



Cite this: *RSC Adv.*, 2020, 10, 3402

Received 17th December 2019

Accepted 6th January 2020

DOI: 10.1039/c9ra10628f

rsc.li/rsc-advances

# DMAP-stabilized bis(silyl)silylenes as versatile synthons for organosilicon compounds†

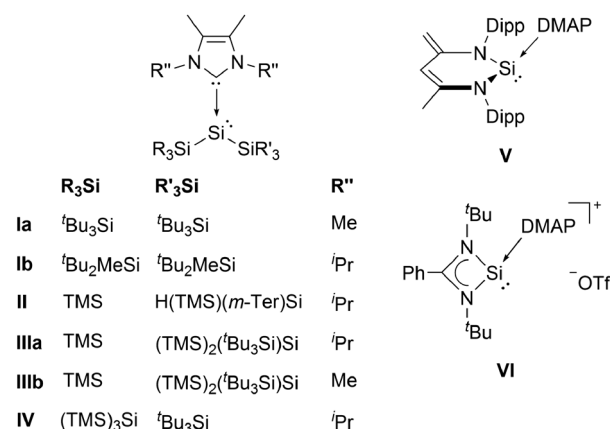
Richard Holzner,‡ Dominik Reiter,‡ Philipp Frisch and Shigeyoshi Inoue \*

DMAP-stabilized silylenes **1a–c** are obtained from the reductive debromination of the corresponding dibromosilanes in the presence of DMAP. Their distinctly different thermal isomerization reactions *via* C–H bond activation, dearomative ring expansion and silyl migration are discussed. Furthermore, complexes **1** dissociate at elevated temperatures, providing the corresponding free silylenes *in situ*, which are even capable of single-site activation of H<sub>2</sub>. Additionally, a potassium-substituted silicon-centered radical **2** is isolated from overreduction of (tBu<sub>3</sub>Si)<sub>2</sub>SiBr<sub>2</sub>.

## Introduction

Silylenes (R<sub>2</sub>Si:), the heavier congeners of carbenes (R<sub>2</sub>C:) have attracted much attention in modern main group chemistry in recent years.<sup>1</sup> The substituents R can either be monodentate, or cyclic, bidentate ligands, as in the case of the extensively studied class of *N*-heterocyclic silylenes (NHSis). In general, silylenes possess a lone pair of electrons and an empty 3p<sub>z</sub> orbital and can therefore display ambiphilic reaction behaviour both as Lewis bases and Lewis acids. This particular reactivity profile even enables the facile activation of small molecules.<sup>2</sup> Thus, silylenes are considered to be promising candidates for metal-free catalysis.<sup>3</sup> In contrast to carbenes, however, the singlet ground state is energetically favoured for almost all reported silylenes. The two sole exceptions are transient silylenes bearing two bulky and strongly electropositive supersilyl (tBu<sub>3</sub>Si) substituents, or both supersilyl groups and alkali metal substituents. However, these species were only generated and analyzed *in situ* at temperatures below 15 K.<sup>3</sup> These reports already underline the peculiarity of bis(silyl)silylenes. In fact, no room temperature stable, two-coordinate derivative has been isolated to date. In all synthetic attempts the extremely reactive bis(silyl)silylene was not stable and either silyl migration<sup>4</sup> or C–H bond activation occurred, even at low temperatures.<sup>3a</sup> Very recently, we presented a bis(silyl)silylene that undergoes reversible isomerization to the corresponding tetra(silyl)disilene.<sup>5</sup> Although this compound is relatively stable, it eventually decomposes *via* insertion of the silylene moiety into a C–H bond of a substituent. A convenient method to stabilize silylenes is to

