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A Unique Transition Metal-Stabilized Silicon Cation

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Supporting Information

ABSTRACT: Trivalent silicon cations are exceptionally strong electron pair acceptors that react, either desired or undesired, with almost any σ and π basic molecule. One way of intramolecular attenuation of the Lewis acidity of these superelectrophiles is by installation of a ferrocene unit at the electron-deficient silicon atom. While well-understood for isoelectronic α-ferrocenyl-substituted carbenium ions and also boranes, the stabilizing interactions between the ferrocene backbone and a positively charged silicon atom are not clear due to the challenge of crystallizing such cations. The structural characterization of our ferrocene-stabilized silicon cation now reveals an unprecedented bonding motif different from its analogues. An extreme dip angle of the silicon atom toward the iron atom is explained by two three-center-two-electron (3c2e) bonds through participation of both the upper and the lower aromatic rings of the ferrocene sandwich structure. The positive charge is still localized at the silicon atom that also retains a quasi-planar configuration.

Understanding the structure and the stabilization of reactive intermediates is a fundamental task for synthetic chemistry. As such, the isolation and the characterization of trivalent silicon cations in the condensed phase pose a perpetual challenge, largely due to its pronounced electrophilicity.[1−3] Unlike the electron-deficient carbon atom in isoelectronic carbenium ions, the positive charge is essentially localized on the silicon atom, and that makes silylium ions exceptionally potent electron pair acceptors. That *voracious appetite for nucleophiles*[4] had fueled a controversy over the existence of truly three-coordinate silicon cations for years, and crystallographic as well as spectroscopic evidence exposed π basic solvents (intermolecular)[5] and groups (intramolecular)[6,7] or even weakly σ coordinating counteranions (intermolecular)[8] and halogen atoms (intramolecular)[9] as donors to the empty orbital at the silicon atom. Intra-[10−12] and intermolecular[13] three-center-two-electron (3c2e) $[\mathrm{Si}\cdots\mathrm{H}\cdots\mathrm{Si}]^+$ bridges are also known. Aside from these beautiful examples of inter- and intramolecularly stabilized silylium ions,[14] Lambert's $\mathrm{Mes_3Si^+}$ cation[15] crystallized with Reed's $[\mathrm{HCB_{11}Me_5Br_6}]^-$ anion[16] remains the sole example of a, in a strict sense of the word, free silylium ion.[17]

An approach to intramolecular stabilization of isoelectronic charged and, likewise, neutral atoms with an electron sextet is realized in α-ferrocenylcarbenium ions[18] and related boranes[19] (**I** and **II**, Figure 1). The concept itself dates back several decades,[20] and it had long been assumed that a bonding interaction between the electron-rich transition metal atom and the electron-poor α-substituent lends these electrophilic compounds increased stability. It was a seminal paper by Behrens[21] that established direct iron−α-carbon bonding in the molecular structure of a ferrocene-stabilized methylium ion. The ferrocene backbone is bent by 9.3°, and the former substituted Cp ligand shows fulvene character, indicating delocalization of the positive charge. There was an early (unsuccessful) attempt to access a silicon analogue (with R = Ph),[23] that is an α-ferrocenylsilylium ion (**III**, Figure 1), but that structural motif[24] had been unprecendented until our laboratory recently reported its synthesis and spectroscopic characterization [$\mathbf{1} \rightarrow \mathbf{3}^+\cdot[\mathrm{B(C_6F_5)_4}]^-$, left, Scheme 1].[25]

For the present investigation, we replaced the $[\mathrm{B(C_6F_5)_4}]^-$ by the easy-to-access $[\mathrm{B_{12}Cl_{12}}]^{2-}$ counteranion[26,27] [$\mathbf{1} \rightarrow (\mathbf{3}^+)_2\cdot[\mathrm{B_{12}Cl_{12}}]^{2-}$, right, Scheme 1] and we now accomplished the crystallization of that ferrocene-stabilized silylium ion. We wish to report its unique molecular structure with both the bonding situation and the charge distribution being distinctly different from the related carbenium ion.[21] Quantum-chemical calculations assist the interpretation of the experimental data and allow for comparison of the silylium ion and the carbenium ion.

