopic and anisochronous at room temperature in a wide range of solvents. The benzyl protons in **2** are accidentally isochronous even at 270 MHz. The isopropyl methyl groups remain anisochronous in both the silyl (**1**) and the germyl (**3**) systems as the temperature is raised to 185 °C in diglyme. Because the <sup>7</sup>Li resonances of **1** and **3** are very similar to that of diisopropylphenylcarbonyllithium (**5**), the ionicities of the Si-Li and Ge-Li bonds cannot be greatly different from that of the C-Li bond. A lower limit to inversion about trivalent silicon and germanium can therefore be set at about 24 kcal/mol.

Barriers have been measured for pyramidal inversion about carbon, nitrogen, oxygen, phosphorus, sulfur, arsenic, and selenium.<sup>2</sup> In the group 4 series, formal trivalency (required for pyramidal inversion) is found in negatively charged species, such as carbanions. Such materials are prone to aggregation,<sup>3</sup> although exchange out of the aggregate is probably fast on the NMR time scale.<sup>4</sup> Bimolecular ligand exchange is possible within the aggregate, so that higher order processes other than unimolecular pyramidal inversion might bring about spectral equivalence.<sup>3</sup> Before inversion can take place, it is necessary for the partially covalent bond between the metal and the central atom to break. Thus the process of inversion can involve up to three steps, exchange out of the aggregate, cleavage of the metal-X covalent bond, and pyramidal inversion.<sup>5</sup> If spectral changes are observed that can be attributed to pyramidal inversion, further experiments would be necessary to specify which of these three steps is rate determining.

In the present paper, we are considering the inversion properties of silicon and germanium. By analogy with phosphines and arsines,<sup>2</sup> it is to be expected that pyramidal inversion about trivalent silicon and germanium is slow on the NMR time scale. The slowness of inversion, however, has never been demonstrated by experiment. Thus it is possible that, although unimolecular inversion is indeed slow, bimolecular exchange within an aggregate rapidly inverts Si and Ge configuration. The only information on the subject is an LCAO-MO-SCF

calculation on SiH<sub>3</sub><sup>-</sup>, which gave a barrier of 39.6 kcal/mol.<sup>6</sup> This figure of course refers to a gas phase-like operation, so that the effects of aggregation are not considered.

The two most common methods for studying inversion barriers are temperature variation of the NMR spectrum and loss of optical activity.<sup>2</sup> Although in principle it is possible to follow the racemization or epimerization of a silyl or germyl anion, in practice these processes can also occur during the formation of the anion. If the inversion process were to be followed by quenching the anion, e.g., with CO<sub>2</sub>, the quenching reaction must be stereospecific, its stereochemistry must be known, and the optical purity of the quenching product must be determinable. The dynamic NMR experiment suffers from none of these limitations, since in its usual form, it only requires the exchange of diastereotopic groups via the inversion process. In order to determine the configurational stability of silyl or germyl anions, we have chosen the DNMR method as the more likely to yield interpretable results.

For the silyl or germyl anion to have sufficient stability, it must be tertiary and possess at least one aromatic substituent. One or both of the remaining substituents must possess groups that are diastereotopic when atomic inversion is slow. Interconversion of these groups would serve as the monitor on the inversion process. The aromatic substituent also would lower the barrier slightly.<sup>2</sup> The systems diisopropylphenylsilyllithium, C<sub>6</sub>H<sub>5</sub>(*i*-Pr)<sub>2</sub>SiLi (**1**), and dibenzylphenylsilyllithium, C<sub>6</sub>H<sub>5</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SiLi (**2**), possess these structural require-