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A Dihydrodisilene Transition Metal Complex from an N-Heterocyclic Carbene-Stabilized Silylene Monohydride

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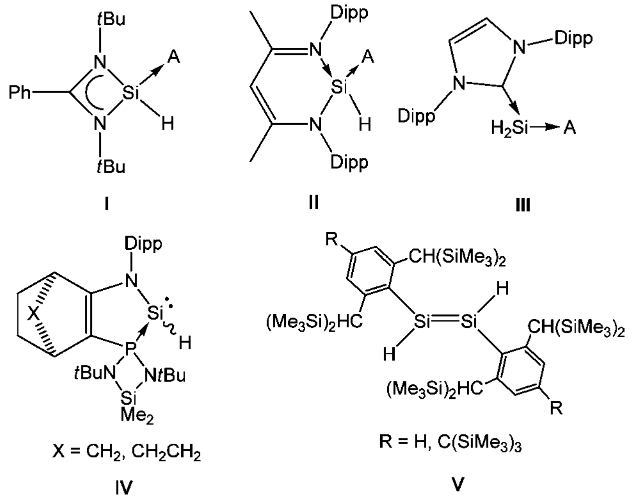
Supporting Information

ABSTRACT: Through the use of an N-heterocyclic carbene (NHC) and the super-silyl group ($t\mathrm{Bu_3Si}$), the novel silylene hydride **2** could be synthesized and isolated in 41% yield. The reaction of **2** with bis(1,5-cyclooctadiene)nickel(0) afforded complex **3**, which represents the first example of a dihydrodisilene transition metal complex. Compounds **2** and **3** were fully characterized, including single-crystal X-ray diffraction analysis. The reaction mechanism for the formation of **3** from **2** was investigated by density functional theory calculations, which showed that migration of the NHC from silicon to nickel takes place in this reaction.

Main-group metal hydrides have recently attracted widespread attention because of their applications in organic synthesis and also in material sciences.[1,2] For example, hydrosilylation using hydrosilanes has developed into one of the most important synthetic methods.[3] In contrast to tetravalent hydrosilanes, the chemistry of silicon(II) hydrides has been much less developed because of their highly reactive properties. Most silicon(II) hydrides have been isolated through donor−acceptor-type stabilization (Chart 1).[4−7] For instance, various donor ligands [amidinate ligand **I**,[4] β-diketiminato ligand **II**,[5] N-heterocyclic carbene (NHC) **III**[6]] and Lewis acids (transition metals,[4b,c,5] boron[4a,6a,b]) have been employed. Only one striking example of a base-stabilized silylene(II) hydride without any stabilization by a Lewis acid, compound **IV**, has been reported.[7] In addition, studies of the reactivity of these silicon(II) hydrides toward alkenes and alkynes have also been reported.[4c,5b,7,8] In contrast to hydridosilylenes, the chemistry of dihydrodisilenes [R(H)Si═Si(H)R], the dimers of hydridosilylenes, is largely unexplored.[9,10] Wiberg and co-workers postulated the formation of the 1,2-dihydrodisilene R(H)Si═Si(H)R [R = SiH($\mathrm{Si}t\mathrm{Bu_3}$)$_2$] as a possible intermediate, but it was not possible to isolate this species because of its thermal decomposition.[11] Very recently, Tokitoh and co-workers reported the successful isolation of dihydrodisilene **V**, which is kinetically stabilized by the bulky aryl group (Chart 1).[12] However, since facile access to dihydrodisilene is synthetically still challenging, new methods are needed to stabilize or intercept these reactive species. In this contribution, we present the synthesis and characterization of a novel NHC-stabilized silylene monohydride and its chemical transformation into an unprecedented dihydrodisilene transition metal complex.

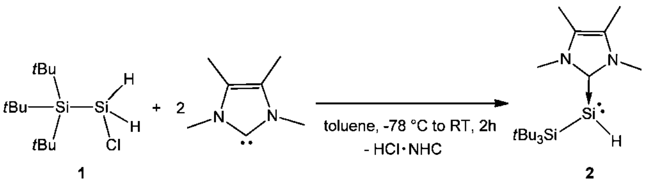
Chart 1. Examples of Recently Reported Hydridosilylenes and Dihydrodisilene



Recently, much progress has been made in the synthesis and isolation of silylenes by applying NHCs as ligands to stabilize the silicon(II) center.[13−15] On the other hand, the introduction of a silyl group to low-valent silicon could lead to remarkable steric and electronic perturbations.[16] On that basis, taking into account an NHC ligand as a strong σ donor and a bulky silyl group as an electron-donating and protecting substituent, we set out to stabilize the terminal Si(II)−H moiety of a hydridosilylene.

