DE GRUYTER Main Group Met. Chem. 2019; 42: 121–124

Short Communication **Open Access**

Anastas Sidiropoulos, Andreas Stasch* and Cameron Jones*

Thermal rearrangement of a 1,2-bis(silylene): Synthesis and crystal structure of a silyl-silylene

https://doi.org/10.1515/mgmc-2019-0013
Received March 21, 2019; accepted May 07, 2019.

Abstract: Thermal rearrangement of the 1,2-bis(silylene), $[\{(4\text{-Bu}^t\text{Ph})\text{C}(\text{NDip})_2\}\text{Si}–]_2$ (Dip = 2,6-diisopropylphenyl, leads to the silyl-silylene, $\{(4\text{-Bu}^t\text{Ph})\text{C}(\text{NDip})_2\}\text{Si}–\text{Si}(\text{H})\{\text{N}(\text{Dip})\text{C}(=\text{NDip})(4\text{-Bu}^t\text{Ph}^{-\text{H}})\}$, *via* an intramolecular C–H activation reaction. The X-ray crystal structure, and limited spectroscopic data, for the compound are reported. The structure of the silyl-silylene incorporates an exocyclic imine fragment, which is unprecedented for this compound class.

Keywords: silylene; silyl-silylene; bis(silylene); low-oxidation state; X-ray crystallography

West's 1981 synthesis of the first stable disilene, $\text{Mes}_2\text{Si}=\text{SiMes}_2$ (Mes = mesityl), *via* dimerization of a transient silylene, $:\text{SiMes}_2$, is considered by many as one of the pivotal results in the development of low oxidation state main group element chemistry (West et al., 1981). It was not until 1994 that the same group reported the first example of an isolable silylene, the two-coordinate silicon center of which was stabilized by incorporation within an N-heterocyclic framework (Denk et al., 1994). Since that time numerous heterocyclic and Lewis base stabilized silylenes have been reported, and their chemistry extensively explored (Asay et al., 2011). In 2012 the first acyclic two-coordinate silylenes were reported in simultaneous papers, one of which described the enhanced reactivity of silylene **1a** (Figure 1) towards H-H and C-H bond activations (Protchenko et al., 2012; Rekken et al., 2012). Several two-coordinate acyclic silylenes have followed, including the highly reactive silyl-silylene **1b** (Protchenko et al., 2013).

Our interest in low oxidation state silicon chemistry is not restricted to silylenes such as **1**, but also includes the stabilization of formally silicon(I) species. In 2011 we were able to prepare such a species, *viz.* the 1,2-bis(silylene) **2** (Scheme 1), which was stabilized by incorporation of a bulky amidinate ligand developed in the group (Jones et al., 2011). It is noteworthy that Roesky and co-workers had prepared a closely related, but less bulky, amidinate substituted 1,2-bis(silylene), $[\{\text{PhC}(\text{NBu}^t)_2\}\text{Si}–]_2$ two years earlier (Sen et al., 2009). During the exploration of the further chemistry of **2**, we have found that the compound slowly thermally isomerizes to yield a rare example of an amidinate substituted silyl-silylene, the X-ray crystal structure of which we report herein.

The deep blue 1,2-bis(silylene) **2** was dissolved in toluene, and subsequently heated at reflux for 4 days. During this time the initially deep blue solution lightened in color, eventually becoming yellow. Layering of this yellow solution with pentane led to the deposition of yellow crystals of the silyl-silylene **3** in an isolated yield of 34% (Scheme 1). It is of note that attempts to thermally isomerize the 1,2-bis(germylene) and 1,2-bis(stannylene) analogues of **2**, led only to deposition of elemental germanium or tin, respectively, and generation of the protonated amidine, $(4\text{-Bu}^t\text{C}_6\text{H}_4)\text{C}(\text{NDip})\{\text{N}(\text{H})\text{Dip}\}$ (Dip = 2,6-diisopropylphenyl).

