

## Cyclobutadiene Dianions Consisting of Heavier Group 14 Elements: Synthesis and Characterization

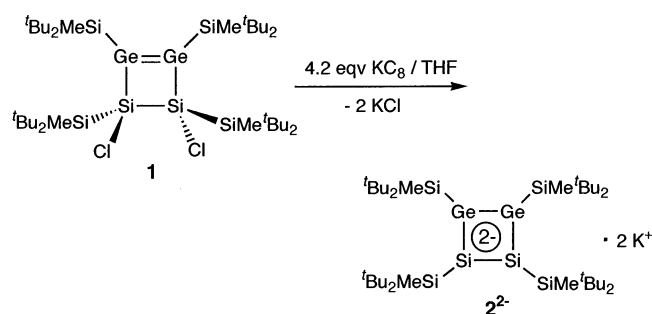
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Among the aromatic charged  $6\pi$ -electron species, cyclobutadiene dianion ( $\text{CBD}^{2-}$ ) is the least studied and the most intriguing.<sup>1</sup> The question of its aromaticity is very important, since multiply charged  $6\pi$ -aromatic cyclic systems behave quite differently from neutral and singly charged systems because of the Coulombic repulsion of the two additional electrons.<sup>2</sup> A folded  $\text{CBD}^{2-}$  structure with one localized and one allylic delocalized negative charge was predicted by early calculations.<sup>3</sup> Later, another model, a trapezoid  $\text{CBD}^{2-}$  structure with 1,2-localized negative charges and a  $\text{C}=\text{C}$  double bond, was suggested.<sup>4</sup> Schleyer et al. have predicted a planar delocalized  $\text{CBD}^{2-}$  structure stabilized by coordination of the two Li cations.<sup>5</sup> Very recently, we have succeeded in isolating the first stable  $\text{Me}_3\text{Si}$ -substituted  $\text{CBD}^{2-}\cdot 2\text{Li}^+$ , which has a square-planar delocalized aromatic structure.<sup>6</sup> However, until now the  $\text{CBD}^{2-}$  analogues consisting of heavier group 14 elements were unexplored, both experimentally and theoretically. Here we report the synthesis and structural characterization of the first “heavy”  $\text{CBD}^{2-}$ 's consisting of Si and Ge atoms.

The two “heavy”  $\text{CBD}^{2-}$  species were synthesized containing two Si and two Ge atoms for  $2^{2-}$ , and containing all Si atoms for  $4^{2-}$ . The first compound was synthesized from disiladigermene **1**<sup>7</sup> by reduction with 4.2 equiv of  $\text{KC}_8$  in THF to furnish very cleanly and quickly the desired tetrakis(di-*tert*-butylmethylsilyl)-1,2-disila-3,4-digermacyclobutadiene dianion  $2^{2-}$  (Scheme 1).<sup>8</sup> The