control their excessive electrophilicity by coordination of a Lewis base, as already recognized by Tokitoh and co-workers in 1997.<sup>6</sup> In fact, electron donation from *N*-heterocyclic carbenes (NHCs) was the only way so far to isolate bis(silyl)silylenes.<sup>7</sup> Sekiguchi *et al.* successfully employed this approach and obtained the NHC-stabilized silylenes **I** (Fig. 1).<sup>8</sup> Lately, several additional examples of acyclic bis(silyl)silylene NHC complexes were reported by Cowley (**II**)<sup>9</sup> and by our group (**III** and **IV**).<sup>5</sup> Besides those acyclic representatives, the groups of Scheschkewitz<sup>10</sup> and Lips<sup>11</sup> synthesized NHC-stabilized silylenes with the low-coordinate silicon center being embedded in a three-membered silicon cycle. Although electron-donation of NHCs to the vacant p-orbital of silylenes is an effective method to allow isolation of these compounds, it brings the downside of a significantly reduced reactivity. Accordingly, none of the



TMS = Me<sub>3</sub>Si; DMAP = 4-*N,N*-dimethylaminopyridine,  
*m*-Ter = 2,6-(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>; Dipp = 2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>

Fig. 1 Acyclic NHC-stabilized bis(silyl)silylenes I–IV and low-coordinate silicon DMAP complexes V and VI.

Department of Chemistry, WACKER-Institute of Silicon Chemistry and Catalysis Research Center, Lichtenbergstraße 4, 85748 Garching bei München, Germany. E-mail: s.inoue@tum.de

† Electronic supplementary information (ESI) available: Experimental details and crystallographic data. CCDC 1967942–1967945. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ra10628f

‡ R. H. and D. R. contributed equally to this work.



examples listed is capable of activating small molecules such as dihydrogen. Therefore, a weaker donor–acceptor interaction is necessary to achieve a balance between reactivity and stability of the respective bis(silyl)silylene compounds. 4-*N,N*-Dimethylaminopyridine (DMAP) is a much weaker Lewis base, compared to NHCs and was already applied by the groups of Driess<sup>12</sup> and So<sup>13</sup> to isolate the low-coordinate silicon donor–acceptor complexes **V** and **VI**. Thus, we envisioned DMAP to be a suitable Lewis base, strong enough to stabilize elusive bis(silyl)silylenes, yet weak enough to partially maintain their reactivity. Very recently, we reported the first acyclic bis(silyl)silylene–DMAP adduct **1a** (cf. Scheme 1).<sup>5</sup>

Herein, we extend this class of donor-stabilized, highly reactive bis(silyl)silylenes. Decomposition pathways and reactivity of these novel silylenes are presented and discussed in detail. Additionally, we report the synthesis and characterization of the potassium-substituted silyl radical **2**.

## Results and discussion

### Synthesis of novel DMAP–silylene complexes **1** and radical **2**

In an approach analogue to the synthesis of **1a**, we obtained the donor-stabilized bis(silyl)silylene **1b** from the reductive debromination of the corresponding dibromosilane with  $\text{KC}_8$  in presence of DMAP (Scheme 1). Silylene **1b** was obtained as red-brown crystals in excellent yield (92%) and fully characterized. Neither the formation of any decomposition products, nor of the disilene  $(^t\text{Bu}_2\text{MeSi})_2\text{Si}=\text{Si}(^t\text{Bu}_2\text{Me})_2$ <sup>14</sup> was observed during the synthesis. Compared to compound **1a**, the <sup>29</sup>Si NMR signal of the silylene Si atom in **1b** is slightly upfield-shifted to 61.5 ppm (68.8 ppm in **1a**). Single crystal X-ray diffraction (SC-XRD) analysis revealed a Si:–N<sup>DMAP</sup> bond length in compound **1b** of 1.937(5) Å (Fig. 2). This value is essentially identical to that in **1a** (1.942(2) Å)<sup>5</sup> and clearly within the range of previously reported low-coordinate silicon–DMAP donor–acceptor complexes (1.84–2.01 Å).<sup>9,12,13,15</sup> The high degree of pyramidalization around the silylene center in **1b** (sum of bond angles  $\Sigma\theta = 318.1^\circ$ ) results from the stereo-chemically active electron lone pair and also compares very well to **1a** ( $\Sigma\theta = 318.7^\circ$ ).<sup>5</sup>

