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# Facile Bond Activation of Small Molecules by an Acyclic Imino(silyl)silylene

Huaiyuan Zhu,[a] Franziska Hanusch,[a] and Shigeyoshi Inoue*[a]

*Dedicated to Professor Helmut Schwarz on the occasion of his 80th birthday.*

**Abstract:** The activation of small molecules by silylenes bearing unique electronic properties has been well established in the past few decades. Here, we disclose the reactivity study of acyclic imino(silyl)silylene **1** with an *N*-heterocyclic imine ligand (NHI) towards various small molecules. Silylene **1** undergoes facile activation of gaseous molecules like dihydrogen, ethylene, and carbon dioxide. While the cycloaddition of carbonyl compounds to **1** was shown as a straightforward synthetic approach of oxasilacycles, reaction with silane as well as borane led to the corresponding E–H (E=Si, B) insertion products. Moreover, reaction with heavier chalcogens allow the isolation of neutral three-coordinate silicon-heavier chalcogen double bond complexes.

**Keywords:** silylene · small molecule activation · cycloaddition · oxasilacycle · silicon chalcogenides

Since the isolation of decamethylsilicocene $Cp^*_2Si(II)$ by Jutzi in 1986,[1] silylenes, the silicon analogues of carbenes, have emerged as transition metal mimics since its ambiphilic nature with a lone pair and a vacant p-orbital.[2] With the deep investigations in the past decades, silylenes have been a promising candidate in small molecule activations, especially simple two-coordinate acyclic silylenes, which firstly isolated at ambient temperature until 2012 (*e.g.* **I** and **II**, Chart 1).[3] In contrast to their cyclic counterparts, acyclic silylenes are structurally flexible and possess a smaller HOMO-LUMO gap (~2–4 eV).[2a,4] Both key advantages facilitate rigid σ-bond cleavage or oxidative addition of small molecules. For instance, the direct cleavage of strong σ-bond of dihydrogen was achieved by **I** at room temperature.[3a] while cyclic dialkylsilylene need cooperate with another Lewis acids or bases to form Frustrated Lewis Pairs.[5] And the homologation of carbon monoxide also accomplished by **I** under mild condition.[6] In the following years, the extensions of acyclic silylenes with different substituents, such as aminosilyl **III**,[7] diamino **IV**,[8] and diboryloxy **V**,[9] were achieved by the Aldridge group. Bulky vinyl silylsilylene **VI**[10] and divinylsilylene **VII**[11] were isolated and studied by Rivard *et al.* recently (Chart 1).

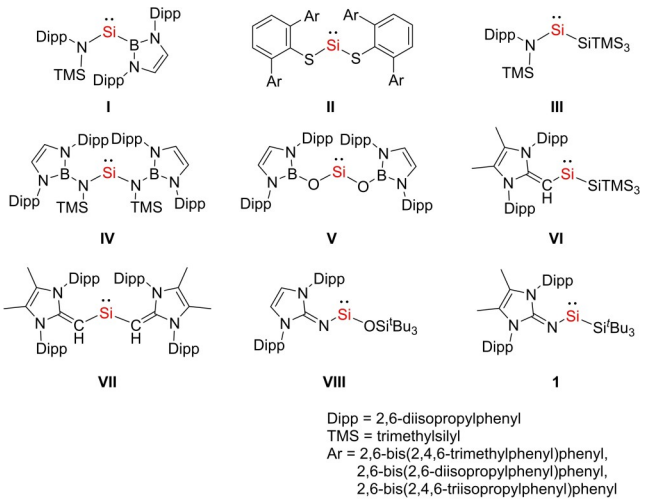


**Chart 1**. Reported isolable two-coordinate acyclic silylenes

[a] *H. Zhu, Dr. F. Hanusch, Prof. Dr. S. Inoue*
School of Natural Sciences, Department of Chemistry, Catalysis Research Center and Institute of Silicon Chemistry, Technische Universität München
Lichtenbergstraße 4, 85748, Garching bei München, Germany
E-mail: s.inoue@tum.de

