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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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A Stable Two-Coordinate Acyclic Silylene

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Supporting Information

ABSTRACT: Simple two-coordinate acyclic silylenes, SiR_2, have hitherto been identified only as transient intermediates or thermally labile species. By making use of the strong σ-donor properties and high steric loading of the $B(NDippCH)_2$ substituent (Dipp = 2,6-$^iPr_2C_6H_3$), an isolable monomeric species, $Si\{B(NDippCH)_2\}\{N(SiMe_3)Dipp\}$, can be synthesized which is stable in the solid state up to 130 °C. This silylene species undergoes facile oxidative addition reactions with dihydrogen (at sub-ambient temperatures) and with alkyl C−H bonds, consistent with a low singlet−triplet gap (103.9 kJ mol^{-1}), thus demonstrating fundamental modes of reactivity more characteristic of transition metal systems.

Simple sub-valent silicon compounds are typically highly reactive and have short lifetimes at temperatures close to ambient.[1] Thus, West's observation of the transient divalent silylene, $SiMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$), which dimerizes to give the disilene, $Mes_2Si{=}SiMes_2$, at 77 K represented a landmark event in the renaissance of modern Main Group chemistry.[2] Since that groundbreaking discovery, only silylene systems stabilized by incorporation into a cyclic framework,[3−8] or by means of an increased coordination number at silicon, have been reported,[9−18] while simple isolable acyclic silylenes, SiR_2, remain a chemical "Holy Grail".[19−26] Thus, for example, although the heavier Group 14 compounds $E\{N(SiMe_3)_2\}_2$ (E = Ge, Sn, and Pb) have been known since the 1970s to be thermally stable monomeric species,[27] and stable acyclic diaminocarbenes have been reported more recently,[28] the analogous silicon-containing species, $Si\{N(SiMe_3)_2\}_2$, is stable in solution only at low temperatures and decomposes rapidly at 0 °C.[29]

With regard to reactivity, singlet tetrelenes ($:ER_2$) possess many attractive features for small molecule activation, up until now almost exclusively the preserve of transition metals. Thus, a vacant coordination site, together with the availability of both a lone pair of electrons and a formally vacant orbital, provide a platform for the activation even of strong, relatively nonpolar linkages, such as H−H and C−H bonds.[30−34] Consistently, recent work on the chemistry of isolable singlet carbenes, CR_2, has led to the development of systems capable of NH_3 activation and H_2 cleavage at 35 °C.[32] While existing N-heterocyclic silylene compounds are less reactive toward such substrates, acyclic derivatives (featuring a more obtuse angle at silicon) have been predicted computationally to offer enhanced reactivity.[35] Such systems, possessing a lower lying excited electronic state and providing coordinative and oxidative flexibility, might therefore be expected to show modes of reactivity more typical of transition metals.[36]

