Hydrosilylation with Silicon(II)

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Hydrosilylation of Alkynes by $Ni(CO)_3$-Stabilized Silicon(II) Hydride**

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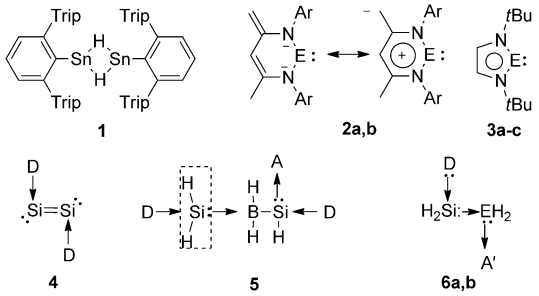
Dedicated to Professor Robert West

The chemistry of low-valent main-group compounds of the heavier Group 14 elements has been a prominent and highly challenging topic in molecular chemistry for several decades.[1a,b] By taking advantage of steric protection through bulky substituents at the low-valent center and/or donor–acceptor stabilization, tremendous progress has been achieved over the last 30 years. Nevertheless, divalent species with element(II)–hydrogen bonds [H_2E: and R(H)E:, E = Si, Ge, Sn, Pb; R = organic groups, amines] are particularly difficult to stabilize because of the lack of steric protection.[1c,g] The first tin(II) hydride **1** without donor substituents was reported by Power et al. in 2000.[2] This hydride has a dimeric structure with bridging hydrido ligands, even though a very large terphenyl group was employed.

As mentioned above, donor–acceptor stabilization is another powerful method and can easily be combined with bulky substituents. The N-heterocyclic heavier Group 14 carbene analogues **2a**,**b**[3a,b] and **3a–c**[4] (Scheme 1) bear N-bound organic groups of considerable size. Additionally, it has been shown that the latter compounds benefit from 6π-electron delocalization.[5]

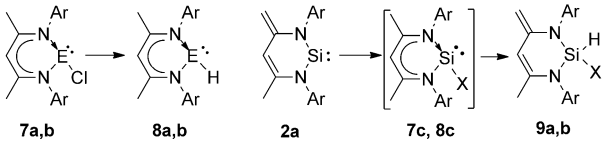
Recently, intra- and intermolecular donor–acceptor stabilization has also allowed the isolation and characterization of several elusive low-valent Group 14 molecules, such as disilicon **4**,[6] the parent silylene **5**,[7] and related alkene analogues **6a,b** (E = Ge, Sn; Scheme 1).[8] Main-group and transition-metal hydrides are of special interest because of their key role for numerous synthetic transformations (for example, hydrometalations of unsaturated organic substrates) on a laboratory and industrial scale and as intermediates in various reactions.[9]

With respect to hydrometalations using Group 14 element hydrides, hydrosilylation has developed into one of the most important and versatile synthetic method in materials and fine-chemical syntheses.[10] Accordingly, the suitability of



Scheme 1. Dimeric tin(II) hydride **1** and N-heterocyclic carbene analogues **2a**,**b** (E = Si, Ge) and **3a–c** of heavier Group 14 elements with 6π electron systems. Donor-stabilized $(Si^0)_2$ **4**, and donor–acceptor-stabilized H_2Si: **5** and $H_2Si{=}EH_2$ **6a**,**b**. D = :C{N(2,6-*i*Pr$_2$C$_6$H$_3$)CH}$_2$, A = B_3H_7, A′ = $W(CO)_5$. **3a–c**: E = Si, Ge, Sn; **6a**,**b**: E = Ge, Sn. Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

tetravalent Group 14 element hydrides (e.g. $R_3E{-}H$) for hydrometalations has been widely investigated.[1g,11] This is in contrast to the chemistry of divalent group 14 hydrides which is far less explored (Ge, Sn) or even hitherto unknown for silicon. The first terminal monomeric hydrides of Ge^{II} and Sn^{II}, LGeH (**8a**; Scheme 2; L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) and LSnH (**8b**), were reported by Roesky et al.[12] in 2006, and their reactivity towards homo- and heteronuclear multiple bonds has been investigated.[13] Both compounds **8a**,**b** are accessible from the corresponding germanium(II) and tin(II) chloride, $LGe^{II}Cl$ (**7a**) and $LSn^{II}Cl$ (**7b**), through a Cl/H metathesis reaction (Scheme 2).