Additionally, the steric hindrance of the silylene center was increased by introducing bulky hypersilyl groups ((TMS)<sub>3</sub>Si), resulting in complex **1c**. Compound **1c**, which is the first stable bis(hypersilyl)silylene species, was identified by the characteristic <sup>29</sup>Si NMR signal of the low-coordinate silicon nucleus (72.5 ppm), similar to the resonances of **1a** and **1b**.<sup>5</sup> Remarkably, in

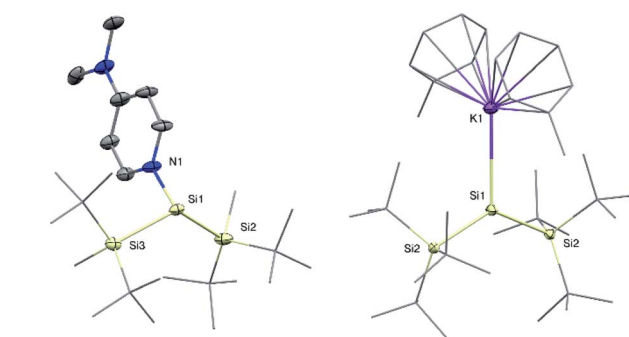
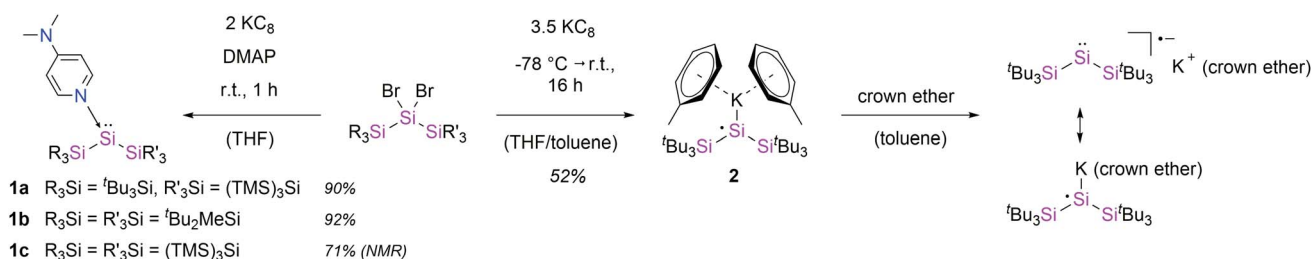


Fig. 2 Molecular structures of silylene **1b** (left) and silyl radical **2** (right) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **1b**: Si1–N1 1.937(5), Si1–Si2 2.390(3), Si1–Si3 2.378(3), Si2–Si1–Si3 123.1(1), Si2–Si1–N1 96.2(2), Si3–Si1–N1 98.8(2); **2**: Si1–Si2 2.3936(14), Si1–K1 3.315(2), K1–Si1–Si2 114.91(2), Si2–Si1–Si2\* 130.19(3).

this case, the facile TMS-migrations were prevented by the coordination of DMAP and the silylene could be stabilized successfully. In sharp contrast, we were not able to isolate the bis(hypersilyl)silylene moiety with NHCs. This result underlines the difference in reactivity between NHCs and the weaker Lewis base DMAP. Unfortunately, the reaction was accompanied by the by-product formation of hexakis(trimethylsilyl)trisilirane (**4**) and  $\text{Si}(\text{TMS})_4$ , reflecting the high propensity of hypersilyl groups towards TMS-group migrations.