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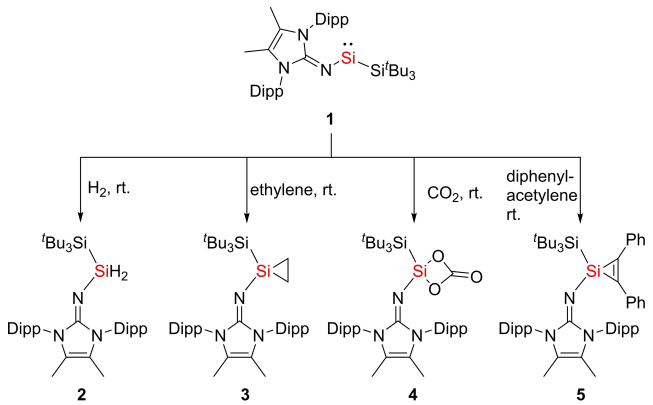
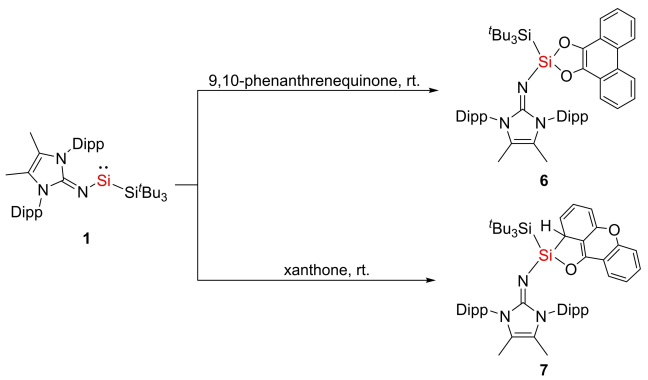
Our group has been focusing on the research of low-valent silicon species, especially two-coordinate acyclic silylenes. In 2017, We demonstrated the reversible intramolecular C=C bond activation of its ligand's aromatic framework by a transient acyclic silylene, which can be used as synthetic equivalent of the corresponding silylene in the activation of small molecules.[12] It is worth mentioning that iminosiloxysilylene **VIII** was obtained by oxygen migration from silanone, which formed by the reaction of the silepin and $N_2O$.[13] We also reported the equilibrium of silepin and silylene, in which both isomers can be observed at ambient conditions.[14] Very recently, we reported the synthesis and isolation of the acyclic imino(silyl)silylene **1** bearing a methylated backbone NHI ligand, which reflects both high σ-donor and π-acceptor abilities.[15] Furthermore, **1** prevents the intramolecular C=C bond activation of its aromatic framework. Instead, it exhibits intermolecular dearomatization of arenes at ambient temperature forming corresponding silepins, which possess almost planar geometry. DFT calculations reveal Büchner-ring-expansion type mechanisms for these transformations with energy barriers achievable at ambient conditions. Besides, we are still interested in the differences in reactivity between the isolated silylene **1**, the masked silylene (silepin),[12,14] and the siloxysilylene.[13,16] Herein, we present the reactivity study of **1** towards small gaseous molecules, alkyne, ketones, silane, borane, and chalcogens.

According to NMR studies, exposure of a freshly prepared solution of **1** to dihydrogen (1 bar) at room temperature led to a color change from blue to pale yellow within 5 minutes (Scheme 1). $^1$H NMR analysis showed the quantitative formation of a sole product with a new triplet Si–H resonance observed at 4.70 ppm ($^1J_{Si-H}$ = 178.4 Hz) and its corresponding $^{29}$Si{$^1$H} NMR signal to be found at −69.2 ppm. The observed red shift of the Si–H stretching vibration frequencies in the IR spectrum of **2** (2044 cm$^{-1}$) compared to those known substituted hydrosilanes could be attributed to the stronger electron donating ability of the NHI and silyl ligand.[17] Dihydrosilane **2** also could be obtained by treating silylene **1** with 1,4-cyclohexadiene at ambient temperature. Subsequently, exposure of a freshly prepared solution of **1** to ethylene (1 bar) and carbon dioxide (1 bar) at room temperature, respectively, led to a rapid color change from blue to pale yellow. The cycloaddition products silirane **3** and carbonate silane **4** were isolated finally through the reaction with ethylene (**3**) and $CO_2$ (**4**) (Scheme 1). The tetracoordinate central silicon nuclei resonate at −110.8 ppm and −45.6 ppm in $^{29}$Si{$^1$H} NMR, respectively, about 10 ppm upfield shifted compared with previously reported silepin's results,[12,14] indicating higher π-donor ability of the methylated backbone NHI. However, further or reversible activation of ethylene could not detect even heated to 120 °C.[14,18] Compared with our reversible silepins ("masked silylenes"), the milder condition and faster reaction periods of oxidative reactions, indicate the higher reactivity of **1**. Furthermore, we also investigated the reactivity toward alkynes. Treatment of silylene **1** with an equivalent diphenylacetylene at room temperature resulted the cycloadduct silacyclopropene **5** (Scheme 1). The $^{29}$Si{$^1$H} NMR spectrum displayed a signal at −129.3 ppm for the central silicon, which is more upfield shifted than the corresponding cycloadduct using **II** (−72.8 ppm)[19] and **III** (−100.1 ppm).[20]

