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

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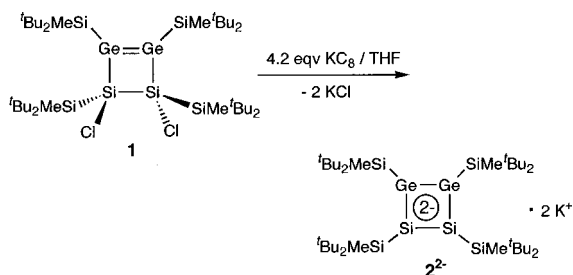
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Among the aromatic charged 6π -electron species, cyclobutadiene dianion (CBD^{2-}) is the least studied and the most intriguing.¹ The question of its aromaticity is very important, since multiply charged 6π -aromatic cyclic systems behave quite differently from neutral and singly charged systems because of the Coulombic repulsion of the two additional electrons.² A folded CBD^{2-} structure with one localized and one allylic delocalized negative charge was predicted by early calculations.³ Later, another model, a trapezoid CBD^{2-} structure with 1,2-localized negative charges and a $\text{C}=\text{C}$ double bond, was suggested.⁴ Schleyer et al. have predicted a planar delocalized CBD^{2-} structure stabilized by coordination of the two Li cations.⁵ Very recently, we have succeeded in isolating the first stable Me_3Si -substituted $\text{CBD}^{2-}\cdot 2\text{Li}^+$, which has a square-planar delocalized aromatic structure.⁶ However, until now the 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” CBD^{2-} ’s consisting of Si and Ge atoms.

The two “heavy” 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 disiladigermetene **1** by reduction with 4.2 equiv of 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).⁸ The

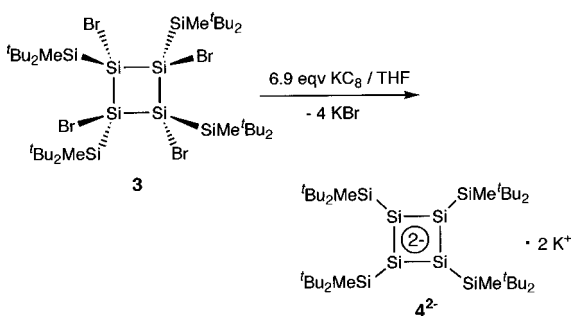
Scheme 1



second 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 KC_8 in THF (Scheme 2).⁹ Both “heavy” 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,^{10,11} 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° for $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$) with two η^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 $^t\text{Bu}_2\text{MeSi}$ groups.

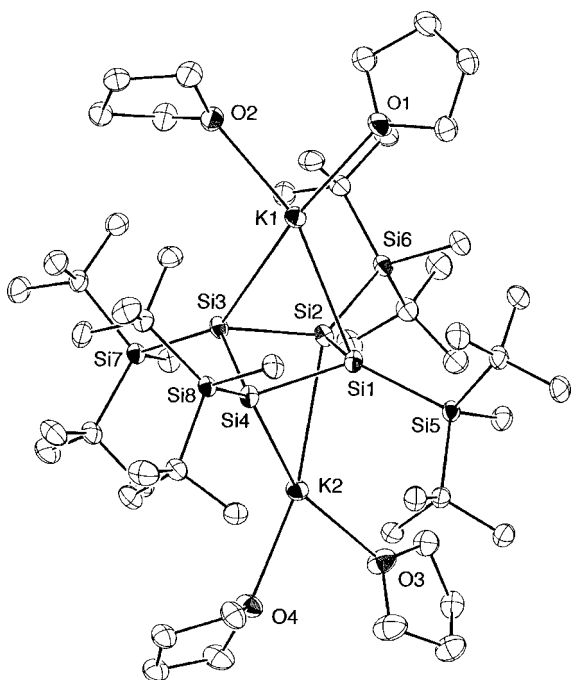
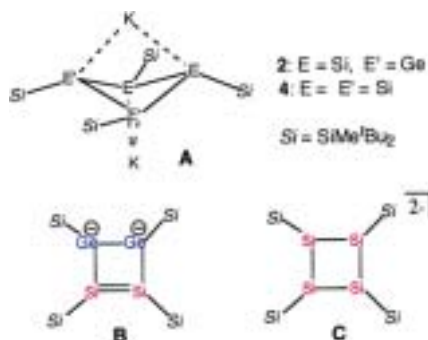


Figure 1. ORTEP drawing of $[\text{K}^+(\text{thf})_2]_2\cdot 4^{2-}$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.2989(8), Si2–Si3 = 2.3300(8), Si3–Si4 = 2.3576(8), Si1–Si4 = 2.3301(8), Si1–Si5 = 2.3602(8), Si2–Si6 = 2.3597(8), Si3–Si7 = 2.3728(7), Si4–Si8 = 2.3719(7);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

