

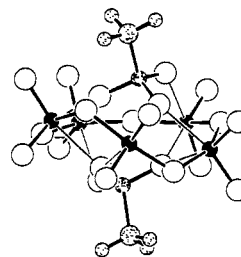
from the  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> structure by removal of W<sub>3</sub>O<sub>6</sub><sup>6+</sup> units from the top of **14** and **15**, respectively, shown in Scheme II. The  $\beta$ -A-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> isomer, **18**, is derived from the  $\beta$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> structure in a similar fashion.<sup>44</sup> The three isomers shown in Scheme III can all be interconverted by reorientation of the PO<sub>4</sub><sup>3-</sup> unit within the W<sub>9</sub>O<sub>30</sub><sup>6-</sup> framework. The  $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> isomer (**16**) is converted to the  $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> isomer (**17**) by rotation of the PO<sub>4</sub><sup>3-</sup> unit 90° about any one of its local C<sub>2</sub> axes (cf. Scheme II). The  $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> isomer (**16**) is converted to the  $\beta$ -A-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> isomer (**18**) by rotation of the PO<sub>4</sub><sup>3-</sup> unit 60° about the anion's C<sub>3</sub> axis. Note that the PO<sub>4</sub><sup>3-</sup> units in PW<sub>9</sub>O<sub>34</sub><sup>6-</sup> isomers, in contrast to the PO<sub>4</sub><sup>3-</sup> unit in the  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> anion, are no longer encapsulated within cages and are therefore relatively mobile. The processes shown in Scheme III are likely to be observable under the appropriate experimental conditions, and we believe that they provide a mechanistic basis for the PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> transformations described by Finke et al.<sup>45</sup> and Knoth et al.<sup>46</sup>

**Generalizations: (MO<sub>3</sub>)<sub>n</sub> Ring Inversion.** The present study has provided detailed evidence for rapid intramolecular Mo<sub>6</sub>O<sub>18</sub> ring inversion in C<sub>6</sub>H<sub>5</sub>AsMo<sub>7</sub>O<sub>25</sub><sup>4-</sup>. Numerous other compounds containing larger or smaller M<sub>n</sub>O<sub>3n</sub> ring subunits are known that might undergo similar rearrangements.<sup>47</sup> As representative species, we have selected the (CH<sub>3</sub>)<sub>2</sub>AsMo<sub>4</sub>O<sub>15</sub>H<sup>2-</sup>,<sup>32,48,49</sup> and (C<sub>6</sub>H<sub>5</sub>P)<sub>2</sub>W<sub>5</sub>O<sub>21</sub><sup>4-</sup><sup>50</sup> anions.

The C<sub>2v</sub> (CH<sub>3</sub>)<sub>2</sub>AsMo<sub>4</sub>O<sub>15</sub>H<sup>2-</sup> anion, **19**, contains (CH<sub>3</sub>)<sub>2</sub>AsO<sub>2</sub><sup>-</sup> and OH<sup>-</sup> subunits connected by weak bonds to opposite sides of an Mo<sub>4</sub>O<sub>12</sub> ring and can be structurally formulated {[(CH<sub>3</sub>)<sub>2</sub>AsO<sub>2</sub><sup>-</sup>](Mo<sub>4</sub>O<sub>12</sub>)(OH<sup>-</sup>)} see Scheme IV). The Mo<sub>4</sub>O<sub>12</sub> ring subunit is puckered and could undergo ring inversion if the inversion were synchronized with a 90° rotation of the (CH<sub>3</sub>)<sub>2</sub>AsO<sub>2</sub><sup>-</sup>

unit about the anion's C<sub>2</sub> axis. This degenerate isomerization exchanges the sites of the OMo<sub>2</sub> bridging oxygens labeled O<sub>A</sub> and O<sub>B</sub> in Scheme IV. Ring inversion, if it occurs, is relatively slow, however, since the <sup>17</sup>O NMR spectrum of (CH<sub>3</sub>)<sub>2</sub>AsMo<sub>4</sub>O<sub>15</sub>H<sup>2-</sup> at 80 °C shows two well-resolved resonances for OMo<sub>2</sub> oxygens.<sup>9</sup>

The (C<sub>6</sub>H<sub>5</sub>P)<sub>2</sub>W<sub>5</sub>O<sub>21</sub><sup>4-</sup> anion contains two C<sub>6</sub>H<sub>5</sub>PO<sub>3</sub><sup>2-</sup> subunits connected by weak bonds to opposite sides of a W<sub>5</sub>O<sub>15</sub> ring and can be structurally formulated [(C<sub>6</sub>H<sub>5</sub>PO<sub>3</sub><sup>2-</sup>)<sub>2</sub>(W<sub>5</sub>O<sub>15</sub>)] (see **21**).

**21**

As has been pointed elsewhere by others,<sup>50</sup> the W<sub>5</sub>O<sub>15</sub> ring is puckered and could undergo ring inversion if the inversion were accompanied by twisting of the C<sub>6</sub>H<sub>5</sub>PO<sub>3</sub><sup>2-</sup> subunits. Although there is no direct evidence for ring inversion in terms of rate-dependent NMR line-shape behavior, the <sup>183</sup>W and <sup>17</sup>O solution NMR spectra reported for (C<sub>6</sub>H<sub>5</sub>P)<sub>2</sub>W<sub>5</sub>O<sub>21</sub><sup>4-</sup> are consistent with fluxional behavior that is immeasurably rapid on the NMR time scale.<sup>50</sup>

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**Registry No.** [(C<sub>6</sub>H<sub>5</sub>As)<sub>2</sub>Mo<sub>6</sub>O<sub>24</sub>][(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>, 60187-14-6; [(C<sub>6</sub>H<sub>5</sub>As)Mo<sub>7</sub>O<sub>24</sub>][(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>, 98509-06-9; (α-Mo<sub>8</sub>O<sub>26</sub>)[(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>, 59054-50-1; <sup>17</sup>O, 13968-48-4.

## X-ray Crystal Structure and Conformational Analysis of Tetradecamethylcycloheptasilane, (Me<sub>2</sub>Si)<sub>7</sub>

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**Abstract:** The crystal and molecular structure of tetradecamethylcycloheptasilane (**1**) has been determined. Crystals of **1** are monoclinic, space group P2<sub>1</sub>/c (*a* = 16.936 Å, *b* = 10.851 Å, *c* = 16.451 Å, β = 114.52°). Molecules of **1** are of approximate C<sub>2</sub> symmetry and adopt a twist-chair conformation. Empirical force field (EFF) calculations indicate that while cycloheptane and **1** adopt similar twist-chair ground-state structures, these molecules show significant differences in the structures of other possible conformations (chair, twist-boat, and boat) and the barriers to their interconversion. The average Si-Si-Si angle in **1** (116.2°) is larger than that found for other cyclosilanes.