The treatment of 2 equiv of NHC$^{\mathrm{Me}}$ (NHC$^{\mathrm{Me}}$ = 1,3,4,5-tetramethylimidazol-2-ylidene) with the super-silyl-substituted dihydrosilane $t\mathrm{Bu_3SiSiH_2Cl}$[17] in toluene at room temperature furnished the desired silicon(II) monohydride **2** as an air- and moisture-sensitive yellow powder in 41% yield (Scheme 1). Compound **2** represents a silylene monohydride NHC adduct

Scheme 1. Synthesis of NHC-Stabilized Silylene Monohydride 2



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without any stabilization by a Lewis acid. In the ^{1}H NMR spectrum of **2**, the signal corresponding to the terminal Si(II)−H appears at 3.17 ppm. The ^{29}Si NMR spectrum of **2** reveals two sharp signals at 25.4 ppm (Si*t*Bu$_3$) and −137.8 ppm (Si−H). The highly upfield-shifted signal can be assigned to the Si(II) silicon and is comparable to those of NHC-stabilized bis(silyl)silylenes NHC−SiR$_2$ (−128.9 ppm for R = Si*t*Bu$_3$ and −132.3 ppm for R = SiMe*t*Bu$_2$).[13] The silicon−hydrogen coupling constant of **2** ($^{1}J_{\mathrm{Si-H}}$ = 101.3 Hz) is smaller than those observed for donor−acceptor-stabilized silylene hydrides **I**−**III** (127.0−235.0 Hz)[4−6] but larger than that observed for base-stabilized silylene hydrides **IV** (85.1 and 85.7 Hz).[7] The IR spectrum of **2** exhibits a sharp band at 1984 cm^{-1}, which is assigned as a Si−H stretching mode. This value is similar to that observed for silylene hydride **IV** (1954 cm^{-1}).[7]

Single crystals of **2** suitable for X-ray diffraction analysis were grown in 1:1 toluene/hexane solution at 4 °C, and the monomeric structure of **2** in the solid state was confirmed crystallographically (Figure 1). The Si(II) atom in **2** is threefold-coordinated by the silicon atom of the super-silyl group, the carbon atom of the NHC, and one hydrogen atom. The tricoordinate Si(II) center is highly pyramidalized, as indicated by the sum of the bond angles around the Si(II) atom (290.84°). The Si1−C1 distance of 1.942(3) Å in **2** is slightly longer than that in the NHC-stabilized bis(super-silyl)silylene NHC−Si(Si*t*Bu$_3$)$_2$ [1.933(4) Å][13] but significantly shorter than those in NHC−SiX$_2$ [X = Cl, 1.985(4) Å; X = Br, 1.985(4) Å; X = I, 1.997(4) Å].[14] The Si1−Si2 bond length in **2** [2.4151(8) Å] is shorter than those in NHC−Si(Si*t*Bu$_3$)$_2$ [2.4542(15) and 2.4419(14) Å],[13] indicating that there is less steric hindrance around the silicon center in **2** because of the small hydrogen substituent. In addition, the calculated HOMO of **2** clearly presents a lone-pair orbital at the silicon center (see the Supporting Information).

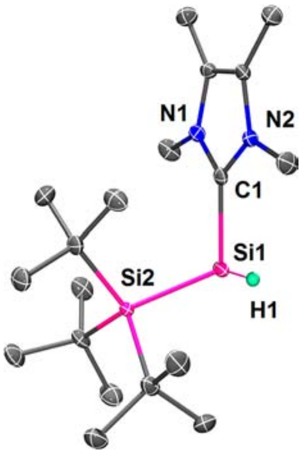
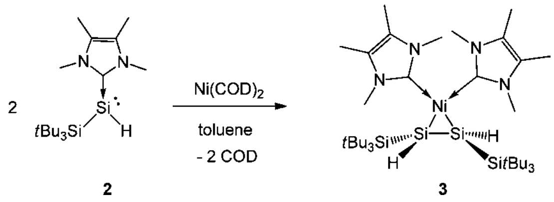


Figure 1. Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms except for H1 have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Si1−C1 1.942(3), Si1−Si2 2.4151(8), Si1−H1 1.21(4), C1−Si1−Si2 104.84(8), Si2−Si1−H1 95(2), C1−Si1−H1 91(2).

