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Reactivity of a Disilylene [{PhC(NBu^t)$_2$}Si]$_2$ toward Bromine: Synthesis and Characterization of a Stable Monomeric Bromosilylene

Hui-Xian Yeong,[†] Kai-Chung Lau,[‡] Hong-Wei Xi,[§] Kok Hwa Lim,[§] and Cheuk-Wai So*,[†]

[†] *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore,* [‡] *Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, and* [§] *Division of Chemical and Biomolecular Engineering, School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore*

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The reaction of the disilylene [{PhC(NBu^t)$_2$}Si]$_2$ (**1**) with 1 equiv of bromine in toluene afforded novel monomeric bromosilylene [{PhC(NBu^t)$_2$}SiBr] (**2**). The result shows that the Si^I−Si^I bond in **1** was cleaved by bromine. An X-ray structure of compound **2** has been determined.

Stable heavier group 14 alkyne analogues of composition RMMR (R = supporting ligand; M = Si, Ge, Sn, Pb) have attracted much attention in the past several decades.[1] These complexes can be synthesized successfully by incorporating sterically hindered substituents at the heavier group 14 elements.[2] The X-ray structures of heavier group 14 alkyne analogues show that they have a trans-bent and planar geometry in which the R−M−M angle decreases from silicon to lead. Theoretical and reactivity studies show that the Si−Si bond order in the disilyldisilyne [R′SiSiR′] (R′ = SiPr^i{CH(SiMe$_3$)$_2$}$_2$) is significantly greater than 2.[3] The Ge−Ge bond in the digermyne [ArGeGeAr] (Ar = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$) has a bond order of about 2 and partial singlet diradical character.[4,6c] The Pb−Pb bond order in the diplumbyne [RPbPbR] (R = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Pr$^i_3$)$_2$) is close to 1 with a lone pair (LP) of electrons at each Pb atom.[2f] Therefore, diplumbyne is considered as diplumbylene. Distannyne can adopt a multiply bonded structure similar to that of the germanium analogue or a singly bonded structure similar to that of the lead analogue, depending on the bulkiness of the supporting ligand.[5] Because of their unique electronic structures, digermyne and distannyne show different reactivities.[6] For example, the treatment of [ArMMAr] [M = Ge, Sn; Ar = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$] with N$_3$SiMe$_3$ afforded the cyclic singlet diradicaloid [ArGe{μ_2-N-(SiMe$_3$)}$_2$GeAr] and the imide-bridged complex [ArSn{μ_2-N(SiMe$_3$)}SnAr], respectively.[6c] It is suggested that distannyne has much less diradical character compared with digermyne, which leads to different reactivities.

Recently, Roesky and his co-workers reported the first example of the amidinate-stabilized disilylene [{PhC-(NBu^t)$_2$}Si]$_2$ with a Si^I−Si^I single bond and an LP of electrons at each Si atom.[7] That the disilylene has an unprecedented electronic structure prompted our interest in exploring its chemical reactivity. In this Communication, we report the synthesis and characterization of a stable bromosilylene from the reaction of [{PhC(NBu^t)$_2$}Si]$_2$ (**1**) with bromine. The theoretical studies of **1** are also described in order to understand its bonding nature and, hence, its reactivity.

The treatment of **1** with 1 equiv of bromine in toluene for 2 h afforded novel monomeric bromosilylene [{PhC(NBu^t)$_2$}-SiBr] (**2**; Scheme 1). The Si−Si bond in **1** was cleaved by bromine in the reaction. It is noteworthy that the LP of

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*To whom correspondence should be addressed. E-mail: CWSo@ntu.edu.sg.

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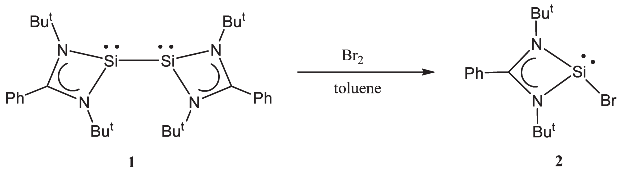
Scheme 1. Synthesis of **2**



