Pentasilatricyclo[2.1.0.02,5]pentane and Its Anion

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Pentasilatricyclo[2.1.0.0²,⁵]pentane and Its Anion

Vladimir Ya. Lee, Taka Yokoyama, Kazunori Takanashi, and Akira Sekiguchi*[a]

Dedicated to Professor Yitzhak Apeloig on the occasion of his 65th birthday

In their comprehensive review, Michl and co-workers listed bicyclo[1.1.1]pentanes, [1.1.1]propellanes and tricyclo[2.1.0.0²,⁵]pentanes among the most highly strained polycyclic compounds, otherwise known as cages.[1] The nonclassical nature and unusual hybridization mode of the bridging bonds in [1.1.1]propellanes and tricyclo[2.1.0.0²,⁵]pentanes, sharply deviating from the normal sp³ states, as well as the nontrivial interbridgehead nonbonding interaction in bicyclo[1.1.1]pentanes, make them very attractive targets for both experimental and computational pursuits. Even though the field of organic derivatives of such cage compounds is rather well investigated from both synthetic and theoretical sides, the field of their analogues of the heavy Group 14 elements is still largely unknown. Thus, for example, only four stable heavy [1.1.1]propellanes of the type R_6E_5 (E = heavy Group 14 element) have been reported to date, representing examples of pentastanna-, digermatristanna- and pentagerma[1.1.1]propellanes.[2] As for the heavy tricyclo[2.1.0.0²,⁵]pentanes, the only known stable representative featuring an extremely long Ge−C bridge bond was reported by us several years ago.[3] The latter compound revealed structural peculiarities that are sharply distinctive from those of its organic counterparts.[4] However, the particularly attractive all heavy Group 14 element-consisting analogues of tricyclo[2.1.0.0²,⁵]pentane were still unknown prior to our studies,[5] and in this communication we wish to report the synthesis of the first pentasilatricyclo[2.1.0.0²,⁵]pentane derivative and its subsequent reduction to produce a rather unusual anionic derivative manifesting a number of unprecedented structural features.

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Synthesis of 3-chloro-3-phenyl-1,2,4,5-tetrakis(di-*tert*-butylmethylsilyl)pentasilatricyclo[2.1.0.0²,⁵]pentane (**2**) was accomplished by the reaction of the calcium salt of 1,2,3,4-tetrakis(di-*tert*-butylmethylsilyl)tetrasilabicyclo[1.1.0]butan-2,4-diide $\mathbf{1^{2-}\cdot Ca^{2+}}$[6] with an excess of PhSiCl₃ in THF (Scheme 1).[7] After purification by silica gel/toluene column chromatography carried out in a glove box, **2** was isolated as yellow crystals in 32% yield. In accordance with its tricyclic structure, **2** exhibited (in both ¹H and ¹³C NMR spectra) a set of three signals for the Me groups and a set of four signals for the *t*Bu groups, along with resonances of the phenyl ring atoms. The resonances of both bridgehead silicon atoms in **2** at −222.4 and −217.1 ppm were observed in the high-field region diagnostic of highly strained polycyclic compounds,[8] whereas the signal of the bridging silicon atoms was observed at −117.0 ppm.
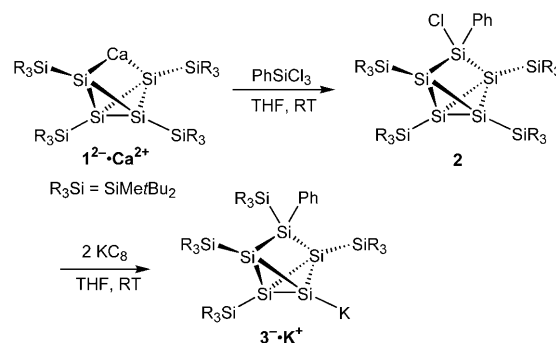
Scheme 1. Synthesis of pentasilatricyclo[2.1.0.0²,⁵]pentane **2** and its subsequent reduction to form anionic derivative **3⁻·K⁺**.