Single crystals suitable for X-ray diffraction were obtained from a solution of our silicon cation $\mathbf{3}^+$ and the $[\mathrm{B_{12}Cl_{12}}]^{2-}$ counteranion in 1,2-$\mathrm{Cl_2C_6D_4}$ at room temperature (cf. Figure S1 in the Supporting Information). There are two independent molecules of $\mathbf{3}^+$ in the solid state, and one of these silicon cations is depicted in Figure 2 (see Table S1 in the Supporting Information for a comparison with the other one). All data obtained were exactly reproduced in an independent experiment. The tilt angle of the Cp rings of 11.6° is in the same order of magnitude as for the tilted sandwich structure of the above-mentioned carbenium ion.[21] However, the dip angle of $\alpha^* = 44.8°$ is dramatically enlarged compared to $\alpha^* = 20.7°$ of the carbenium ion[21] (cf. Figure S2 in the Supporting Information for calculated dip angles). The geometry at the silicon atom also deserves attention. The average C−Si−C angle is 117.8° (116.3° for the other molecule), and that is closer to trigonal planarity (120.0°) than to a tetrahedron (109.5°). Despite that quasi-planarity, there is a bonding interaction between Si and Fe with a bond length of 2.492 Å. These angles compare well with those of all representative classes of intermolecularly stabilized silylium ions: $\mathrm{Et_3Si(toluene)^+}\cdot[\mathrm{B(C_6F_5)_4}]^-$ (114.0°),[5] i-$\mathrm{Pr_3Si^+}\cdot[\mathrm{HCB_{11}H_5Cl_6}]^-$ (117.3°),[28] and $[\mathrm{Me_3Si\cdots H\cdots SiMe_3}]^+\cdot[\mathrm{HCB_{11}Cl_{11}}]^-$ (116.7).[13]

Our density functional theory (DFT) calculations (TPSS-D3/def2-TZVPP, see the Supporting Information for details)[29−31] of

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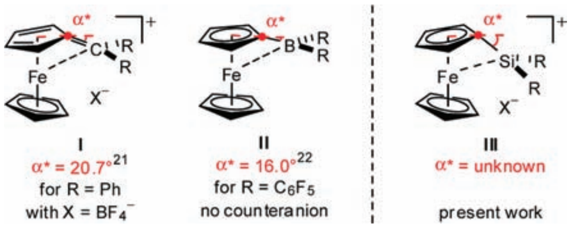
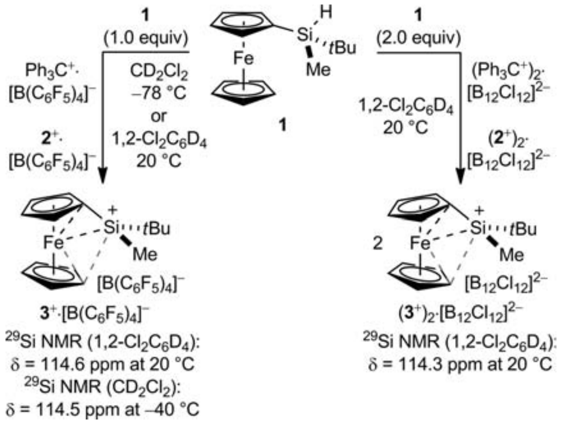


Figure 1. Isoelectronic charged and neutral ferrocene-based systems with an electron sextet at the α atom.

Scheme 1. Execution of the Silicon Cation Generation with Different Counteranions



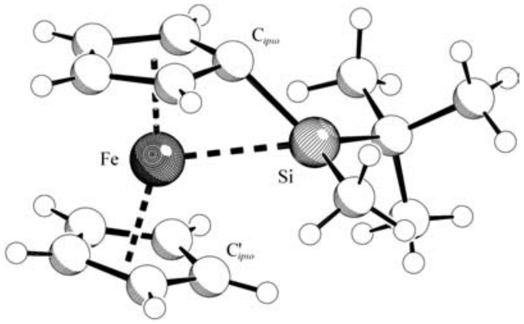


Figure 2. Crystal structure analysis of $\mathbf{3}^+$: Schakal plot of the molecular structure (counteranion omitted for the sake of clarity). Selected experimental bond lengths (Å): Si−C_{ipso}, 1.829(9); Si−Fe, 2.492(2); Si−C'_{ipso}, 2.784(9). Selected calculated bond lengths (Å): Si−C_{ipso}, 1.823; Si−Fe, 2.461; Si−C'_{ipso}, 2.647.

the isolated silylium ion $\mathbf{3}^+$ resulted in an optimized geometry which is in excellent agreement with the solid state structure (Figure 2). The unusual bonding situation in the ferrocene-stabilized silylium ion is apparent in the Wiberg bond orders b_W[32] between the silicon atom and its neighbors. While a single bond is clearly present between the silicon atom and the carbon atom C_{ipso} (b_W = 1.03), both the Si−Fe bond (b_W = 0.51) and the Si−C'_{ipso} bond (b_W = 0.26) have partial covalent bonding character, indicative of delocalized bonding. The nature of this bonding becomes visible when localized molecular orbitals (LMOs)[33] are calculated and drawn (Figure 3). In addition to a 3c2e bond of C_{ipso} of the upper Cp ring, Si and Fe (LMO_A, Figure 3A), there is another one (LMO_B, Figure 3B) involving the carbon atom C'_{ipso} of the lower Cp ring. That involvement of bonding interactions between the silicon atom and the lower ring clearly distinguishes our silylium ion from the corresponding carbenium ion.[18] It also explains the extraordinarily large dip angle between the Si−C_{ipso} bond and the upper Cp plane.