Despite several attempts, we were not able to isolate the DMAP-stabilized bis(supersilyl) silylene  $(^t\text{Bu}_3\text{Si})_2\text{Si} \leftarrow \text{DMAP}$  with the same approach used for the syntheses of **1**. Even at low temperatures, the reduction of the corresponding dibromosilane only afforded the decomposition product of the free silylene (disiletane from C–H bond activation).<sup>3a</sup> With an excess of 3.5 equivalents of  $\text{KC}_8$ , however the potassium-substituted silyl radical **2** was generated, even in the presence of DMAP. The solid state structure of **2** was unambiguously determined by SC-XRD analysis (Fig. 2). Silyl radical **2** exhibits a completely planar geometry (sum of bond angles  $\Sigma\theta = 360.0^\circ$ ) which is typical for alkali metal-substituted silyl radicals.<sup>16</sup> The Si–K bond distance (3.315(2) Å) is in the same range as observed in four-coordinate potassium silanides, such as hypersilyl potassium (3.352(4) Å).<sup>4a</sup> Thus compound **2** is clearly a contact ion pair in the solid state. Unfortunately, **2** is extremely sensitive and decomposes in toluene solution. Therefore, no satisfactory spectroscopic data was obtained. After synthesis in absence of DMAP and



Scheme 1 Synthesis of DMAP-stabilized silylenes **1a–c** and silyl radical **2**.



stabilization by crown ether (18-C-6) however, we were able to obtain an EPR spectrum which contains a signal with a  $g$  value of 2.0056 and a hyperfine coupling  $a(\alpha\text{-}^{29}\text{Si}) = 2.92$  mT (see ESI, Fig. S7†). Coupling with the  $\beta\text{-}^{29}\text{Si}$  nuclei was not observable. This  $g$  value is in the same range, as it was reported for other alkali metal-substituted silyl radicals.<sup>16,17</sup> Furthermore, no signal splitting from coupling of the unpaired electron with the K nucleus was observed. Presumably, in solution, compound **2** in presence of crown ether exists as solvent-separated ion pair. This observation is consistent with reports of a potassium substituted silyl radical.<sup>16</sup>

### Thermally induced isomerization of **1**

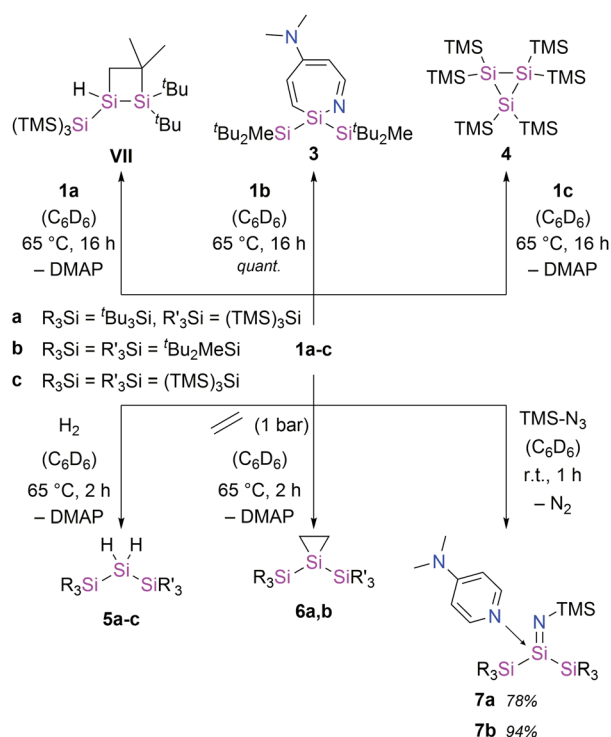
With the novel silylene complexes **1** in hand, we initially tested their thermal stability. Silylene **1a** isomerizes to the respective disilene **VII** *via* DMAP dissociation and subsequent C–H bond activation at elevated temperatures (Scheme 2). The same product, that was observed for the decomposition of the donor-free disilene/silylene equilibrium mixture.<sup>5</sup> Surprisingly, upon heating compound **1b** to 65 °C, the silylene fragment inserts into the pyridine ring of DMAP, generating azasilepin **3** by dearomative ring expansion in quantitative yield. Silepin formation *via* insertion of a silylene into an aromatic ring system has previously been reported,<sup>18</sup> oftentimes either thermally<sup>19</sup> or photochemically<sup>20</sup> induced. After transformation from **1b** to **3** and thus increase of the coordination number, the  $^{29}\text{Si}$  NMR signal of the central silicon atom is strongly upfield-shifted to –28.1 ppm. This value is comparable to that of a similar compound, reported by Tokitoh *et al.* from the