While rather interesting in itself, pentasilatricyclo[2.1.0.0²,⁵]pentane (**2**) served as a good precursor for the even more exciting anionic derivative, 3-phenyl-2,3,4,5-tetrakis(di-*tert*-butylmethylsilyl)pentasilatricyclo[2.1.0.0²,⁵]pentan-1-ide, isolated in the form of its potassium salt **3⁻·K⁺** (Scheme 1).[7] One should mention that no stable representatives of tricyclo[2.1.0.0²,⁵]pentanide derivatives are known in organic chemistry.[1,4] As expected, the anionic bridgehead

silicon in $\mathbf{3^-\cdot K^+}$ was more shielded than that in the neutral precursor **2**, being observed at the very high field of −253.9 ppm.[9]

In the crystalline form, potassium pentasilatricyclo[2.1.0.0^{2,5}]pentan-1-ide exists as a contact ion pair, in which potassium lacks coordination to a nucleophilic solvent. As is typical for unsolvated anionic derivatives R$_3$EM (E = heavy Group 14 element; M = alkali metal),[9] potassium pentasilatricyclo[2.1.0.0^{2,5}]pentan-1-ide forms a dimeric aggregate $[\mathbf{3^-\cdot K^+}]_2$, featuring a central parallelogram consisting of two Si and two K atoms (Figure 1).[10] Thus, each

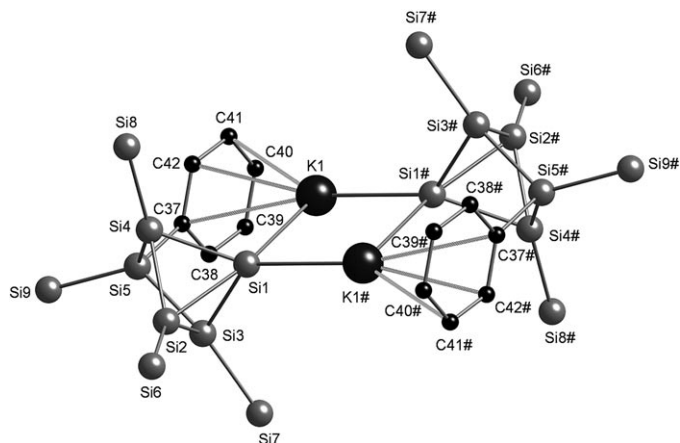Figure 1. CrystalMaker view of $[\mathbf{3^-\cdot K^+}]_2$ (hydrogen atoms and alkyl (methyl, *tert*-butyl) groups are omitted). Structural parameters are given in Table 1.

potassium is coordinated to a pair of silicons with different bond lengths of 3.2742(6) Å (Si1–K1) and 3.3540(6) Å (Si1–K1#),[11] in addition to an agostic interaction with one of the Me$_{tBu}$ groups manifested in the K1–C18 bonding contact of 3.301(2) Å (Figure 1). Particularly important was K-aromatic ring π-interaction, which was seen in the bonding of potassium to three of the ring carbons: K1−C37 3.4384(17), K1−C42 3.220(2) and K1−C41 3.285(2) Å.[11] In the absence of solvation effects, the potassium ions in $[\mathbf{3^-\cdot K^+}]$ could be most efficiently stabilized by intramolecular π-coordination to the aromatic ring. Such an interaction causes a significant bending of the Si1–K1 bond toward the benzene ring, resulting in the rather unusual and structurally unfavorable inverted tetrahedral configuration of the anionic Si1 center (the so-called umbrella configuration).[12] The importance of such a K$^+$–arene π-interaction, which outbalanced the obvious disadvantage of geometrical constraints resulting in the overall stabilization of the anionic derivative, was supported by DFT computations on the $[\mathbf{3^-\cdot K^+}]_{model}$, which well reproduced the real structure of $[\mathbf{3^-\cdot K^+}]$ with the diagnostic umbrella configuration of the anionic Si1 center and K$^+$–arene π-interaction (Figure 2).[13]

