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# $SiBr_2$(Idipp): A Stable N-Heterocyclic Carbene Adduct of Dibromosilylene**

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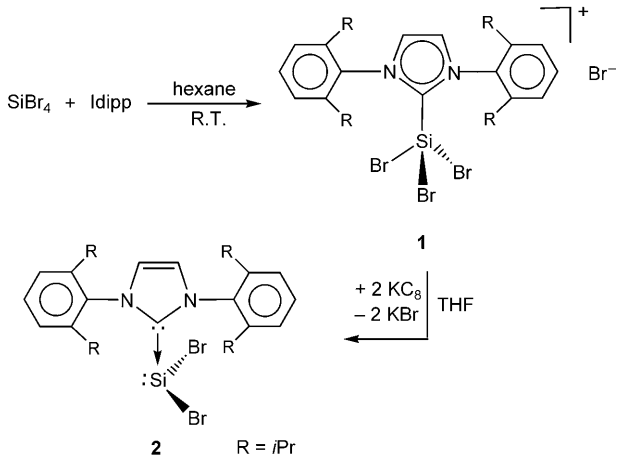
Silicon dihalides are high-temperature molecules of major academic and industrial interest.[1] For example, $SiF_2$ is one of the major products in plasma etching of silicon-containing films used in the manufacture of microelectronic devices, $SiCl_2$ is an important intermediate in the industrial synthesis 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 $SiX_2$ are highly unstable with respect to their disproportionation products, namely elemental silicon and $SiX_4$, at ambient temperature.[4] They are also very reactive, polymerizing rapidly even at low temperatures to give perhalopolysilanes, $[SiX_2]_n$.[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 $GeCl_2$(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 $SiBr_2$, $SiBr_2$(Idipp) **2** (Idipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), are described.

Compound **2** was obtained in two steps starting from $SiBr_4$ (Scheme 1). In the first step, $SiBr_4$ was treated with one equivalent of the N-heterocyclic carbene Idipp in hexane at ambient temperature to give the ionic product $[SiBr_3$(Idipp)]Br (**1**). Reduction of **1** with 2.5 equivalents of potassium graphite ($KC_8$) 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 $CH_2Cl_2$. 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 in hexane, and is stable under vigorous exclusion of air in benzene solution at ambient temperature for at least one week.




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

Compounds **1** and **2** were fully characterized. The crystal structure of **1**·3 $CH_2Cl_2$ reveals the presence of tetrahedral $[SiBr_3$(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, $SiCl_4$ forms a neutral, trigonal bipyramidal adduct with Idipp.[9] The mean Si–Br bond length in **1**·3 $CH_2Cl_2$ (2.175(3) Å)[15] compares well with that

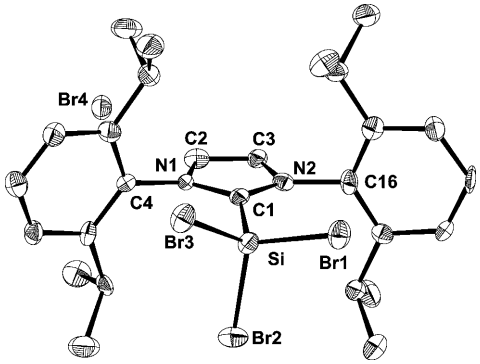



***Figure 1.*** DIAMOND plot of the structure of **1**·3 $CH_2Cl_2$ in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si–Br1 2.171(3), Si–Br2 2.180(2), Si–Br3 2.175(3), Si–C1 1.880(9), C1–N1 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-Br2 109.0(1), Br1-Si-Br3 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($sp^2$) single bonds (1.872 Å).[17] From the bonding parameters, **1**·3 $CH_2Cl_2$ can be described as an imidazolium salt bearing a $SiBr_3$ substituent at the $C^2$ position. The $^1H$ and $^{13}C$ NMR spectra provide additional support for the ionic nature of **1** in $CH_2Cl_2$. Thus, the $^1H$ and $^{13}C$ NMR signals of **1** in $CD_2Cl_2$ appear at similar frequencies to those of the imidazolium salt [(Idipp)H]Br (**3**),[18] and the $^{29}Si\{^1H\}$ NMR spectrum of **1** shows in $CD_2Cl_2$ a singlet resonance at lower field ($\delta = -63.9$ ppm) than that of $SiBr_4$ ($C_6D_6$: $\delta = -90.8$ ppm). In comparison, the $^{29}Si$ NMR signal of the neutral adduct $SiCl_4$(Idipp) appears at considerably higher field in $CD_2Cl_2$ ($\delta = -108.9$ ppm)[9] than that of $SiCl_4$ ($\delta = -18.5$ 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