electrons at the Si^I center in **1** did not undergo an oxidative addition reaction with bromine. In contrast, the reaction of [:Si{(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2}] or [R′SiSiR′] (R′ = SiPr^i{CH(SiMe$_3$)$_2$}$_2$) with bromine gave [SiBr$_2${(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2}] and [R′SiBr$_2$−SiBr$_2$R′], respectively.[2a,8] Power and his co-workers have reported that the reaction of [ArMMAr] [M = Ge, Sn; Ar = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-Pr^i$_2$)$_2$] with PhN=NPh resulted in the complete cleavage of the M−M bond, and an LP of electrons was found at the metal centers in the product [ArM{(Ph)N−N(Ph)}MAr].[6c] Similar results can be found in the reaction of [ArSnSnAr] with N$_3$SiMe$_3$ to form [ArSn{μ_2-N(SiMe$_3$)}SnAr].[6c] Recently, an amidinate-stabilized chlorosilylene [{PhC(NBu^t)$_2$}SiCl] was synthesized by the reaction of [{PhC(NBu^t)$_2$}SiCl$_3$] with potassium.[9] Density functional theory (DFT) calculations of [{PhC(NBu^t)$_2$}SiCl] have been performed. Carbene-stabilized dihalosilylenes [L → SiX$_2$] (L = :C{N(C$_6$H$_3$-2,6-Pr^i$_2$)CH}$_2$; X = Cl, Br) have also been synthesized by the reaction of [L → SiCl$_4$] or [{L → SiBr$_3$}Br] with potassium graphite.[10]

Compound **2** was isolated as a highly air- and moisture-sensitive pale-yellow crystalline solid, which is soluble in toluene and tetrahydrofuran. It is stable in solution or the solid state at room temperature in an inert atmosphere. It has been characterized by elemental analysis, spectroscopic methods, and X-ray crystallography. The ^{1}H and ^{13}C NMR spectra of **2** display resonances due to the amidinate ligand. The ^{29}Si NMR signal of **2** (18.6 ppm) shows an upfield shift compared with that of **1** (76.3 ppm). It is comparable with that of [{PhC(NBu^t)$_2$}SiCl][9] (14.6 ppm) and [L → SiBr$_2$] (10.9 ppm).[10b]

The molecular structure of **2** with an atomic numbering scheme is shown in Figure 1.[11] The amidinate ligand is bonded in a N,N′-chelate fashion to the silicon center and displays a trigonal-pyramidal geometry. The sum of the bond angles at the silicon center is 255.0°, which is comparable with that of the three-coordinated chlorosilylene [{PhC(NBu^t)$_2$}SiCl] (260.7°).[9] This geometry is consistent with a stereoactive LP at the silicon center. The phenyl group is orthogonally arranged to the four-membered Si1−N1−C1−N1A ring. The Si1−Br1 bond [2.326(3) Å] is comparable to those of [L → SiBr$_2$] [2.3379(8) and 2.3607(8) Å][10b] but is longer than that of gaseous silicon dibromide (2.243 Å).[12]

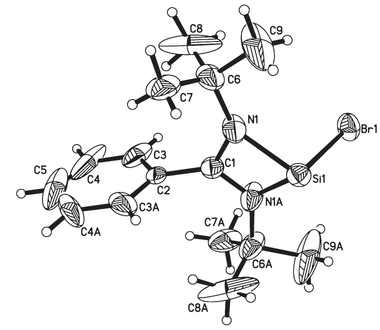


Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (deg): Si1−Br1 2.326(3), Si1−N1 1.971(5), Si1−N1A 1.882(5), C1−N1 1.331(5); N1−Si1−N1A 66.9(2), N1A−Si1−Br1 93.3(2), N1−Si1−Br1 94.8(2), Si1−N1−C1 88.5(3), N1−C1−N1A 105.9(6).

Table 1. Theoretical Topological Features at the BCP of **1** and [H$_3$Si−SiH$_3$][a]

bond	ρ	$\nabla^2\rho$	G	H	$\|V\|$
		Compound **1**			
Si−Si′	0.52	−2.29	0.06	−0.22	0.27
Si−N	0.59	6.87	0.72	−0.24	0.96
Si−N′	0.59	7.06	0.73	−0.23	0.96
N−C	2.25	−24.56	1.72	−3.49	5.21
N′−C	2.27	−24.92	1.86	−3.60	5.46
		[H$_3$Si−SiH$_3$]			
Si−Si	0.63	−3.91	0.04	−0.31	0.36

[a] Units: ρ, e Å^{-3}; $\nabla^2\rho$, e Å^{-5}; H, G, $|V|$, hartree Å^{-3}.