The NHC-stabilized silylene hydride **2** bears three potentially reactive sites: (i) a lone pair at the silicon center (coordination chemistry), (ii) the terminal Si−H (hydrosilylation), and (iii) the NHC (carbene abstraction). Interestingly, silylene hydride **2** readily reacts with bis(1,5-cyclooctadiene)nickel(0) to give the dihydrodisilene nickel complex **3** in 86% yield (Scheme 2). The ^{1}H NMR spectrum of **3** shows a singlet at 2.08 ppm that can be assigned to the terminal Si−H protons. This value is upfield-shifted relative to those of precursor **2** (3.17 ppm) as a result of the coordination to nickel. The observed $^{1}J_{\mathrm{Si-H}}$ values in complex **3** (149.3 and 167.6 Hz) are smaller than those of stable dihydrodisilenes **V** (216 and 210 Hz)[12] but larger than that of compound **2** (101.3 Hz). In the ^{13}C NMR spectrum of **3**, the carbene carbon signal (198.5 ppm) appears considerably downfield relative to that of **2** (176.9 ppm). The ^{29}Si NMR spectrum of complex **3** exhibits two signals at 24.4 and −115.0 ppm. The latter value corresponds to the skeletal silicon atoms and is shifted downfield by ca. 20 ppm relative to that in **2** (−137.8) and in the range of those in disilene transition metal complexes (−159.7 to +65.3 ppm).[10,18−20]

Scheme 2. Synthesis of Dihydrodisilene Nickel Complex 3



Complex **3** crystallized from a hexane solution of the reaction mixture at 4 °C as yellow crystals. The X-ray diffraction analysis of **3** (Figure 2) revealed that two carbon atoms (C1 and C8) and two silicon atoms (Si2 and Si3) are coordinated to the nickel center with a C1−Ni−C8 angle of 103.10(7)° and a Si2−Ni−Si3 angle of 58.631(16)°. The geometry around the nickel atom is planar (sum of the bond angles around nickel = 359.99°). The Si−Ni bonds in **3** [2.3004(5) and 2.3101(5) Å] are longer than those in silylene−nickel complexes [2.0369(6)−2.275(1) Å].[21] The central Si2−Si3 bond distance in **3** [2.2574(6) Å] is relatively short but in the range of those

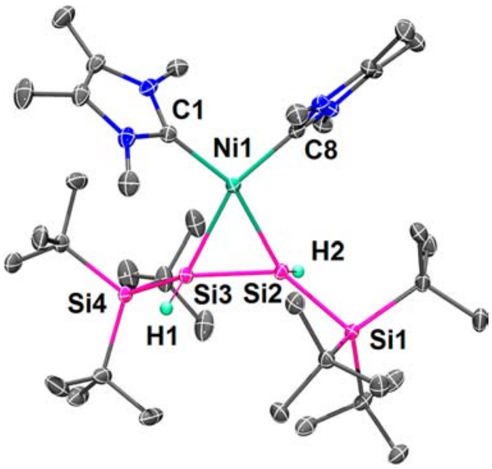


Figure 2. Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms except for H1 and H2 have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ni1−Si2 2.3004(5), Ni1−Si3 2.3101(5), Si1−Si2 2.3515(6), Si2−Si3 2.2574(6), Si3−Si4 2.3572(6), Si2−H2 1.38(2), Si3−H1 1.39(2), C1−Ni1−C8 103.10(7), Si2−Ni1−Si3 58.631(16), Si3−Si2−Ni1 60.899(16), Si1−Si2−Si3, 127.98(2), Si3−Si2−H2 113(9), Si2−Si3−H1 113.3(8), Si4−Si3−H1 107.7(8), Si2−Si3−Si4 125.52 (2).