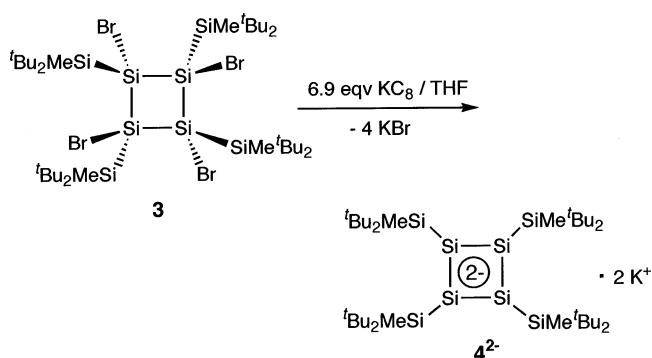
### Scheme 1



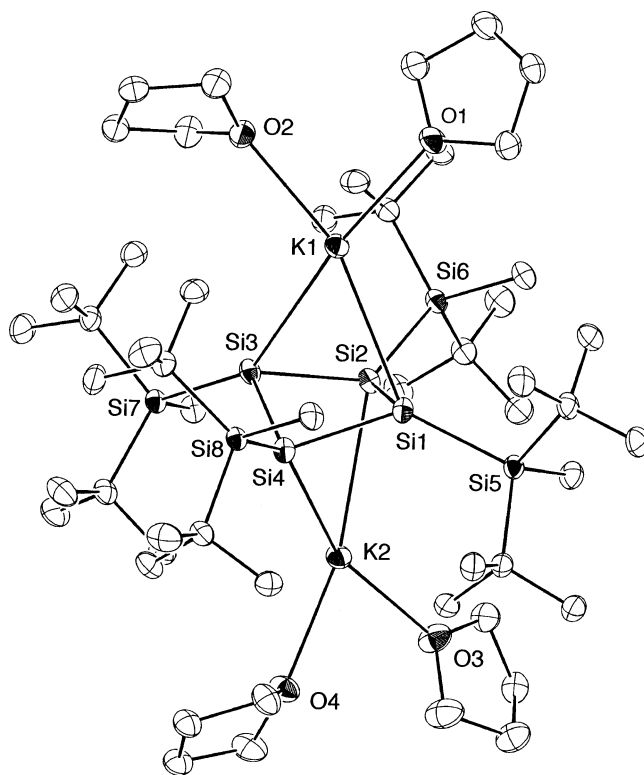
second  $\text{CBD}^{2-}$  species, tetrakis(di-*tert*-butylmethylsilyl)-1,2,3,4-tetrasilacyclobutadiene dianion  $4^{2-}$ , was obtained similarly by the reduction of tetrabromocyclobutasilane **3** with 6.9 equiv of  $\text{KC}_8$  in THF (Scheme 2).<sup>9</sup> Both “heavy”  $\text{CBD}^{2-}$  species  $[\text{K}^+(\text{thf})_2]_2\cdot 2^{2-}$  and  $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$ , isolated as extremely air- and moisture-sensitive dark-green crystals in 70 and 73% yields, respectively, exhibited simple NMR spectra, in agreement with their symmetrical structure.

The structures of  $2^{2-}$  and  $4^{2-}$  were unequivocally determined by X-ray analysis. Crystals of  $[\text{K}^+(\text{thf})_2]_2\cdot 2^{2-}$  and  $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$  with four THF molecules are crystallographically isomorphous,<sup>10,11</sup> the ORTEP drawing of  $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$  being shown in Figure 1. Both cases showed folded four-membered rings (folding angle:  $34^\circ$  for  $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$ ) with two  $\eta^2$ -1,3-coordinated potassium cations accommodated above and below the ring. The Si–Si bond lengths

### Scheme 2

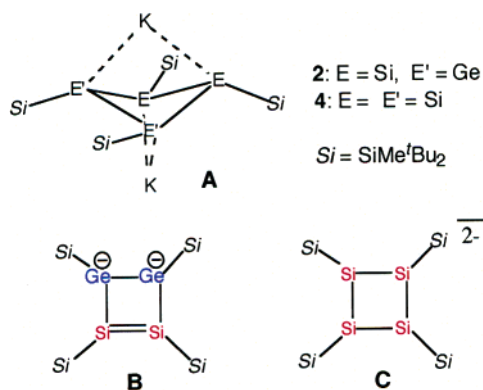


in the four-membered ring of  $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$  are not equal, with the Si1–Si2 bond being somewhat shortened (2.2989(8) Å) and the Si3–Si4 bond being somewhat lengthened (2.3576(8) Å) as a consequence of the different orientation of the  $\text{tBu}_2\text{MeSi}$  groups.



**Figure 1.** ORTEP drawing of  $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$ . Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.2989(8), Si2–Si3 = 2.3300(8), Si3–Si4 = 2.3576(8), Si1–Si4 = 2.3301(8), Si1–Si5 = 2.3602(8), Si2–Si6 = 2.3597(8), Si3–Si7 = 2.3728(7), Si4–Si8 = 2.3719(7); Selected bond angles (deg): Si2–Si1–Si4 = 88.09(3), Si1–Si2–Si3 = 88.12(3), Si2–Si3–Si4 = 86.72(3), Si1–Si4–Si3 = 86.74(3); Dihedral angle (deg): Si1–Si2–Si3/Si1–Si3–Si4 = 34.16(2).