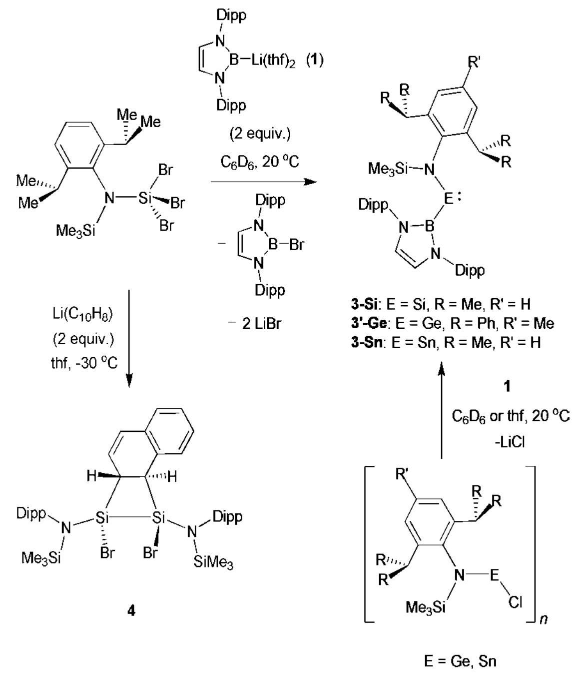
In recent work we have utilized the lithium reagent $(thf)_2Li\{B(NDippCH)_2\}$ (**1**; Dipp = 2,6-$^iPr_2C_6H_3$)[37] as a nucleophilic source of the boryl (BR_2) fragment in the synthesis of novel E−B chemical bonds.[38] The extremely strong σ donor properties and high steric loading of the formally anionic $[B(NDippCH)_2]^-$ ligand, and the ability of **1** to react with metal electrophiles,[37,38] appear ideally suited to the syntheses of monomeric Group 14 systems of the types $E(boryl)_2$ and E(boryl)X (E = Si, Ge, and Sn). In the current study this hypothesis is borne out by the syntheses of the mononuclear tin(II) systems $Sn\{B(NDippCH)_2\}_2$ (**2-Sn**) and $Sn\{B(NDippCH)_2\}\{N(SiMe_3)Dipp\}$ (**3-Sn**) from $(thf)_2Li\{B(NDippCH)_2\}$ (**1**) and $SnCl_2$ or $[Sn\{N(SiMe_3)Dipp\}(\mu\text{-}Cl)]_2$, respectively (Scheme 1 and Supporting Information (SI)). X-ray crystallography and density functional theory (DFT) calculations on these systems are consistent (i) with bent monomeric structures [**2-Sn**: ∠B−Sn−B = 118.8(3)° (X-ray), 115.7° (DFT); **3-Sn**: ∠N−Sn−B = 106.7(2)°, 107.0(1)° (X-ray), 108.1° (DFT)]; (ii) with singlet ground states ($\Delta E_{s\to t}$ = 39.2 and 121.7 kJ mol^{-1}, respectively); and (iii) with tin-centered HOMOs featuring appreciable 5p-orbital character (e.g., 38.8% Sn 5p, 18.3% Sn 5s for **3-Sn**) (SI).

Analogous DFT calculations carried out for the lighter Group 14 congeners $E\{B(NDippCH)_2\}_2$ (**2-Ge**, **2-Si**) and $E\{B(NDippCH)_2\}\{N(SiMe_3)Dipp\}$ (**3-Ge**, **3-Si**) suggest that, while the singlet−triplet gaps for the bis(boryl) systems are prohibitively low (17.9 and −0.27 kJ mol^{-1} for **2-Ge** and **2-Si**, respectively), those for the (amido)boryl systems (123.0 and 103.9 kJ mol^{-1}) are consistent with potentially isolable germylene/silylene species. Furthermore, when compared to the gaps calculated for more heavily π-stabilized bis(amido)germylenes and silylenes [e.g., 209.3 kJ mol^{-1} for the model system $Si(NMe_2)_2$, using the same method], the data for **3-Ge**