With regard to a mechanism for the formation of **3**, it seems reasonable that there is an initial de-complexation of one arm of one amidinate ligand from a silicon center to give the transient bis(silylene) intermediate, **4**. Rotation of the ligand backbone about its N-C single bond could then bring the *tert*-butyl phenyl substituent into close proximity with the acyclic two-coordinate silylene center of **4**. The phenyl then undergoes an intramolecular C-H activation at one of its *ortho*-positions to give **3**. Such a process is not dissimilar to intramolecular C–H activation processes previously reported for silylenes **1** (Protchenko et al., 2012; Protchenko et al., 2013).

As compound **3** has limited solubility in normal non-coordinating deuterated solvents once crystallized, only its ^{1}H NMR spectrum could be obtained. That spectrum is consistent with the compound retaining its unsymmetrical solid state structure in solution, in that it exhibits two sets of

---

*** Corresponding authors: Andreas Stasch and Cameron Jones,** School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria, 3800, Australia, e-mail: as411@st-andrews.ac.uk (Andreas Stasch); cameron.jones@monash.edu (Cameron Jones).
Anastas Sidiropoulos, School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria, 3800, Australia

ligand resonances. In addition, a broad signal at δ 6.39 ppm was assigned to the hydride ligand, close to where the hydride resonance for the only other example of an amidinato substituted hydridosilyl-silylene, $\{PhC(NBu^t)_2\}Si–Si(H)\{(Bu^tN)_2C(H)Ph\}$, occurs, *viz.* δ 6.70 ppm (Zhang et al., 2010). It is of note that this silylene was not prepared by thermal rearrangement of a 1,2-bis(silylene), but by reduction of the silicon(IV) precursor compound, $\{PhC(NBu^t)_2\}Si(H)Cl_2$.

The X-ray crystal structure of compound **3** was obtained, and its molecular structure is depicted in Figure 2 (see also Table 1). This shows it to possess a three-coordinate pyramidal silylene center, Si(2), that is chelated by an amidinate ligand with an electronically delocalised NCN backbone. Further ligation comes from a hydridosilyl fragment that results from the aforementioned intramolecular thermal isomerization. That fragment is a five-membered heterocycle, which encompasses a distorted tetrahedral silicon center, Si(1). The backbone of the five-membered ring is substituted at planar C(1) by an exo-cyclic imino moiety. To the best of our knowledge, this structural motif is unprecedented in silyl-silylene chemistry. The Si–Si distance in **3**, 2.394(1) Å, lies in the known range for such interactions, and is comparable to Si–Si distances in related silyl-silylenes, e.g. 2.386(1) Å in **1b**, and 2.377(5) Å in $\{PhC(NBu^t)_2\}Si\text{-}Si(H)\{(Bu^tN)_2C(H)Ph\}$ (Protchenko et al., 2013; Rodriguez et al., 2015; Yamaguchi and Sekiguchi, 2011; Zhang et al. 2010).