Over the past decades, oxasilacycles are widely used as cross-linker reagents in polymer chemistry.[21] However, the common methods for the synthesis of oxasilacycles is still limited to intramolecular hydrosilylation, catalyzed by metalloid catalyst,[22] or direct salt metathesis.[23] With the appearance of silylenes, the regio- and stereo-selective oxidation reaction of silylenes with carbonyl compounds, provides a promising approach for the preparation of oxasilacycles.[24] Therefore, the investigation of silylene **1** with carbonyl compounds is presented. Different with the reaction of **1** and carbon dioxide forming silanone intermediate, treatment of **1** with 9,10-phenanthrenequinone in benzene at room temperature, corresponding [1+4] cycloaddition adduct **6** was isolated as the sole product (Scheme 2). The central nucleus was observed in $^{29}$Si{$^1$H} NMR at −31.1 ppm. It represents the rare example of rearomatization of phenanthrene, mediated by silylene.[25] When **1** was treated with xanthone in benzene




**Scheme 1.** Small molecule activation of silylene **1** with $H_2$, ethylene, $CO_2$, and diphenylacetylene.




**Scheme 2.** Reaction of silylene **1** with quinone and xanthone.

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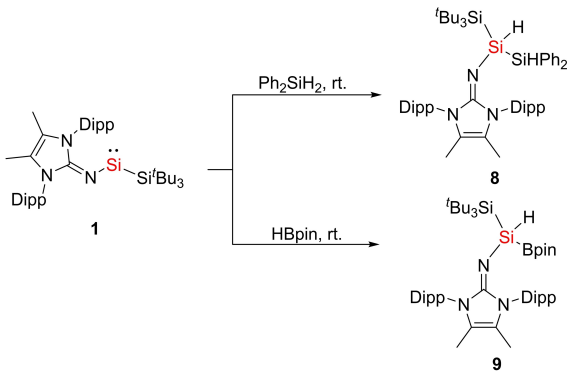
at room temperature, dearomative cycloaddition adduct **7** was isolated as orange powder in 93% yield (Scheme 2). The $^{29}$Si{$^{1}$H} NMR displayed a resonance at −30.2 ppm for the central silicon. A new singlet signal appeared at 3.55 ppm in $^{1}$H NMR, corresponding to the dearomative C–H signal of the benzene ring, is similar with known dearomatization of arylketones by silylenes.[24,26]

While silylene **1** underwent intramolecular C–H bond activation upon heating to 75 °C for 5 days, more reactive




