The First Isolation of 1,3-Diaza-2-sila-4-cyclopentene Radical Cation Salt: The X-ray Structure and Electronic Properties

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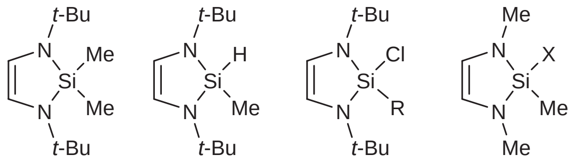
The first TPFPB salt of 1,3-diaza-2-sila-4-cyclopentene (DASCP) radical cation was isolated as an orange crystalline solid by one-electron oxidation of the neutral DASCP with Ag(I) ion. The X-ray structural analysis and theoretical studies showed that the silicon atom plays an important role in stabilization of this cationic species.

Silacyclopentadiene (silole) has been the subject of extensive recent studies.[1,2] A characteristic of silole lies in its low-lying LUMO resulting from the interaction between σ^* orbital of exocyclic Si–C bonds and a π^* orbital of the butadiene moiety.[2] In comparison, chemistry of dithiasilole[3] and 1,3-diaza-2-sila-4-cyclopentene (DASCP)[4,5] has not received so much attention. Tom Dieck et al. reported that DASCP **1** and **2** have low ionization potentials and are readily oxidized with $AlCl_3$ to give stable radical cations in solution.[5] However, their isolation as stable salts has not been reported so far. Here we report the structure and property of a radical cation salt of chloro derivative **3** and electronic structure of DASCP.



R = $CH(SiMe_3)_2$

1 **2** **3** **4** (X = Cl) **5** (X = Me)

Chart 1.

In the course of our study on 2-silaimidazolium ion,[6] we found that chlorosilane **3** can be readily oxidized, similarly to **1** and **2**. Cyclic voltammetry of **3** in MeCN showed a reversible first oxidation wave at a remarkably low potential ($E_{1/2} = -0.06$ V vs Fc/Fc^+) and an irreversible second oxidation peak ($E_{pa} = +0.75$ V). The former is comparable to *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, a well-known electron donor ($E_{1/2} = -0.10$ V vs Ag/Ag^+).[7] Accordingly, one-electron oxidation instead of chloride-ion abstraction took place when **3** was treated with Ag(I) ion.[8] When chlorosilane **3** was allowed to react with $Ag^+(benzene)_3{\cdot}TPFPB^-$ ($TPFPB^- = (F_5C_6)_4B^-$)[9] in CH_2Cl_2 at room temperature under argon, the color of the solution turned to orange and elemental silver precipitated. Silver powder was removed by filtration, and then filtrate was evaporated. After the resulting orange crystals were washed by hexane for several times, an analytically pure orange crystal of radical cation salt $\mathbf{3}^{\bullet+}{\cdot}TPFPB^-$[10] was obtained in 98% yield (Eq 1). Salt $\mathbf{3}^{\bullet+}{\cdot}TPFPB^-$ is thermally stable up to the melting point (89–91 °C) and tolerant toward oxygen, but slowly decomposed upon contact with aerial moisture.

$$\mathbf{3} \xrightarrow[CH_2Cl_2,\ rt]{Ag^+(benzene)_3{\cdot}TPFPB^-} \mathbf{3}^{\bullet+}{\cdot}TPFPB^- + Ag(0) \quad (1)$$

A solution of $\mathbf{3}^{\bullet+}{\cdot}TPFPB^-$ in CH_2Cl_2 displayed an ESR spectrum ($g = 2.0029$) shown in Figure 1a. The observed hyperfine splitting was analyzed as coupling with two equivalent olefinic protons and with two equivalent nitrogen and one chlorine atoms by computer simulation (Figure 1b).[11] The hyperfine coupling constants a(N) and a(H) of $\mathbf{3}^{\bullet+}$ (0.451 and 0.729 mT, respectively) are similar to those reported for radical cations $\mathbf{1}^{\bullet+}$ (0.460 and 0.695 mT) and $\mathbf{2}^{\bullet+}$ (0.455 and 0.703 mT).[5a] Since the spectrum pattern and intensity are independent on a change in the concentration of $\mathbf{3}^{\bullet+}{\cdot}TPFPB^-$ and no coupling with ^{19}F ($I = 1/2$) and/or ^{11}B ($I = 3/2$) is observed, $\mathbf{3}^{\bullet+}$ does not have any significant interaction with counter-anions or other molecules in solution.

