Synthesis and Structure of a Tetrasilacyclohexyne

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Synthesis and Structure of a Tetrasilacyclohexyne

Abstract
Although strained cycloalkynes have received considerable experimental and theoretical attention for many years, the smallest isolable rings are seven-membered. We report here the synthesis, chemical and structural characterization, and ab initio calculations of the first isolable six-membered ring containing a carbon-carbon triple bond.

Disciplines
Chemistry

Comments
these atoms, in contrast to other examples of \( \pi \)-bridging CO ligands.\(^{1,5,7}\) Each ligand serves as a four-electron donor. Two electrons are donated by the carbon atom to the pair of metal atoms that it bridges, and two electrons from the oxygen are donated to the metal Ru(8). Since the oxygen atoms of both bridging carbonyl ligands are bonded to the same metal atom, the carbon atoms are brought into an unusually close nonbonding contact: C(53)–C(63) = 2.46 (2) Å. Similar close contacts have been shown to facilitate the formation of carbon–carbon bonds between CO ligands under reducing conditions.\(^{15}\) Efforts to achieve this are in progress.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (27 pages); tables of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Table I. NMR Comparison of Cycloalkynes 2, 4, and 5

<table>
<thead>
<tr>
<th>cycloalkyne</th>
<th>(^{13})C NMR</th>
<th>(^{29})Si NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me,SiMe=CSiMe</td>
<td>113.02/0.10</td>
<td>-35.4, -38.9, -39.9</td>
</tr>
<tr>
<td>c-(Me,Si)₂C=C</td>
<td>117.77/3.10, -5.14, -6.24</td>
<td>33.3, -34.7, -38.7</td>
</tr>
<tr>
<td>2</td>
<td>123.22/3.16, -5.91, -6.04</td>
<td>-17.8, -30.6</td>
</tr>
<tr>
<td>4</td>
<td>135.66/3.02, -6.31</td>
<td>-17.8, -30.6</td>
</tr>
</tbody>
</table>

Figure 1. ORTEP diagram of octaisopropyldisilacyclohexyne (8). The methyl groups have been omitted for clarity.

tetrasilacyclohexyne (4) in 65% yield as a colorless liquid, easily purified by chromatography on silica gel.\(^{6}\)

Pure, neat 4 slowly decomposes or polymerizes at room temperature but is completely stable when stored as a 20% solution in hexane at 0 °C. The structure of cyclohexyne 4 was initially deduced from its mass (calcd for \( \text{C}_8\text{H}_{16}\text{Si}_4\), \( m/z \) 256.09522, found \( m/z \) 256.09561). \(^{1}\) \(^{1}\)H NMR (two singlets; \( \delta \) 0.224, 0.175), \(^{13}\)C NMR, and \(^{29}\)Si NMR spectra. The \(^{1}\)C NMR and \(^{29}\)Si NMR spectral data for permethylhexasilacyclooctyne (5), \(^{2}\) and 4 are tabulated for comparison in Table I. As anticipated, the most dramatic effect is observed in \(^{13}\)C NMR absorption of the acetylenic carbons, which steadily shifts downfield to the remarkable value of \( \delta \) 135.7 for 4. This corresponds to a downfield shift of ca. 23 ppm from the acetylenic resonance of Me,Si=SiMe

Repeated attempts to obtain crystalline 4 were unsuccessful even at low temperatures. Thus, to obtain X-ray structural data


\(^{(2)}\) 1,4-dichlorooctamethyltetrasilane (3) afforded octamethyl-permeethylhexasilacyclooctyne (5), 72, and 4 are deduced from its mass (calcd for \( \text{C}_8\text{H}_{16}\text{Si}_4\), \( m/z \) 256.09522, found \( m/z \) 256.09561). \(^{1}\)H NMR (two singlets; \( \delta \) 0.224, 0.175), \(^{13}\)C NMR, and \(^{29}\)Si NMR spectra. The \(^{1}\)C NMR and \(^{29}\)Si NMR spectral data for permethylhexasilacyclooctyne (5), \(^{2}\) and 4 are tabulated for comparison in Table I. As anticipated, the most dramatic effect is observed in \(^{13}\)C NMR absorption of the acetylenic carbons, which steadily shifts downfield to the remarkable value of \( \delta \) 135.7 for 4. This corresponds to a downfield shift of ca. 23 ppm from the acetylenic resonance of Me,Si=SiMe

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\(^{(8)}\) Both we and Professor W. Ando reported at the 9th International Symposium on Organosilicon Chemistry, Edinburgh, Scotland, July 1990, GCMS evidence for the synthesis but not isolation of 4. After this communication was submitted, we learned that the isolation of 4 had been reported the previous month by Professor Ando.\(^{9}\) Very recently a paper has appeared describing in detail Professor Ando's work in this area, which includes theoretical generation of 4 from 2.\(^{10}\)
it was necessary to synthesize the more bulky derivative 8. Synthesis of 8\(^{11}\) (colorless crystals, mp 67-68 °C) was accomplished by PCl\(_3\)-induced ring opening of cycloctetrasilane \(^{6,12}\) followed by condensation of the resulting 1,4-dichlorotetrasilane 7 with Li=CCl in 25% yield from 6.

\[
\begin{array}{c}
\text{i-Pr}_2\text{SiCl}_2 \\
\text{ref. 12}
\end{array}
\]

\[
\text{SiCC} \\
\text{SCF}
\]

Experimental structures for scattering factors and anomalous scattering corrections were taken from the theoretical study was supported by a grant from the National Science Foundation, CHE-8911911. The calculations were performed on an IBM RS6600/530 computer, purchased in part with a major instrument grant from the National Science Foundation.

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Neighboring Tin Effect in Electron Transfer from Thioethers

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The neighboring silyl substituents in \(\alpha\)-silyl ethers are known to significantly decrease the electrochemical oxidation potential of ethers,\(^{13,14}\) but not thioethers.\(^{3,5}\) Neighboring stannyl substituents with appropriate geometry in \(\alpha\)-stannyl thioethers are now shown in this paper to dramatically render the anodic peak potential of the representative thioether 1,3-dithiane less positive.

\[
\begin{align*}
11 & : \text{mass spectrum calcd for C}_{28}\text{H}_{28}\text{Si}_4, m/z 480.3451, \text{found 480.3459; C}_{26}\text{H}_{56}\text{Si}_4, \text{calcd 575.0525, found 575.0511.} \\
12 & : \text{Data were collected at } 25^\circ\text{C, } >50\%\text{ infrared, } 1 \text{ h, } >50\%\text{ infrared, } 1 \text{ h.}
\end{align*}
\]