observed for known disilene transition metal complexes [2.2569(5)−2.336(2) Å].[19,20] In general, disilene transition metal complexes bear a character between a metallacycle (type **A**) and π-complex (type **B**), but most of the disilene complexes prefer to form the metallacycle rather than π-complex since stronger σ donation to the metal and stronger π back-donation from the metal to the ligand can be considered due to the higher HOMO and lower LUMO of the Si−Si double bond (Chart 2). In fact, only two examples of disilene complexes having a real π-complex character were hitherto reported by Kira and Iwamoto et al.[18] In the case of **3**, the bent back angles θ (θ_{si1} = 35.05° and θ_{si2} = 34.7°) are significantly larger than those in disilene π-complexes **B** (4.4−9.7°)[19] and comparable to those in reported metallacycles **A** (9.2−30.2°).[20] Accordingly, these structural observations in addition to the highly shielded resonance of the skeletal silicon atoms (−115.0 ppm) clearly indicate the metallacyclopropane character of the dihydrodisilene nickel complex **3**.

Chart 2. Metallacycle versus π-Complex in Disilene Transition Metal Complexes

A reaction mechanism for the formation of **3** involving the coordination of nickel to silicon and the migration of the NHCs is proposed. Density functional theory calculations at the B3LYP/6-31G(d)/LANL2DZ[Ni] level for simplified model compounds (NHC = 1,3-dimethylimidazol-2-ylidene, R = $SiMe_3$) were performed in order to obtain further mechanistic insight. The potential energy surface is depicted in Figure 3. The reaction commences with the coordination of hydridosilylene **2′** to the nickel center, resulting in the formation of hydridosilylene nickel complex intermediate **IT1** (+5.0 kcal/mol) via the dissociation of one COD ligand on nickel (+16.6 kcal/mol). The coordination of the second silylene to **IT1** produces the bis(silylene)nickel complex **IT2** (+13.3 kcal/mol), which is rather less stable and can release one COD to give the bis(silylene) complex **IT3** (+7.6 kcal/mol). Subsequently, **IT3** undergoes migration of the two NHCs and Si−Si bond formation to yield the dihydrodisilene nickel complex **3′**. The NHC migration transition states **TS1** (+9.5 kcal/mol) and **TS2** (+9.6 kcal/mol) lie merely higher in energy than **2′**, thus revealing a low barrier step. Consequently, the pathway from **2′** to **3′** is highly exothermic by −21.4 kcal/mol.

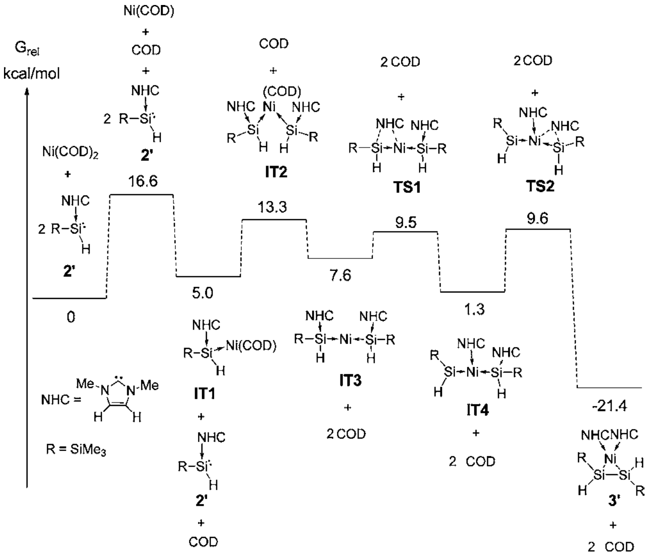


Figure 3. Potential energy surface for the reaction of NHC-stabilized silylene hydride **2′** with $Ni(COD)_2$.

In summary, we have here reported for the first time the dihydrodisilene nickel complex **3**, which was successfully synthesized starting from the novel NHC-stabilized silylene monohydride **2**. Notably, new methodology to intercept the reactive dihydrodisilene starting from the hydridosilylene assisted by a transition metal is presented. On the basis of structural observations, complex **3** has a metallacycle character. Further applications of hydridosilylene **2** as a promising new building block for low-valent organosilicon compounds are currently underway in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis and spectroscopic data of **2** and **3** and crystallographic data for **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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