Scheme 2. Monomeric germanium(II) and tin(II) chlorides **7a**,**b** and hydrides **8a**,**b**. Synthesis of silicon(IV) compounds **9a**,**b** from silylene **2a** via the elusive 1,4-adduct **7c**, **8c. 7a**, **8a**: E = Ge; **7b**, **8b**: E = Sn; **7c**, **9a**: X = Cl, **2a** + HCl; **8c**, **9b**: X = H, **2a** + NH_3BH_3.

However, the same strategy cannot be applied for the synthesis of the analogous silicon(II) hydride **8c** because the analogous silicon(II) precursor **7c** is not accessible. Thus, the reaction of stable silylene **2a** with HCl in Et_2O at ambient temperature yields, via the elusive 1,4-adduct **7c**, chlorosilane **9a** almost quantitatively. Likewise, the direct hydrogenation of the germylene analogue **2b**[3b] with ammonia–borane

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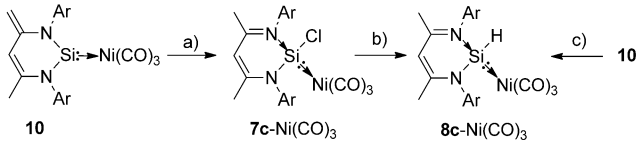
(H_3BNH_3) affords solely the 1,4-adduct LGeH (**8a**),[14] whereas the similar hydrogenation reaction of silylene **2a** with ammonia–borane leads merely to the corresponding 1,1-addition product, silicon(IV) dihydride **9b** (Scheme 2).

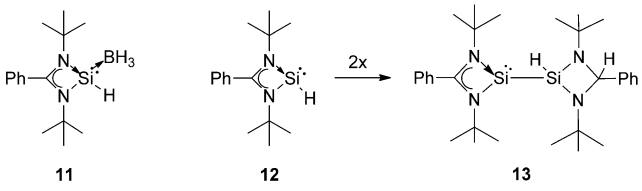
Recently, we have shown that the formation of the thermodynamically preferred 1,1-adduct of silylene **2a** from the initially formed, kinetically favored 1,4-addition product can be prevented by coordination of the Si^{II} donor center of **2a** to the {$Ni(CO)_3$} complex fragment, leading to the corresponding silylene precursor complex **10**.[15] Applying this chemical trick has now enabled us to synthesize the first isolable silicon(II) hydride nickel(0) complex [(**8c**)$Ni(CO)_3$] (Scheme 3), which turned out to be suitable for a silicon(II)-hydrosilylation of alkynes.



Scheme 3. Synthesis of donor–acceptor-stabilized silicon(II) hydride [(**8c**)$Ni(CO)_3$] from silylene–{$Ni(CO)_3$} complex **10** in one step or two steps via donor–acceptor stabilized silicon(II) chloride [(**7c**)$Ni(CO)_3$]. a) HCl, b) Li[BEt_3H], c) NH_3BH_3.

Two pathways to synthesize the new silicon(II) hydride nickel(0) complex [(**8c**)$Ni(CO)_3$] from the precursor **10** in acceptable yields have been established. A two-step method starts with the 1,4-addition of HCl to complex **10** to yield the desired [LSi(Cl)–$Ni(CO)_3$] complex [(**7c**)$Ni(CO)_3$], followed by a substitution of the chloride by hydride to yield the isolable silicon(II) hydride complex [(**8c**)$Ni(CO)_3$]. This complex is also directly accessible from **10** with ammonia–borane as hydrogen source under mild reaction conditions in good yields (Scheme 3).

A related, BH_3-protected silicon(II) hydride, $L'Si^{II}(H)BH_3$ (**11**)[16] with a different ligand has been synthesized recently from $L'Si^{II}(Cl)BH_3$ ($L' = PhC(NtBu)_2$) by reaction with K-selectride (K[$B(sBu)_3H$]; Scheme 4). No reactivity of the hydride **11** has yet been reported. Reaction of the unprotected precursor $L'Si^{II}Cl$, however, gave the dimeric silicon(II) compound **13**. So et al. suggested the formation of silicon(II) hydride **12** as an intermediate, which undergoes dimerization by hydrosilylation.[17]



Scheme 4. BH_3-protected silicon(II) hydride **11** and formation of silyl silylene **13** by intermolecular hydrosilylation of free silicon(II) hydride **12**.