**Scheme 3.** Reaction of silylene **1** with silane and borane.

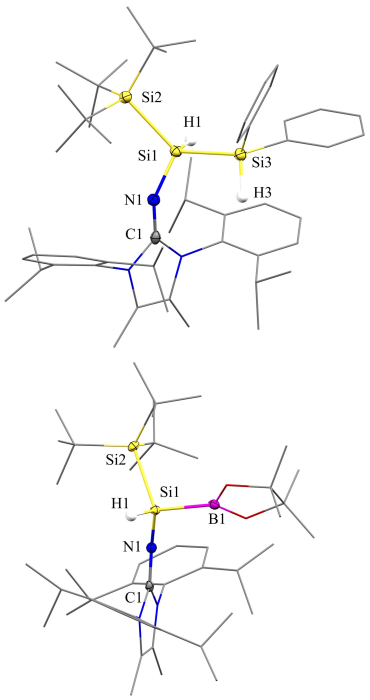



**Figure 1.** Molecular structures of **8** and **9**. Ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity, expect for the respective Si–H nuclei of silane. Selected bond lengths [Å] and angles [°]: **8**: Si1–Si2 2.3944(7), Si1–Si3 2.3779(6), Si1–N1 1.7004(14), N1–Si1–Si2 111.04(5), Si2–Si1–Si3 120.65(2); **9**: Si1–Si2 2.4094(11), Si1–B1 2.043(3), Si1–N1 1.702(2), N1–Si1–Si2 110.87(8), Si2–Si1–B1 108.70(8).

Si–H and B–H bonds are worth to investigated as well. When silylene **1** is treated with one equivalent of diphenylsilane (Scheme 3), two triplet Si–H resonances were observed at 4.93 ppm ($^{1}J_{Si-H}$ = 160.8 Hz) and 5.90 ppm ($^{1}J_{Si-H}$ = 160.8 Hz) in $^{1}$H NMR spectrum, indicating the formation of a new Si–H bond, the signals belong to the central silicon and biphenylsilyl group, respectively. The corresponding $^{29}$Si{$^{1}$H} NMR resonances appeared at −68.6 and −28.0 ppm. Upon treatment of silylene **1** with one equivalent of pinacolborane (Scheme 3), a new triplet Si–H resonance was observed at 4.84 ppm ($^{1}J_{Si-H}$ = 170.8 Hz) in $^{1}$H NMR spectrum, and in $^{11}$B{$^{1}$H} NMR a broad signal was observed at 35.7 ppm, indicating a three-coordinate boron species. However, only one signal was observed at 5.6 ppm in $^{29}$Si{$^{1}$H} NMR, related to the *t*-butylsilyl groups. SC-XRD analysis revealed the Si–H and B–H bonds insertion afforded silane **8** and borylsilane **9** (Figure 1). In **8**, the Si1–Si2 and Si1–Si3 distance of 2.3944(7) and 2.3779(6) Å are almost identical. In **9**, The Si1–B1 distance of 2.043(3) Å is similar to our previously reported silylborane (2.02 Å).[27] Infrared spectroscopy showed Si–H stretching mode of **8** (2058, 2140 cm$^{-1}$) and **9** (2034 cm$^{-1}$), respectively. These are red-shifted than related compound.[17f,g] However, further attempt of hydrosilylation and hydroboration of alkenes, alkynes, carbon dioxide or ketones mediated by silylene **1** failed.[28]

With the widespread establishment of neutral three-coordinate silanones in the past five years,[13,29] the research of its heavy congeners is still continuing. Different to oxygen, heavier chalcogens possess smaller electronegativity difference values with silicon, resulting less polarized Si=E bond and more feasible to isolate monomeric $R_2Si$=E complexes (E=S, Se, and Te).[30] In 1989, Corriu *et al.* demonstrated the isolation of silanethione with a silicon sulfur double bond.[31] Since then, a plethora of donor stabilized terminal silicon-heavy chalcogenides were presented.[6,32] However, among these, only a few neutral three-coordinate silicon-heavy chalcogen double bond compounds (**IX–XI**) were isolated and studied (Scheme 4, a).[6,33] To compare silylene **1** with our previously reported silepin[13] in the formation of silanone and its successful application in Sila-Wittig olefination,[34] a hexane solution of silylene **1** was degassed and exposed to $N_2O$ at −78 °C. However, it just led to an ill-defined mixture, possibly due to the high reactivity of acyclic silylene **1** and its corresponding silanone. Subsequently, treatment of **1** with one equivalent of the weaker oxygen source triethylphosphine oxide at room temperature for 24 h (Scheme 4, b) formed a pale green solution. Colorless crystals were obtained by recrystallization from a saturated pentane solution and fully characterized. The $^{29}$Si{$^{1}$H} NMR spectrum displayed a signal at 59.3 ppm for the central silicon atom, which is almost similar with our previously reported siloxysilylene (58.9 ppm).[13] SC-XRD analysis revealed the structure of iminosiloxysilylene **10** (Figure 2). Similar to the formation of siloxysilylene **VIII**, silylene **1** reacted with triethylphosphine oxide to afford a more polarized silanone intermediate, due to the electronic effect of the methylated backbone NHI, which