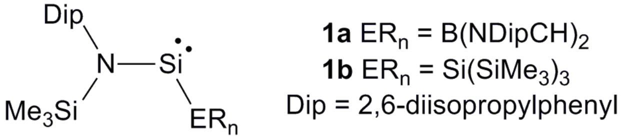


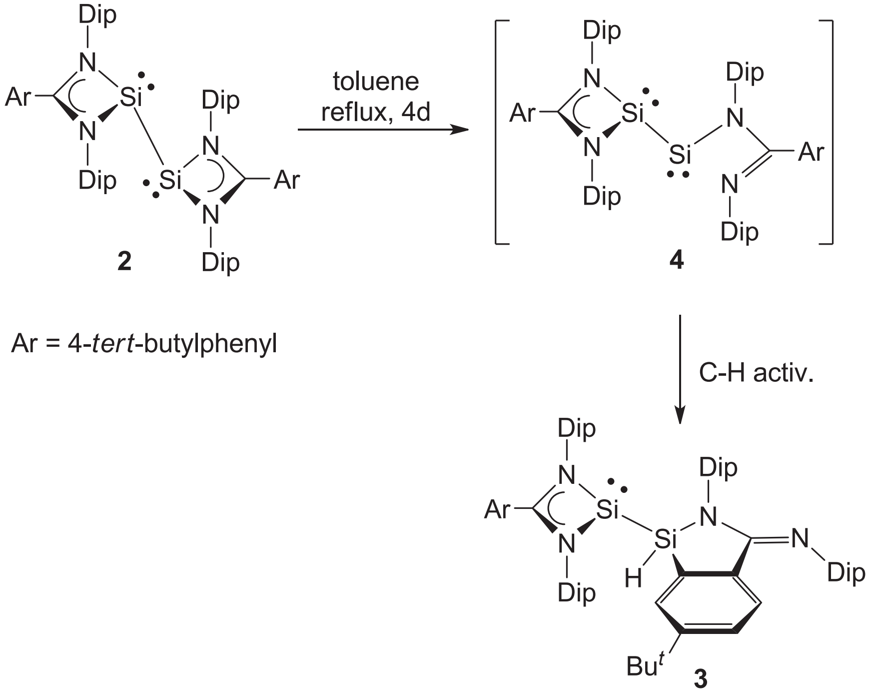
Figure 1: Examples of previously reported acyclic two-coordinate silylenes.

In summary, an unusual amidinate coordinated silyl-silylene has been prepared by thermal rearrangement of a 1,2-bis(silylene). The mechanism of the rearrangement is thought to include a transient intermediate that possesses a reactive acyclic two-coordinate silylene center. This undergoes an intramolecular C-H activation of one of its phenyl substituents to ultimately yield the isolated silyl-silylene. In the solid state this is shown to incorporate a five-membered heterocyclic silyl fragment that is substituted by an imine moiety. We continue to explore the stabilization and reactivity of low oxidation state silicon compounds in our laboratory.

Experimental

General

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of



Scheme 1: Synthesis of silyl-silylene **3**.