Received: February 1, 2012
Published: March 23, 2012

dx.doi.org/10.1021/ja301042u | J. Am. Chem. Soc. 2012, 134, 6500−6503

Scheme 1. Synthesis of Silylene 3-Si and Related Germylene/Stannylene Compounds



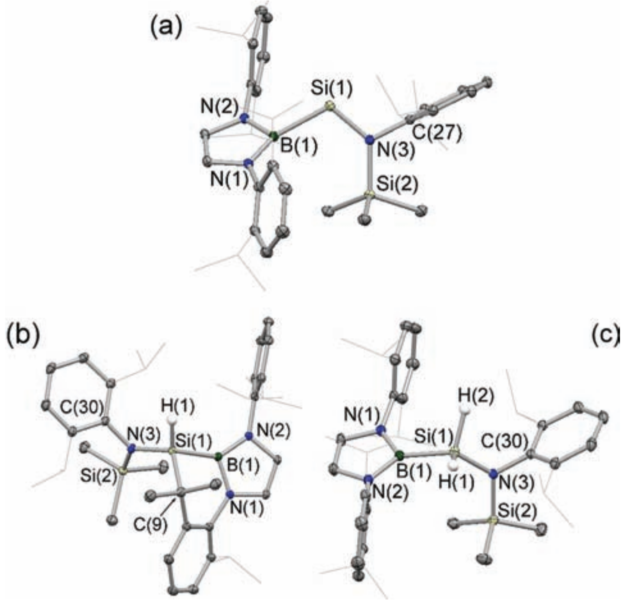


Figure 1. Molecular structures of (a) **3-Si**, (b) **5**, and (c) **6** (ellipsoids shown at the 40% probability level; C-bound hydrogen atoms omitted and ^{i}Pr groups shown in wireframe format for clarity). Selected bond lengths and angles: for **3-Si**, Si(1)−B(1) 2.066(1) Å, Si(1)−N(3) 1.731(1) Å, B(1)−Si(1)−N(1) 109.7(1)°; for **5**, Si(1)−B(1) 2.000(1) Å, Si(1)−N(3) 1.748(1) Å, Si(1)−C(9) 1.937(1) Å, Si(1)−H(1) 1.388(14) Å, B(1)−Si(1)−N(3) 118.1(1)°; and for **6**, Si(1)−B(1) 2.016(2) Å, Si(1)−N(3) 1.751(2) Å, B(1)−Si(1)−N(1) 120.1(1)°.

and **3-Si** imply that mixed (amido)boryl systems might be even better candidates for small-molecule activation chemistry under mild conditions.

Synthetically, an (amido)boryl germanium(II) complex has so far only been accessible by employing the sterically even more demanding N(SiMe$_3$)Dipp* amido group [Dipp* = 2,6-(Ph$_2$CH)$_2$-4-Me-C$_6$H$_2$], since the precursor Ge{N(SiMe$_3$)Dipp*}Cl is readily available, while Ge{N(SiMe$_3$)Dipp}hal (hal = Cl, Br) can be synthesized only in low yield.[39] Reaction of Ge{N(SiMe$_3$)Dipp*}Cl with **1** gives the desired monomeric germylene Ge{B(NDippCH)$_2$}{N(SiMe$_3$)Dipp*} (**3′-Ge**) in reasonable (55%) yield as an exceedingly thermally stable red-purple crystalline solid, decomposing at $T > 240$ °C (Scheme 1 and SI). Corresponding Si^{II} precursors are not available as tractable species, but, remarkably, the reaction of the Si^{IV} trihalide Si{N(SiMe$_3$)Dipp}Br$_3$ with 2 equiv of **1** cleanly generates the analogous silylene Si{B(NDippCH)$_2$}{N(SiMe$_3$)Dipp} (**3-Si**) as the only silicon-containing product (as judged by ^{29}Si NMR spectroscopy). The co-products from this reaction are LiBr and 1 equiv of the bromoborane BrB(NDippCH)$_2$, and ^{1}H NMR monitoring of the reaction implies that the conversion is quantitative (SI); this transformation therefore implies spontaneous formation of Si^{II} via net reductive elimination.[40−43] The key, and unprecedented, role of the boryl reagent in this process in providing both ligation and reduction is illuminated by the contrasting reactivity toward simple lithium-based reductants; reaction of Si{N(SiMe$_3$)Dipp}Br$_3$ with lithium naphthalenide, for example, gives the Si−Si bonded dibromodisilane **4** (SI), possibly via the highly reactive transient Si^{II} bromide [Si{N(Dipp)SiMe$_3$}Br]$_n$.

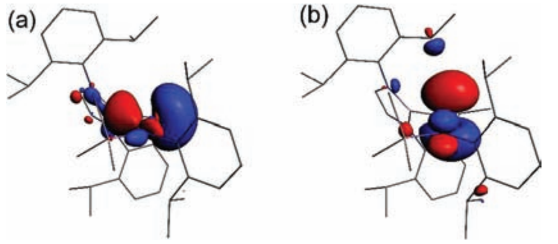
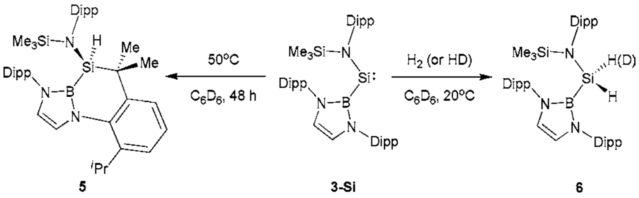


Figure 2. DFT-calculated (left) HOMO ($E = -4.64$ eV) and (right) LUMO ($E = -2.60$ eV) of **3-Si**.