The family of compounds known as permethylated cyclopolysilanes of general formula [Si(CH<sub>3</sub>)<sub>2</sub>]<sub>*n*</sub> (where *n* = 4-35)<sup>1</sup> are of interest for a number of reasons. Of particular interest is the fact that these compounds show unique electronic and spectroscopic

properties<sup>2,3</sup> arising from electron delocalization in the σ-framework. For example, they readily form delocalized anion<sup>4</sup> and cation<sup>5</sup> radicals and charge-transfer complexes with π-acceptors.<sup>6</sup>

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Table I. Experimental Crystallographic Details and Crystal Data for 1

parameter	1
crystal dimensions, mm	0.9 × 1.0 × 1.1
temp, °C	-70 ± 5
cell parameters	
a, Å	16.936 (2)
b, Å	10.851 (2)
c, Å	16.451 (2)
β, deg	114.52 (2)
V, Å <sup>3</sup>	2750.6
space group	P2 <sub>1</sub> /c
Z	4
density (calcd), g/cm <sup>3</sup>	0.985
density (meas), <sup>a</sup> g/cm <sup>3</sup>	0.912
radiation	graphite monochromated Mo Kα (λ = 0.71073 Å)
absorption coeff, cm <sup>-1</sup>	3.02
scan range (deg below 2θ Kα <sub>1</sub> )	0.8
scan range (deg above 2θ Kα <sub>2</sub> )	0.8
scan rate, deg/min	2.0–24.0
2θ limits, deg	2.5–54.9
sin θ/λ <sub>max</sub> , Å <sup>-1</sup>	0.649
unique data, theor	6290
obsd, F <sub>o</sub> > 3σ(F <sub>o</sub> )	4704

<sup>a</sup>The measured density was determined by flotation at room temperature.

Despite interest in these molecules, detailed structural information is only available for a limited number of compounds in the series. The crystal structures of octamethylcyclotetrasilane, (Me<sub>2</sub>Si)<sub>4</sub>,<sup>7</sup> and dodecamethylcyclohexasilane, (Me<sub>2</sub>Si)<sub>6</sub>,<sup>8</sup> have been reported, but attempts to obtain crystals of decamethylcyclopentasilane, (Me<sub>2</sub>Si)<sub>5</sub>, suitable for X-ray molecular structure determination have been unsuccessful.<sup>9</sup>

Structures of two organometallic derivatives of (Me<sub>2</sub>Si)<sub>5</sub>, c-Si<sub>5</sub>Me<sub>8</sub>[Fe(CO)<sub>2</sub>Cp]SiMe<sub>2</sub>[Fe(CO)<sub>2</sub>Cp] and c-Si<sub>5</sub>Me<sub>9</sub>SiMe<sub>2</sub>[Fe(CO)<sub>2</sub>Cp] have been reported,<sup>11</sup> as has that of a bicyclo compound, hexamethylbicyclo[3.3.1]nonasilane.<sup>12</sup>

Comparison of the structures of permethylcyclosilanes with those obtained for cyclic hydrocarbons reveals a number of interesting similarities. For example, the derivatives of (Me<sub>2</sub>Si)<sub>5</sub> adopt C<sub>3</sub> conformations,<sup>11</sup> and (Me<sub>2</sub>Si)<sub>6</sub> has the familiar chair structure<sup>8</sup> associated with cyclohexane. In order to see if these similarities extend to the higher homologues, we have obtained the X-ray molecular structure and performed empirical force field calculations on tetradecamethylcycloheptasilane, (Me<sub>2</sub>Si)<sub>7</sub> (**1**). In this paper we report the results of this study and compare the static and dynamic stereochemistry of **1** to that obtained for its hydrocarbon analogue, cycloheptane.

### X-ray Crystallography

Compound **1** was prepared from the mixture of permethylcyclosilanes obtained by the reaction of dimethyldichlorosilane with lithium.<sup>3</sup> At room temperature **1** exists in a plastic crystalline phase, so it was necessary to obtain data below the plastic transition temperature. Accordingly, crystals were grown at -78 °C by vapor diffusion of methanol into a dimethyl ether solution of **1**. A crystal was mounted directly in a stream of nitrogen at -70 ± 5 °C and maintained at this temperature during irradiation. Data were collected on a Syntex-Nicolet P<sub>1</sub> four-circle diffractometer equipped with a modified LT-1 low-temperature device, using Mo Kα radiation. Crystals of **1** are monoclinic, space group P2<sub>1</sub>/c.

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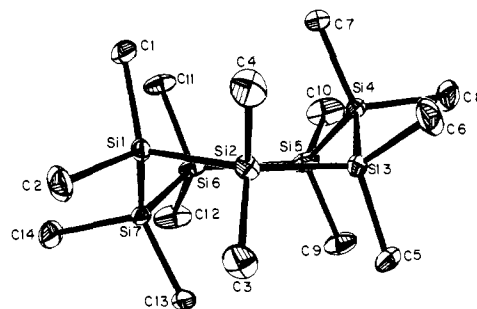


Figure 1. X-ray molecular structure of **1** viewed along the approximate C<sub>2</sub> symmetry axis. Hydrogen atoms have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Unit cell parameters were obtained from least-squares refinements based on 60 reflections collected at ±2θ (2θ = 35°). Other pertinent crystal data are collected in Table I. Delaunay cell reduction revealed no hidden symmetry.

Intensity data were collected with the crystal used for the preliminary examinations. Details of intensity measurements are given in Table I. Four standard reflections from diverse regions of reciprocal space were measured every 50 reflections throughout data collection to monitor the long-term stability. No significant trend was observed for **1**. Structure amplitudes and their standard deviations were collected from the intensity data by procedures similar to those described previously.<sup>13</sup>

The structure was solved by direct methods with use of the MULTAN package.<sup>14</sup> The positions of the silicon atoms were revealed by the E maps and the carbon atoms were located by the subsequent electron density difference maps. The full-matrix least-squares refinement of the structure was based on F<sub>o</sub> and used the reflections with F<sub>o</sub> > 3σ(F<sub>o</sub>). The structure was initially refined to convergence, using isotropic thermal parameters for the non-hydrogen atoms. Difference electron density maps revealed the positions for all the hydrogen atoms. In the final cycles of refinement all hydrogen atoms were assumed to vibrate isotropically. Atomic form factors were taken from Cromer and Waber<sup>15</sup> and that for hydrogen was taken from Stewart, Davidson, and Simpson.<sup>16</sup>

The hydrogen atom parameters were refined in the final cycles.<sup>17</sup> The final values of the discrepancy indices were R<sub>1</sub> = ∑||F<sub>o</sub> - |F<sub>c</sub>||/|F<sub>o</sub>| = 0.039 and R<sub>2</sub> = [∑w(|F<sub>o</sub> - |F<sub>c</sub>||)<sup>2</sup>/∑w(F<sub>o</sub>)<sup>2</sup>]<sup>1/2</sup> = 0.054 for 4704 observed reflections. The estimated standard deviation of an observation of unit weight was 1.75, with a final data/variable ratio of 13.1. The final difference electron density map was featureless.