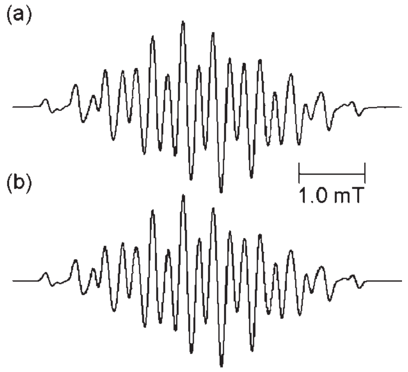


Figure 1. (a) ESR spectrum of $\mathbf{3}^{\bullet+}{\cdot}TPFPB^-$ in CH_2Cl_2 solution at room temperature. (b) Computer simulation spectrum obtained by the use of $a(N) = 0.451$ mT, $a(=CH) = 0.729$ mT, $a(^{35}Cl) = 0.492$ mT, $a(^{37}Cl) = 0.409$ mT, and half-line width $= 0.090$ mT.

X-ray crystallography was conducted on a single crystal of $\mathbf{3}^{\bullet+}{\cdot}TPFPB^-{\cdot}CH_2Cl_2$ obtained by recrystallization from CH_2Cl_2 at −20 °C.[12] Any interaction of $\mathbf{3}^{\bullet+}$ with other molecule was not found and therefore $\mathbf{3}^{\bullet+}$ exists as a free cation in the solid state (Figure 2). The structural parameters are shown in Table 1. The values of Σ_{Ring}, Σ_N, and dihedral angle θ for both compound **3** and radical cation $\mathbf{3}^{\bullet+}$ are close to 540, 360, and 0°, respectively, indicating that they have almost planar five-membered rings. The planarity of $\mathbf{3}^{\bullet+}$ is slightly higher than that of neutral **3**. The original C=C and Si–N bonds (1.372(4) Å and 1.781(2) Å respectively) are elongated as compared with those of neutral **3** (1.320(4) and 1.729(2) Å),[13] while the C–N bond is significantly shortened (1.336(4) Å as compared with 1.415(4) Å for **3**). These structural changes can be rationalized by taking the nature of the relevant bonds in HOMO in neutral

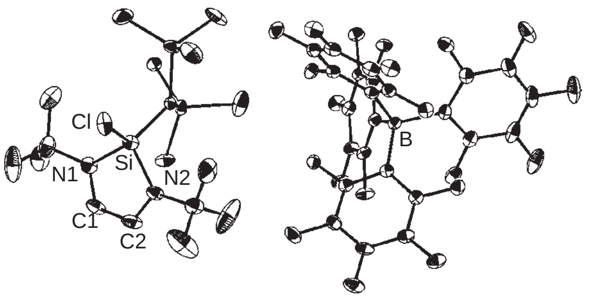


Figure 2. Molecular structure of $\mathbf{3}^{\bullet+}\cdot$TPFPB$^{-}\cdot$CH$_2Cl_2$. One of the disordered molecules is displayed at the 30% probability level. Hydrogen and solvent are omitted for clarity.

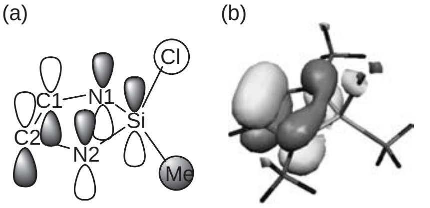


Figure 3. (a) Schematic representation of the $\sigma_{(\mathrm{Si-X})}{}^{*}$–$\pi$ interaction in **4**. (b) KS-HOMO of **4**.

Table 1. Bond lengths (Å), angles (deg), and other structural parameters for **3** and $\mathbf{3}^{\bullet+}$ by X-ray crystallography and for **4** and $\mathbf{4}^{\bullet+}$ by DFT calculations[a]

Compd	Si–N	C–N	C=C	Σ_{N}[a]	Σ_{Ring}[b]	θ[c]
3	1.729(2) 1.728(2)	1.415(4) 1.412(4)	1.320(4)	357.4(2) 359.2(2)	539.8(2)	4.5(3) 3.9(3)
$\mathbf{3}^{+\bullet}$	1.782(2) 1.780(2)	1.336(4) 1.333(4)	1.372(4)	359.2(2) 360.0(2)	539.9(2)	0.7(3) 0.2(3)
4	1.738	1.414	1.350	357.9	538.8	9.8
$\mathbf{4}^{+\bullet}$	1.798	1.347	1.406	359.9	540.0	2.1

[a]Ref. 14. [b]Sum of the angle around nitrogen. [c]Sum of the interior angles. [d]Dihedral angles of C1–N1–Si–N2 and N1–Si–N2–C2.