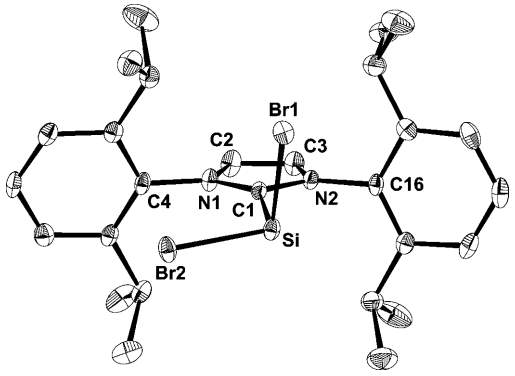


***Figure 2.*** DIAMOND plot of the molecular structure of **2** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si–Br1 2.3607(8), Si–Br2 2.3379(8), Si–C1 1.989(3), C1–N1 1.358(4), C1–N2 1.363(3), N1–C2 1.388(3), 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-$(NCH_2tBu)_2C_6H_4$),[22] but longer than the Si=C bonds of the silenes $Me_2Si{=}C(SiMe_3)SiMetBu_2$ (1.702(5) Å)[23] and $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (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 $SiBr_2$, 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 $SiBr_2$ ($r_g$(Si-Br) = 2.245(3) Å, $r_e$(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 $SiBr_2$ and carbene planes (75.5(1)°) shows that the molecule is folded, and there is significant torsion of the $N_2CSiBr_2$ 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 $^{13}C\{^1H\}$ NMR spectra of **2** in $C_6D_6$ have a single set of resonances for the Idipp group, indicating a rapid rotation of the $SiBr_2$ fragment about the Si–C bond on the NMR timescale. A distinctive signal for the silicon-bonded carbon atom is observed in the $^{13}C\{^1H\}$ 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 $C_6D_6$)[26] and of **1** ($\delta$ = 136.3 ppm in $CD_2Cl_2$). Finally, compound **2** has a characteristic $^{29}Si$ NMR signal in solution at a similar position ($\delta$ = 10.9 ppm in $C_6D_6$) 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/Ib | 2.037 | 2.3892 | 2.3580 | 1.368 | 1.373 | 1.388 | 1.384 | 1.357 | 93.3 | 100.7 | 100.8 |
| BP86/I | 2.036 | 2.3916 | 2.3647 | 1.371 | 1.375 | 1.395 | 1.390 | 1.367 | 93.4 | 100.4 | 100.2 |
| B3LYP/I | 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 "I": TZVPP for Si, Br and C1, 6-31G* for the other atoms; basis set "Ib": TZ2P for all atoms (see the Supporting Information).

  

*Table 2:* Selected results of the NBO analysis for **2** (B3LYP/I).[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 $SiBr_2$ upon complexation, which reduces the positive partial charge at the silicon atom from +0.71 in $SiBr_2$ to +0.59 in **2**, and increases the negative partial charges of the bromine atoms from −0.36 in $SiBr_2$ to −0.43/−0.44 in **2**.[31]

*Table 3:* NPA partial charges for **2**, Idipp, and $SiBr_2$ (B3LYP/I).