Final atomic parameters are reported in Table II, and selected bonding parameters are reported in Table III. A view of the final structure of **1** is shown in Figure 1. A listing of observed and calculated structure factors and a table of anisotropic thermal parameters are available as supplementary material.

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Table II. Final Atomic Parameters for **1**<sup>a</sup>

atom	x	y	z	<i>B</i> <sub>iso</sub>
Si(1)	0.29931 (4)	0.27066 (5)	0.56367 (4)	3.41
Si(2)	0.16663 (4)	0.26567 (6)	0.43766 (4)	3.83
Si(3)	0.11484 (3)	0.44537 (6)	0.35306 (4)	3.69
Si(4)	0.21606 (4)	0.59671 (6)	0.36068 (4)	3.60
Si(5)	0.27069 (4)	0.72022 (6)	0.48869 (5)	4.17
Si(6)	0.36562 (4)	0.62063 (6)	0.61906 (4)	3.67
Si(7)	0.31199 (3)	0.44037 (6)	0.65595 (3)	3.29
C(1)	0.39316 (18)	0.2537 (3)	0.53142 (18)	4.80
C(2)	0.3001 (3)	0.1286 (3)	0.63075 (23)	6.37
C(3)	0.08015 (23)	0.2115 (4)	0.47426 (25)	6.23
C(4)	0.1786 (3)	0.1416 (3)	0.36240 (24)	6.84
C(5)	0.02799 (16)	0.5153 (4)	0.38215 (22)	5.38
C(6)	0.06212 (23)	0.3948 (4)	0.23215 (18)	6.46
C(7)	0.30972 (17)	0.5264 (3)	0.34520 (19)	4.81
C(8)	0.15886 (25)	0.7035 (4)	0.26169 (27)	6.53
C(9)	0.17928 (23)	0.7954 (3)	0.50758 (26)	5.87
C(10)	0.3370 (3)	0.8447 (3)	0.4642 (3)	7.05
C(11)	0.47111 (16)	0.5888 (3)	0.60970 (23)	5.07
C(12)	0.38814 (22)	0.7335 (4)	0.71363 (27)	6.03
C(13)	0.20128 (15)	0.47221 (27)	0.65223 (17)	4.29
C(14)	0.38612 (21)	0.3971 (4)	0.77511 (16)	5.76
H(13A)	0.2082 (17)	0.5228 (26)	0.6977 (18)	6.7 (6)
H(11B)	0.4598 (15)	0.5367 (24)	0.5549 (16)	5.6 (6)
H(10C)	0.3619 (21)	0.892 (3)	0.5229 (20)	8.4 (8)
H(7A)	0.3517 (21)	0.585 (3)	0.3450 (19)	8.2 (8)
H(1A)	0.3968 (19)	0.318 (3)	0.4878 (19)	7.4 (7)
H(5B)	0.0465 (19)	0.5385 (28)	0.4449 (20)	7.7 (7)
H(14A)	0.4455 (24)	0.395 (4)	0.7737 (22)	9.9 (9)
H(7C)	0.3362 (19)	0.476 (3)	0.3923 (20)	7.9 (7)
H(14A)	0.3899 (20)	0.457 (3)	0.8103 (21)	8.1 (7)
H(13B)	0.1775 (18)	0.394 (3)	0.6689 (17)	7.3 (7)
H(9A)	0.1526 (20)	0.736 (3)	0.5271 (19)	7.3 (7)
H(12C)	0.4263 (24)	0.694 (4)	0.7676 (23)	9.7 (9)
H(4B)	0.1262 (24)	0.140 (3)	0.3112 (23)	9.5 (9)
H(10B)	0.3773 (20)	0.803 (3)	0.4426 (19)	7.5 (7)
H(2C)	0.3530 (20)	0.113 (3)	0.6764 (20)	7.7 (7)
H(8A)	0.1128 (27)	0.738 (4)	0.2688 (23)	10.6 (11)
H(9B)	0.2026 (18)	0.8457 (27)	0.5607 (18)	6.7 (6)
H(3B)	0.0319 (23)	0.196 (3)	0.4150 (23)	9.9 (9)
H(1C)	0.4431 (21)	0.2506 (28)	0.5895 (21)	8.1 (8)
H(11C)	0.4963 (22)	0.668 (3)	0.6082 (21)	9.0 (8)
H(7B)	0.2900 (21)	0.493 (3)	0.2902 (23)	9.3 (8)
H(2B)	0.2554 (17)	0.1349 (24)	0.6485 (16)	5.6 (6)
H(4A)	0.2172 (17)	0.1812 (25)	0.3425 (16)	5.8 (6)
H(11A)	0.4995 (20)	0.553 (3)	0.6510 (19)	7.6 (7)
H(6A)	0.0397 (26)	0.469 (4)	0.2025 (25)	11.4 (11)
H(3A)	0.0745 (21)	0.266 (3)	0.5190 (21)	8.2 (8)
H(1B)	0.3877 (23)	0.184 (4)	0.5030 (23)	10.0 (9)
H(12B)	0.4113 (25)	0.805 (4)	0.7057 (23)	9.9 (9)
H(3C)	0.0922 (22)	0.144 (3)	0.5000 (22)	9.2 (9)
H(10A)	0.3037 (24)	0.897 (4)	0.4243 (23)	10.7 (10)
H(14C)	0.3695 (23)	0.315 (4)	0.7969 (24)	9.7 (9)
H(6C)	0.0205 (26)	0.347 (4)	0.2254 (23)	10.4 (10)
H(8B)	0.2003 (26)	0.775 (4)	0.2737 (24)	10.7 (10)
H(5A)	-0.0160 (21)	0.454 (3)	0.3691 (19)	8.1 (8)
H(4C)	0.191 (4)	0.065 (6)	0.380 (4)	18.5 (18)
H(2A)	0.289 (3)	0.060 (4)	0.5927 (27)	13.5 (13)
H(13C)	0.1636 (16)	0.4952 (24)	0.5912 (16)	5.6 (6)
H(6B)	0.1060 (21)	0.374 (3)	0.2124 (19)	8.2 (8)
H(9C)	0.1426 (23)	0.845 (3)	0.4534 (21)	9.9 (9)
H(5C)	0.0054 (20)	0.585 (3)	0.3467 (19)	7.8 (7)
H(12A)	0.3403 (27)	0.736 (4)	0.7122 (25)	10.4 (10)
H(8C)	0.154 (3)	0.669 (5)	0.217 (3)	14.8 (14)

<sup>a</sup>Standard deviations in parentheses. Isotropic equivalents are given for the atoms that were refined anisotropically.

