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Ambiphilicity of Dichlorosilylene in a Single Molecule

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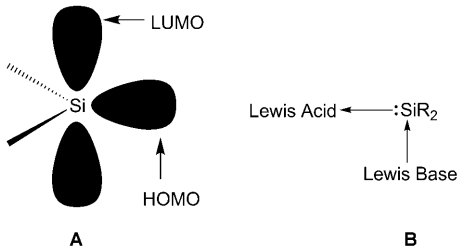
Dedicated to Professor Josef Michl on the occasion of his 70th birthday

In general, silylenes (R_2Si, in which R = H, halogen, alkyl, or aryl) are divalent neutral silicon species with the lone pair of electrons as the HOMO and an empty p orbital as the LUMO in the singlet ground (^1A) state. Therefore, silylenes can in principle behave as Lewis acids as well as Lewis bases, depending on the substituents. Silylenes are known to have an ambiphilic[1] nature (**A** and **B** in Scheme 1). The availability of simultaneously electrophilic and nucleophilic



Scheme 1. Ambiphilic nature of $L{\rightarrow}SiCl_2{\rightarrow}B(C_6F_5)_3$ **2**.

center in the same molecule such as a silylene (**A**), has been intriguing both to theoretical[1] and experimental[2] scientists during the last few decades. A fair number of examples of insertion or addition reactions of stable silylenes have been reported.[3] The reactions in which silylenes function as Lewis bases are limited.[4,5]

The base-catalyzed generation of silylenes as reaction intermediates and their trapping products are known.[6] Many transient silylene complexes with Lewis bases were postulated in low-temperature matrices,[7] but the first stable silylene Lewis base complex was isolated by Okazaki et al. in 1997 by the reaction of disilene with isocyanide.[8] A variety of transition-metal–silylene complexes[9] are reported in the literature in which they exhibit metal–silicon multiple bond character. Very recently, we isolated and reported on stable N-heterocyclic carbene (NHC)-base-stabilized dichlorosilylenes[10a] $L{\rightarrow}SiCl_2$ (**1**; in which L = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene in **1** or 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) under very mild reaction conditions. Subsequently, NHC-stabilized dibromosilylene was also reported.[10b] The NHC in **1** behaves as a σ-donor ligand and the stereochemically active lone pair resides at the silicon atom. A N-heterocyclicsilylene–borane adduct[5] $[(CHtBuN)_2Si]{\rightarrow}B(C_6F_5)_3$, with a half life of one month to convert to silylborane is known, but it could not be characterized by X-ray diffraction. Furthermore, the reaction of the silylene–isocyanide complex with borane resulted in the formation of a silylborane–isocyanide complex[11] instead of a silylene–borane adduct. Herein we report on the use of NHC-stabilized dichlorosilylene $L{\rightarrow}SiCl_2$ (**1**) as a base in the reaction to give the silylene–borane adduct $L{\rightarrow}SiCl_2{\rightarrow}B(C_6F_5)_3$ (**2**). Adduct **2** is a novel example showing both acidic and basic properties of dichlorosilylene in a single molecule, as a σ-acceptor as well as a σ-donor.

The reaction of **1** and $B(C_6F_5)_3$ in toluene (Scheme 2) and subsequent concentration of the resulting solution afforded colorless crystals of **2** on storage at −35 °C for two days.

Compound **2** is soluble in common organic solvents and is stable under inert gas atmosphere; it has been characterized by elemental analyses, ^1H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si NMR spectroscopic studies, and EI mass spectrometry. The molecular structure of **2** was established by single-crystal X-ray diffraction and DFT calculations with subsequent topological analysis.