On the other hand, skeletal Si−Si bonds to the anionic Si1 center (Si1−Si3 2.4160(6) and Si1−Si4 2.4025(6) Å) are markedly stretched compared with other skeletal bonds involving the neutral Si2 atom (Si2−Si3 2.3182(6) and Si2−Si4
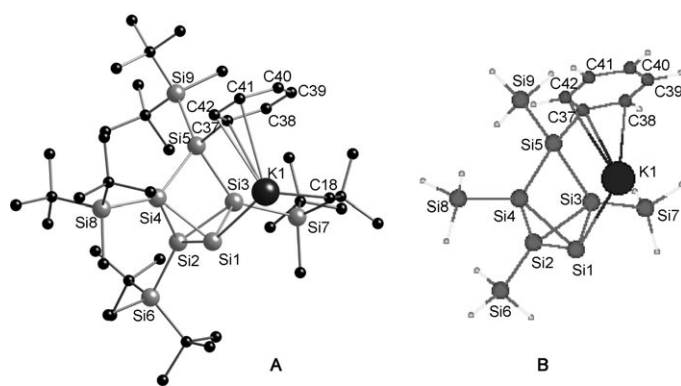

Figure 2. Comparison of the X-ray structure of $\mathbf{3^-\cdot K^+}$ **A** (monomeric half-molecule is shown, hydrogen atoms are omitted) and optimized geometry of $[\mathbf{3^-\cdot K^+}]_{model}$ **B** (H$_3$Si groups instead of *t*Bu$_2$MeSi substituents). For the structural parameters of both $\mathbf{3^-\cdot K^+}$ **A** and $[\mathbf{3^-\cdot K^+}]_{model}$ **B**, see Table 1.

2.3321(6) Å, see Table 1). Calculated values of the skeletal Si−Si bonds follow the same trend: long bonds to anionic Si1 (Si1−Si3 = Si1−Si4 2.499 Å) and short bonds to neutral Si2 (Si2−Si3 = Si2−Si4 2.313 Å). This definitely demonstrates the situation where the anionic Si1 center holds its negative charge in the exocyclic orbital with a large s-orbital contribution, whereas the endocyclic bonds from Si1 to Si2, Si3 and Si4 are formed by high *p*-character hybrids. Accordingly, NBO calculations on $[\mathbf{3^-\cdot K^+}]_{model}$ revealed the high *p*-character of the endocyclic Si1 orbitals compared with those of Si2 atom, Si1(sp$^{15.5}$)-Si3/Si4(sp$^{3.4}$) versus Si2(sp$^{2.9}$)-Si3/Si4-(sp$^{4.6}$).[13] It is interesting to note that although the R$_3$Si(Ph)Si bridge in $\mathbf{3^-\cdot K^+}$ fixes a very acute interplanar angle Si3-Si1-Si2/Si4-Si1-Si2 of 93.45(10)°, the bridging Si1−Si2 bond of 2.3801(6) Å is quite normal, in contrast to typical tricyclo[2.1.0.0^{2,5}]pentanes featuring extremely short C−C bridges.[1,4] This again should be ascribed to the presence of an anionic center at the bridgehead Si1 and the resulting high *p*-character of the Si1−Si2 bridge bond (Si1(sp$^{7.4}$)-Si2-(sp$^{6.6}$)).
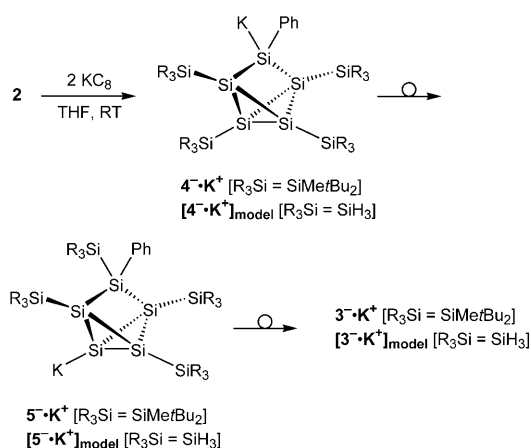
The mechanism of the formation of anionic $\mathbf{3^-\cdot K^+}$ is not evident; however, it may involve several consecutive steps.