**Crystal Structure of 1.** From visual inspection of the X-ray molecular structure of **1** presented in Figure 1, it is immediately apparent that **1** adopts a twist-chair conformation in the solid state. Although the two halves of the molecule are crystallographically independent (since **1** does not reside on a crystallographic site of *C*<sub>2</sub> symmetry), deviations are sufficiently small that one may

(24) Chen, S.-M.; David, L. D.; Haller, K. J.; Wadsworth, C. L.; West, R. *Organometallics* **1983**, *2*, 409.

(25) Dräger, V. M.; Walter, K. G. *Z. Anorg. Allg. Chem.* **1981**, *479*, 65.

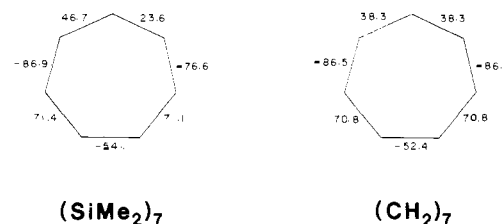


Figure 2. Left: Ring torsion angles for the X-ray molecular structure of **1**. Right: Ring torsion angles for the electron diffraction structure of the TC conformation of cycloheptane. The signs of all of the torsion angles for cycloheptane have been changed to allow for comparison to **1**.

properly describe **1** in terms of approximate *C*<sub>2</sub> symmetry. The approximate *C*<sub>2</sub> axis in **1** passes through Si(2) and bisects the Si(5)–Si(6) bond. The bonding parameters which are equivalent under this assumption have been grouped in symmetry-related pairs in Table III. Further analysis of the crystal structure of **1** reveals that a number of intermolecular C...C distances are less than the methyl–methyl van der Waals contact distance of 400 pm (Table III). It is possible that the deviations from *C*<sub>2</sub> symmetry observed for **1** (Table III) are due to the slight crystal packing forces resulting from these contacts.

It is interesting to compare the molecular structure of **1** with structures obtained for other cyclopolysilanes. To allow for such a comparison, relevant structural parameters for selected organosilicon ring compounds have been assembled in Table IV. The average Si–Si and Si–C bond lengths in **1** of 234.0 and 188.9 pm, respectively, are within the normal range for unstrained cyclopolysilanes. The average Si–Si bond length is somewhat shorter than that observed for three- and four-membered ring compounds, and while the average Si–C bond length is similar to that found for four- and five-membered rings, it is slightly shorter than that observed in [(*t*-Bu)<sub>2</sub>Si]<sub>3</sub>, (Me<sub>2</sub>Si)<sub>6</sub>, and Si<sub>9</sub>Me<sub>16</sub>. The average Si–Si–Si bond angle of 116.2° obtained for **1** is significantly larger than any of the previously reported values for cyclopolysilanes. This large average angle may be the result of transannular ring strain in **1**, which results in angle expansion. It is interesting to note that the bond angles in cycloalkanes show a similar trend, with medium-ring compounds exhibiting expanded average C–C–C angles relative to strain-free values.<sup>26</sup> It is possible that this larger Si–Si–Si angle will prove to be typical of medium-ring cyclopolysilanes as well.<sup>27</sup>

The larger Si–Si–Si bond angles in **1** do not appear to affect the C–Si–C angles. The average of 107.6° obtained for this parameter is within the normal range when compared to other cyclopolysilanes (Table IV). By contrast the Si–Si–C angles of **1**, averaging 107.6°, are somewhat smaller than any of the corresponding averages previously reported for this bond angle.

The structure of **1** can also be usefully compared with that of cycloheptane and its closely related derivatives. Cycloheptane has been investigated extensively by molecular mechanics calculations,<sup>29</sup> and an electron-diffraction study has been published.<sup>30</sup> In addition, the X-ray molecular structures of a number of cycloheptane derivatives<sup>31</sup> have been reported. It is generally agreed

(26) See, for example: Bixon, M.; Lifson, S. *Tetrahedron* **1967**, *23*, 769. Dunitz, J. D. In "Perspectives in Structural Chemistry"; Dunitz, J. D., Ibers, J. A., Eds.; John Wiley & Sons: New York, 1968; Vol. II, p 1.

(27) However, recent empirical force field calculations on dodecamethylpentasilane obtained average Si–Si–Si bond angles of 114.2°, 115.4°, and 116.6° in the trans, gauche-trans, and gauche conformations, respectively.<sup>28</sup>

(28) Damewood, J. R., Jr.; West, R. *Macromolecules* **1985**, *18*, 159.

(29) For example, see: (a) Ivanov, P. M.; Osawa, E. *J. Comput. Chem.* **1984**, *5*, 307 and references therein. (b) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D.C., 1981; p 98ff and references therein. (c) Favini, C. *J. Mol. Struct.* **1983**, *93*, 139. (d) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis", Amer. Chem. Soc., Washington, D. C., 1981, p 189.

(30) Dillen, J.; Geise, H. J. *J. Chem. Phys.* **1979**, *70*, 425.

(31) A search of the Cambridge Crystallographic Database<sup>32</sup> (CCD) updated to January 1984 revealed that 482 compounds meet this description.