Chart 1

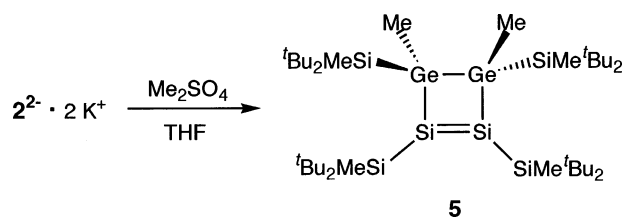


The Si–K bond distances, ranging from 3.3011(8) to 3.4044(7) Å, are typical for silyl potassium derivatives.<sup>12</sup> All skeletal Si atoms are significantly pyramidalized; for example, the sum of the three Si–Si–Si angles around Si1 (or Si2) and Si3 (or Si4) atoms are 341 and 326 °, respectively. Consequently, the bulky 'Bu<sub>2</sub>MeSi-substituents occupy alternating up and down positions, minimizing steric congestion around the CBD<sup>2-</sup> ring. Such structural features of [K<sup>+</sup>(thf)<sub>2</sub>]<sub>2</sub>·4<sup>2-</sup>, as well as those of [K<sup>+</sup>(thf)<sub>2</sub>]<sub>2</sub>·2<sup>2-</sup>, do not meet the classical criteria for aromaticity (ring planarity, cyclic bonds equalization),<sup>1</sup> thus providing evidence for their nonaromatic nature.<sup>13</sup> Magnetic criteria for aromaticity also support such a conclusion: NICS,<sup>14</sup> commonly recognized as an effective aromaticity probe, was calculated for 2<sup>2-</sup> and 4<sup>2-</sup> as +4.3 and +6.1, respectively [NICS(1)], indicating the absence of a diatropic ring current.<sup>15</sup>

Although both “heavy” CBD<sup>2-</sup>'s 2<sup>2-</sup> and 4<sup>2-</sup> in the solid state have very similar geometries, as depicted in **A** (Chart 1), their solution behavior is significantly different based on their <sup>29</sup>Si NMR spectra. The <sup>29</sup>Si NMR spectrum of 2<sup>2-</sup> showed three resonances (5.3, 20.8, and 113.7 ppm), from which the latter one, due to the skeletal Si atoms, is in the range for sp<sup>2</sup>-type Si atoms. This provides evidence for the preferential accommodation of the two negative charges on the more electronegative Ge atoms, making the two endocyclic Si atoms doubly bonded, which corresponds to structure **B**. However, the <sup>29</sup>Si NMR spectrum of 4<sup>2-</sup> shows a set of only two signals at 10.0 for 'Bu<sub>2</sub>MeSi and 17.0 ppm for the skeletal Si.<sup>9</sup> The latter resonance is clearly outside the range for sp<sup>2</sup>-type Si atoms, which provides evidence for appreciable delocalization of the negative charges inside the CBD<sup>2-</sup> ring, as depicted in **C**. Apparently, in polar THF, the Si–K bonds can be easily broken to form solvated ion pairs, whose structural behavior is dictated mainly by the relative electronegativities of the skeletal elements (Si vs. Ge): the electronegativity difference favors electron localization.

The “heavy” CBD<sup>2-</sup>'s are highly and selectively reactive. Thus, 2<sup>2-</sup> smoothly and cleanly reacts with Me<sub>2</sub>SO<sub>4</sub> to form the cyclic disilene **5** in 95% yield, where the Me groups are bound to Ge atoms (Scheme 3).<sup>16</sup> The formation of **5** provides clear evidence for the 1,2-localization of the two negative charges on the Ge atoms in 2<sup>2-</sup>.