reaction of a transient, *in situ* generated bis(aryl)silylene with DMAP (–20.8 ppm).<sup>21</sup> In comparison to **1b**, the Si–N bond distance in **3** is shortened by 10% to 1.750(1) Å, indicating a covalent bonding-type instead of the dative interaction in **1b**. This bond length is identical to that in Tokitoh's azasilepin.<sup>21</sup> Furthermore, the Si center adopts a tetrahedral coordination sphere within the boat-shaped, seven-membered heterocyclic ring (*cf.* Fig. 3). In sharp contrast to the related compounds **1a** and **1b** however, the thermal decomposition of silylene **1c** does not proceed *via* C–H, or C–N bond activation, but in fact by silyl migration. At 65 °C, **1c** isomerizes under liberation of DMAP to the cyclic silane **4**, which was already observed from rearrangement of  $((\text{TMS})_3\text{Si})_2\text{Si}$ : in the attempted synthesis of the free silylene.<sup>4a,d</sup>

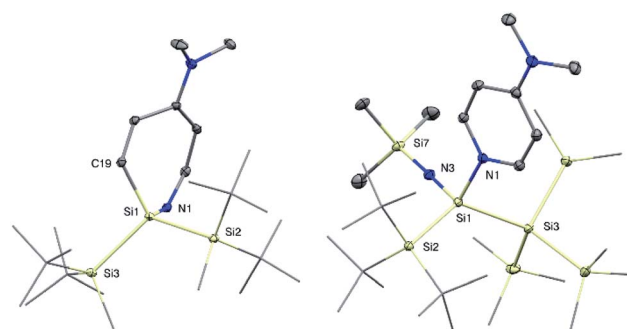
### Small molecule activation by silylenes **1**

Single-site activation of the enthalpically strong, apolar dihydrogen molecule remains a challenging task for low-coordinate silicon compounds. So far, this was only achieved by few acyclic, donor-free silylenes and a masked iminosilyl silylene.<sup>5,18a,22</sup> In fact, to date, there are no reports of  $\text{H}_2$  activation by a silylene base complex.

Although, the thermal decomposition reactions of **1a–c** strongly depend on the silyl substituents and proceed *via* three different mechanisms, they are all based on the extreme reactivity of the respective free silylene. Furthermore, the calculated Gibbs free bond-dissociation energy of **1a** (15.3 kcal mol<sup>–1</sup>),<sup>5</sup> which is lower than for the analogous, NHC-coordinated (hypersilyl)(supersilyl)silylene **IV**<sup>5</sup> (16.3 kcal mol<sup>–1</sup>)<sup>5</sup> also suggests a higher reactivity of the DMAP–silylene complexes, compared to the NHC-stabilized bis(silyl)silylenes. Therefore, we conceived compounds **1a–c** to be easily accessible synthetic equivalents for these unstable, elusive, donor-free bis(silyl)silylenes and conducted a reactivity study towards activation of small molecules. Indeed, all three DMAP–silylenes underwent dihydrogen addition reactions upon heating to 65 °C, furnishing the reported corresponding dihydrosilanes **5a–c** in



**Scheme 2** Thermally-induced decomposition of silylenes **1** and synthesis of hydrosilanes **5**, siliranes **6** and silaimines **7**.