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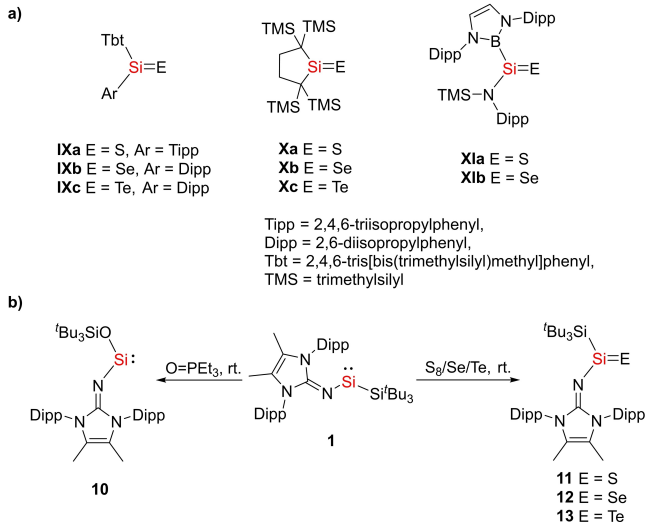


**Scheme 4.** a) Reported neutral three-coordinate silicon-heavy chalcogenides; b) Reaction of silylene **1** with phosphine oxide and heavy chalcogens.

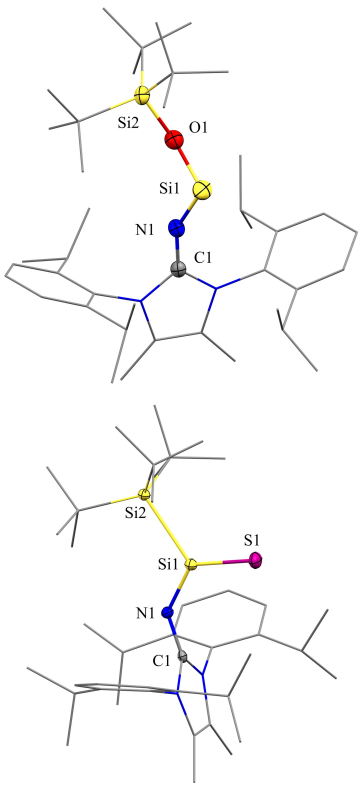


**Figure 2.** Molecular structures of **10** and **11**. Ellipsoids of **10** set at 30% probability; Ellipsoids of **11** set at 50% probability. Hydrogen atoms are omitted for clarity Selected bond lengths [Å] and angles [°]: **10**: Si1–O1 1.613(3), Si1–N1 1.644(3), N1–Si1–O1 104.33(15); **11**: Si1–Si2 2.3700(6), Si1–S1 1.9838(5), Si1–N1 1.6416(13), N1–Si1–Si2 116.48(5), Si2–Si1–S1 118.21(2), N1–Si1–S1 125.30(5).

more easily undergoes oxygen migration to the silicon-silicon single bond, resulting in siloxysilylene **10**. The Si1–O1 distance of 1.613(3) Å, and N1–Si1–O1 angle of 104.33(15)° are also similar with **VIII**.[13]

Next, 1 : 1 reaction of **1** with S, Se, and Te were conducted, to afford the desired monomeric Si=E compounds **11** (E=S), **12** (E=Se), **13** (E=Te), respectively (Scheme 4, b). The $^{29}$Si {$^{1}$H} NMR spectrums display signals at 105.5, 109.9, and 101.9 ppm for the central silicon atom, respectively. These $^{29}$Si {$^{1}$H} NMR signals are upfield shifted compared to known neutral three-coordinate silicon-chalcogen double bond compounds (133.4–229.5 ppm),[6,33] indicating a more electron dense silicon center donated by the NHI and silyl ligand. SC-XRD analysis confirmed the monomeric form of **11** with a planar silicon center (Figure 2). The Si1–S1 distance of 1.9838(5) Å is slightly longer than known three-coordinate silanethiones (1.948(4) and 1.960(1) Å),[6,33] but still much shorter than some known Si–S single bond lengths (2.093–2.182(11) Å).[18,32t,35]

