

Push–Pull Stabilization of Parent Monochlorosilylenes

Hunter P. Hickox, Yuzhong Wang, Yaoming Xie, Pingrong Wei, Henry F. Schaefer III, and Gregory H. Robinson*

Department of Chemistry and the Center for Computational Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States

S Supporting Information

ABSTRACT: While reaction of carbene-stabilized disilicon $L:Si=Si:L$ ($L = C\{N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) (**8**) with $\text{HCl}\cdot\text{NC}_5\text{H}_5$ results in carbene-stabilized Si_2Cl_2 (**2**) and substituted 1*H*-imidazole (**9**), combination of the corresponding $\text{Fe}(\text{CO})_4$ -modified disilicon carbene complex $L:Si=Si[\text{Fe}(\text{CO})_4]:L$ (**6**) with pyridine hydrochloride gives a species containing two push–pull-stabilized parent monochlorosilylenes that are bridged by an $\text{Fe}(\text{CO})_3$ unit (**7**). The nature of **7** was further elucidated by spectroscopic, crystallographic, and computational methods. Spectroscopic data suggest that **7** exists as two diastereoisomers.

The chemistry of silylenes ($:SiR_2$),¹ silicon analogues of carbenes, has experienced impressive growth since the initial experimental observation of these transient divalent silicon species nearly half a century ago.^{1–7} Since the seminal discovery of stable silylenes, such as $:Si(\eta^5\text{-C}_5\text{Me}_5)_2$ and $:Si\{N(t\text{Bu})\text{-CH}\}_2$,^{4,8,9} these species have evolved into potent ligands for synthesis of the corresponding transition metal complexes.^{10–27} Furthermore, these compounds have attracted considerable attention due to their catalytic potential.^{11,12} The parent silylene ($:SiH_2$)²⁸ and chlorosilylenes [$:SiCl_2$ and $:Si(H)Cl$]^{29–31} have been observed as reactive intermediates in chemical vapor deposition of silicon from silane (SiH_4) and chlorosilanes, respectively.³² However, the quest to stabilize these elusive silylenes under ambient conditions has long challenged chemists.

Lewis bases, particularly N-heterocyclic carbenes, were recently employed for this purpose (Figure 1).^{33,34} While Roesky reported a Lewis-base-complexed chlorosilylene (**1**),³⁵ this laboratory reported that potassium graphite reduction of $L:SiCl_4$ ($L = C\{N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) afforded a carbene-stabilized dichlorobis-silylene (**2**).³⁶ Subsequently, carbene-stabilized $:SiCl_2$ (**3**) was synthesized via both N-heterocyclic carbene-mediated reductive elimination of HCl from HSiCl_3 and potassium graphite reduction of $L:SiCl_4$ ($L = C\{N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$).³⁷ It is noteworthy that $L:SiCl_2$ complexes have exhibited interesting reactivity toward organic and organometallic substrates.³³ In addition, the elusive $:SiH_2$ moiety has been stabilized by donor (carbene)–acceptor (group 13 Lewis acids) coordination (**4** and **5**, $L = C\{N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$).^{38,39} Despite recent attempts to access carbene-stabilized SiHCl via N-heterocyclic carbene-mediated HCl elimination from SiH_2Cl_2 ,⁴⁰ carbene stabilization of SiHCl has yet to be achieved.