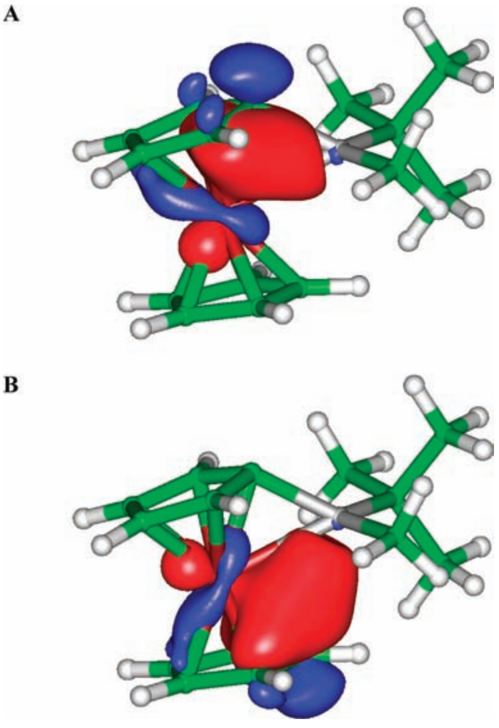


Figure 3. Localized molecular orbitals. (A) LMO_A and (B) LMO_B involving silicon, iron, and ring carbon atoms (isosurfaces are displayed at a value of 0.05 $e/a_0^{3/2}$). The Mulliken populations of the silicon atomic orbitals in the LMOs are 19.2% for LMO_A and 12.5% for LMO_B.

The intramolecular stabilization through the ferrocene donor makes any intermolecular interaction redundant. Neither the solvent (shortest Si−Cl distance 5.261 Å) nor the counteranion (shortest Si−Cl distance 3.624 Å) coordinate to the cationic silicon atom in the solid state (cf. sum of the van der Waals radii is 3.68 Å). These data are in accordance with ^{29}Si NMR measurements (Scheme 1) where the chemical shift is independent of solvent (CD_2Cl_2 or 1,2-$Cl_2C_6D_4$ with $[B(C_6F_5)_4]^-$ as counteranion) and counteranion (with $[B(C_6F_5)_4]^-$ or $[B_{12}Cl_{12}]^{2-}$ in 1,2-$Cl_2C_6D_4$ as solvent). The silicon atom is significantly deshielded in the ^{29}Si NMR spectrum ($\delta \approx 114.5$ ppm), indicating a localized positive charge. The ^{29}Si NMR chemical shift calculated with GIAO−DFT (BP86)[34−36] is $\delta_{TMS} = 116.4$ ppm, a clear indication that the solid state structure of the silicon cation also prevails in solution. The electrostatic potential of the silylium ion also alludes to the presence of a positive charge at the silicon atom (Figure 4A), especially when compared to the related carbenium ion (Figure 4B).

Quantum-chemical calculations unravelled a unique bonding situation in our silylium ion $\mathbf{3}^+$ with its ferrocene backbone.[37] It is two 3c2e bonds with participation of both the upper (expected) and the lower (unexpected) Cp rings that account for the unconventional molecular structure. By this mode of stabilization, an almost planar geometry and a positive charge located at

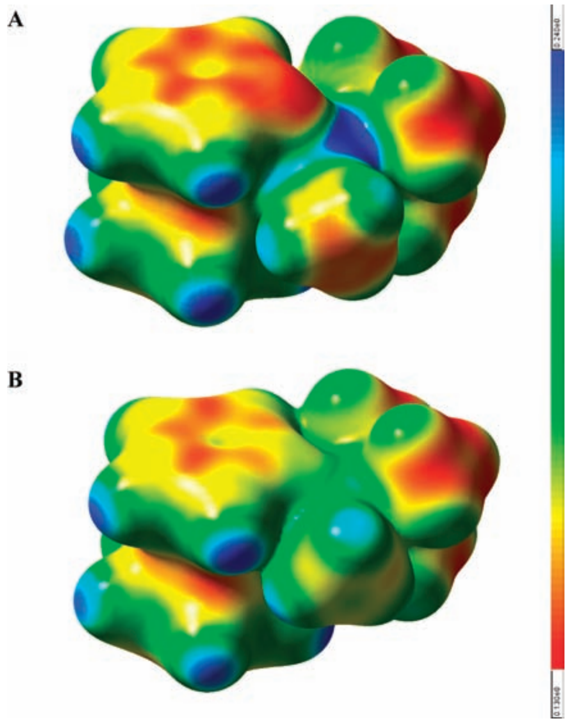


Figure 4. Electrostatic potentials. (A) *tert*-Butylferrocenyl methylsilylium ion (3^+) and (B) *tert*-butylferrocenylmethyl carbenium ion. Isovalue surfaces are displayed at an electron density of 0.08 au.

the silicon atom is retained, also helping to understand its reactivity in catalysis.[25,38]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, characterization data as well as ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{29}Si NMR spectra for all compounds, X-ray data of $(3^+)_2\cdot[B_{12}Cl_{12}]^{2-}$, and quantum-chemical calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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