The synthesis of [(**7c**)$Ni(CO)_3$] from **10** with HCl in Et_2O proceeds even at low temperature (−78 °C). The ^1H NMR spectrum of [(**7c**)$Ni(CO)_3$] is consistent with the suggested 1,4-addition product. Accordingly, the ^{29}Si NMR chemical shift ($\delta = 44.1$ ppm) is similar to that of related complexes.[15a] In a subsequent step, [(**7c**)$Ni(CO)_3$] was allowed to react with Li[$HBEt_3$] to give the desired silicon(II) hydride [(**8c**)$Ni(CO)_3$] as well as lithium chloride and BEt_3, which were removed by filtration and evaporation of all volatile components, respectively. Alternatively, silicon(II) hydride [(**8c**)$Ni(CO)_3$] can also be synthesized directly from **10** with ammonia–borane as a convenient hydrogenation reagent.[16,18] The hydrogenation of the silylene complex **10** proceeds at room temperature. The ^1H NMR spectrum of [(**8c**)$Ni(CO)_3$] shows a new singlet at $\delta = 6.15$ ppm ($^1J_{Si,H} = 154$ Hz), which can be assigned to the Si–H proton. The ^{29}Si NMR chemical shift ($\delta = 45.1$ ppm) is close to that of complex [(**7c**)$Ni(CO)_3$]. The Si–H stretching frequency cannot be assigned precisely because the bands are superimposed by the strong CO bands in the range 2050–1950 cm^{-1}; however, it can be concluded that they are shifted to lower wavenumbers in comparison to compounds **9a**,**b** ($\tilde{\nu} = 2238$, 2168 cm^{-1}; Scheme 2) and most typical Si^{IV} hydrides ($\tilde{\nu} = 2300$–1950 cm^{-1}). The comparison of the CO stretching vibrations of compounds [(**7c**)$Ni(CO)_3$] and [(**8c**)$Ni(CO)_3$] (A_1 mode: $\tilde{\nu} = 2057$ [(**7c**)$Ni(CO)_3$], 2045 cm^{-1} [(**8c**)$Ni(CO)_3$]) clearly indicates a stronger σ-donor capability of the silicon(II) hydride ligand in [(**8c**)$Ni(CO)_3$] compared to the silicon(II) chloride ligand in [(**7c**)$Ni(CO)_3$]. In fact, the CO stretching frequency of [(**8c**)$Ni(CO)_3$] is shifted to even lower wavenumbers, as observed for the strongest σ-donor ligand of this type known to date.[15a]

The solid-state structures of compounds [(**7c**)$Ni(CO)_3$] and [(**8c**)$Ni(CO)_3$] were confirmed by single-crystal X-ray analyses.[19] Suitable crystals of [(**7c**)$Ni(CO)_3$] (Figure 1) and [(**8c**)$Ni(CO)_3$] (Figure 2) were obtained from concentrated toluene solutions at −20 °C. Both compounds crystallize in

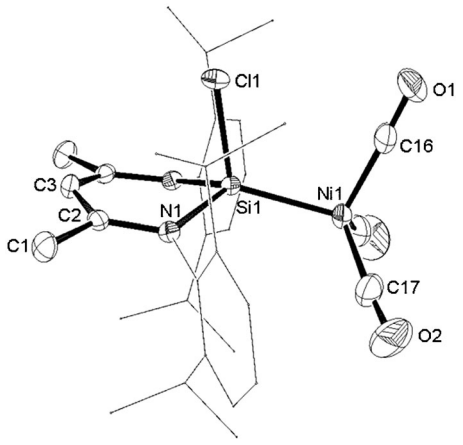


Figure 1. Molecular structure of [(**7c**)$Ni(CO)_3$]. Thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–Ni1 223.6(1), Si1–Cl1 214.3(1), Si1–N1 183.0(2), N1–C2 134.1(3), C1–C2 150.4(3), C2–C3 138.9(3); N1-Si1-N1 95.95(9), N1-Si1-Ni1 122.85(7), N1-Si1-Cl 97.65(7), Ni-Si-Cl 114.40(5).