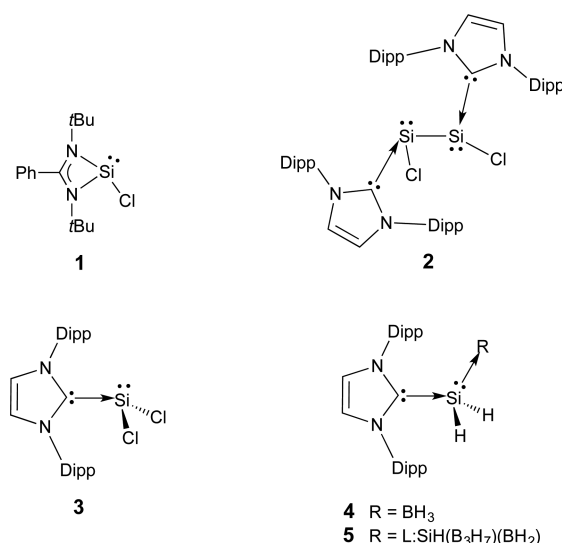


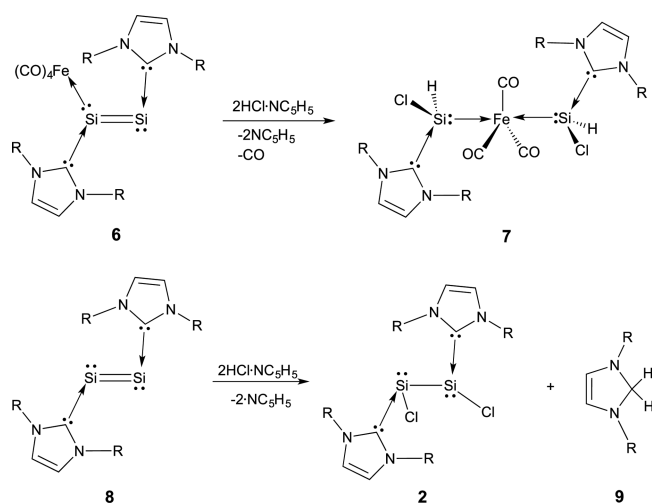
Figure 1. Lewis base-stabilized chlorosilylenes (**1–3**) and push–pull-stabilized parent silylene ($:SiH_2$) (**4** and **5**).

To explore the intriguing transition metal chemistry of carbene-stabilized disilicon, $L:Si=Si:L$ ($L = C\{N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) (**8**),³⁶ both $L:Si=Si(\text{CuCl}):L$ and $L:Si=Si[\text{Fe}(\text{CO})_4]:L$ (**6**) were recently prepared.^{41,42} Herein, we report the synthesis,⁴³ molecular structure,⁴³ and computations⁴³ of a “push–pull”-stabilized parent monochlorosilylene [$:Si(H)Cl$] (**7**) via reaction of **6** with pyridine hydrochloride ($\text{HCl}\cdot\text{NC}_5\text{H}_5$), which represents the first experimental realization of HSiCl stabilization under ambient conditions.

Reaction of carbene-stabilized disilicon (**8**) with electrophilic Brookhart’s acid⁴⁴ ($[\text{H}(\text{Et}_2\text{O})_2][\text{B}(\text{Ar}^F)_4]$, $\text{Ar}^F = \text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2$) gave a carbene-complexed HSi_2^+ cation.⁴⁵ Pyridine hydrochloride was recently utilized by this laboratory in the preparation of the carbene-complexed HP_2^+ cation via protonation of carbene-stabilized diphosphorus, $L:P=P:L$ ($L = C\{N(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$).⁴⁶ In contrast, low-temperature reaction of **6** (purple) with $\text{HCl}\cdot\text{NC}_5\text{H}_5$ (1:2 ratio) in toluene gave neutral **7** (orange, 58.0% yield; Scheme 1). The corresponding 1:1 reaction afforded a mixture containing both **7** and unreacted starting material **6**. Notably, bis(carbene-silylene) transition metal compounds, involving a $[L: \rightarrow \text{silylene}]_2 \rightarrow \text{TM}$ (i.e., transition metal) bonding motif, are interesting because they

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Scheme 1. Synthesis of 7 and Parallel Reaction of 8 with HCl·NC₅H₅ (R = 2,6-*i*-Pr₂C₆H₃)


have been postulated as intermediates in the synthesis of disilene transition metal complexes.⁴⁷ By comparison, parallel reaction of 8 with HCl·NC₅H₅ was also conducted (Scheme 1). The 1:2 (8:HCl·NC₅H₅) reaction gave a complicated mixture, from which 2 and 9, along with byproducts [i.e., free carbene (L) and its precursor (L·H⁺Cl⁻)], were detected and characterized by ¹H NMR spectroscopy.^{36,48} Compared to the Si(0)₂ core in 8, the iron–carbonyl-modified disilicon core in 6 exhibits unique reactivity toward HCl·NC₅H₅. Although the mechanisms of the two reactions shown in Scheme 1 remain unclear, based on the formation of HSiCl units in 7, we propose that L:Si(H)Cl (L = C{N(2,6-*i*-Pr₂C₆H₃)CH₂}) may exist as an unstable intermediate in the reaction of 8 with HCl·NC₅H₅, which then decomposes to give a mixture containing 2, 9, and other byproducts.

