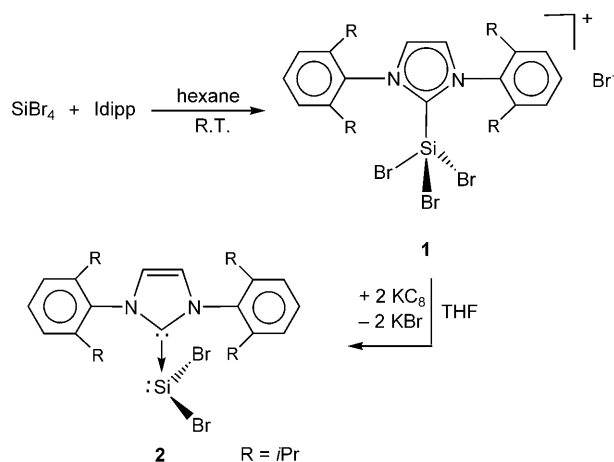


SiBr₂(Idipp): A Stable N-Heterocyclic Carbene Adduct of Dibromosilylene**

Alexander C. Filippou,* Oleg Chernov, and Gregor Schnakenburg

Silicon dihalides are high-temperature molecules of major academic and industrial interest.^[1] For example, SiF₂ is one of the major products in plasma etching of silicon-containing films used in the manufacture of microelectronic devices, SiCl₂ is an important intermediate in the industrial synthesis of elementary silicon from chlorosilanes and hydrogen,^[2] and silicon dihalides are involved in the chemical transport of silicon.^[3] Thermochemical studies have shown that silicon dihalides SiX₂ are highly unstable with respect to their disproportionation products, namely elemental silicon and SiX₄, at ambient temperature.^[4] They are also very reactive, polymerizing rapidly even at low temperatures to give perhalopolysilanes, [SiX₂]_n.^[5] Therefore, it is not surprising that all attempts to isolate monomeric silicon dihalides that can be handled at ambient temperature have been unsuccessful to date. Their isolation would have a similar impact in molecular silicon(II) chemistry^[6] as GeCl₂(1,4-dioxane)^[7] in the chemistry of divalent germanium.^[8] N-heterocyclic carbenes have been recently shown to bind strongly to silicon^[9] and germanium centers^[10] in low oxidation states. Herein, the synthesis, structure, and first reactions of a stable carbene adduct of SiBr₂, SiBr₂(Idipp) **2** (Idipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), are described.

Compound **2** was obtained in two steps starting from SiBr₄ (Scheme 1). In the first step, SiBr₄ was treated with one equivalent of the N-heterocyclic carbene Idipp in hexane at ambient temperature to give the ionic product [SiBr₃(Idipp)]Br (**1**). Reduction of **1** with 2.5 equivalents of potassium graphite (KC₈) in THF at ambient temperature then gave the silicon(II) compound **2**. Compound **1** was isolated as a white solid in high yield.^[11] It is sparingly soluble in benzene and soluble in CH₂Cl₂. Its solutions hydrolyze rapidly upon exposure to air to afford the imidazolium salt [(Idipp)H]Br (**3**).^[12] Compound **2** was purified by crystallization from benzene and isolated in 48% yield as a yellow, air-sensitive solid. It is soluble in THF and benzene, but insoluble



Scheme 1. Synthesis of the carbene dibromosilylene adduct **2**.

in hexane, and is stable under vigorous exclusion of air in benzene solution at ambient temperature for at least one week.

Compounds **1** and **2** were fully characterized. The crystal structure of **1**·3CH₂Cl₂ reveals the presence of tetrahedral [SiBr₃(Idipp)]⁺ cations, which are well-separated from the bromide counterions (Figure 1).^[13]

The shortest Si...Br interionic contacts (4.68 Å) are considerably longer than the sum of the van der Waals radii of the involved atoms (3.95 Å),^[14] excluding any covalent bonding. In comparison, SiCl₄ forms a neutral, trigonal bipyramidal adduct with Idipp.^[9] The mean Si–Br bond length in **1**·3CH₂Cl₂ (2.175(3) Å)^[15] compares well with that