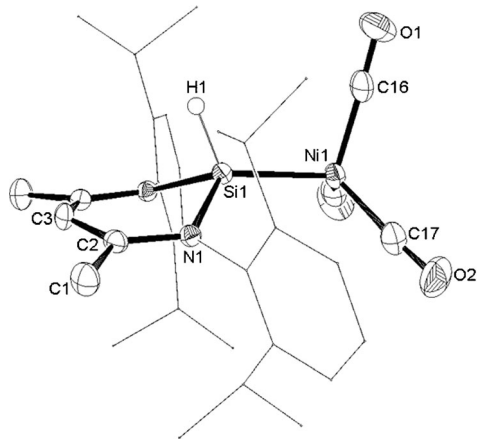


Figure 2. Molecular structure of $[(\mathbf{8c})Ni(CO)_3]$. Ellipsoids set at 50% probability; hydrogen atoms except that of Si1 are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–Ni1 225.24(8), Si1–N1 183.43(16), N1–C2 134.0(3), C1–C2 150.4(3), C2–C3 139.1(2); N1-Si1-N1 95.42(8), N1-Si1-Ni1 121.67(6).

the monoclinic space group $P2_1/m$ with two molecules in the asymmetric unit. The atoms of the C_3N_2 backbones of $[(\mathbf{7c})Ni(CO)_3]$ and $[(\mathbf{8c})Ni(CO)_3]$ are nearly co-planar.

The silicon centers of the complexes are coordinated in a distorted-tetrahedral fashion and the silicon atoms are out of the mean plane of the ligand backbone by 69.4 pm and 71.2 pm, respectively. The acute N-Si-N angles (96°, $[(\mathbf{7c})Ni(CO)_3]$ and 95°, $[(\mathbf{8c})Ni(CO)_3]$) indicate an increased p character of the Si–N bonds, whereas the larger Ni-Si-N angles (122–123°) point to increased s character of the Si–Ni bonds.

As mentioned above, the Ge^{II} and Sn^{II} hydrides **8a**,**b** are able to undergo hydrometalation reactions (for example with alkynes and CO_2) at room temperature without the presence of a catalyst.[13] The facile access to $[(\mathbf{8c})Ni(CO)_3]$ prompted us to investigate whether the silicon(II) hydride complex is suitable to undergo hydrosilylation reactions with stoichiometric amounts of alkynes even without an exogenous catalyst. Silicon(II) hydrides and silylene metal complexes have been employed directly or suggested as intermediates in hydrosilylations of C–C and C–N multiple bonds on the basis of experimental data and DFT calculations by Tilley,[20] Tobita,[21] and others. In fact, $[(\mathbf{8c})Ni(CO)_3]$ reacts in a straightforward manner with diaryl-substituted alkynes at 90 °C in toluene solution, even though the space around the Si–H bond is highly crowded by two bulky aryl ligands and a $\{Ni(CO)_3\}$ fragment (Scheme 5). The hydrosilylation of the symmetrical alkyne diphenylacetylene with $[(\mathbf{8c})Ni(CO)_3]$ proceeds stereoselectively and affords only the *cis* addition product $[(LSi(PhC{=}CHPh)Ni(CO)_3)$ (**14a**) bearing a Si^{II}-alkenyl subunit. The structure was confirmed by X-ray diffraction analysis (see Figure 3).[19] The ^1H NMR spectrum of compound **14a** shows the presence of a new singlet at $\delta =$ 8.14 ppm, which can be assigned to the proton of the alkene moiety. The resonance in the ^{29}Si NMR spectrum appears at $\delta = 64.9$ ppm.

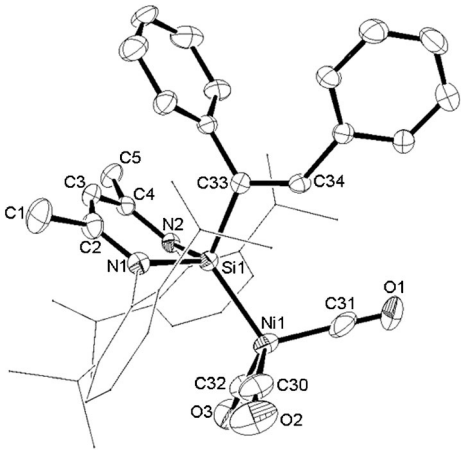
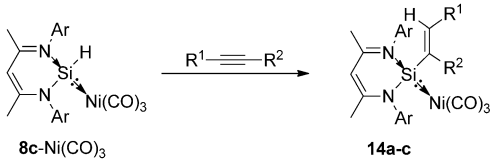


Figure 3. Molecular structure of **14a**. Ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–Ni1 227.5(1), Si1–N1 185.3(4), Si1–N2 184.6(3), N1–C2 133.9(5), N2–C4 135.6(5), C1–C2 149.4(5), C2–C3 140.5(5), C3–C4 136.4(5), C4–C5 151.3(5), Si1–C33 193.8(5), C33–C34 134.1(7); N1-Si1-N2 95.6(1), N1-Si1-Ni1 115.8(1), N2-Si1-Ni1 118.2(1), N1-Si1-C33 100.5(2), N2-Si1-C33 101.5(2), Ni1-Si1-C33 121.0(1).