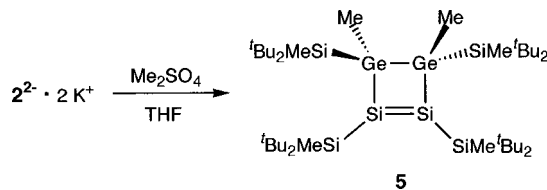


The Si–K bond distances, ranging from 3.3011(8) to 3.4044(7) Å, are typical for silyl potassium derivatives.¹² All skeletal Si atoms are significantly pyramidalized; for example, the sum of the three Si–Si–Si angles around Si1 (or Si2) and Si3 (or Si4) atoms are 341 and 326°, respectively. Consequently, the bulky ^tBu₂MeSi-substituents occupy alternating up and down positions, minimizing steric congestion around the CBD²⁻ ring. Such structural features of [K⁺(thf)₂]₂·4²⁻, as well as those of [K⁺(thf)₂]₂·2²⁻, do not meet the classical criteria for aromaticity (ring planarity, cyclic bonds equalization),¹ thus providing evidence for their nonaromatic nature.¹³ Magnetic criteria for aromaticity also support such a conclusion: NICS,¹⁴ commonly recognized as an effective aromaticity probe, was calculated for 2²⁻ and 4²⁻ as +4.3 and +6.1, respectively [NICS(1)], indicating the absence of a diatropic ring current.¹⁵

Although both “heavy” CBD²⁻’s 2²⁻ and 4²⁻ in the solid state have very similar geometries, as depicted in A (Chart 1), their solution behavior is significantly different based on their ²⁹Si NMR spectra. The ²⁹Si NMR spectrum of 2²⁻ 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 sp²-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 ²⁹Si NMR spectrum of 4²⁻ shows a set of only two signals at 10.0 for ^tBu₂MeSi and 17.0 ppm for the skeletal Si.⁹ The latter resonance is clearly outside the range for sp²-type Si atoms, which provides evidence for appreciable delocalization of the negative charges inside the CBD²⁻ 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” CBD²⁻’s are highly and selectively reactive. Thus, 2²⁻ smoothly and cleanly reacts with Me₂SO₄ to form the cyclic disilene 5 in 95% yield, where the Me groups are bound to Ge atoms (Scheme 3).¹⁶ The formation of 5 provides clear evidence for the 1,2-localization of the two negative charges on the Ge atoms in 2²⁻.

Scheme 3



Supporting Information Available: Experimental procedures, spectral data of 2²⁻ and 4²⁻, and tables of crystallographic data including atomic positional and thermal parameters for [K⁺(thf)₂]₂·4²⁻ (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Spectral data for [K⁺(thf)₂]₂·2²⁻: ¹H NMR (THF-*d*₈, δ) 0.28 (s, 6 H), 0.31 (s, 6 H), 1.13 (s, 36 H), 1.15 (s, 36 H); ¹³C NMR (THF-*d*₈, δ) −1.7, 0.7, 22.3, 23.3, 31.6, 31.7; ²⁹Si NMR (THF-*d*₈, δ) 5.3, 20.8, 113.7 (skeletal Si atoms).
- (9) Spectral data for [K⁺(thf)₂]₂·4²⁻: ¹H NMR (THF-*d*₈, δ) 0.34 (s, 12 H), 1.20 (s, 72 H); ¹³C NMR (THF-*d*₈, δ) −0.4, 22.6, 31.7; ²⁹Si NMR (THF-*d*₈, δ) 10.0, 17.0 (skeletal Si atoms). The assignment of the ²⁹Si NMR signals was made on the basis of comparison between ²⁹Si inverse gated and ²⁹Si DEPT NMR techniques.
- (10) Although the crystal structure of [K⁺(thf)₂]₂·2²⁻ was determined by X-ray analysis, we do not discuss its structural parameters due to unsatisfactory refinement.
- (11) Crystal data for [K⁺(thf)₂]₂·4²⁻ at 120 K: MF = C₅₂H₁₁₆K₂O₄Si₈, MW = 1108.37, triclinic, *P*-1, *a* = 13.0830(7) Å, *b* = 13.3180(4) Å, *c* = 22.070(10) Å, α = 89.659(3)°, β = 88.870(2)°, γ = 61.283(3)°, *V* = 3392.7(3) Å³, *Z* = 2, *D*_{calc} = 1.085 g·cm^{−3}. The final *R* factor was 0.0532 for 12184 reflections with *I*_o > 2σ(*I*_o) (R_w = 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.; Englich, 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” CBD²⁻’s is expected to be great: the smaller Li cations, which are more prone to form covalent bonds than K, can approach the CBD²⁻’s ring more closely than other cations, thus counteracting the Coulombic repulsion and making the CBD²⁻ ring more planar and more aromatic.
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- (15) NICS calculations were performed at the B3LYP/6-31G(d) level for the model Me₃Si-substituted CBD²⁻’s 2²⁻ and 4²⁻ at 1 Å above the center of the rings [NICS(1)].
- (16) Spectral data for 5: orange crystals, mp 175–177 °C; ¹H NMR (C₆D₆, 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); ¹³C NMR (C₆D₆, δ) −5.0, −4.0, 5.5, 21.4, 21.6, 22.2, 22.4, 29.9, 30.28, 30.30, 30.5; ²⁹Si NMR (C₆D₆, δ) 19.0, 23.0, 167.6 (Si=Si); UV/vis (hexane) λ_{max}/nm (ε) 337 (820), 388 (1160), 441 (2890); Anal. Calcd for C₃₈H₉₀Ge₂Si₆: C, 53.02; H, 10.54. Found: C, 53.33; H, 10.28.

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