Push−Pull Stabilization of Parent Monochlorosilylenes

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Ⓢ *Supporting Information*

ABSTRACT: While reaction of carbene-stabilized disilicon L:Si═Si:L (L: = C{N(2,6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$) (**8**) with HCl·NC$_5$H$_5$ results in carbene-stabilized Si$_2$Cl$_2$ (**2**) and substituted 1*H*-imidazole (**9**), combination of the corresponding Fe(CO)$_4$-modified disilicon carbene complex L:Si═Si[Fe(CO)$_4$]:L (**6**) with pyridine hydrochloride gives a species containing two push−pull-stabilized parent monochlorosilylenes that are bridged by an Fe(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.

Figure 1. Lewis base-stabilized chlorosilylenes (**1**−**3**) and push−pull-stabilized parent silylene (:SiH$_2$) (**4** and **5**).

T he 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(η^5-C$_5$Me$_5$)$_2$ and :Si{N(*t*Bu)-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-^{i}Pr$_2$C$_6$H$_3$)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-^{i}Pr$_2$C$_6$H$_3$)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-^{i}Pr$_2$C$_6$H$_3$)-CH}$_2$).[38,39] Despite recent attempts to access carbene-stabilized SiHCl via N-heterocyclic carbene-mediated HCl elimination from SiH$_2$Cl$_2$,[40] carbene stabilization of SiHCl has yet to be achieved.
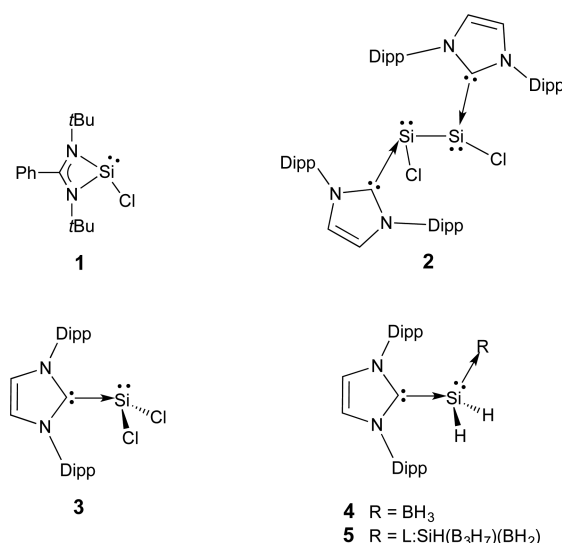
To explore the intriguing transition metal chemistry of carbene-stabilized disilicon, L:Si═Si:L (L: = C{N-(2,6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$) (**8**),[36] both L:Si═Si(CuCl):L and L:Si═Si[Fe(CO)$_4$]:L (**6**) were recently prepared.[41,42] Herein, we report the synthesis,[43] molecular structure,[43] and computations[43] of a "push−pull"-stabilized parent monochlorosilylene [:Si(H)Cl] (**7**) via reaction of **6** with pyridine hydrochloride (HCl·NC$_5$H$_5$), which represents the first experimental realization of HSiCl stabilization under ambient conditions.

Reaction of carbene-stabilized disilicon (**8**) with electrophilic Brookhart's acid[44] ([H(Et$_2$O)$_2$][B(Ar^F)$_4$], Ar^F = C$_6$H$_3$-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-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$).[46] In contrast, low-temperature reaction of **6** (purple) with HCl·NC$_5$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: → silylene:]$_2$ → TM (i.e., transition metal) bonding motif, are interesting because they

