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# “Inverse Sandwich” Complexes of Perhalogenated Cyclohexasilane

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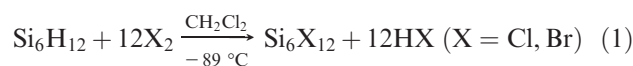
**Summary:** Perhalogenated cyclohexasilanes, Si<sub>6</sub>X<sub>12</sub> (X = Cl, Br), were prepared by reaction of Si<sub>6</sub>H<sub>12</sub> with molecular chlorine or bromine in cold (−89 °C) dichloromethane. Single-crystal structural determination by X-ray analysis shows that the six silicon atoms comprising Si<sub>6</sub>Br<sub>12</sub> adopt a chair conformation in the solid state. The addition of *p*-tolunitrile to Si<sub>6</sub>X<sub>12</sub> (X = Cl, Br) leads to the rapid formation of colorless precipitates. Si<sub>6</sub>Br<sub>12</sub>·2(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN) adopts an “inverse sandwich” structure where the N atoms of the *p*-tolunitrile molecules are μ<sub>6</sub> bonded and are located above and below the planar hexagonal Si<sub>6</sub> ring.

While the chemistry of hypercoordinate silicon complexes has been well documented and is the subject of several review articles,<sup>1</sup> there are only a few examples where two or more neutral silicon atoms are bridged by donor ligands. Tamao et al. reported a number of pentacoordinate complexes based upon *o*-C<sub>6</sub>H<sub>4</sub>(SiF<sub>3-x</sub>R<sub>x</sub>)(SiF<sub>3-x</sub>R'<sub>x</sub>) where the fluoride ion bridges two Si atoms to give a five-membered ring.<sup>2</sup> Similar bridging between two acceptor Si atoms has been reported for other halides such as chloride<sup>3</sup> and bromide<sup>4</sup> as well as oxygen.<sup>5</sup> Jung and Xia reported that three Si atoms in 12-silacrown-3 could complex with either Cl<sup>−</sup> or Br<sup>−</sup>.<sup>6</sup> Corriu et al. found that F<sup>−</sup> quickly exchanges among the three silicon atoms in trisilacyclohexane.<sup>7</sup> In all of these examples, the donor atom bridges no more than three silicon acceptor atoms.

We reported the synthesis of neutral and cationic hexacoordinated silane complexes when trichlorosilane was reacted with aliphatic diamines and triamines.<sup>8</sup> That research led to the discovery of cyclohexasilane-based salts such as

[Si<sub>6</sub>Cl<sub>14</sub>]<sup>2−</sup>,<sup>9</sup> where an “inverse sandwich” structure was observed. Each of two spaces above and below the middle of the Si<sub>6</sub> ring are strong Lewis acid sites. We now report the formation of cyclohexasilane-based “inverse sandwich” complexes that feature neutral Lewis base atoms in the apical positions.

The perhalogenated cyclohexasilanes Si<sub>6</sub>X<sub>12</sub> (X = Cl (1), Br (2)) have previously been synthesized via the reaction of Si<sub>6</sub>Ph<sub>12</sub> with HCl or HBr in the presence of AlCl<sub>3</sub>.<sup>10</sup> The Si<sub>6</sub>Ph<sub>12</sub> synthon is typically prepared via Wurtz coupling of Ph<sub>2</sub>SiCl<sub>2</sub> using active metals, where low yields and the formation of numerous cyclic products complicate the effective production of the six-membered ring. Given the availability of Si<sub>6</sub>H<sub>12</sub> via reduction of the dianion [Si<sub>6</sub>Cl<sub>14</sub>]<sup>2−</sup>,<sup>9b</sup> we considered molecular halogenation as a straightforward route to Si<sub>6</sub>X<sub>12</sub>, where Cl<sub>2</sub> or Br<sub>2</sub> reacts with Si–H to yield Si–Cl<sup>11</sup> or Si–Br<sup>11b,d,12</sup> with elimination of HCl or HBr, respectively, without breaking Si–Si bonds (eq 1). Accordingly, pure chlorine gas was slowly added to Si<sub>6</sub>H<sub>12</sub> in CH<sub>2</sub>Cl<sub>2</sub> at −89 °C. When the reaction was complete, solvent was removed, giving crude product in 89% yield. Si<sub>6</sub>Br<sub>12</sub> was prepared analogously in 93% yield using ~25 wt % bromine in CH<sub>2</sub>Cl<sub>2</sub>. Better control of the reaction was observed for Si<sub>6</sub>Br<sub>12</sub>, presumably as a consequence of the lower vapor pressure of Br<sub>2</sub>, allowing more quantitative addition. (Note: Si<sub>6</sub>H<sub>12</sub> is a pyrophoric liquid that burns upon contact with air and should be treated as an ignition source and handled under inert conditions.)