Suitable crystals of compound **14a** (Figure 3) were obtained from a concentrated *n*-hexane solution at −20 °C. Compound **14a** crystallizes in the triclinic space group $P\bar{1}$. The metric of the backbone of **14a** is comparable to that of $[(\mathbf{8c})Ni(CO)_3]$ and thus nearly co-planar. Remarkably, the alkyne insertion into the Si–H bond in $[(\mathbf{8c})Ni(CO)_3]$ leads merely to a marginal change of the N-Si-N angle compared to the precursor. However, the sterically congested alkene subunit produces smaller Ni-Si-N angles (115°, 118°). The Si–Ni distance (227.5(1) pm) indicates a somewhat weaker bond after the hydrosilylation.

DFT calculations (see the Supporting Information for further details) of model compounds **15**–**18** (Figure 4) were



Scheme 5. Hydrosilylation of diarylacetylenes with compound $[(\mathbf{8c})Ni(CO)_3]$. Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; **14a**: R^1 = R^2 = Ph, **14b**: R^1 = *p*-Tol, R^2 = Ph, **14c**: R^1 = Ph, R^2 = *p*-Tol.

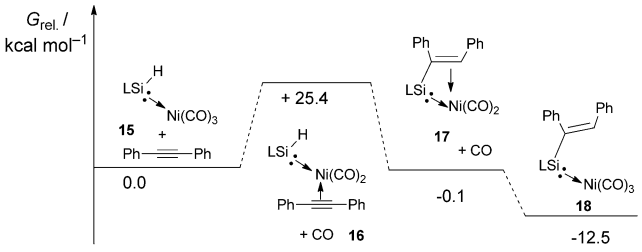


Figure 4. Relative energies of model compounds **15**–**18** as derived from DFT calculations. L = HC(MeCNPh)$_2$.

performed at the B3LYP level using 6-31G(d) basis set for Si, N, C, O, and H atoms and the LANL2DZ level for the Ni atom with the Gaussian 03 program package to gain insight into the mechanism of the hydrosilylation of alkynes with the silicon(II) hydride complex [(**8c**)Ni(CO)$_3$]. Because no reasonable pathway could be found for the alkyne to approach the Si–H bond of model compound **15**, we propose that the hydrosilylation is mediated by the nickel center. This proposal is in accordance with results from calculations that revealed that the initial step of the reaction could be a facile ligand exchange of CO at the Ni center by the alkyne to give the model compound **16** bearing a {Ni(CO)$_2$(alkyne)} subunit; this step requires $+25.4$ kcal mol^{-1}. Subsequently, the Si–H bond can add across the Ni-coordinated C–C triple bond to yield the Ni(CO)$_2$(Si^{II}-alkenyl) olefin complex **17** in a slightly exothermic reaction. A similar mechanism was reported for the metal-catalyzed hydrosilylation of ethene with a ruthenium silylene complex.[24] Finally, the Si^{II}-alkenyl olefin ligand can be replaced by CO in an exothermic reaction ($\Delta G_{rel} = -12.5$ kcal mol^{-1}), affording complex **18** (Figure 4). A nickel hydride species that could connect compounds **16** and **17** as an intermediate was located on the hypersurface. However, this structure seems to be too high in energy ($\Delta G_{rel} = +44.8$ kcal mol^{-1}) to be relevant for this reaction (see the Supporting Information).

To support the proposed mechanism, the hydrosilylation reaction was studied in an atmosphere of CO under conditions otherwise identical to those applied before. The presence of excess CO (about 60 equivalents as estimated from the volume of the reaction vessel; see the Supporting Information) completely suppressed the formation of compound **14a**, as judged by ^{1}H NMR spectroscopy. This gives some evidence that dissociation of a CO ligand and coordination of diphenylacetylene is involved in the rate-determining step.

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package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Absorption corrections were performed by using the SCALE3 ABSPACK program.[23] CCDC 837329 (**7c**), 837327 (**8c**), and 837328 (**14a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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