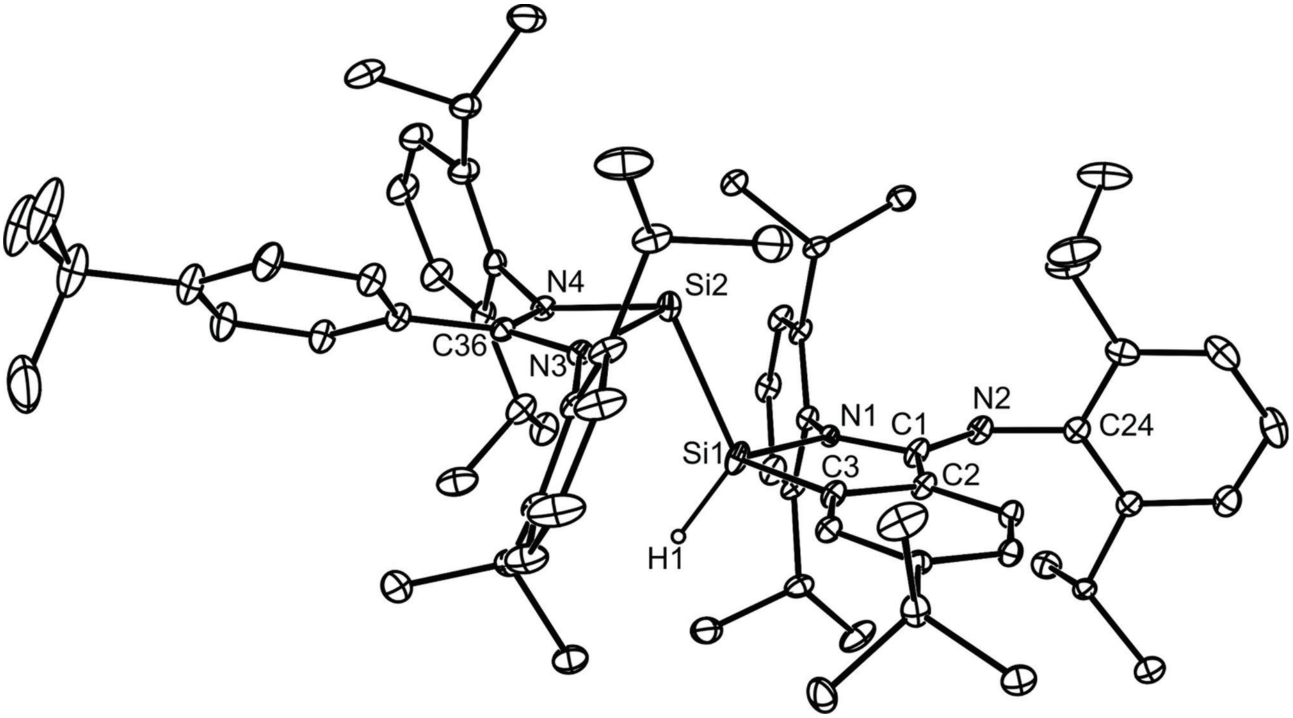


Figure 2: Thermal ellipsoid plot (25% probability surface) of the molecular structure of **3** (hydrogen atoms, except the hydride, omitted). Selected bond lengths (Å) and angles (°): Si(1)-N(1) 1.849(10), Si(1)-C(3) 1.875(2), Si(1)-Si(2) 2.394(1), Si(1)-H(1) 1.43(2), N(1)-C(1) 1.335(11), C(1)-N(2) 1.275(3), C(1)-C(2) 1.494(3), Si(2)-N(3) 1.8662(18), Si(2)-N(4) 1.8836(16), C(2)-C(3) 1.404(3), N(1)-Si(1)-C(3) 89.8(3), Si(2)-Si(1)-H(1) 121.1(9), N(3)-Si(2)-N(4) 69.39(7), N(3)-Si(2)-Si(1) 96.97(6), N(4)-Si(2)-Si(1) 106.08(6), C(1)-N(2)-C(24) 124.56(18).

Table 1: Summary of crystallographic data for **3**.

	3
empirical formula	$C_{70}H_{94}N_4Si_2$
formula weight	1047.67
crystal system	triclinic
space group	*P*-1
a (Å)	12.7450(3)
b (Å)	15.6776(3)
c (Å)	18.5694(4)
α (deg.)	67.456(2)
β (deg)	75.511(2)
γ (deg.)	69.741(2)
vol (Å^3)	3185.18(13)
Z	2
ρ (calcd) (g.cm^{-3})	1.092
μ (mm^{-1})	0.098
F(000)	1140
reflections collected	24075
unique reflections	11461
R_{int}	0.0338
R1 indices [$I > 2\sigma(I)$]	0.0540
*w*R2 indices (all data)	0.1560
largest peak/hole (e/Å^3)	0.58, -0.35
CCDC No.	1904293

high purity dinitrogen. Toluene was distilled over molten potassium, while pentane was distilled from 1:1 Na/K alloy. The ^{1}H NMR spectrum was recorded on a Bruker AvanceIII 400 spectrometer and was referenced to the residual proton resonance of the solvent used. Compound **2** was prepared by the literature procedure, while all other reagents were used as received (Jones et al., 2011).

Preparation of {(4-Bu^{t}Ph)C(NDip)$_2$}Si-Si(H){N(Dip)C(=NDip)(4-Bu^{t}Ph^{-H})} 3

A solution of **2** (0.094 g, 0.090 mmol) was dissolved in toluene (20 mL) and the resultant blue solution heated at reflux for 4 d. During this time, the color of the solution gradually changed to yellow. The solution was then concentrated to *ca.* 2 mL *in vacuo* and layered with pentane (*ca.* 15 mL) in a long Schlenk tube. Yellow crystals of the title compound deposited overnight (0.032 g, 34%). M.p. 231-236°C (decomp.) Data for **3**: ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ 0.96 (s, 9H, C(CH_3)$_3$), 1.00 (s, 9H, C(CH_3)$_3$), 1.00-1.41 (many overlapping doublets, 48H, CH(CH_3)$_2$), 3.34 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.58 (sept, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 3.62 (sept, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 3.72 (sept, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 6.39 (br. s, 1H, Si*H*), 6.76-7.37 (overlapping m, 19H, Ar*H*). A reproducible microanalysis could not be obtained for the compound as it consistently co-crystallized with small amounts of the amidine, (4-$\mathrm{Bu^t}$Ph)C(NDip){N(H)Dip}, which could not be separated.