**Fig. 3** Molecular structures of azasilepin **3** (left) and silaimine **7a** (right) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: Si1–N1 1.750(1), Si1–C19 1.878(1), Si1–Si2 2.4144(6), Si2–Si1–Si3 113.74(2), Si2–Si1–N1 109.08(4), N1–Si1–C19 104.71(5); **7a**: Si1–Si2 2.453(1), Si1–N1 1.928(2), Si1–N3 1.616(2), N3–Si7 1.660(2), Si2–Si1–Si3 125.08(3), N1–Si1–N3 106.08(8), Si1–N3–Si7 177.1(1).

quantitative yields. (Scheme 2).<sup>5,23</sup> Remarkably, the oxidative addition of dihydrogen to the DMAP-silylene complexes proceeds in a selective fashion, without the formation of the respective decomposition products. Free DMAP was simply removed from the product by precipitation with one equivalent of SiBr<sub>4</sub> and subsequent filtration. Notably, no reaction was observed upon exposure of NHC-stabilized bis(silyl)silylenes **1a** and **11a** to H<sub>2</sub>, even at elevated temperatures. This result underlines the inherently high reactivity of bis(silyl)silylene–DMAP complexes upon thermal dissociation of the stabilizing donor. Presumably, the H<sub>2</sub> addition to the silylene fragments of **1** proceeds *via* a bimolecular reaction similar to that proposed for the free silylene (<sup>t</sup>Bu<sub>3</sub>Si)((TMS)<sub>3</sub>Si)Si.<sup>5</sup>

Additional reactivity investigations were carried out with **1a** and **1b** due to their easier accessibility. Silirane formation – another classical silylene reactivity – was observed after treatment of **1a** and **1b** with ethylene, yielding compounds **6**. The <sup>29</sup>Si NMR shift of the central Si-atom in **6b** (–174.5 ppm) is similar to that of the earlier reported **6a** (–164.3 ppm).<sup>5</sup>

Since the isolation of the first silaimine by Wiberg *et al.* in 1985,<sup>24</sup> a number of these heavier imine analogues have been published. Besides donor free examples,<sup>25</sup> many silaimines need additional stabilization by a coordinating Lewis base, such as NHCs.<sup>7</sup> Interestingly, reaction of **1a** and **1b** with trimethylsilyl azide furnishes the DMAP-coordinated silaimines **7** under liberation of gaseous N<sub>2</sub>. The <sup>29</sup>Si NMR signals of the central Si atoms in **7a** and **7b** were observed at –25.9 ppm and –25.5 ppm, respectively. Compared to a silaimine–pyridine adduct ( $\delta^{29}\text{Si} = -12.6$  ppm),<sup>25b</sup> these resonances are slightly upfield-shifted, presumably due to the electropositive silyl groups. In the solid state, compound **7a** displays a tetrahedral coordination sphere around the silicon center. Silaimine **7a** contains three unique Si–N bonds, distinguishable by their characteristic lengths: a short Si=N bond (1.616(2) Å), a significantly longer Si7–N3 single bond to the TMS group (1.660(2) Å) and an even further elongated, dative Si–N<sup>DMAP</sup> bond (1.928(2) Å). The central Si=N distance is slightly longer, than in the donor-free silaimines, from the groups of Wiberg and Kira (1.57–1.59 Å)<sup>25a,25c</sup> and essentially identical to Klingebiel's silaimine–pyridine adduct (1.611(2) Å).<sup>25b</sup> Interestingly, the geometry of the imino group is almost linear ( $\theta = 177.1(1)^\circ$ ). A similar observation was reported by Kira *et al.* and attributed to the electronic properties of the TMS group.<sup>25c</sup> Notably, compound **7a** slowly decomposes in solution under liberation of DMAP and probably formation of the donor-free silaimine, which decomposes further to a mixture of unidentified species. Complex **7b** instead is stable in solution.