| | 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 $D^o(0)$ of **2** (123.7 kJ mol$^{-1}$)[32] compares well with that of ammonia–borane, $H_3NBH_3$ (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 $SiBr_2$ and Idipp at 298 K, as shown by the calculated Gibbs free dissociation energy $\Delta G^o = +57.3$ 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 $SiCp^*_2$ ($Cp^* = C_5Me_5$)[33] and Idipp. Rapid substitution reactions of **2** also occur, with NaCp ($Cp = C_5H_5$), $NaL_{OEt}$ ($L_{OEt} = [CpCo\{P(O)(OEt)_2\}_3]$),[34] and KTp′ ($Tp' = HB(3,5\text{-}Me_2pz)_3$].[35] The outcome of these reactions is currently under investigation.

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**Keywords:** carbene ligands · density functional calculations · donor–acceptor systems · silicon · silylenes

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[11] The Supporting Information contains the experimental section, details of the computational methods, tables of selected calculated and experimental geometrical parameters of **2**, $SiBr_2$, and

  

Idipp, and the cartesian atomic coordinates of the minimum structures of **2**, $SiBr_2$, and Idipp.

[12] NMR spectroscopic data for **3**: $^1$H NMR (300.1 MHz, $CD_2Cl_2$, 298 K, ppm): $\delta = 1.22$ (d, $^3J(H,H) = 6.8$ Hz, 12 H, $4 \times CH(CH_3)_A(CH_3)_B$), 1.24 (d, $^3J(H,H) = 6.8$ Hz, 12 H, $4 \times CH(CH_3)_A(CH_3)_B$), 2.39 (sept, $^3J(H,H) = 6.8$ Hz, 4 H, $4 \times CH(CH_3)_A(CH_3)_B$), 7.34 (d, $^3J(H,H) = 7.8$ Hz, 4 H, $4 \times m$-H, $C_6H_3$), 7.57 (t, $^3J(H,H) = 7.8$ Hz, 2 H, $2 \times p$-H, $C_6H_3$), 7.86 (d, $^4J(H,H) = 1.6$ Hz, 2 H, $H^{4,5}$), 11.2 ppm (t, $^4J(H,H) = 1.6$ Hz, 1 H, $H^2$). $^{13}$C{H} NMR (75.47 MHz, $CD_2Cl_2$, 298 K, ppm): $\delta = 23.6$ (s, $4 \times CH(CH_3)_A(CH_3)_B$), 24.7 (s, $4 \times CH(CH_3)_A(CH_3)_B$), 29.3 (s, $4 \times CH(CH_3)_A(CH_3)_B$), 124.8 (s, $4 \times m$-C, $C_6H_3$), 126.0 (s, $C^{4,5}$), 130.2 (s, $2 \times$ *ipso*-C, $C_6H_3$), 132.1 (s, $2 \times p$-C, $C_6H_3$), 140.3 (s, $C^2$), 145.3 ppm (s, $4 \times o$-C, $C_6H_3$).

[13] Suitable single crystals of $\mathbf{1}\cdot 3\,CH_2Cl_2$ were obtained upon cooling a $CH_2Cl_2$ 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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[18] Most distinctive is the NMR signal of the imidazole ring carbon atom $C^2$ of **1** and **3** in $CD_2Cl_2$, which is shifted to considerably lower frequency ($\delta = 136.3$ and 140.3 ppm, respectively) than that of Idipp ($\delta = 220.6$ ppm in $C_6D_6$), and the NMR signals of the $H^{4,5}$ imidazole ring protons of **1** and **3** in $CD_2Cl_2$, which appear at considerably higher frequency ($\delta = 8.79$ and 7.86 ppm, respectively) than that of Idipp ($\delta = 6.62$ ppm in $C_6D_6$). It is noteworthy that a solvent change from $CD_2Cl_2$ to $C_6D_6$ causes a dramatic shielding of the $H^{4,5}$ imidazole ring protons of **1** from $\delta = 8.79$ ppm to $\delta = 6.46$ ppm, which indicates that **1** might be composed of neutral $SiBr_4$(Idipp) molecules in less polar solvents, such as benzene.

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