Scheme 2. C−H and H−H Bond Activation by 3-Si



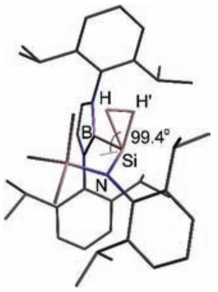


Figure 3. Transition state for oxidative addition of dihydrogen to **3-Si**. Key distances: Si−H 1.697 Å, Si−H′ 1.587 Å, H···H′ 1.045 Å, Si−B 2.034 Å, Si−N 1.787 Å.

Spectroscopic data for **3-Si**, in particular the very low-field ^{29}Si resonance [δ_{Si} = 439.7 (meas), 421.9 ppm (calc)], are consistent with the formation of a two-coordinate silylene [cf. δ_{Si} = 567 and 224 ppm for Si{C(SiMe$_3$)$_2$CH}$_2$ and Si{N(SiMe$_3$)$_2$}$_2$, respectively],[5,29] and a monomeric structure in the solid state was confirmed crystallographically (Figure 1). As such, **3-Si** is revealed to be the first example of a room-temperature-stable simple two-coordinate acyclic silylene. The Si−B and Si−N distances [2.066(1), 1.731(1) Å] fall within precedented ranges; the B−Si−N angle [109.7(1)°] is very similar to that calculated for $Si\{N(SiMe_3)_2\}_2$ (110.2°),[29] but slightly wider than that in the isosteric stannylene system **3-Sn** [106.7(2), 107.0(1)°], consistent with established trends in p-block chemistry.[44] By contrast, significant widening of the angle at silicon is observed compared to N-heterocyclic silylenes [e.g., 90.5(10)° for $Si(N^tBuCH)_2$],[3] consistent with quantum chemical predictions of a narrower singlet−triplet gap and, by implication, enhanced reactivity for **3-Si.**[35] Despite the presence of both potentially *π*-donor amido and *π*-acceptor boryl substituents at Si(1), DFT calculations reveal minimal delocalization of key molecular orbitals across the B−Si−N framework. Thus, although the amido substituent is aligned approximately parallel to the B−Si−N plane (interplane torsion angle = 9.9°), there is little N 2p contribution to the LUMO (70.1% Si 3p, 8.3% N 2p; Figure 2). Similarly, there is little B 2p contribution to the HOMO, which again is largely localized at Si(1) (41.7% Si 3p, 22.8% Si 3s, 8.2% B 2p).[45]

In the solid state, **3-Si** exhibits remarkable thermal robustness, being stable at temperatures up to 130 °C. Even at 50 °C in benzene solution, only slow decomposition occurs (48 h to reach completion), the exclusive product being the cyclo-metalated species **5** (Scheme 2). This highly selective formal intramolecular insertion of the silylene function into one of the methine C−H bonds of the boryl ligand Dipp substituents is reminiscent of the well-established ortho-metalation of aryl rings by lower oxidation state transition metal compounds—a signature reaction for these elements. Given this latent reactivity, and the moderate singlet−triplet gap calculated for **3-Si**, the potential for the more challenging intermolecular activation of other E−H bonds at or below room temperature has been examined.