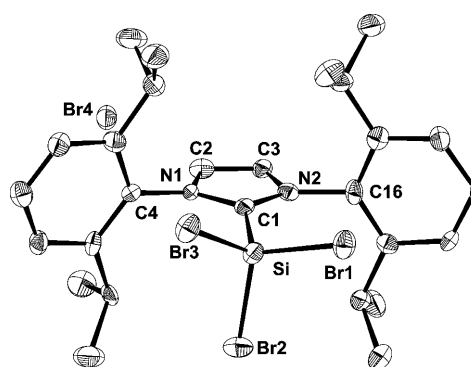


Figure 1. DIAMOND plot of the structure of **1**·3CH₂Cl₂ in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si–Br1 2.171(3), Si–Br2 2.180(2), Si–Br3 2.175(3), Si–C1 1.880(9), C1–N1 1.379(11), C1–N2 1.363(10), N1–C2 1.364(11), N2–C3 1.384(11), C2–C3 1.350(12); Br1–Si–Br3 109.0(1), Br1–Si–Br2 108.9(1), Br2–Si–Br3 109.0(1), C1–Si–Br1 111.4(3), C1–Si–Br2 106.2(2), C1–Si–Br3 112.3(3), N1–C1–N2 104.8(7).

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of SiBr_4 (2.183(4) Å),^[16] and the Si–C1 bond (1.880(9) Å) is similar to those of Si–C(sp²) single bonds (1.872 Å).^[17] From the bonding parameters, **1**·3CH₂Cl₂ can be described as an imidazolium salt bearing a SiBr₃ substituent at the C² position. The ¹H and ¹³C NMR spectra provide additional support for the ionic nature of **1** in CH₂Cl₂. Thus, the ¹H and ¹³C NMR signals of **1** in CD₂Cl₂ appear at similar frequencies to those of the imidazolium salt [(Idipp)H]Br (**3**),^[18] and the ²⁹Si{¹H} NMR spectrum of **1** shows in CD₂Cl₂ a singlet resonance at lower field ($\delta = -63.9$ ppm) than that of SiBr₄ (C₆D₆: $\delta = -90.8$ ppm). In comparison, the ²⁹Si NMR signal of the neutral adduct SiCl₄(Idipp) appears at considerably higher field in CD₂Cl₂ ($\delta = -108.9$ ppm)^[9] than that of SiCl₄ ($\delta = -18.5$ ppm)^[19] as a result of the higher silicon coordination number.^[20]

The crystal structure of **2** shows that the dibromosilylene-carbene adduct is composed of monomers that have a rather short Si–C bond (1.989(3) Å, Figure 2).^[13] The carbon atom is

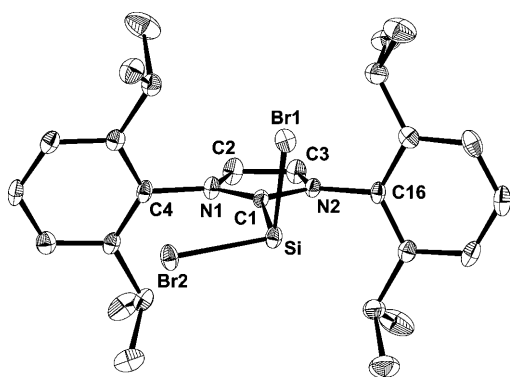


Figure 2. DIAMOND plot of the molecular structure of **2** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si–Br1 2.3607(8), Si–Br2 2.3379(8), Si–C1 1.989(3), C1–N1 1.358(4), C1–N2 1.363(3), N1–C2 1.388(3), N2–C3 1.378(4), C2–C3 1.346(4); Br1–Si–Br2 97.94(3), C1–Si–Br1 94.86(8), C1–Si–Br2 99.93(8), N1–C1–N2 104.7(2).

in an almost planar environment (sum of angles at C1 = 358.9°, fold angle at C1 = 9.0(2)°), whereas the silicon center is distinctly trigonal pyramidal (sum of angles at Si = 292.7°, fold angle^[21] at Si = 78.2(1)°) indicating the presence of a stereochemically active lone pair of electrons on silicon. The Si–C bond of **2** is considerably shorter than that of the silylene-carbene adduct [(NN)SiC(NN)] (Si–C = 2.162(5) Å; NN = 1,2-(NCH₂tBu)₂C₆H₄),^[22] but longer than the Si=C bonds of the silenes Me₂Si=C(SiMe₃)SiMe₃ (1.702(5) Å)^[23] and (Me₃Si)₂Si=C(OSiMe₃)Ad (1.764(3) Å; Ad = 1-adamantyl).^[24] These bonding parameters indicate

the presence of a rather strong C→Si donor-acceptor single bond in **2** resulting from the donation of the carbene carbon lone pair into the vacant silicon p orbital of SiBr₂, which is in full agreement with the results of the quantum chemical calculations (see below).