The ^1H NMR spectrum of **2** exhibits resonances for the NHC ligand bound to the Si atom (δ = 0.80 ($CHMe_2$), 1.15 ($CHMe_2$), 2.62 ($CHMe_2$), 6.29 (NC*H*), 6.89 (*m*-C_6H_3), 7.02–7.07 ppm (*p*-C_6H_3)) with upfield shifted resonances relative to **1** (δ = 1.01 ($CHMe_2$), 1.43 ($CHMe_2$), 2.79 ($CHMe_2$), 6.36

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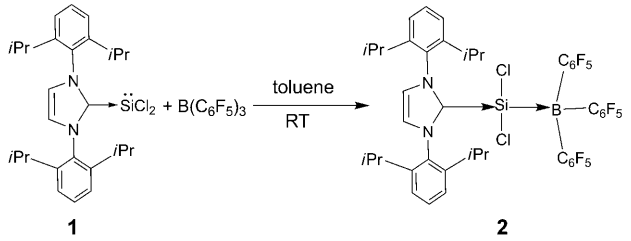

Scheme 2. Synthesis of $L{\rightarrow}SiCl_2{\rightarrow}B(C_6F_5)_3$ (**2**), (L = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene).

(NC*H*), 7.05–7.22 ppm (C_6H_3)). The ^{11}B NMR spectrum of **2** shows a broad resonance consistent with a four-coordinate boron atom.[5,12] The ^{19}F NMR spectrum exhibits the resonances in the expected region. The formation of the adduct **2** is accompanied by a large shift ($\Delta\delta = 72.25$ ppm) to higher field ($\delta = -53.19$ ppm) in the ^{29}Si NMR spectrum relative to the dichlorosilylene **1** ($\delta = 19.06$ ppm).

The solid-state structure of **2** was determined by single-crystal X-ray diffraction and is shown in Figure 1. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ as a twin

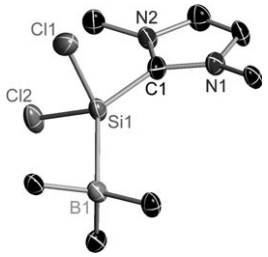

Figure 1. Molecular structure of **2**; anisotropic displacement parameters depicted at the 50% probability level. Only the *ipso*-carbon atoms of the 2,6-diisopropylphenyl substituents at the NHC ligand and the three carbon atoms of each of the three C_6F_5 rings at the boron atom are depicted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)–C(1) 1.965(5), Si(1)–Cl(1) 2.066(2), Si(1)–Cl(2) 2.0568(18), Si(1)–B(1) 2.106(6); C(1)-Si(1)-B(1) 132.3(2), Cl(1)-Si(1)-Cl(2) 102.59(8).

with toluene molecules in the crystal lattice. The silicon and boron atoms in **2** are each four coordinate and in the center of a distorted tetrahedral coordination polyhedron. The C→Si bond length in **2** (1.965(5) Å) is only marginally shorter than in **1** (1.985(4) Å) while the average Si–Cl bond length (2.06195(19) Å) in **2** is noticeably shorter than that in **1** (2.1664(16) Å). The Si→B bond length of 2.1135(6) Å in **2** is comparable with a Si–B single bond in silylboranes (2.038–2.1249 Å),[13] but larger than that observed in silaborene[14] (1.8379(17) Å). The C→Si bond includes an angle of 109.6° with the $SiCl_2$ plane. The Si→B bond includes an angle of 130.1° with that plane.

Reactions with $B(OPh)_3$ and $BF_3{\cdot}Et_2O$ with **1** were not successful. In both cases no adduct formation with **1** was observed. The reactions proceed with the formation of insoluble dichlorosilylene $(SiCl_2)_x$ and soluble NHC adducts of borane.