Single-crystal X-ray structural analysis shows that each disordered HSiCl unit in 7 (Figure 2) contains a four-coordinate silicon(II) center. Each silicon atom accepts one pair of electrons from the carbene ligand while also donating an electron pair to

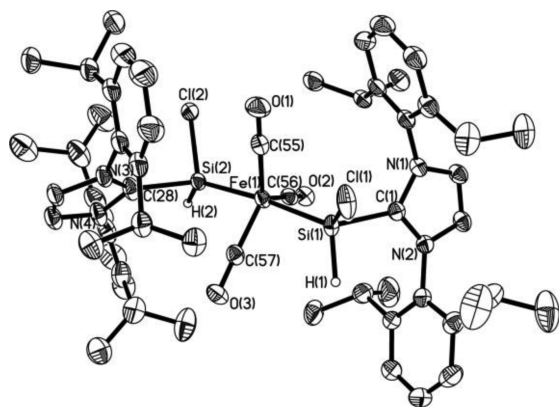


Figure 2. Molecular structure of 7. Thermal ellipsoids represent 30% probability. Hydrogen atoms attached to carbons have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–C(1), 1.955(5); Si(1)–Cl(1), 2.135(5); Si(1)–Fe(1), 2.213(3); Si(2)–C(28), 1.957(5); Si(2)–Cl(2), 2.127(3); Si(2)–Fe(1), 2.189(3); C(1)–Si(1)–Cl(1), 98.7(2); Cl(1)–Si(1)–Fe(1), 117.03(19); C(1)–Si(1)–Fe(1), 120.42(18); Si(1)–Fe(1)–Si(2), 172.77(18); Si(1)–Fe(1)–C(55), 91.7(2); C(28)–Si(2)–Cl(2), 95.14(18); Cl(2)–Si(2)–Fe(1), 117.97(15); C(28)–Si(2)–Fe(1), 122.49(19).

the Fe(CO)₃ unit [only the bonding parameters involving the H(1)Si(1)Cl(1) set (85.2% occupancy) and the H(2)Si(2)Cl(2) set (71.9% occupancy) are listed in the caption of Figure 2].⁴³ The Si–C (1.958 Å, av.), Si–Cl (2.128 Å, av.), and Si–Fe (2.213 Å, av.) bond distances in 7 are comparable to those [*d*_{Si–C} = 1.958(3) Å; *d*_{Si–Cl} = 2.0890(12) and 2.0965(14) Å; *d*_{Si–Fe} = 2.229(11) Å] for L:SiCl₂[Fe(CO)₄] (L = C{N(2,6-*i*-Pr₂C₆H₃)CH₂})₂.⁴⁹ Notably, the Si–Fe bond for 6 [2.3265(10) Å] is obviously longer than that for 7 (2.213 Å, av.).⁴² The central iron atom in 7 adopts a distorted trigonal bipyramidal geometry, wherein two carbene-complexed HSiCl silylene ligands reside at the axial positions about an Fe(CO)₃ equatorial plane.

While the two SiCl₂ units in [Co(CO)₃-(SiCl₂L)₂]⁺[CoCl₃(THF)]⁻ (L = C{N(2,6-*i*-Pr₂C₆H₃)CH₂})₂, 10) only show one singlet at 44.11 ppm in the ²⁹Si{¹H} NMR spectrum,⁵⁰ compound 7, containing two chiral silicon centers, exhibits two adjacent ²⁹Si{¹H} NMR resonances at 44.02 and 45.32 ppm (Figure 3a) due to the presence of two

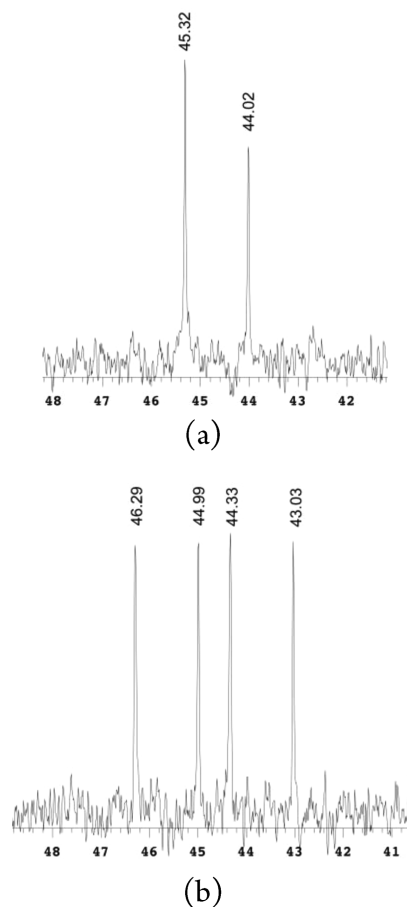


Figure 3. (a) Proton-decoupled ²⁹Si NMR spectrum of 7; (b) proton-coupled ²⁹Si NMR spectrum of 7.