The Si–Br bonds of **2** (2.3379(8) and 2.3607(8) Å) are considerably longer than those of SiBr₂ ($r_g(\text{Si-Br}) = 2.245(3)$ Å, $r_e(\text{Si-Br}) = 2.227(6)$ Å)^[25] owing to the higher silicon coordination number. The angles at silicon (Br1–Si–Br2 97.94(3), C1–Si–Br1 94.86(8), and C1–Si–Br2 99.93(8)°) suggest that the silicon atom uses mainly p orbitals for the bonding to the three substituents. The angle between the SiBr₂ and carbene planes (75.5(1)°) shows that the molecule is folded, and there is significant torsion of the N₂CSiBr₂ skeleton, as seen by the quite different dihedral angles N1–C1–Si–Br2 (–5.1(3)°) and N2–C1–Si–Br1 (89.5(2)°). The solution NMR spectra are in agreement with the solid-state structure of **2**. The ¹H and ¹³C{¹H} NMR spectra of **2** in C₆D₆ have a single set of resonances for the Idipp group, indicating a rapid rotation of the SiBr₂ fragment about the Si–C bond on the NMR timescale. A distinctive signal for the silicon-bonded carbon atom is observed in the ¹³C{¹H} NMR spectrum at $\delta = 164.5$ ppm, a value that is between that of the corresponding carbon atom in Idipp ($\delta = 220.6$ ppm in C₆D₆)^[26] and of **1** ($\delta = 136.3$ ppm in CD₂Cl₂). Finally, compound **2** has a characteristic ²⁹Si NMR signal in solution at a similar position ($\delta = 10.9$ ppm in C₆D₆) to that found in the solid state ($\delta = 15.8$ ppm, $\Delta\nu_{1/2} = 120$ Hz), which suggests that compound **2** adopts a similar structure in solution and in the solid state.

Gradient-corrected density functional theoretical (DFT) calculations for **2** were carried out at different levels of theory, and the electronic structure of **2** was analyzed by the natural bond orbital (NBO) partitioning scheme^[27] and natural resonance theory (NRT).^[28] The computed bond lengths and bond angles of **2** compare well with the experimental values (Table 1), and even the twisted conformation of **2** is reproduced well by the theoretical calculations.^[11] Only the experimental Si–C1 bond length differed noticeably, being 0.04–0.06 Å shorter than that predicted by theory (Table 1). This bond shortening has been observed for a variety of other donor-acceptor bonds of Lewis base–Lewis acid complexes in the solid state (rather than the gas phase), and may be the result of short range dipole–dipole interactions between the molecules in the solid state.^[29]

NBO analysis of **2** leads to an optimal Lewis structure with a highly filled (1.96e) σ -type natural bond orbital for the Si–C1 bond, which is strongly polarized towards the carbon atom (%C = 79.9%; Table 2). This finding indicates the donor-acceptor character of the Si–C1 bond, which results from the overlap of a filled sp^{1.36} hybrid orbital of the C1 atom

Table 1: Computed and experimental bond lengths [Å] and angles [°] for **2**.^[a]

	Si–C1	Si–Br1	Si–Br2	C1–N1	C1–N2	N1–C2	N2–C3	C2–C3	C1–Si–Br1	C1–Si–Br2	Br1–Si–Br2
BP86/lb	2.037	2.3892	2.3580	1.368	1.373	1.388	1.384	1.357	93.3	100.7	100.8
BP86/l	2.036	2.3916	2.3647	1.371	1.375	1.395	1.390	1.367	93.4	100.4	100.2
B3LYP/l	2.051	2.3915	2.3645	1.360	1.364	1.388	1.385	1.355	93.5	100.9	99.8
Exp.	1.989(3)	2.3607(8)	2.3379(8)	1.358(4)	1.363(3)	1.388(3)	1.378(4)	1.346(4)	94.86(8)	99.93(8)	97.94(3)

[a] Basis set "l": TZVPP for Si, Br and C1, 6-31G* for the other atoms; basis set "lb": TZ2P for all atoms (see the Supporting Information).

Table 2: Selected results of the NBO analysis for **2** (B3LYP/II).^[a]

Si–X	Occ.	%(Si)	Hyb.	%(X)	Hyb.	WBI
Si–C1	1.960	20.1	p	79.9	sp ^{1.36}	0.65
Si–Br1	1.968	22.4	p	77.6	sp ^{4.96}	0.76
Si–Br2	1.980	23.1	p	76.9	sp ^{6.64}	0.82
Si (LP)	1.947		sp ^{0.27}			

[a] NBO occupancy (Occ.), bond polarization in %(Si) and %(X), orbital hybridization (Hyb.), and Wiberg bond index (WBI).

with an empty p valence orbital of the silicon atom. The presence of a stereochemically active lone pair at silicon in an NBO orbital of high s character and of strongly polarized Si–Br bonds complement the bonding picture of **2** as a dibromosilylene–carbene adduct (Table 2). Furthermore, application of the NRT formalism suggests that compound **2** is a strongly delocalized system.^[30] The NRT Si–C1 bond order of 1.02 clearly indicates the presence of a localized donor–acceptor single bond.