After the remarkable room temperature intermolecular dearomatization of arenes by imino(silyl)silylene **1**, a variety of small molecule activations of **1** was demonstrated. More facile activation of dihydrogen, ethylene, and carbon dioxide pinpoint the higher reactivity of **1** than the "masked silylene" (silepin) reported by us before could show. Different to carbon dioxide, regioselective rearomatization and dearomatization of carbonyl compounds, provides a promising approach for the preparation of oxasilacycles. Even the activation of a representative hydrosilane and hydroborane were easily achieved by **1**, catalytic hydrosilylation and hydroboration, however, could not be achieved. In addition, the reaction of silylene **1** with heavier chalcogen elements afforded the monomeric $R_2Si$=E (E=S, Se, and Te), which represent rare examples of three-coordinate silicon-heavier chalcogen double bond complexes. Further reactivity studies of **1** towards the activation of various small molecules are currently underway.

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## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

## References

[1] P. Jutzi, D. Kanne, C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 164.

[2] a) S. Fujimori, S. Inoue, *Eur. J. Inorg. Chem.* **2020**, *2020*, 3131–3142; b) C. Shan, S. Yao, M. Driess, *Chem. Soc. Rev.* **2020**, *49*, 6733–6754; c) L. Wang, Y. Li, Z. Li, M. Kira, *Coord. Chem. Rev.* **2022**, *457*, 214413.
[3] a) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500–6503; b) B. D. Rekken, T. M. Brown, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 6504–6507; c) B. D. Rekken, T. M. Brown, J. C. Fettinger, F. Lips, H. M. Tuononen, R. H. Herber, P. P. Power, *J. Am. Chem. Soc.* **2013**, *135*, 10134–10148.
[4] M. Driess, *Nat. Chem.* **2012**, *4*, 525–526.
[5] Z. Dong, Z. Li, X. Liu, C. Yan, N. Wei, M. Kira, T. Müller, *Chem. Asian J.* **2017**, *12*, 1204–1207.
[6] A. V. Protchenko, P. Vasko, D. C. H. Do, J. Hicks, M. Á. Fuentes, C. Jones, S. Aldridge, *Angew. Chem. Int. Ed.* **2019**, *58*, 1808–1812; *Angew. Chem.* **2019**, *131*, 1822–1826.
[7] A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Angew. Chem. Int. Ed.* **2013**, *52*, 568–571; *Angew. Chem.* **2013**, *125*, 596–599.
[8] T. J. Hadlington, J. A. B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones, *Chem. Commun.* **2016**, *52*, 1717–1720.
[9] Y. K. Loh, L. Ying, M. Á. Fuentes, D. C. H. Do, S. Aldridge, *Angew. Chem. Int. Ed.* **2019**, *58*, 4847–4851; *Angew. Chem.* **2019**, *131*, 4901–4905.
[10] M. M. D. Roy, M. J. Ferguson, R. McDonald, Y. Zhou, E. Rivard, *Chem. Sci.* **2019**, *10*, 6476–6481.
[11] M. M. D. Roy, S. R. Baird, E. Dornsiepen, L. A. Paul, L. Miao, M. J. Ferguson, Y. Zhou, I. Siewert, E. Rivard, *Chem. Eur. J.* **2021**, *27*, 8572–8579.
[12] D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 8134–8137.
[13] D. Wendel, D. Reiter, A. Porzelt, P. J. Altmann, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 17193–17198.
[14] T. Eisner, A. Kostenko, F. Hanusch, S. Inoue, *Chem. Eur. J.* **2022**, *28*, e202202330.
[15] H. Zhu, A. Kostenko, D. Franz, F. Hanusch, S. Inoue, *J. Am. Chem. Soc.* **2023**, *145*, 1011–1021.