The reaction of **3-Si** with dihydrogen in hydrocarbon solution occurs readily (even at 0 °C) to give the dihydrosilane, $H_2Si\{B(NDippCH)_2\}\{N(Dipp)SiMe_3\}$ (**6**), in quantitative yield (Scheme 2), which has been characterized by spectroscopic methods and by X-ray crystallography (Figure 1). The formation of **6** from **3-Si** represents single-site activation of dihydrogen by a well-defined Main Group compound below room temperature and the first experimentally observed activation of H_2 by a silylene. Thermodynamically, this H_2 activation reaction is calculated to be strongly exergonic ($\Delta G = -122.2$ kJ mol^{-1}), in line with the experimental observation of irreversibility, and with previous calculations on dihydrogen addition to hypothetical model silylenes.[35] Mechanistically, a concerted bimolecular process is suggested not only by DFT calculations, but also by the analogous reaction with HD, which yields $H(D)Si\{B(NDippCH)_2\}\{N(Dipp)SiMe_3\}$ as the sole product. Kinetically, the computed value of $\Delta G^{\ddagger}$ (+97.2 kJ mol^{-1}) is consistent with the observed activation at or below room temperature; moreover, it is markedly lower than the activation energies calculated for dihydrogen addition to bis(amido)silylenes [e.g., 190.0, 277.8 kJ mol^{-1} for $Si(NH_2)_2$ and $Si(NHCH)_2$, respectively], in line with the smaller singlet−triplet gap calculated for **3-Si.**[35] Interestingly, the transition state calculated for the **3-Si**+H_2 system (Figure 3) reveals approach of the H_2 molecule side-on to the silylene and with a trajectory essentially perpendicular to the B−Si−N plane (99.4°), consistent with the electrophilic nature of the silylene molecule, and with donation of electron density from HOMO of H_2 into the LUMO of **3-Si**. Such behavior is more reminiscent of the behavior of transition metal systems toward dihydrogen than the *nucleophilic* activation of H_2 by carbenes.[32]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details; synthetic and spectroscopic data for all new compounds; CIF files for **2-Sn**, **3-Si**, **3′-Ge**, **3-Sn**, **4**, **5**, **6**, and $Si\{N(SiMe_3)Dipp\}\{B(NDippCH)_2\}I_2$. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data are also freely available from the Cambridge Crystallographic Data Centre (CCDC 857171−857177 and 857429).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Leverhulme Trust (F/08699/E), the Australian Research Council, and the EPSRC (EP/F019181/1, EP/F055412/1, and computational resources via its National Service for Computational Chemistry Software, http://www.nsccs.ac.uk). We also thank UCL for computing resources via the Research Computing 'Legion' cluster and associated services.

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(40) Mechanistically, Si{N($SiMe_3$)Dipp}Br_3 is seemingly inert to substitution chemistry with bulky nucleophiles [e.g., Li{N($SiMe_3$)Dipp} or K{N($SiMe_3$)$_2$}], as are other sterically encumbered silanes of the type $SiRBr_3$.[41] However, $SiRBr_3$ systems have previously been shown to be susceptible to bromide/lithium exchange in the presence of powerful lithium-containing reductants, to give silylenoid species of the type SiR(Br)$_2$Li, which are then amenable to substitution with anionic nucleophiles [to give SiR(Br)R′(Li)].[41] Given that boryllithium reagent **1** has previously been shown to be capable of halogen/lithium exchange with organic halides,[42] a possible mechanism for the formation of **3-Si** therefore proceeds via formation of Br_2(Li)Si{N($SiMe_3$)Dipp} (via bromine/lithium exchange with the first equivalent of **1**), followed by boryl/bromide metathesis at silicon (using the second equivalent of **1**) to give Br(Li)Si{B(NDippCH)$_2$}{N($SiMe_3$)Dipp}, and finally by elimination of LiBr from this bulky silylenoid. Elimination of LiBr from a lithium silylenoid system as an *in situ* silylene source also finds recent literature precedent.[43] An alternative mechanism proceeding via initial bromide/boryl metathesis to give Br_2Si{B(NDippCH)$_2$}{N($SiMe_3$)Dipp}, followed by elimination of the bromoborane BrB(NDippCH)$_2$ (and subsequent bromide/boryl metathesis), appears less likely. The diiodosilane I_2Si{B(NDippCH)$_2$}{N($SiMe_3$)Dipp}, prepared independently from **3-Si** and I_2 (SI), is resolutely stable to reductive elimination.

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