Natural population analysis of **2** (Table 3) shows that a charge transfer of 0.29e occurs from the Lewis base Idipp to the Lewis acid SiBr₂ upon complexation, which reduces the positive partial charge at the silicon atom from +0.71 in SiBr₂ to +0.59 in **2**, and increases the negative partial charges of the bromine atoms from –0.36 in SiBr₂ to –0.43/–0.44 in **2**.^[31]

Table 3: NPA partial charges for **2**, Idipp, and SiBr₂ (B3LYP/II).

	Si	C1	N1	C2	C3
Idipp		+0.07	–0.43	–0.09	–0.09
SiBr ₂	+0.71				
2	+0.59	+0.08	–0.37	–0.06	–0.06
	N2	Br1	Br2	SiBr2	
Idipp	–0.43				
SiBr ₂		–0.36	–0.36	0	
2	–0.37	–0.44	–0.43	–0.29	

The calculated bond dissociation energy $D^0(0)$ of **2** (123.7 kJ mol^{–1})^[32] compares well with that of ammonia–borane, H₃NBH₃ (118.4 kJ mol^{–1}),^[29b] thus providing additional evidence for a strong Si–C bond in **2**. Compound **2** is also thermodynamically stable with respect to its dissociation products SiBr₂ and Idipp at 298 K, as shown by the calculated Gibbs free dissociation energy $\Delta G^0 = +57.3$ kJ mol^{–1} in the gas phase.

Initial reactivity studies show compound **2** to be a very promising starting material in molecular silicon(II) chemistry. In fact, treatment of **2** with two equiv of KCp* in benzene affords selectively SiCp*₂ (Cp* = C₅Me₅)^[33] and Idipp. Rapid substitution reactions of **2** also occur, with NaCp (Cp = C₅H₅), NaLOEt (LOEt = [CpCo{P(O)(OEt)₂}]₃)^[34] and KTp' (Tp' = HB(3,5-Me₂pz)₃)^[35]. The outcome of these reactions is currently under investigation.

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- Idipp, and the cartesian atomic coordinates of the minimum structures of **2**, SiBr₂, and Idipp.
- [12] NMR spectroscopic data for **3**: ¹H NMR (300.1 MHz, CD₂Cl₂, 298 K, ppm): δ = 1.22 (d, ³J(H,H) = 6.8 Hz, 12H, 4 × CH-(CH₃)_A(CH₃)_B), 1.24 (d, ³J(H,H) = 6.8 Hz, 12H, 4 × CH-(CH₃)_B(CH₃)_A), 2.39 (sept, ³J(H,H) = 6.8 Hz, 4H, 4 × CH-(CH₃)_A(CH₃)_B), 7.34 (d, ³J(H,H) = 7.8 Hz, 4H, 4 × *m*-H, C₆H₃), 7.57 (t, ³J(H,H) = 7.8 Hz, 2H, 2 × *p*-H, C₆H₃), 7.86 (d, ⁴J(H,H) = 1.6 Hz, 2H, H^{4,5}), 11.2 ppm (t, ⁴J(H,H) = 1.6 Hz, 1H, H²). ¹³C{H} NMR (75.47 MHz, CD₂Cl₂, 298 K, ppm): δ = 23.6 (s, 4 × CH-(CH₃)_A(CH₃)_B), 24.7 (s, 4 × CH-(CH₃)_A(CH₃)_B), 29.3 (s, 4 × CH-(CH₃)_A(CH₃)_B), 124.8 (s, 4 × *m*-C, C₆H₃), 126.0 (s, C^{4,5}), 130.2 (s, 2 × *ipso*-C, C₆H₃), 132.1 (s, 2 × *p*-C, C₆H₃), 140.3 (s, C²), 145.3 ppm (s, 4 × *o*-C, C₆H₃).
- [13] Suitable single crystals of **1**·3CH₂Cl₂ were obtained upon cooling a CH₂Cl₂ solution of **1** from ambient temperature to −60 °C. The crystals deteriorate rapidly owing to the loss of the included solvent molecules and should be handled at very low temperature. Suitable yellow crystals of **2** were grown by diffusion of hexane into a benzene solution of **2** at room temperature. CCDC 729736 and CCDC 729737 contain 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.
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