## Conclusions

In summary, we utilized our recently published method to synthesize two novel DMAP-stabilized silylenes **1b** and **1c**. Compound **1c** is the first stable bis(hypersilyl)silylene complex, which could be synthesized so far. Surprisingly, silyl radical **2** was obtained in a related fashion from the over-reduction of the corresponding dibromosilane. The silylene complexes **1a–c** turned out to undergo facile oxidative addition with dihydrogen

and ethylene at relatively mild conditions. This remarkable reactivity originates from the respective free silylenes, which are generated *in situ* from dissociation of complexes **1**. Stabilization of transient bis(silyl)silylenes with DMAP is the only method so far to isolate these species and reactivate their extreme reactivity upon dissociation. Therefore, complexes **1** can be considered easily accessible, stable synthetic equivalents of otherwise elusive bis(silyl)silylenes. Additionally, the unprecedented, DMAP-coordinated silaimines **7** were isolated from the reactions of the silylene complexes with trimethylsilyl azide.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

We are exceptionally grateful to the WACKER Chemie AG and the European Research Council (SILION 637394) for continued financial support. We thank Dr Oksana Storcheva for the EPR measurements.

## Notes and references

- For selected reviews on silylenes see: (a) M. Haaf, T. A. Schmedake and R. West, *Acc. Chem. Res.*, 2000, **33**, 704–714; (b) B. Gehrhus and M. F. Lappert, *J. Organomet. Chem.*, 2001, **617–618**, 209–223; (c) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457–492; (d) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511; (e) M. Kira, *Chem. Commun.*, 2010, **46**, 2893–2903; (f) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396; (g) S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767; (h) S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578–587; (i) S. S. Sen, S. Khan, P. P. Samuel and H. W. Roesky, *Chem. Sci.*, 2012, **3**, 659–682; (j) B. Blom and M. Driess, in *Functional Molecular Silicon Compounds II*, ed. D. Scheschkewitz, Springer, Cham, 2013, vol. 156, pp. 85–123.
- (a) P. P. Power, *Nature*, 2010, **463**, 171–177; (b) C. Weetman and S. Inoue, *ChemCatChem*, 2018, **10**, 4213–4228.
- (a) A. Sekiguchi, T. Tanaka, M. Ichinohe, K. Akiyama and S. Tero-Kubota, *J. Am. Chem. Soc.*, 2003, **125**, 4962–4963; (b) A. Sekiguchi, T. Tanaka, M. Ichinohe, K. Akiyama and P. P. Gaspar, *J. Am. Chem. Soc.*, 2008, **130**, 426–427.
- (a) K. W. Klinkhammer, *Chem.–Eur. J.*, 1997, **3**, 1418–1431; (b) M. Ichinohe, R. Kinjo and A. Sekiguchi, *Organometallics*, 2003, **22**, 4621–4623; (c) K. Hassler, A. Dzambaski and J. Baumgartner, *Silicon Chem.*, 2008, **3**, 271–288; (d) C. Marschner, *Eur. J. Inorg. Chem.*, 2015, **2015**, 3805–3820; (e) S. K. Mueller, A. Dzambaski, N. Altenhuber, A. Torvisco, K. Hassler and M. Flock, *J. Mol. Struct.*, 2015, **1099**, 197–203; (f) M. Haas, A. Knoechl, T. Wiesner, A. Torvisco, R. Fischer and C. Jones, *Organometallics*, 2019, **38**, 4158–4170.