Compound **2** contains two interesting bonding modes in the same molecule. First, there is the C→Si donor bond from the NHC ligand to the silylene and, second, the silylene itself acts as a donor to the Lewis acceptor atom B1. To shed light on the bonding situation of the C1-Si1-B1 unit we performed computational studies. After a gas-phase optimization at the B3LYP-TZVP level of theory, a topological analysis of the resulting electron density according to Bader's quantum theory of atoms in molecules[15] (QTAIM) was carried out. In principle this methodology can be applied to experimentally obtained charge densities as well, making it a very powerful tool to compare quantum theoretical and experimental approaches. Unfortunately the crystals required for the experiment need to be of superb quality, which is not the case for compound **2**. However, the twinned crystal structure could be determined unequivocally. Both C→Si and Si→B donor bonds are confirmed by bond critical points (BCPs). The characteristics of a bond can be deduced by evaluating the density and its derivatives at the BCP.[16] While the electron density at the critical points is in both cases nearly identical (0.55 and 0.57 e Å^{-3}), the Laplacians differ considerably. While the Laplacian at the C→$Si_{(BCP)}$ adopts a slightly positive value of 2.67 e Å^{-5}, that at the Si→$B_{(BCP)}$ is overall the same value but with negative sign (−2.66 e Å^{-5}). As can be seen from Figure 2 the latter resides clearly in a region of charge accumulation, while the former is located close to a region where $\nabla^2\rho(\mathbf{r})$ changes sign. In this case, the rough interpretation of a negative Laplacian at the BCP as an indicator for predominately covalent bonding and a positive Laplacian for predominantly polar or ionic bonding clearly misses out the main point.[17] Compared to the carbene, the silylene is the much softer donor

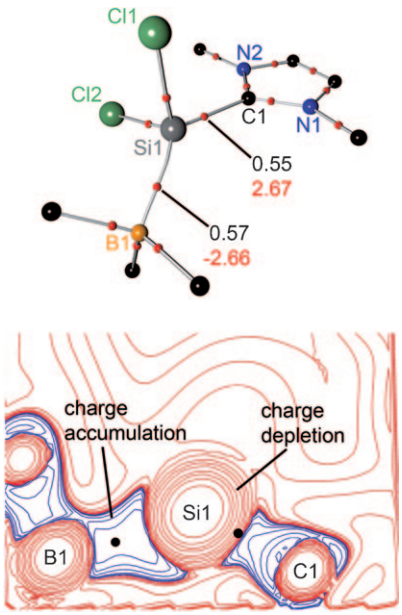

Figure 2. Molecular graph of **2** (top) obtained from a gas phase optimization (B3LYP/TZVP). The small black spheres indicate BCPs, with $\rho(\mathbf{r}_{BCP})$ [e Å^{-3}] (upper number) and $\nabla^2\rho(\mathbf{r}_{BCP})$ [e Å^{-5}] (bottom number) and contour plot of $\nabla^2\rho(\mathbf{r})$ (bottom) for the C1-Si1-B1 plane.

because the BCP at the C→Si bond is located much closer to the silicon (0.77) than the BCP at the Si→B bond (1.26 Å).

This is further illustrated by monitoring $\nabla^2\rho(\mathbf{r})$ along the bond paths. While the Laplacian along the bond path between the carbon and the silicon atom is considerably negative in the carbon basin and only changes sign close to the BCP (Figure 3, left) the related function along the Si→B

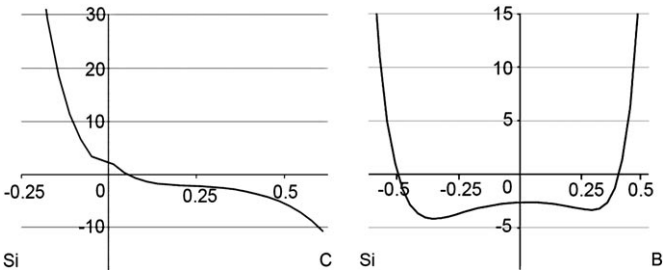

Figure 3. $\nabla^2\rho(\mathbf{r})$ [e Å^{-5}] of the C1–Si1 bond (left) and along the bond path Si1B1 (right), [Å] (0 = BCP).

bond shows much more balanced behavior, indicative for a covalent bond. These QTAIM results are in accordance with the differences in electronegativity; the electronegativity of Si is smaller than that of carbon by 0.8 and is smaller by 0.3 with respect to that of boron.

In summary the charge density analysis of the silylene donor–acceptor complex **2** revealed that the two C→Si and Si→B donor bonds are of considerably different quality, although the bare bond lengths might suggest simple C–Si and Si–B single bonds. While the C→Si bond is very polar and indicative for the hard NHC ligand the Si→B bond is much more covalent and confirms the silylene donor to be much softer.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen gas using standard Schlenk line technique and in a glove box.