Table III. Selected Bonding Parameters for **1**

Bond Lengths <sup>a,c</sup>					
Si(1)-Si(2)	234.0 (1)	Si(1)-C(1)	187.9 (3)	Si(4)-C(8)	190.3 (3)
Si(2)-Si(3)	234.4 (1)	Si(3)-C(5)	188.2 (3)	Si(7)-C(14)	189.6 (3)
Si(1)-Si(7)	233.9 (1)	Si(1)-C(2)	189.3 (3)	Si(5)-C(9)	188.4 (3)
Si(3)-Si(4)	233.8 (1)	Si(3)-C(6)	189.2 (3)	Si(6)-C(11)	188.5 (2)
Si(4)-Si(5)	233.8 (1)	Si(2)-C(4)	189.6 (3)	Si(5)-C(10)	190.2 (3)
Si(6)-Si(7)	233.9 (1)	Si(2)-C(3)	189.1 (3)	Si(6)-C(12)	189.0 (3)
Si(5)-Si(6)	234.2 (1)	Si(4)-C(7)	186.8 (2)	Si-C(av)	188.9
		Si(7)-C(13)	188.0 (2)		
Si-Si(av)	234.0				
Bond Angles <sup>b,c</sup>					
Si(1)-Si(7)-Si(6)	115.6 (1)	C(1)-Si(1)-C(2)	106.4 (2)		
Si(3)-Si(4)-Si(5)	117.3 (1)	C(5)-Si(3)-C(6)	107.9 (2)		
Si(2)-Si(1)-Si(7)	112.9 (1)	C(7)-Si(4)-C(8)	107.0 (1)		
Si(2)-Si(3)-Si(4)	117.9 (1)	C(13)-Si(7)-C(14)	107.6 (1)		
Si(4)-Si(5)-Si(6)	115.1 (1)	C(9)-Si(5)-C(10)	108.9 (2)		
Si(5)-Si(6)-Si(7)	115.5 (1)	C(11)-Si(6)-C(12)	108.1 (1)		
Si(1)-Si(2)-Si(3)	119.4 (1)	C(3)-Si(2)-C(4)	107.0 (2)		
Si-Si-Si(av)	116.2	C-Si-C(av)	107.6		
Si(1)-Si(2)-C(3)	108.0 (1)	Si(3)-Si(4)-C(8)	106.3 (2)	Si(5)-Si(4)-C(7)	108.4 (1)
Si(3)-Si(2)-C(4)	108.6 (1)	Si(1)-Si(7)-C(14)	108.6 (1)	Si(6)-Si(7)-C(13)	109.0 (1)
Si(1)-Si(2)-C(4)	105.8 (1)	Si(4)-Si(3)-C(5)	109.5 (1)	Si(5)-Si(4)-C(8)	107.0 (2)
Si(3)-Si(2)-C(3)	107.4 (1)	Si(7)-Si(1)-C(1)	113.5 (1)	Si(6)-Si(7)-C(14)	108.3 (2)
Si(2)-Si(1)-C(1)	111.1 (1)	Si(4)-Si(3)-C(6)	106.0 (1)	Si(5)-Si(6)-C(11)	108.8 (1)
Si(2)-Si(3)-C(5)	108.9 (1)	Si(7)-Si(1)-C(2)	106.7 (1)	Si(6)-Si(5)-C(9)	110.3 (1)
Si(2)-Si(1)-C(2)	105.6 (1)	Si(4)-Si(5)-C(9)	110.6 (1)	Si(5)-Si(6)-C(12)	106.4 (2)
Si(2)-Si(3)-C(6)	106.2 (2)	Si(7)-Si(6)-C(11)	110.5 (1)	Si(6)-Si(5)-C(10)	106.3 (2)
Si(3)-Si(4)-C(7)	110.4 (1)	Si(4)-Si(5)-C(10)	105.3 (2)	Si-Si-C(av)	107.6
Si(1)-Si(7)-C(13)	107.6 (1)	Si(7)-Si(6)-C(12)	107.2 (1)		
Torsion Angles <sup>b,c</sup>					
Si(1)-Si(2)-Si(3)-Si(4)				23.6 (1)	
Si(7)-Si(1)-Si(2)-Si(3)				46.7 (1)	
Si(2)-Si(3)-Si(4)-Si(5)				-76.6 (1)	
Si(6)-Si(7)-Si(1)-Si(2)				-86.9 (1)	
Si(3)-Si(4)-Si(5)-Si(6)				71.1 (1)	
Si(5)-Si(6)-Si(7)-Si(1)				71.4 (1)	
Si(4)-Si(5)-Si(6)-Si(7)				-54.1 (1)	
Si(1)-Si(2)-Si(3)-C(5)	-101.9 (1)	Si(3)-Si(4)-Si(5)-C(10)	-172.2 (1)	Si(6)-Si(7)-Si(1)-C(1)	40.7 (1)
Si(3)-Si(2)-Si(1)-C(1)	-82.1 (1)	Si(1)-Si(7)-Si(6)-C(12)	-170.3 (1)	Si(5)-Si(4)-Si(3)-C(5)	48.6 (1)
Si(1)-Si(2)-Si(3)-C(6)	142.2 (1)	Si(4)-Si(5)-Si(6)-C(11)	70.8 (1)	Si(6)-Si(7)-Si(1)-C(2)	157.5 (1)
Si(3)-Si(2)-Si(1)-C(2)	162.9 (1)	Si(7)-Si(6)-Si(5)-C(9)	71.8 (1)	Si(5)-Si(4)-Si(3)-C(6)	164.7 (1)
Si(2)-Si(3)-Si(4)-C(7)	48.3 (1)	Si(4)-Si(5)-Si(6)-C(12)	-172.9 (1)	Si(7)-Si(1)-Si(2)-C(3)	-76.3 (1)
Si(2)-Si(1)-Si(7)-C(13)	35.1 (1)	Si(7)-Si(6)-Si(5)-C(10)	-170.2 (1)	Si(4)-Si(3)-Si(2)-C(4)	-97.6 (1)
Si(2)-Si(3)-Si(4)-C(8)	163.9 (2)	Si(5)-Si(6)-Si(7)-C(13)	-49.8 (1)	Si(7)-Si(1)-Si(2)-C(4)	169.4 (2)
Si(2)-Si(1)-Si(7)-C(14)	151.3 (2)	Si(6)-Si(5)-Si(4)-C(7)	-54.7 (1)	Si(4)-Si(3)-Si(2)-C(3)	147.0 (2)
Si(3)-Si(4)-Si(5)-C(9)	-54.7 (1)	Si(5)-Si(6)-Si(7)-C(14)	-166.6 (1)		
Si(1)-Si(7)-Si(6)-C(11)	-52.6 (1)	Si(6)-Si(5)-Si(4)-C(8)	-169.7 (1)		
Selected C...C Distances <sup>a</sup>					
Intermolecular					
	C(2)...C(7)'			384.8	
	C(4)...C(13)'			383.5	
	C(5)...C(13)'			368.1	
	C(7)...C(11)'			368.4	
	C(7)...C(12)'			395.0	

<sup>a</sup> In picometer units. <sup>b</sup> In degrees. <sup>c</sup> Parenthesized values are esd's.

that cycloheptane, like **1**, adopts the twist-chair conformation in the ground state.<sup>29</sup> In order to examine how far the similarity between **1** and cycloheptane extends, a comparison of the ring torsion angles of these compounds, as determined by X-ray

crystallography and electron diffraction, respectively, is shown in Figure 2. In general, the torsional parameters obtained for these two molecules agree fairly well, but two of the torsion angles of **1**, Si(1)-Si(2)-Si(3)-Si(4) and Si(2)-Si(3)-Si(4)-Si(5), deviate