- 5 D. Reiter, R. Holzner, A. Porzelt, P. J. Altmann, P. Frisch and S. Inoue, *J. Am. Chem. Soc.*, 2019, **141**, 13536–13546.
- 6 N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki and S. Nagase, *J. Am. Chem. Soc.*, 1997, **119**, 1456–1457.
- 7 V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678–9842.
- 8 H. Tanaka, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2012, **134**, 5540–5543.
- 9 M. W. Stanford, J. I. Schweizer, M. Menche, G. S. Nichol, M. C. Holthausen and M. J. Cowley, *Angew. Chem., Int. Ed.*, 2019, **58**, 1329–1333.
- 10 A. Jana, I. Omlor, V. Huch, H. S. Rzepa and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2014, **53**, 9953–9956.
- 11 B. J. Guddorf, A. Hepp and F. Lips, *Chem.–Eur. J.*, 2018, **24**, 10334–10338.
- 12 Y. Xiong, S. Yao, R. Müller, M. Kaupp and M. Driess, *J. Am. Chem. Soc.*, 2010, **132**, 6912–6913.
- 13 H.-X. Yeong, H.-W. Xi, Y. Li, K. H. Lim and C.-W. So, *Chem.–Eur. J.*, 2013, **19**, 11786–11790.
- 14 A. Sekiguchi, S. Inoue, M. Ichinohe and Y. Arai, *J. Am. Chem. Soc.*, 2004, **126**, 9626–9629.
- 15 T. Yamaguchi and A. Sekiguchi, *J. Am. Chem. Soc.*, 2011, **133**, 7352–7354.
- 16 S. Inoue, M. Ichinohe and A. Sekiguchi, *Organometallics*, 2008, **27**, 1358–1360.
- 17 (a) D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, M. Botoshansky, B. Tumanskii and Y. Apeloig, *Angew. Chem., Int. Ed.*, 2005, **44**, 739–743; (b) S. Ishida, T. Iwamoto and M. Kira, *J. Am. Chem. Soc.*, 2003, **125**, 3212–3213; (c) G. Molev, D. Bravo-Zhivotovskii, M. Karni, B. Tumanskii, M. Botoshansky and Y. Apeloig, *J. Am. Chem. Soc.*, 2006, **128**, 2784–2785; (d) S. Inoue, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2007, **129**, 6096–6097.
- 18 (a) D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue and B. Rieger, *J. Am. Chem. Soc.*, 2017, **139**, 8134–8137; (b) S. Ishida, T. Tamura and T. Iwamoto, *Dalton Trans.*, 2018, **47**, 11317–11321.
- 19 (a) H. Suzuki, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11572–11573; (b) H. Suzuki, N. Tokitoh and R. Okazaki, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2471–2481.
- 20 (a) M. Kira, S. Ishida, T. Iwamoto and C. Kabuto, *J. Am. Chem. Soc.*, 2002, **124**, 3830–3831; (b) M. Kira, S. Ishida, T. Iwamoto, A. de Meijere, M. Fujitsuka and O. Ito, *Angew. Chem., Int. Ed.*, 2004, **43**, 4510–4512; (c) T. Kosai, S. Ishida and T. Iwamoto, *Chem. Commun.*, 2015, **51**, 10707–10709.
- 21 Y. Mizuhata, T. Sato and N. Tokitoh, *Heterocycles*, 2012, **84**, 413–418.
- 22 (a) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503; (b) A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Angew. Chem., Int. Ed.*, 2013, **52**, 568–571.
- 23 (a) T. Gross, H. Reinke and H. Oehme, *Can. J. Chem.*, 2000, **78**, 1399–1404; (b) A. Sekiguchi, T. Fukawa, M. Nakamoto, V. Y. Lee and M. Ichinohe, *J. Am. Chem. Soc.*, 2002, **124**, 9865–9869.
- 24 N. Wiberg, K. Schurz and G. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 1053–1054.
- 25 (a) N. Wiberg, K. Schurz, G. Reber and G. Müller, *J. Chem. Soc., Chem. Commun.*, 1986, 591–592; (b) J. Niesmann, U. Klingebiel, M. Schäfer and R. Boese, *Organometallics*, 1998, **17**, 947–953; (c) T. Iwamoto, N. Ohnishi, Z. Gui, S. Ishida, H. Isobe, S. Maeda, K. Ohno and M. Kira, *New J. Chem.*, 2010, **34**, 1637–1645; (d) S. Inoue and K. Leszczyńska, *Angew. Chem., Int. Ed.*, 2012, **51**, 8589–8593; (e) J. Keuter, A. Hepp, C. Mück-Lichtenfeld and F. Lips, *Angew. Chem., Int. Ed.*, 2019, **58**, 4395–4399; (f) A. V. Protchenko, P. Vasko, D. C. H. Do, J. Hicks, M. Ángeles Fuentes, C. Jones and S. Aldridge, *Angew. Chem., Int. Ed.*, 2019, **58**, 1808–1812.