3 into consideration (see below).

In order to examine the intrinsic electronic nature of DASCP, DFT calculations were conducted for neutral and radical cation states of a model compound **4**.[14] As shown in Table 1, the calculated result for DASCP **4** and its radical cation $\mathbf{4}^{\bullet+}$ reproduced the observed tendency for the structural change upon one-electron oxidation. In the HOMO of neutral **4**, the C=C and C–N bonds are in-phase and out-phase, respectively. Moreover, the rigidly fixed arrangement of exocyclic Si–C/Cl bonds is favorable for the in-phase $\sigma_{(\mathrm{Si-X})}{}^{*}$–$\pi$ (X = C, Cl) interaction (Figure 3).[15] The elongation of C=C and Si–N bonds and shortening of the C–N bond upon one-electron oxidation of DASCP **3** can be explained by consideration of the phase of HOMO. Furthermore, this orbital interaction stabilizes the radical cation state of DASCP and planar structure of the five-membered ring in both the neutral and cation radical states.[15]

According to the above discussion, energy level of the HOMO in DASCP should be controlled by substituents on the silicon atom. For example, the energy level of the Kohn–Sham HOMO in dimethyl-DASCP **5** (−4.31 eV) becomes higher than that in chloro-DASCP **4** (−4.91 eV). Although the HOMO of DASCPs is stabilized by the $\sigma_{(\mathrm{Si-X})}{}^{*}$–$\pi$ interaction, DASCP was found to have relatively high-lying HOMO. The results of the present study suggest that DASCP may be used as new functionality molecules such as hole-transport materials.

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8 This is in sharp contrast to the formation of 2-silaimidazolium ion by chloride-ion abstraction upon treatment of **3** with Et$_3$Si^{+}TPFPB^{-} (Ref. 6). The strong bond energy of Si–Cl (93.4 kcal mol^{-1}) relative to that of C–Cl (78.0 kcal mol^{-1}) should be one major reason.

9 K. Ogawa, T. Kitagawa, S. Ishida, and K. Komatsu, submitted for publication.

10 Anal. Calcd for C$_{41}$H$_{39}$BClF$_{20}$N$_2$Si$_3$: C, 46.01; H, 3.67; N, 2.62%. Found: C, 45.73; H, 3.75; N, 2.69%. The electronic spectrum in CH$_2$Cl$_2$ displayed two broad bands at 418 nm (1500) and 322 nm (5200). According to TDDFT calculation of model compound $\mathbf{4}^{\bullet+}$, these bands could be assigned to the HOMO → SOMO and SOMO → LUMO transitions, respectively.

11 Computer simulations were performed using SimFonia software.

12 Although there is some disorder around chlorine and bis(trimethylsilyl)methyl groups, (see supporting information) discussion on structural features of five-membered ring can be safely made. Crystal data for $\mathbf{3}^{\bullet+}\cdot$TPFPB$^{-}\cdot$CH$_2Cl_2$: FM = C$_{42}H_{41}BCl_3F_{20}N_2Si_3$, MW = 1155.2, monoclinic, $a = 16.939(3)$, $b = 17.258(3)$, $c = 17.5640(18)$ Å, $\beta = 102.831(7)°$, $V = 5006.3(13)$ Å^3, $P2_1/n$, $Z = 4$, $D_{\mathrm{calcd}} = 1.533$ g/cm^3, $R = 0.0614$, $wR_2 = 0.1229$, $T = 100$ K, GOF = 1.026.

13 Crystal data for **3**: FM = C$_{17}$H$_{39}$ClN$_2$Si$_3$, MW = 391.22, monoclinic, $a = 11.6084(14)$, $b = 11.1827(13)$, $c = 17.954(2)$ Å, $\beta = 90.219(2)°$, $V = 2330.7(5)$ Å^3, $P2_1/c$, $Z = 4$, $D_{\mathrm{calcd}} = 1.115$ g/cm^3, $R = 0.0649$, $wR_2 = 0.1354$, $T = 100$ K, GOF = 1.054.

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