[16] D. Reiter, P. Frisch, D. Wendel, F. M. Hörmann, S. Inoue, *Dalton Trans.* **2020**, *49*, 7060–7068.
[17] a) J.-M. Denis, Z. Pellerin, P. Guenot, M. Letulle, J.-L. Ripoll, *Chem. Ber.* **1992**, *125*, 1397–1399; b) H. Cui, C. Cui, *Chem. Asian J.* **2011**, *6*, 1138–1141; c) K. Schwedtmann, M. Quest, B. J. Guddorf, J. Keuter, A. Hepp, M. Feldt, J. Droste, M. R. Hansen, F. Lips, *Chem. Eur. J.* **2021**, *27*, 17361–17368; d) Y. Ding, Y. Li, J. Zhang, C. Cui, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205785; e) M. R. Hurst, A. G. Davis, A. K. Cook, *Organometallics* **2022**, *41*, 997–1005; f) T. Kajiwara, N. Takeda, T. Sasamori, N. Tokitoh, *Organometallics* **2004**, *23*, 4723–4734; g) P. T. K. Lee, M. K. Skjel, L. Rosenberg, *Organometallics* **2013**, *32*, 1575–1578.
[18] F. Lips, J. C. Fettinger, A. Mansikkamäki, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2014**, *136*, 634–637.
[19] F. Lips, A. Mansikkamäki, J. C. Fettinger, H. M. Tuononen, P. P. Power, *Organometallics* **2014**, *33*, 6253–6258.
[20] A. V. Protchenko, M. P. Blake, A. D. Schwarz, C. Jones, P. Mountford, S. Aldridge, *Organometallics* **2015**, *34*, 2126–2129.
[21] a) C. A. Anger, K. Hindelang, T. Helbich, T. Halbach, J. Stohrer, B. Rieger, *ACS Macro Lett.* **2012**, *1*, 1204–1207; b) C. Anger, F. Deubel, S. Salzinger, J. Stohrer, T. Halbach, R. Jordan, J. G. C. Veinot, B. Rieger, *ACS Macro Lett.* **2013**, *2*, 121–124; c) C. A. Anger, J. Kehrle, K. Hindelang, J. G. C. Veinot, J. Stohrer, B. Rieger, *Macromolecules* **2014**, *47*, 8497–8505.
[22] R. Shchepin, C. Xu, P. Dussault, *Org. Lett.* **2010**, *12*, 4772–4775.
[23] F. S. Tschernuth, T. Thorwart, L. Greb, F. Hanusch, S. Inoue, *Angew. Chem. Int. Ed.* **2021**, *60*, 25799–25803.
[24] K. Uchida, S. Ishida, T. Iwamoto, *Eur. J. Org. Chem.* **2022**, *2022*, e202200522.
[25] T. Kosai, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2016**, *55*, 15554–15558; *Angew. Chem.* **2016**, *128*, 15783–15787.
[26] a) Y. Xiong, S. Yao, M. Driess, *Chem. Eur. J.* **2009**, *15*, 5545–5551; b) S. Ishida, T. Iwamoto, M. Kira, *Organometallics* **2010**, *29*, 5526–5534.
[27] D. Franz, T. Szilvási, A. Pöthig, S. Inoue, *Chem. Eur. J.* **2019**, *25*, 11036–11041.
[28] a) S. Yadav, S. Saha, S. S. Sen, *ChemCatChem* **2016**, *8*, 486–501; b) T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, *47*, 4176–4197; c) M. M. D. Roy, A. A. Omaña, A. S. S. Wilson, M. S. Hill, S. Aldridge, E. Rivard, *Chem. Rev.* **2021**, *121*, 12784–12965.
[29] a) I. Alvarado-Beltran, A. Rosas-Sánchez, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 10481–10485; *Angew. Chem.* **2017**, *129*, 10617–10621; b) A. Rosas-Sánchez, I. Alvarado-Beltran, A. Baceiredo, N. Saffon-Merceron, S. Massou, D. Hashizume, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 15916–15920; *Angew. Chem.* **2017**, *129*, 16132–16136; c) R. Kobayashi, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2019**, *58*, 9425–9428; *Angew. Chem.* **2019**, *131*, 9525–9528; d) S. Takahashi, K. Nakaya, M. Frutos, A. Baceiredo, N. Saffon-Merceron, S. Massou, N. Nakata, D. Hashizume, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2020**, *59*, 15937–15941; *Angew. Chem.* **2020**, *132*, 16071–16075.