Table 1. Comparison of the experimentally observed (for $[\mathbf{3^-\cdot K^+}]$) and computed (for $[\mathbf{3^-\cdot K^+}]_{model}$) bond lengths [Å].

| Bond length	Experimental	Calculated
Si1−Si2	2.3801(6)	2.366
Si1−Si3	2.4160(6)	2.499
Si1−Si4	2.4025(6)	2.499
Si2−Si3	2.3182(6)	2.313
Si2−Si4	2.3321(6)	2.313
Si3−Si5	2.3698(6)	2.362
Si4−Si5	2.3607(6)	2.362
Si1−K1	3.2742(6)	3.180
K1−C37	3.4384(17)	3.050
K1−C38	3.691(3)[a]	3.207
K1−C41	3.285(2)	3.503[a]
K1−C42	3.220(2)	3.207

[a] Non-bonding distance.

One can suggest that in the first-step reductive dehalogenation of **2** with potassium graphite produces the expected silylpotassium **4⁻·K⁺** featuring an anionic charge at the bridge Si (Scheme 2). Then, the following 1,3-migration transforms **4⁻·K⁺** into the novel silylpotassium **5⁻·K⁺**, in which the negative charge is now located at the bridgehead Si. Such isomerization might be driven by a general tendency for accommodation of the anionic charge in an orbital of greater s-character. Final bridgehead-to-bridgehead 1,2-migration, providing strongly favorable π-coordination of the K⁺ ion to the aromatic ring, would complete the reaction sequence resulting in the formation of **3⁻·K⁺**. Both intermediate silylpotassiums [**4⁻·K⁺**]$_{model}$ and [**5⁻·K⁺**]$_{model}$ were located as minimum structures (for H$_3$Si-substituted models), destabilized compared with the final [**3⁻·K⁺**]$_{model}$ by 13.7 and 5.7 kcal mol^{-1}, respectively (Scheme 2).[13] In sharp contrast, computations on the free cage anions with no Si−K bonding revealed a marked stabilization of the final [**3⁻**]$_{model}$ over the initially formed [**4**]$^-_{model}$ by 11.8 kcal mol^{-1} and rather insignificant destabilization of the final [**3**]$^-_{model}$ compared with the intermediate [**5**]$^-_{model}$ by 0.2 kcal mol^{-1}. Indeed, lacking bonding to potassium and, consequently, a favorable K⁺-arene π-interaction, silyl anion [**3**]$^-_{model}$ is no longer stabilized compared with silyl anion [**5**]$^-_{model}$. Thus, the π(K⁺-arene) stabilization energy in [**3⁻·K⁺**]$_{model}$ could be estimated as about 5.9 kcal mol^{-1}.

Scheme 2. Possible reaction mechanism for the formation of anionic derivative **3⁻·K⁺**.

Silylpotassium **3⁻·K⁺** serves as a convenient source for further persilapolycyclic derivatives inaccessible in any other way. Thus, reacting with trimethylchlorosilane in THF, **3⁻·K⁺** produced a novel Me$_3$Si-substituted pentasilatricyclo[2.1.0.0^{2,5}]pentane **6** featuring characteristic high-field resonances of the bridgehead (−182.3 and −178.6 ppm) and bridging (−121.1 ppm) silicons (Scheme 3).[7]

To conclude, we have synthesized 3-chloro-3-phenyl-1,2,4,5-tetrakis(di-*tert*-butylmethylsilyl)pentasilatricyclo[2.1.0.0^{2,5}]pentane **2** by the reaction of the calcium salt of tetrasilabicyclo[1.1.0]butan-2,4-diide **1²⁻·Ca²⁺** with PhSiCl$_3$. Reduction of **2** with KC$_8$ resulted in the unexpected forma-
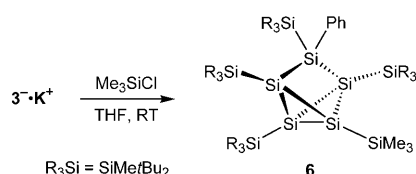
Scheme 3. Synthesis of a pentasilatricyclo[2.1.0.0^{2,5}]pentane **6** from the anionic derivative **3⁻·K⁺**.

tion of the pentasilatricyclo[2.1.0.0^{2,5}]pentan-1-ide derivative **3⁻·K⁺**, which is stabilized by the K⁺−arene(Ph) π-interaction.