diastereoisomers.⁵¹ Two silicon hydride ¹H NMR resonances of 7 (at 6.20 and 6.22 ppm in C₆D₆) indicate approximate 1:2 population ratio of these two diastereoisomers. The ¹H-coupled ²⁹Si NMR spectrum of 7 is shown in Figure 3b with ¹J_{Si–H} = 195 Hz (av.), which is in accordance with the Si–H coupling constant [¹J_{Si–H} = 192 Hz (av.)] obtained from low-intensity ²⁹Si satellites observed in the ¹H NMR spectrum of 7. The Si–H stretching band (*ν* = 2103 cm⁻¹) in the IR spectrum of 7 is close to that (*ν* = 2118 cm⁻¹) for L₂SiH₂Cl₂ (L = C{N(2,6-*i*-Pr₂C₆H₃)CH₂})₂.⁴⁰ In

addition, the three carbonyls in **10** are characterized as a singlet ^{13}C NMR resonance at 199.3 ppm, along with three distinct IR bands (1969, 1994, 2052 cm^{-1}). In contrast, the three carbonyl groups of **7** exhibit two adjacent ^{13}C NMR resonances (at 216.2 and 216.5 ppm) and five IR stretching bands [1823, 1832, 1856 (br), 1934, and 1941 cm^{-1}], further supporting the presence of two diastereoisomers of **7**.

Density functional theory computations at the B3LYP/6-311+G** level were performed on the simplified model **7-H** [optimized in C_2 symmetry, L: = :C(NHCH) $_2$].⁴³ The computed Si–C (1.963 Å), Si–Cl (2.178 Å), and Si–Fe (2.227 Å) distances for **7-H** agree well with the experimental values for **7** ($d_{\text{Si-C}} = 1.958$ Å, av.; $d_{\text{Si-Cl}} = 2.128$ Å, av.; $d_{\text{Si-Fe}} = 2.213$ Å, av.). The selected localized molecular orbitals of **7-H** (Figure 4) include

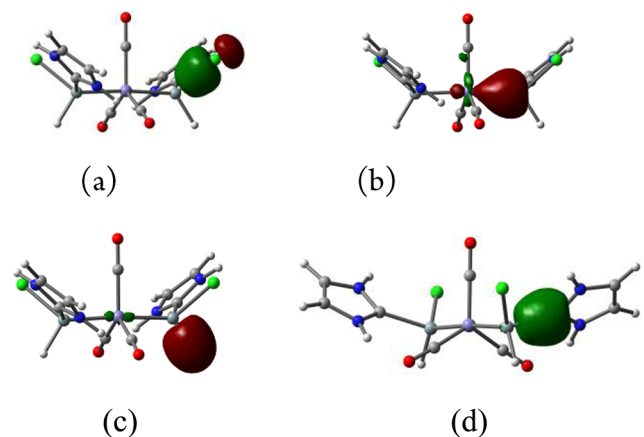


Figure 4. Selected localized molecular orbitals of **7-H**: (a) Si–Cl σ -bonding orbital; (b) Si–Fe σ -bonding orbital; (c) Si–H σ -bonding orbital; (d) Si–C_{NHC} σ -bonding orbital.

the Si–C, Si–H, Si–Cl, and Si–Fe σ -bonding orbitals. The 0.43 Wiberg bond index of the Si–Fe bond in **7-H** compares to that (0.69) for the Si–Fe single bond in **6-Me** [L: = :C(N(Me)-CH) $_2$].⁴² Both the positive natural charge (+0.89) on each silicon atom and the negative charge (–0.74) on the central iron atom indicate the dative character of the Si–Fe bonds in **7-H**.

The iron–carbonyl-modified disilicon carbene complex **6** provides a unique platform to access donor–acceptor-stabilized parent monochlorosilylene (HSiCl) **7**, which exists as two diastereoisomers. In contrast, reaction of carbene-stabilized disilicon **8** with HCl–NC $_3$ H $_5$ did not give the expected carbene-stabilized HSiCl product but rather a mixture containing both **2** and **9**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06726.

Complete ref 43, full details of the syntheses, computations, and X-ray crystal determination (PDF)
X-ray data for **7** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*robinson@uga.edu

Notes

The authors declare no competing financial interest.

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