Synthesis of 2: Toluene (30 mL) was added to a 100 mL flask containing **1** (0.77 g, 1.58 mmol) and $B(C_6F_5)_3$ (0.81 g, 1.58 mmol) and the reaction mixture was stirred at ambient temperature for 5 h. The resulting colorless solution was concentrated to 20 mL and stored at −35°C in a freezer. Colorless crystals of **2** (1.03 g, 65%) were obtained after two days. M.p. 144–145°C; ^{1}H NMR (200 MHz, C_6D_6, 25°C): δ = 0.80 (d, J = 6.80 Hz, 12H; CHMe_2), 1.15 (d, J = 6.60 Hz, 12H; CHMe_2), 2.56–2.69 (m, 4H; CHMe$_2$), 6.29 (s, 2H; NCH), 6.89 (d, J = 7.80 Hz, 4H; m-C_6H_3), 7.02–7.07 ppm (m, 2H; p-C_6H_3); ^{11}B NMR (96 MHz, C_6D_6, 25°C): δ = 14.10 ppm; ^{13}C NMR (125 MHz, C_6D_6, 25°C): δ = 21.98 (CHMe_2), 26.10 (CHMe_2), 29.14 (CHMe$_2$), 124.64(NCH), 125.64 (m-C_6H_3), 128.51 (p-C_6H_3), 129.28, 131.97, 134.57 (o-C_6H_3), 145.27 (*ipso*-C_6H_3), 136.23, 137.85, 138.17, 138.87,140.83, 148.15, 150.05 ppm (C_6F_5); ^{19}F NMR (188 MHz, C_6D_6, 25°C): δ = −124.86 (d, J = 23.4 Hz, 6F; o-C_6F_5), −158.36 (t, J = 21.1 Hz, 3F; p-C_6F_5), −164.34 ppm (m, 6F; m-C_6F_5); ^{29}Si NMR (99 MHz, C_6D_6, 25°C) δ = 53.19 ppm; EI-MS (70 eV): m/z: 832 $[M-C_6F_5]^+$, 512 $[B(C_6F_5)_3]^+$; elemental analysis (%) calcd for $C_{45}H_{36}BCl_2F_{15}N_2Si$ (999.56): C 54.07, H 3.63, N 2.80; found: C 54.13, H 3.51, N 2.72

X-ray structure analysis: Crystals of **2** were selected at low temperature and applied in an oil drop at the tip of a fiber[18] and the data were collected at 100.0(5) K on a Bruker TXS-Mo rotating anode with INCOATEC Helios mirror optics and APEX II detector. The integration was performed with SAINT V7.46 A,[19] which was followed by an empirical absorption correction with TWINABS-2008/2.[20] The structures were solved by direct methods and refined with SHELXL[21] against F^2. Data for **2**: $(C_{45}H_{36}BCl_2F_{15}N_2Si)_2\cdot(toluene)_3$, M_r = 2275.52 g mol^{-1}, crystal size 0.20 × 0.15 × 0.05 mm, triclinic, $P\bar{1}$, a = 11.615(2), b = 21.069(4), c = 22.573(4) Å, V = 5263.7(15) Å^3; Z = 2, ρ_{calcd} = 1.436 mg m^{-3}, μ = 0.240 mm^{-1}, θ_{max} = 25.45°, 84398 reflections measured, 19865 independent reflections, R_{int} = 0.0634, $R1$ = 0.0737 [$I > 2\sigma(I)$], $wR2$ = 0.1846 (all data), 0.803/−0.558 e Å^{-3} residual densities.

CCDC-747375 (**2**) 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.

Theoretical calculations for 2: The quantum chemical calculations were performed with the TURBOMOLE suite of programs.[22]As Gaussian AO basis, triple-zeta sets of Ahlrichs et al. were employed.[23] The geometry was fully optimized at the DFT level using the B3LYP hybrid density functional.[24] The electron density obtained by the above-described procedure was analyzed according to Baders "Quantum Theory of Atoms in Molecules" (QTAIM)[15] with DGRID-4.4[25].

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Keywords: ambiphilicity · computational chemistry · Lewis acids · Lewis bases · silylenes

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