**Table IV.** Bonding Parameters for Selected Organosilicon Ring Compounds

compound	av bond lengths <sup>a</sup>		av bond angles <sup>b</sup>			ref
	Si-Si	Si-C	Si-Si-Si	Si-Si-C	C-Si-C	
[(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> Si] <sub>3</sub>	240.7	192.0 <sup>c</sup>	60.0			18
[( <i>t</i> -Bu) <sub>2</sub> Si] <sub>3</sub>	251.1	197.0	60.0	121.5	105.7	19
(Me <sub>2</sub> Si) <sub>4</sub>	236.3	189.0	90.0	114.0	110.0	7
[Me( <i>t</i> -Bu)Si] <sub>4</sub>	237.7	Si-C <sub>Me</sub> 189.3	87.0	Si-Si-C <sub>Me</sub> 111.0	107.4	20
		Si-C <sub><i>t</i>-Bu</sub> 191.8		Si-Si-C <sub><i>t</i>-Bu</sub> 119.6		
(Ph <sub>2</sub> Si) <sub>4</sub>	237.7	188.6	89.6	114.4	109.1	21
Si <sub>5</sub> Me <sub>9</sub> SiMe <sub>2</sub> [Fe(CO) <sub>2</sub> CP] <sup>d</sup>	235.3	187.7	104.0	110.3	108.2	11
Si <sub>5</sub> Me <sub>8</sub> [Fe(CO) <sub>2</sub> CP]SiMe <sub>2</sub> [Fe(CO) <sub>2</sub> CP] <sup>d</sup>	236.2	188.7	103.6	109.4	107.6	11
(Ph <sub>2</sub> Si) <sub>5</sub>	239.6	189.5	104.5	111.6	105.9	22
[(CH <sub>2</sub> ) <sub>4</sub> Si] <sub>5</sub>	234.7	190.6	104.5	114.5	94.6	23
[(CH <sub>2</sub> ) <sub>5</sub> Si] <sub>5</sub>	235.9	189.4	102.5	113.1	102.3	23
(Me <sub>2</sub> Si) <sub>6</sub>	233.8	192.4	111.9	109.2	108.1	8
Si <sub>9</sub> Me <sub>16</sub> <sup>e</sup>	234.3	193.5	112.4	108.8	106.4	11
(MePhSi) <sub>6</sub>	235.9	Si-C <sub>Me</sub> 188.2	111.1	Si-Si-C <sub>Me</sub> 110.0	108.7	24
		Si-C <sub>Ph</sub> 189.3		Si-Si-C <sub>Ph</sub> 108.4		
(Ph <sub>2</sub> Si) <sub>6</sub>	239.4	189.8	113.8	109.3	105.5	25
<b>1</b>	234.0	188.9	116.2	107.6	107.6	<i>f</i>

<sup>a</sup> In picometer units. <sup>b</sup> In degrees. <sup>c</sup> Estimated average Si-C bond lengths range from 190.0 to 193.0 pm. <sup>d</sup> Average values for silicon ring only. <sup>e</sup> Hexamethylbicyclo[3.3.1]nonasilane. <sup>f</sup> This work.

significantly (ca. 14.7° and 9.9°, respectively) from their related parameters in cycloheptane.

Cycloheptasulfur,<sup>33</sup> S<sub>7</sub>, provides an example of a homoatomic seven-membered ring of third period atoms for comparison with **1**. This compound crystallizes in four different allotropic forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) whose thermodynamic stability relationships are unknown. The crystal structure of two of these allotropes,  $\gamma$ -<sup>33f</sup> and  $\delta$ -S<sub>7</sub>,<sup>33c</sup> have been reported, however, and both contain molecules that are best described as adopting the chair conformation. A slightly distorted chair conformation has also been observed for three homocyclic derivatives of cycloheptasulfur, S<sub>7</sub>O,<sup>34</sup> S<sub>7</sub>I<sup>+</sup>,<sup>35</sup> and [(S<sub>7</sub>I)<sub>2</sub>I]<sup>3+</sup>.<sup>36</sup> Thus S<sub>7</sub> and its derivatives differ substantially from **1** and cycloheptane in terms of ground-state molecular structure.<sup>37</sup>

**Empirical Force Field Calculations on 1.** In order to more fully explore the conformational hypersurface of **1**, we performed empirical force field (EFF) calculations<sup>29b</sup> using the program MM3<sup>38</sup> and the full relaxation technique. The parameters for silicon contained in MM2 along with those previously developed for polysilanes<sup>28</sup> were employed.

The four basic conformations of seven-membered rings have been identified from studies of cycloheptane<sup>29</sup> as the chair (C), boat (B), twist-chair (TC), and twist-boat (TB). The C and B conformations are both of C<sub>2</sub> symmetry and the TC and TB are of C<sub>2</sub> symmetry. For cycloheptane the TC is the ground-state conformation and enantiomeric TC forms interconvert via pseudorotation through the C transition state. The TB conformation is somewhat higher in energy than the TC and pseudorotation

**Table V.** Calculated Bonding Parameters for Conformations of **1**

	TC					
	calcd	(exptl) <sup>b</sup>	TB	C	B	TT
	Average Bond Lengths <sup>a</sup>					
Si-Si	234.8	(234.0)	235.0	234.9	235.1	234.9
Si-C	186.5	(189.0)	186.6	186.6	186.6	186.6
	Average Bond Angles <sup>c</sup>					
Si-Si-Si	117.1	(116.2)	117.6	117.3	117.3	117.0
Si-Si-C	107.7	(108.2)	107.7	107.7	107.7	107.8
C-Si-C	108.5	(107.5)	108.1	108.3	108.1	108.4

<sup>a</sup> In picometer units. <sup>b</sup> This work. <sup>c</sup> In degrees.

**Table VI.** Calculated and Experimental Ring Torsion Angles for TC Conformation of **1**<sup>a,b</sup>

	calcd	exptl
$\omega_1$	37.4	23.6
$\omega_2$	-79.5	-76.6
$\omega_3$	70.3	71.1
$\omega_4$	-56.6	-54.1
$\omega_5$	70.3	71.4
$\omega_6$	-76.8	-86.9
$\omega_7$	31.5	46.7

<sup>a</sup> In degrees. <sup>b</sup> The central bond between atoms defining  $\omega_4$  is bisected by the C<sub>2</sub> (or approximate C<sub>2</sub>) axis of symmetry of the molecule.

through the B transition state relates enantiomeric forms of the TB conformation as well. In addition the families of TC and TB conformations may interconvert via an axially symmetric mode,<sup>39</sup> through a twisted transition state (TT). In the present calculations we obtain the structures and conformational energies as well as the pseudorotation and interconversion barriers for **1** and compare our results with those obtained previously for cycloheptane.

Using the X-ray structure obtained for **1** as an input structure followed by complete geometry optimization yields the calculated TC structure. The TB structure was similarly obtained starting from an idealized input structure. The C and B forms are calculated to be relative energy maxima for **1**, and their structures were obtained by geometry optimization under the constraint of C<sub>s</sub> symmetry. Removal of the symmetry constraint on these two conformations followed by geometry optimization yields the TC and TB structures, respectively. The TT was obtained by geometry optimization under the constraint of C<sub>2</sub> symmetry. The relative energies and calculated torsion angles obtained for the TC, TB,