The C(1)−N(1) and C(1)−N(1A) bond lengths in **2** [1.331(5) Å] are approximately intermediate between the C−N double and C−N(sp^2) single bond lengths. This geometry shows considerable delocalization throughout the NCN backbone of the ligand. The Si−N bonds in **2** [1.882(5) and 1.971(5) Å] are slightly longer than those of **1** [1.866(4) and 1.874(4) Å].[7]

In order to understand the bonding nature and, hence, reactivity, compound **1** was investigated by means of quantum chemical calculations. The calculations were performed by the DFT[13] B3LYP[14] with the 6-311+G(d,p) basis set[15] as implemented in the *Gaussian 03*[16] program. The calculated structural parameters (Si−Si′ = 2.472 Å, Si−N = 1.903 Å, Si−N′ = 1.905 Å, and N−Si−N′ = 68.5°) are in good agreement with the crystallographic data. The natural bond orbital (NBO)[17] analysis (Table S1; see the Supporting Information) shows that the Si−Si bond is derived from the overlapping of p-rich hybrids (sp$^{7.48}$, 87.8% p character) on the Si atoms. The Wiberg bond index[18] shows that the Si−Si bond (0.923) in **1** has single-bond character. The LP

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(11) Crystal data for **2** (C$_{15}$H$_{23}$BrN$_2$Si): M = 339.35; a = 14.239(1) Å, b = 11.164(8) Å, c = 11.982(9) Å; α = 90°, β = 116.28(4)°, γ = 90°; V = 1707.9(2) Å^3; Z = 4; space group $C2/c$ (monoclinic); T = 103(2) K; λ = 0.710 73 Å; μ = 2.468 mm^{-1}; ρ_{calc} = 1.320 g cm^{-3}; F(000) = 704; 7803 measured reflections, 1507 independent and 100 observed reflections [$I > 2\sigma(I)$]; R1 = 0.0636, wR2 = 0.1665; largest diffraction peak and hole 1.190/−0.380 e Å^{-3}.

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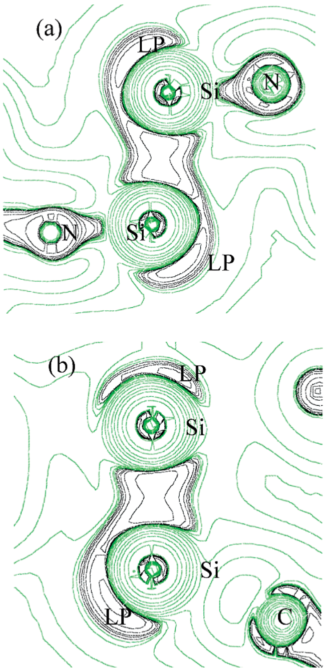

Figure 2. $\nabla^2\rho$ in the (a) SiSiN plane and (b) SiSiC plane in compound **1**. The N atom on the left of part a is slightly off the plane. LP stands for the LP electron on silicon. Green lines indicate negative values in $\nabla^2\rho$, and black lines stand for positive values.

electrons at the silicon centers are high in s character ($sp^{0.43}$, 69.9% s character) with some directionality.

The presence of a π bond in a molecule can be measured by the chemical shift anisotropy (CSA).[3a] Large CSA values indicate the presence of π bonds. When the calculated ^{29}Si CSA of **1** (80.5 ppm) is compared with that of [$H_2Si{=}SiH_2$] (362.6 ppm), it is suggested that the Si$-$Si bond in **1** does not have multiple-bond character (Table S2; see the Supporting Information).

The topological analysis of the electron densities of compound **1** and [$H_3Si{-}SiH_3$] according to Bader's quantum theory of atoms in molecules was performed using the optimized structure at the B3LYP/6-31+G(d) level (Table 1).[19] The Laplacian of the electron density $\nabla^2\rho$ and the total energy density H at the (3, -1) bond critical point (BCP) show that the Si$-$Si bond in compound **1** and [$H_3Si{-}SiH_3$] are nonpolar and covalent (Figure 2). The electron density is locally concentrated between two Si atoms in **1** and [$H_3Si{-}SiH_3$]. The bond strength of the Si$-$Si bond in **1** is weaker than that in [$H_3Si{-}SiH_3$]. There are four valence-shell charge concentrations at the Si atoms. One of them in the nonbonding region is regarded as the LP density. The result shows that the LP of electrons is stereochemically active, consistent with the NBO analysis.

In summary, DFT calculations and the topological analysis of the electron densities show that **1** comprises a Si$-$Si single bond and an LP of electrons at each Si atom. A novel monomeric bromosilylene complex **2** has been synthesized by the reaction of **1** with bromine in toluene. The results show that the $Si^I{-}Si^I$ bond in **1** was cleaved by bromine. The LP of electrons at the Si^I center did not undergo oxidative addition with bromine. Compound **2** can serve as a functionalized silylene in a metathesis reaction.

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Supporting Information Available: Complete citation for ref 16, selected calculation results of **1**, and a CIF file giving X-ray data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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