Scheme 1. Synthesis of 7 and Parallel Reaction of 8 with HCl·NC₅H₅ (R = 2,6-^{i}Pr₂C₆H₃)
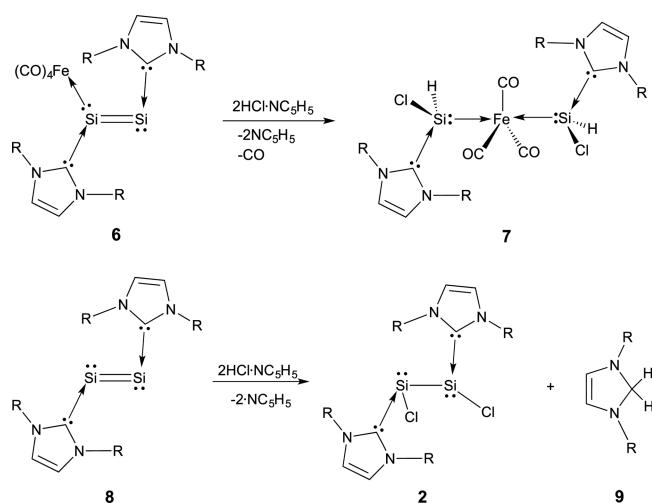
have been postulated as intermediates in the synthesis of disilene transition metal complexes.[47] By comparison, parallel reaction of 8 with HCl·NC₅H₅ was also conducted (Scheme 1). The 1:2 (8:HCl·NC₅H₅) reaction gave a complicated mixture, from which 2 and 9, along with byproducts [i.e., free carbene (L:) and its precursor (L:H⁺Cl⁻)], were detected and characterized by ^{1}H 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)CH}₂) 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
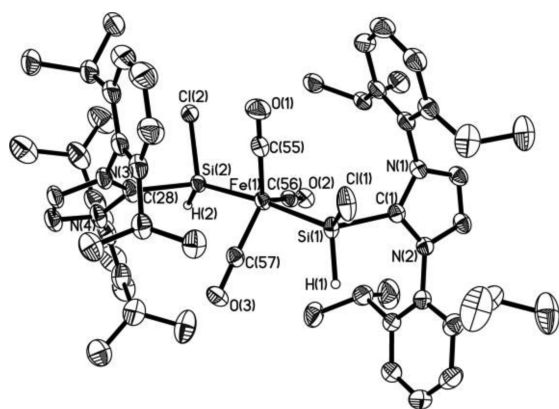
the Fe(CO)₃ unit [only the bonding parameters involving the H(1)Si(1)Cl(1) set (85.2% occupancy) and the H(2)Si(2)Cl(2) set (71.9% occupancy) are listed in the caption of Figure 2].[43] The Si−C (1.958 Å, av.), Si−Cl (2.128 Å, av.), and Si−Fe (2.213 Å, av.) bond distances in 7 are comparable to those [$d_{Si−C}$ = 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)-CH}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)CH}₂, 10) only show one singlet at 44.11 ppm in the ^{29}Si{^{1}H} NMR spectrum,[50] compound 7, containing two chiral silicon centers, exhibits two adjacent ^{29}Si{^{1}H} NMR resonances at 44.02 and 45.32 ppm (Figure 3a) due to the presence of two
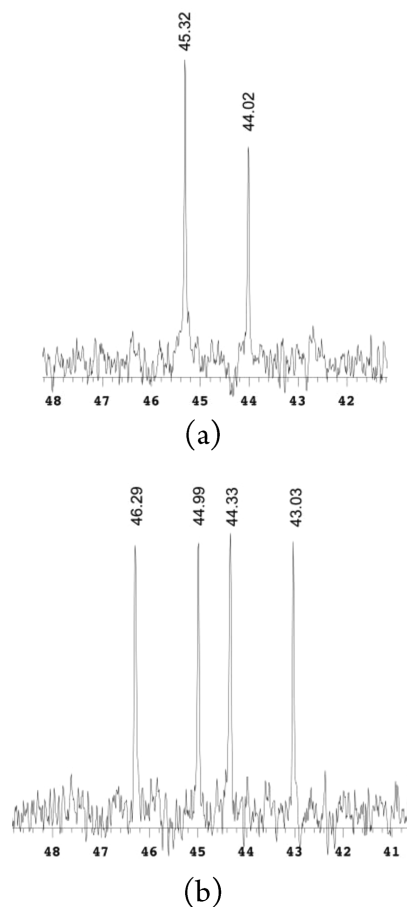

(a)

(b)

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

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).

diastereoisomers.[51] Two silicon hydride ^{1}H NMR resonances of 7 (at 6.20 and 6.22 ppm in C₆D₆) indicate approximate 1:2 population ratio of these two diastereoisomers. The ^{1}H-coupled ^{29}Si 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 ^{29}Si satellites observed in the ^{1}H 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)CH}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_{Si-C} = 1.958 Å, av.; d_{Si-Cl} = 2.128 Å, av.; d_{Si-Fe} = 2.213 Å, av.). The selected localized molecular orbitals of **7-H** (Figure 4) include
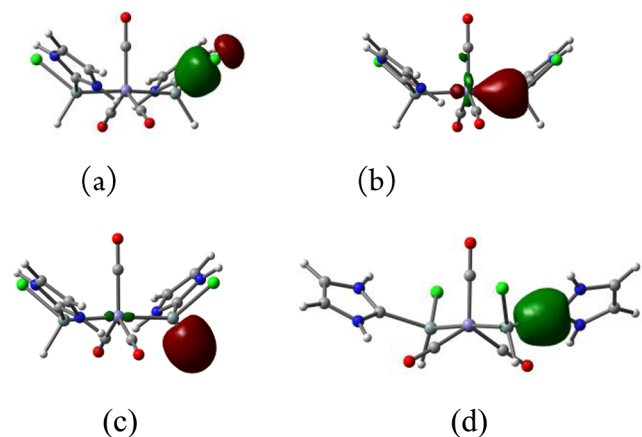

Figure 4. Selected localized molecular orbitals of **7-H**: (a) Si−Cl σ-bonding orbital; (b) Si−Fe σ-bonding orbital; (c) Si−H σ-bonding orbital; (d) Si−C$_{NHC}$ σ-bonding orbital.

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$_5$H$_5$ did not give the expected carbene-stabilized HSiCl product but rather a mixture containing both **2** and **9**.

ASSOCIATED CONTENT

S 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)

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Notes

The authors declare no competing financial interest.

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