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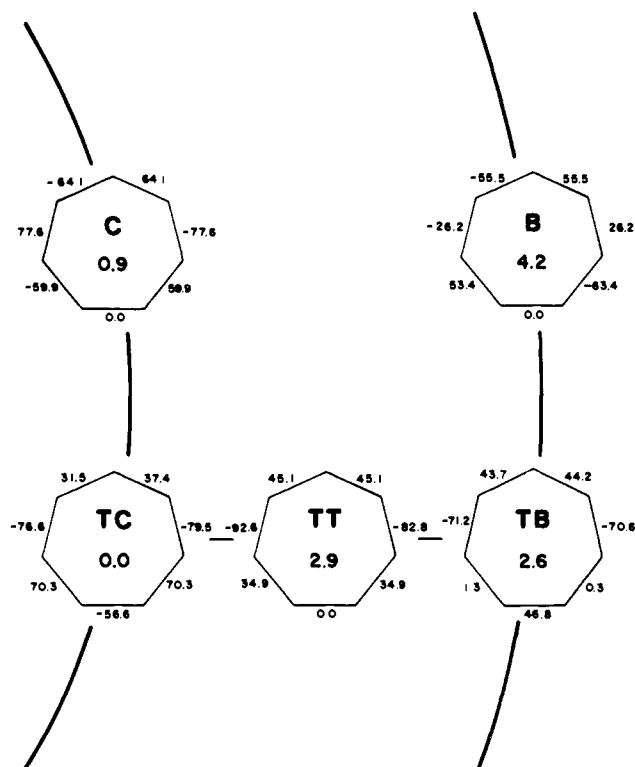
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(38) Allinger, N. L. et al. *QCPE* **1981**, *13*, 359.

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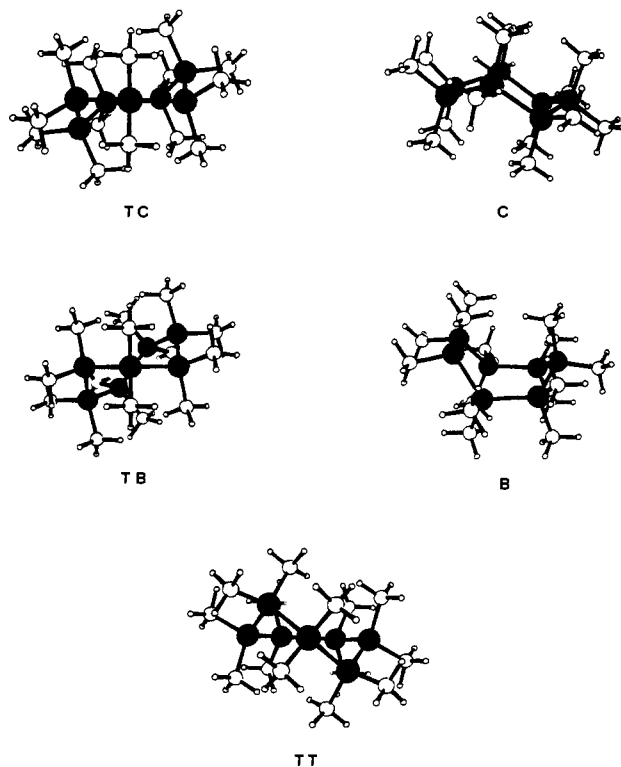
**Figure 3.** Conformational interconversion map for **1**. Inner and outer arcs represent portions of TC-C and TB-B pseudorotation pathways, respectively. The TT interconverts the TC and TB conformations and connects the pseudorotation itineraries. Relative energies for the conformations are shown under the conformational descriptors. Calculated torsion angles are shown around the ring perimeter.

C, and B conformations and the TT of **1** are reported in Figure 3. This figure represents a portion of the conformational interconversion map for **1** and is similar to the representation used by Hendrickson for describing the modes of interconversion in cycloheptane. Selected calculated bonding parameters are reported in Tables V and VI. Views of the five calculated conformations of **1** are shown in Figure 4.

Inspection of Figure 3 reveals that the TC conformation is calculated to be lowest in energy for **1**, and comparison of calculated and observed TC conformations (Tables V and VI) indicates that agreement between the two structures is, in general, good. While deviations from  $C_2$  symmetry are sufficiently small for both calculated and observed TC structures that we may properly speak of approximate  $C_2$  symmetry, the deviation from  $C_2$  symmetry is greatest for the X-ray molecular structure. The differences between calculated and observed TC structures and the deviation of the X-ray molecular structure from  $C_2$  symmetry are most apparent in the ring torsion angles ( $\omega_1$ - $\omega_7$ ). Specifically, the angles  $\omega_1/\omega_7$  and  $\omega_2/\omega_6$  which would be pairwise related under  $C_2$  symmetry differ noticeably in the X-ray structure and upon comparison to the same angles calculated for the TC conformation. These differences may result from the moderate intermolecular contacts which are present in the crystal (see above).

Relative energies for conformations of **1** and of cycloheptane are compared in Table VII. For **1**, the C conformation is the transition state for TC-C pseudorotation and is 0.9 kcal/mol higher in energy than the TC. This barrier height resides within the range of 0.63-1.58 kcal/mol calculated for the TC-C pseudorotation barrier in cycloheptane. As found for the X-ray structure of **1**, the ring torsion angles calculated for the TC and C conformations are similar to the values obtained experimentally by electron diffraction<sup>30</sup> and by EFF calculations<sup>29</sup> for the same conformations of cycloheptane.

The TB conformation of **1** is calculated to be 2.6 kcal/mol higher in energy than the TC and to have approximate  $C_2$  symmetry. This value is within the 2.40-5.64 kcal/mol range calculated for the TB of cycloheptane, but the ring of the TB form



**Figure 4.** Views of the calculated TC, C, TB, B, and TT conformations of **1**. Top left: The TC conformation viewed down the approximate  $C_2$  symmetry axis. Top right: The C conformation viewed approximately normal to the symmetry plane. Center left: The TB conformation viewed down the approximate  $C_2$  symmetry axis. Center right: The B conformation viewed approximately normal to the symmetry plane. Bottom: The TT viewed down the  $C_2$  symmetry axis. Silicon atoms have been shaded for clarity.

**Table VII.** Calculated Relative Energies for Conformations of **1** and Cycloheptane<sup>a,b</sup>

	<b>1</b>	$C_7H_{14}$
TC	0.0	0.0
C	0.9	0.63-1.58
TB	2.6	2.40-5.64
B	4.2	2.60-5.66
TT	2.9	8.1-9.6

<sup>a</sup> In kcal mol<sup>-1</sup>. <sup>b</sup> See ref 29 for literature references to calculations for cycloheptane.