[30] A. L. Allred, *J. Inorg. Nucl. Chem.* **1961**, *17*, 215–221.
[31] P. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot, C. Priou, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1016–1018.
[32] a) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3504; b) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625–630; c) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923; d) S.-H. Zhang, H.-X. Yeong, C.-W. So, *Chem. Eur. J.* **2011**, *17*, 3490–3499; e) F. M. Mück, J. A. Baus, A. Ulmer, C. Burschka, R. Tacke, *Eur. J. Inorg. Chem.* **2016**, *2016*, 1660–1670; f) A. Baceiredo, T. Kato, in *Organosilicon Compounds: Theory and Experiment (Synthesis)* (Ed.: V. Y. Lee), Academic Press, London, **2017**, pp. 533–618; g) A. Burchert, R. Müller, S. Yao, C. Schattenberg, Y. Xiong, M. Kaupp, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 6298–6301; *Angew. Chem.* **2017**, *129*, 6395–6398; h) H. Wang, J. Zhang, Z. Xie, *J. Organomet. Chem.* **2018**, *865*, 173–177; i) M. K. Bisai, V. S. V. S. N. Swamy, T. Das, K. Vanka, R. G. Gonnade, S. S. Sen, *Inorg. Chem.* **2019**, *58*, 10536–10542; j) T. Muraoka, S. Tanabe, K. Ueno, *Organometallics* **2019**, *38*, 735–738; k) S. Sinhababu, M. M. Siddiqui, S. K. Sarkar, A. Münch, R. Herbst-Irmer, A. George, P. Parameswaran, D. Stalke, H. W. Roesky, *Chem. Eur. J.* **2019**, *25*, 11422–11426; l) M. L. Bin Ismail, M. X.-Y. Ong, C.-W. So, *Eur. J. Inorg. Chem.* **2020**, *2020*, 3703–3707; m) M. Ghosh, P. Panwaria, S. Tothadi, A. Das, S. Khan, *Inorg. Chem.* **2020**, *59*, 17811–17821; n) M.-P. Luecke, E. Pens, S. Yao, M. Driess, *Chem. Eur. J.* **2020**, *26*, 4500–4504; o) F. Hanusch, D. Munz, J. Sutter, K. Meyer, S. Inoue, *Angew. Chem. Int. Ed.* **2021**, *60*, 23274–23280; p) X. Sun, C. Röder, P. W. Roesky, *Inorg. Chem.* **2021**, *60*, 13861–13868; q) S. Takahashi, A. Ishii, N. Nakata, *Chem. Commun.* **2021**, *57*, 3203–3206; r) N. Tiessen, N. Schwarze, H.-G. Stammler, B. Neumann, B. Hoge, *Inorg. Chem.* **2021**, *60*, 15112–15117; s) M. Chen, B. Lei, X. Wang, H. Rong, H. Song, Z. Mo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204495; t) M.-P. Luecke, L. Giarrana, A. Kostenko, T. Gensch, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2022**, *61*, e202110398.

[33] a) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, *J. Am. Chem. Soc.* **1998**, *120*, 11096–11105; b) T. Norihiro, S. Tomonori, H. Ken, S. Takayo, T. Nobuhiro, O. Renji, *Chem. Lett.* **2002**, *31*, 34–35; c) T. Iwamoto, K. Sato, S. Ishida, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2006**, *128*, 16914–16920; d) H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11578–11579.

[34] D. Reiter, P. Frisch, T. Szilvási, S. Inoue, *J. Am. Chem. Soc.* **2019**, *141*, 16991–16996.

[35] a) W. Ando, Y. Hamada, A. Sekiguchi, K. Ueno, *Tetrahedron Lett.* **1983**, *24*, 4033–4036; b) K. Kabeta, D. R. Powell, J. Hanson, R. West, *Organometallics* **1991**, *10*, 827–828; c) J. Keuter, K. Schwedtmann, A. Hepp, K. Bergander, O. Janka, C. Doerenkamp, H. Eckert, C. Mück-Lichtenfeld, F. Lips, *Angew. Chem. Int. Ed.* **2017**, *56*, 13866–13871; *Angew. Chem.* **2017**, *129*, 14054–14059.

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