Crystals of Si<sub>6</sub>Br<sub>12</sub> suitable for structural determination by X-ray analysis were prepared by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. In the solid state, Si<sub>6</sub>Br<sub>12</sub> adopts a chair conformation (Figure S1, Supporting Information) with Si–Si and Si–Br distances of 2.34 and 2.20 Å, respectively, and Si–Si–Si angles from 112 to 115°.

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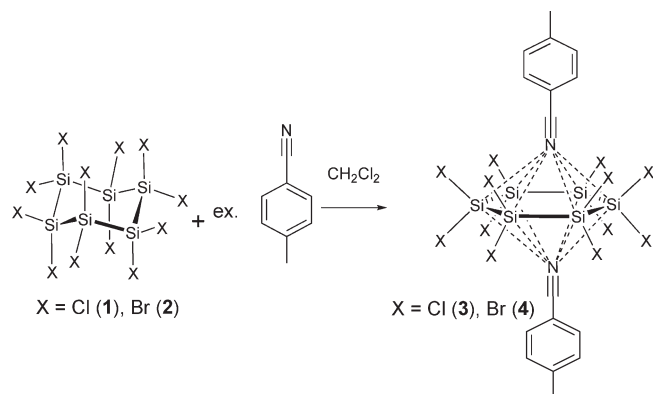
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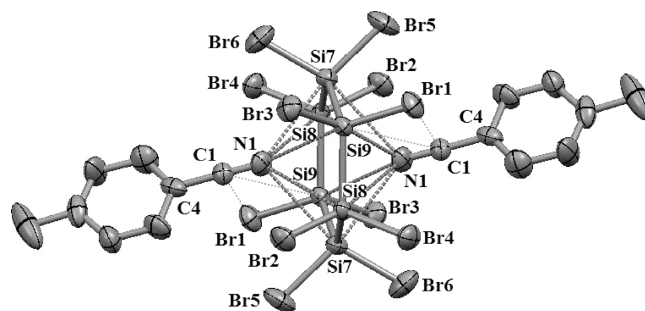
**Figure 1.** Synthesis of  $\text{Si}_6\text{X}_{12} \cdot 2(p\text{-CH}_3\text{C}_6\text{H}_4\text{CN})$ .

Weak intermolecular  $\text{Br} \cdots \text{Br}$  interactions are present in **2**, and each  $\text{Si}_6\text{Br}_{12}$  molecule has four nearest neighbors (Figure S2, Supporting Information) with Br–Br distances of 3.67 Å—a value that is slightly less than twice the van der Waals radius of bromine (3.70 Å).<sup>13</sup> There appears to be no interlayer  $\text{Br} \cdots \text{Br}$  interaction, as the closest  $\text{Br} \cdots \text{Br}$  distance between layers is 3.75 Å. Thus, intermolecular interactions are limited to two dimensions, giving rise to a layered crystal lattice.

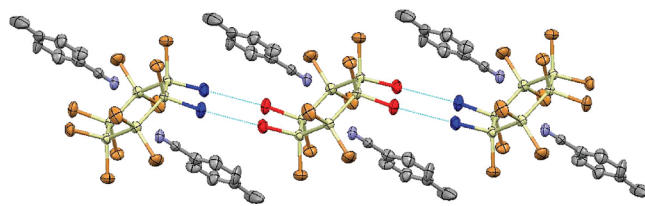
The reactions of **1** and **2** with *p*-tolunitrile in  $\text{CH}_2\text{Cl}_2$  yield colorless precipitates (Figure 1). Elemental analyses indicate that each of these two complexes is comprised of one  $\text{Si}_6\text{X}_{12}$  and two *p*-tolunitrile molecules as  $\text{Si}_6\text{X}_{12} \cdot 2(p\text{-CH}_3\text{C}_6\text{H}_4\text{CN})$  (X = Cl (**3**), Br (**4**)).