X-ray crystallography

A crystal of **3** suitable for X-ray structural determination was mounted in silicone oil. Crystallographic measurements were carried out at 123(2) K, and were made using an Oxford Gemini diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 by full matrix least squares (SHELX16) (Sheldrick, 2016) using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model), except the hydride ligand, the positional parameters of which were freely refined. There is significant disorder in the structure, which involves positional disorder of the methyl groups of one *tert*-butyl substituent, two isopropyl groups, and one whole NDip fragment. This disorder was successfully modelled. Crystal data, details of the data collection and refinement are given in Table 1. Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1904293). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgement: This research was supported by the Australian Research Council.

References

Asay M., Jones C., Driess M., N-Heterocyclic carbene analogues with low-valent group 13 and group 14 elements: Syntheses, structures, and reactivities of a new generation of multitalented ligands. Chem. Rev., 2011, 111, 354-396.

Denk M., Lennon R., Hayashi R., West R., Belyakov V., Verne H.P., et al., Synthesis and structure of a stable silylene. J. Am. Chem. Soc., 1994, 116, 2691-2692.

Jones C., Bonyhady S.J., Holzmann N., Frenking G., Stasch A., Preparation, characterization, and theoretical analysis of group 14 element(I) dimers: A case study of magnesium(I) compounds as reducing agents in inorganic synthesis. Inorg. Chem., 2011, 50, 12315-12325.

Protchenko A.V., Birjkumar K.H., Dange D., Schwarz A.D., Vidovic D., Jones C., et al., A stable two-coordinate acyclic silylene. J. Am. Chem. Soc., 2012, 134, 6500-6503.

Protchenko A.V., Schwarz A.D., Blake M.P., Jones C., Kaltsoyannis N., Mountford P., et al., A generic one-pot route to acyclic two-coordinate silylenes from silicon(IV) precursors: synthesis and structural characterization of a silylsilylene. Angew. Chem. Int. Ed., 2013, 52, 568-571.

Rekken B.D., Brown T.M., Fettinger J.C., Tuononen H.M., Power P.P., Isolation of a stable, acyclic, two-coordinate silylene. J. Am. Chem. Soc., 2012, 134, 6504-6507.

Rodriguez R., Contie Y., Mao Y., Saffron-Merceron N., Baceiredo A., Branchadell V., et al., Reversible dimerization of phosphine-stabilized silylenes by silylene insertion into $\mathrm{Si^{II}}$–H and $\mathrm{Si^{II}}$–Cl s-bonds at room temperature. Angew. Chem. Int. Ed., 2015, 54, 15276-15279.

Sen S.S., Jana A., Roesky H.W., Schulzke C., A remarkable base-stabilized bis(silylene) with a silicon(I)-silicon(I) bond. Angew. Chem. Int. Ed., 2009, 48, 8536-8538.

Sheldrick G.M., SHELX-16. University of Göttingen, 2016.

West R., Fink M.J., Michl J., Tetramesityldisilene, a stable compound containing a silicon silicon double bond. Science, 1981, 214, 1343-1344.

Yamaguchi Y., Sekiguchi A., Unusual reactivity of a disilyne with 4-dimethylaminopyridine: Formation of an intramolecularly N-coordinated silylene and its isomerization to a zwitterionic silyl anion. J. Am. Chem. Soc., 2011, 133, 7352-7354.

Zhang S.-H., Yeong H.-X., Xi H.-W., Lim K.H., So C.-W., Hydrosilylation of a silicon(II) hydride: Synthesis and characterization of a remarkable silylsilylene. Chem. Eur. J., 2010, 16, 10250-10254.