[1] M. D. Levin, P. Kaszynski, J. Michl, *Chem. Rev.* **2000**, *100*, 169.

[2] a) L. R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* **1989**, *111*, 6454; b) C. Drost, M. Hildebrand, P. Lönnecke, *Main Group Met. Chem.* **2002**, *25*, 93; c) A. F. Richards, M. Brynda, P. P. Power, *Organometallics* **2004**, *23*, 4009; d) D. Nied, W. Klopper, F. Breher, *Angew. Chem.* **2009**, *121*, 1439; *Angew. Chem. Int. Ed.* **2009**, *48*, 1411.

[3] V. Y. Lee, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2002**, *124*, 9962.

[4] P. Dowd, H. Irngartinger, *Chem. Rev.* **1989**, *89*, 985.

[5] A CSD search found only one paper describing a (*t*Bu$_3$Si)$_6$Si$_8$ cluster, which consists of two fused pentasilatricyclo[2.1.0.0^{2,5}]pentane fragments (G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem.* **2005**, *117*, 8096; *Angew. Chem. Int. Ed.* **2005**, *44*, 7884). However, the structure of such an unusual compound is greatly affected by the polycyclic fusion, being rather far from that one expected for the isolated pentasilatricyclo[2.1.0.0^{2,5}]pentane.

[6] K. Takanashi, V. Ya. Lee, T. Yokoyama, A. Sekiguchi, *J. Am. Chem. Soc.* **2009**, *131*, 916.

[7] For the experimental procedures and spectral data of **2**, **3⁻·K⁺**, and **6**, see the Supporting Information.

[8] For related compounds, see, for example: V. Ya. Lee, K. Takanashi, M. Ichinohe, A. Sekiguchi, *Angew. Chem.* **2004**, *116*, 6871; *Angew. Chem. Int. Ed.* **2004**, *43*, 6703.

[9] Recent reviews on silyl anions: a) K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1; b) P. D. Lickiss, C. M. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75; c) J. Belzner, U. Dehnert in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, Chapter 14; d) A. Sekiguchi, V. Ya. Lee, M. Nanjo, *Coord. Chem. Rev.* **2000**, *210*, 11; e) V. Ya. Lee, A. Sekiguchi in *Reviews of Reactive Intermediate Chemistry* (Eds.: M. S. Platz, R. A. Moss, M. Jones, Jr.), Wiley, New York, **2007**, Chapter 2.

[10] CCDC 717783 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For further details see also the Supporting Information.

[11] These values can be compared with those of the related *t*Bu$_2$PhSiK-(C$_6$H$_6$) dimer, featuring an intramolecular Si−K bond of 3.3602(11) Å and intermolecular η⁶-(K−C$_{Ph}$) bonding contacts rang-

ing from 3.143(3) to 3.312(3) Å: H.-W. Lerner, S. Scholz, M. Bolte, M. Wagner, *Z. Anorg. Allg. Chem.* **2004**, *630*, 443.

[12] For examples of the inverted tetrahedral configuration at the heavy Group 14 elements, see the following papers: refs. [3,5], and T. Iwamoto, D. Yin, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2001**, *123*, 12730.

[13] All computations, including geometry optimization and NBO calculations, were performed at the B3LYP/6-31G(d) DFT level with the Gaussian 98 program on the model compound [**3⁻·K⁺**]$_{model}$, in which the real tBu$_2$MeSi substituents were replaced with H$_3$Si groups. Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgometry, R. E. Stratman, J. C. Burant, S. Daprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. Martin, D. J. Fox, D. T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.