Both **3** and **4** exhibit very low solubility in common organic solvents, thus complicating low-temperature NMR data collection. Characterization of **3** was incomplete, as neither a  $^{29}\text{Si}$  signal for the  $\text{Si}_6$  ring nor a  $^{13}\text{C}$  resonance for the cyano group were observed after 24 h of data collection at room temperature. NMR and IR data for complex **4** indicated a weak interaction between the  $\text{Si}_6\text{X}_{12}$  ring and *p*-tolunitrile. Toward that end, the carbon atom of the cyano group for **4** was observed at 119.47 ppm in  $\text{CD}_2\text{Cl}_2$ , a value which varies only slightly from that of free *p*-tolunitrile (at 119.12 ppm). The  $^{29}\text{Si}$  resonance for **4** in  $\text{CDCl}_3$  was observed at –25.77 ppm and was very close to that of uncomplexed  $\text{Si}_6\text{Br}_{12}$  at –25.73 ppm.<sup>14a</sup> The IR spectra show  $\text{C}\equiv\text{N}$  stretches at 2211 and 2209  $\text{cm}^{-1}$  for complexes **3** and **4**, respectively. Again, these values were shifted slightly from that of free *p*-tolunitrile at 2229  $\text{cm}^{-1}$ . UV–vis spectroscopic characterization of  $\text{Si}_6\text{Cl}_{12}$  and  $\text{Si}_6\text{Br}_{12}$  was in good agreement with a previous report.<sup>14b</sup> The low-energy bands for both **1** ( $\lambda_{\text{max}}$  287 nm) and **2** ( $\lambda_{\text{max}}$  301 nm) exhibit a decrease in peak intensity and a small red shift when complexed with *p*-tolunitrile to give **3** ( $\lambda_{\text{max}}$  297 nm) and **4** ( $\lambda_{\text{max}}$  309 nm) (Figures S9 and S10, Supporting Information).

The “inverse sandwich” structure of **4** was confirmed by X-ray crystallography (see the Supporting Information; CCDC-752137 submitted Oct 23, 2009). The term “inverse sandwich” was coined by Hoffmann<sup>15</sup> to describe complexes that contain a planar ring that is coordinated by Lewis



**Figure 2.** ORTEP diagram of complex **4** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity.



**Figure 3.** Intermolecular  $\text{Br} \cdots \text{Br}$  interactions of **4**. All  $\text{Br} \cdots \text{Br}$  distances (light blue lines between molecules) are 3.606 Å.

conjugates both above and below the ring. Schmidbaur et al.<sup>16</sup> provided the first experimental evidence of such “inverse sandwich” complexes. Most literature reports have planar Lewis base rings (e.g., benzene, cyclopentadienyl, etc.)<sup>17</sup> coordinated to Lewis acids. In contrast, complex **4** features a planar Lewis acid (i.e.,  $\text{Si}_6\text{Br}_{12}$ ) coordinated to two Lewis base *p*-tolunitrile molecules.

There are several types of contacts observed for complex **4**. A Lewis acid–base interaction has the nitrile groups located just above and below the center of the  $\text{Si}_6\text{Br}_{12}$  ring at a distance of 2.001 Å from the center of the hexagonal  $\text{Si}_6$  plane (Figure 2). In addition, the distances between Si atoms and N atoms (i.e., 3.02–3.17 Å) are significantly shorter than the sum of van der Waals radii ( $r_{\text{vdw}}(\text{Si}–\text{N}) = 3.65$  Å)<sup>14</sup> but longer than the sum of the covalent radii ( $r_{\text{cov}}(\text{Si}–\text{N}) = 1.82$  Å).<sup>18</sup> It is also interesting to note the weak interactions of the cyano carbon atom with one Si–Br moiety, giving  $\text{C1}–\text{Si9} = 3.760$  Å and  $\text{C1}–\text{Br1} = 3.505$  Å. Intermolecular  $\text{Br} \cdots \text{Br}$  interactions are observed for **4**, where each molecule is “edge-connected” to two adjacent molecules (Figure 3).

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In conclusion,  $\text{Si}_6\text{X}_{12}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) was synthesized by molecular halogenation of  $\text{Si}_6\text{H}_{12}$  in high yield and good purity. Perhalogenated cyclohexasilanes react with *p*-tolunitrile to give “inverse sandwich” adducts **3** and **4** with a planar  $\text{Si}_6$  ring upon coordination. Our future reports will detail dianionic adducts based on tetra-*n*-butylammonium halides as well as a monoanionic adamantylazide adduct of  $\text{Si}_6\text{Cl}_{12}$ .<sup>19</sup> It is straightforward to conceptualize the utility of  $\text{Si}_6\text{X}_{12}\cdot\text{L}_n$  chemistry in molecular assembly of silicon-based clusters/tubes/

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wires. Thereby, we proffer that this constitutes a new landscape in Si chemistry.

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**Supporting Information Available:** Text, tables, and figures giving experimental details regarding the synthesis and characterization of complexes **1–4** and CIF files giving crystallographic data for **2** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.