of **1** is somewhat flattened relative to that found for cycloheptane. As a result of this flattening, the TB structure we calculate for **1** is closely similar in conformation to one of the intermediates (TC/TB(c)) encountered by Hendrikson<sup>39</sup> in the TC-TB interconversion pathway of cycloheptane. A search of the potential energy surface of **1** in the vicinity of structures which correspond to the calculated TB ring conformation of cycloheptane revealed no additional minima for **1**. A further difference in the potential energy hypersurface of **1** and cycloheptane is illustrated by the magnitude of the calculated TB-B pseudorotation barrier for **1** of 1.6 kcal/mol. While, like the TB, the relative energy of 4.2 kcal/mol for the B conformation of **1** is within the range of 2.60-5.66 kcal/mol calculated for cycloheptane (Table VII), this TB-B pseudorotation barrier is significantly larger than the 0.02-0.24 kcal/mol range obtained for the similar conformational process in the hydrocarbon system. Such differences are expected between TB-B pseudorotation barriers for **1** and cycloheptane due to the significantly different TB structures, even if one accepts the premise that permethylcyclopolysilanes and cycloalkanes have similar steric requirements. It is interesting to note that the direction of this difference in barrier heights (i.e., **1** > cycloheptane) is that which would be predicted under this approximation, since the TB structure of **1** could then be viewed as being more extensively distorted along the potential energy surface from

the B transition state and therefore expected to have a somewhat higher TB-B pseudorotation barrier.<sup>40</sup>

There are many possible mechanisms for interconversion of the TC and TB conformations (TC-TB) of **1**. The pathway which maintains a  $C_2$  axis of symmetry, going through a TT, is the one energetically favored among those considered for cycloheptane.<sup>29</sup> We obtain a barrier height of 2.9 kcal/mol for TC-TB interconversion via a TT in **1**. This value, which is significantly lower than the 8.1,<sup>39</sup> 8.55,<sup>29a</sup> and 9.6 kcal/mol<sup>41</sup> barriers calculated for cycloheptane, further reflects the differences between **1** and its hydrocarbon analogue. This difference also extends to the structure of the TT. While for cycloheptane the TT is calculated to have a sequence of torsion angles,  $\omega_3$ - $\omega_5$ , which are all of the same sign, the corresponding angles in **1** contain one,  $\omega_4$ , which is eclipsed ( $\omega_4 = 0.0$ ). Thus our TT closely resembles a second intermediate TC/TB(a) encountered by Hendrickson<sup>39</sup> in the

TC-TB interconversion of cycloheptane. Releasing the symmetry constraint on the TT calculated for **1** followed by geometry optimization yields the TC structure. The TB conformation was obtained by increasing the magnitude of  $\omega_4$  in the TT in a driving experiment.<sup>37</sup> No intermediates were encountered between the TT and the TC or TB and we observed a uniform decrease in energy along both pathways. Thus, the calculations indicate that the magnitude of the TC-TB interconversion barrier and the ring structure of the TT calculated for **1** differ from that obtained for cycloheptane. In addition, unlike the interconversion process in cycloheptane, we find no intermediates along the TC-TB itinerary for **1**.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters and values of  $10F_o$  and  $10F_c$  (22 pages). Ordering information is given on any current masthead page.

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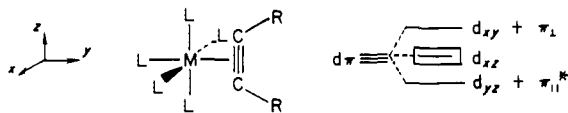
## Mixed Olefin-Alkyne Complexes of Molybdenum(II) and Tungsten(II) Dithiocarbamates<sup>†</sup>

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**Abstract:** Mixed olefin-alkyne complexes of the type  $M(\eta^2\text{-olefin})(\eta^2\text{-alkyne})(S_2CNR_2)_2$  ( $M = Mo$  and  $W$ ) have been prepared from  $M(CO)(\eta^2\text{-alkyne})(S_2CNR_2)_2$  and electron poor olefins (maleic anhydride, tetracyanoethylene, and *trans*-dicyanoethylene). The range of acceptable alkyne ligands spans alkyl, aryl, and terminal alkynes. The motivation for this work was to incorporate a single-faced  $\pi$ -acid ligand into the octahedral position cis to the alkyne ligand of the  $M(\eta^2\text{-alkyne})(S_2CNR_2)_2$  fragment. The resulting family of mixed olefin-alkyne complexes has been characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, infrared, and electronic spectroscopies; cyclic voltammograms have been recorded for a number of the compounds reported here. The structure of  $W(\eta^2\text{-maleic anhydride})(\eta^2\text{-PhC}_2\text{H})(S_2CNMe_2)_2$  has been determined:  $a = 22.744$  (5) Å,  $b = 12.589$  (3) Å,  $c = 21.440$  (8) Å,  $\beta = 121.52$  (2)°,  $Z = 8$ ,  $d_{\text{calcd}} = 1.69$  g cm<sup>-3</sup>, and space group  $C2/c$ . Several of these olefin-alkyne complexes undergo nucleophilic attack by the phosphorus lone pair of phosphites and phosphines at the terminal carbon of the coordinated alkyne to form  $\eta^2$ -vinyl products. The  $\eta^2$ -vinyl ligand present in the  $M(\eta^2\text{-PhCCHPR}_2)$  moiety which results can also be described as a cyclic alkylidene or as a metallacyclopentene. These names are in accord with the considerable carbenoid character of the more tightly bound  $\alpha$ -carbon as reflected in a low-field <sup>13</sup>C chemical shift of 220-230 ppm.

Alkyne ligands in monomeric early transition-metal complexes are particularly sensitive to metal  $d\pi$  orbital occupancies. A neutral alkyne ligand serves simultaneously as an excellent single-faced  $\pi$ -acid through  $\pi_{||}^*$  and as an excellent single-faced  $\pi$ -base through  $\pi_{\perp}$ .<sup>1</sup> For octahedral  $L_5M(RC_2R)$  complexes, these divergent metal-alkyne  $\pi$  interactions dictate the location of two  $d\pi$  energy levels and leave one  $d\pi$ -orbital energy undetermined. In the coordinate system shown below, with the alkyne approaching the metal along the  $y$  axis,  $d_{xz}$  is the flexible  $d\pi$  orbital. The occupancy of this flexible metal-based orbital depends on whether it sees predominantly  $\pi$ -donor or  $\pi$ -acceptor ancillary ligands in the  $xz$  plane, and it follows that either  $d^2$  or  $d^4$  electron configurations will be preferred for  $L_5M(\text{alkyne})$  monomers.



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The *cis*-(CO)(RC<sub>2</sub>R) fragment found in numerous six-coordinate  $d^4$   $L_4M(CO)(RC_2R)$  complexes<sup>2</sup> contains a  $3c-2e$  bond involving  $d_{yz}$ , CO  $\pi^*$ , and alkyne  $\pi_{||}^*$  (see below).<sup>3</sup> This orbital redundancy suggests that a single-faced  $\pi$  acceptor, such as a carbene or an electron-withdrawing olefin, should suffice in place of the cylindrically symmetrical  $\pi$ -acid carbonyl ligand. The bis(alkyne) complexes,  $Mo(RC_2R)_2(S_2CNR_2)_2$ , contain a  $3c-4e$  bond involving  $d_{yz}$  and both filled alkyne  $\pi_{\perp}$  orbitals.<sup>4,5</sup> Since

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