Scheme 3



**Supporting Information Available:** Experimental procedures, spectral data of 2<sup>2-</sup> and 4<sup>2-</sup>, and tables of crystallographic data including atomic positional and thermal parameters for [K<sup>+</sup>(thf)<sub>2</sub>]<sub>2</sub>·4<sup>2-</sup> (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Garratt, P. *Aromaticity*; Wiley: New York, 1986.
- (2) (a) Sommerfeld, T. *J. Am. Chem. Soc.* **2002**, *124*, 1119. (b) Feuerbacher, S.; Cederbaum, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 9531.
- (3) Hess, B. A.; Ewig, C. S.; Schaad, L. J. *J. Org. Chem.* **1985**, *50*, 5869.
- (4) van Zandwijk, G.; Janssen, R. A. J.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 4155.
- (5) (a) Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7929. (b) Balci, M.; McKee, M. L.; Schleyer, P. v. R. *J. Phys. Chem. A* **2000**, *104*, 1246.
- (6) (a) Sekiguchi, A.; Matsuo, T.; Watanabe, H. *J. Am. Chem. Soc.* **2000**, *122*, 5652. (b) Ishii, K.; Kobayashi, N.; Matsuo, T.; Tanaka, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2001**, *123*, 5356.
- (7) Lee, V. Ya.; Takahashi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2003**, *125*, 6012.
- (8) Spectral data for K<sup>+</sup><sub>2</sub>·2<sup>2-</sup>: <sup>1</sup>H NMR (THF-*d*<sub>6</sub>, δ) 0.28 (s, 6 H), 0.31 (s, 6 H), 1.13 (s, 36 H), 1.15 (s, 36 H); <sup>13</sup>C NMR (THF-*d*<sub>6</sub>, δ) -1.7, 0.7, 22.3, 23.3, 31.6, 31.7; <sup>29</sup>Si NMR (THF-*d*<sub>6</sub>, δ) 5.3, 20.8, 113.7 (skeletal Si atoms).
- (9) Spectral data for K<sup>+</sup><sub>2</sub>·4<sup>2-</sup>: <sup>1</sup>H NMR (THF-*d*<sub>6</sub>, δ) 0.34 (s, 12 H), 1.20 (s, 72 H); <sup>13</sup>C NMR (THF-*d*<sub>6</sub>, δ) -0.4, 22.6, 31.7; <sup>29</sup>Si NMR (THF-*d*<sub>6</sub>, δ) 10.0, 17.0 (skeletal Si atoms). The assignment of the <sup>29</sup>Si NMR signals was made on the basis of comparison between <sup>29</sup>Si inverse gated and <sup>29</sup>Si DEPT NMR techniques.
- (10) Although the crystal structure of [K<sup>+</sup>(thf)<sub>2</sub>]<sub>2</sub>·2<sup>2-</sup> was determined by X-ray analysis, we do not discuss its structural parameters due to unsatisfactory refinement.
- (11) Crystal data for [K<sup>+</sup>(thf)<sub>2</sub>]<sub>2</sub>·4<sup>2-</sup> at 120 K: MF = C<sub>52</sub>H<sub>116</sub>K<sub>2</sub>O<sub>4</sub>Si<sub>8</sub>, MW = 1108.37, triclinic, *P*-1, *a* = 13.0830(7) Å, *b* = 13.3180(4) Å, *c* = 22.2070(10) Å, α = 89.659(3)°, β = 88.870(2)°, γ = 61.283(3)°, *V* = 3392.7(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>calcd</sub> = 1.085 g·cm<sup>-3</sup>. The final *R* factor was 0.0532 for 12184 reflections with *I*<sub>0</sub> > 2σ(*I*<sub>0</sub>) (R<sub>w</sub> = 0.1535 for all data, 31807 reflections), GOF = 1.018.
- (12) The typical Si–K bond distances lie in the range 3.31–3.42 Å, which corresponds well with the sum of the covalent radii for Si and K atoms (3.38 Å), see: Jenkins, D. M.; Teng, W.; English, U.; Stone, D.; Ruhland-Senge, K. *Organometallics* **2001**, *20*, 4600.
- (13) The influence of the nature of the counteranion on the degree of aromaticity of the “heavy” CBD<sup>2-</sup>'s is expected to be great: the smaller Li cations, which are more prone to form covalent bonds than K, can approach the CBD<sup>2-</sup>'s ring more closely than other cations, thus counteracting the Coulombic repulsion and making the CBD<sup>2-</sup> ring more planar and more aromatic.
- (14) Schleyer, P. v. R.; Maerker, G.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- (15) NICS calculations were performed at the B3LYP/6-31G(d) level for the model Me<sub>3</sub>Si-substituted CBD<sup>2-</sup>'s 2<sup>2-</sup> and 4<sup>2-</sup> at 1 Å above the center of the rings [NICS(1)].
- (16) Spectral data for **5**: orange crystals, mp 175–177 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.33 (s, 6 H), 0.38 (s, 6 H), 1.08 (s, 6 H), 1.19 (s, 18 H), 1.21 (s, 18 H), 1.22 (s, 18 H), 1.23 (s, 18 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) -5.0, -4.0, 5.5, 21.4, 21.6, 22.2, 22.4, 29.9, 30.28, 30.30, 30.5; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) 19.0, 23.0, 167.6 (Si=Si); UV/vis (hexane) λ<sub>max</sub>/nm (ε) 337 (820), 388 (1160), 441 (2890); Anal. Calcd for C<sub>38</sub>H<sub>90</sub>Ge<sub>2</sub>Si<sub>6</sub>: C, 53.02; H, 10.54. Found: C, 53.33; H, 10.28.

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