

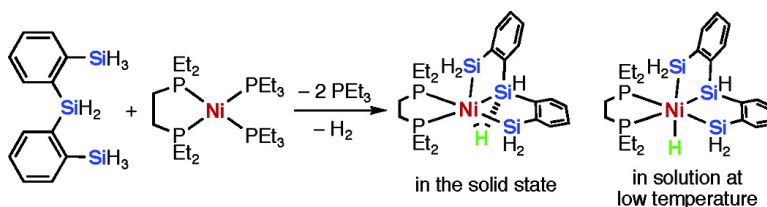
Communication

**Reaction of [2-(SiH)CH]SiH with Ni(EtPCHCHPEt)(PEt):
 Characterization of η -(Si-H)Ni and Ni-H Complexes**

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Reaction of $[2-(\text{SiH}_3)\text{C}_6\text{H}_4]_2\text{SiH}_2$ with $\text{Ni}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)(\text{PEt}_3)_2$: Characterization of $\eta^2-(\text{Si}-\text{H})\text{Ni}$ and $\text{Ni}^{\text{IV}}-\text{H}$ Complexes

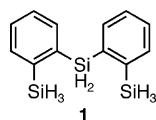
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The chemistry of silyl/silylene transition-metal complexes is rapidly growing because of its importance for understanding and developing transition-metal-catalyzed reactions of silicon compounds as well as its unique properties.¹ One of the most important methods to prepare silyl/silylene transition-metal complexes is the reaction of hydrosilanes with low-valent transition-metal complexes.^{1c} The reaction of a Si–H bond with late transition-metal complexes usually results in oxidative addition to form (silyl)(hydrido)metal species, while it occasionally stops at the stage of Si–H σ -bond coordination to the metal to form $\eta^2-(\text{Si}-\text{H})$ metal complexes.^{1,2} In the case of group 10 metals, oxidative addition of Si–H bond easily takes place, and therefore, $\eta^2-(\text{Si}-\text{H})$ metal complexes are rather rare and are known only in some dinuclear species of platinum³ and palladium.^{3e,4} In this communication, we report the isolation and structure determination of a bis(silyl)[$\eta^2-(\text{Si}-\text{H})$]nickel complex, which proved to exist, in solution at low temperatures, as a tris(silyl)(hydrido)nickel(IV) complex by NMR spectroscopy as well as by theoretical calculation.

In the course of our study on the stabilization of silylmetal complexes in formal high oxidation states by using chelating silyl ligands,⁵ bis(2-silylphenyl)silane (**1**) was prepared as a precursor of tridentate silyl ligand,⁶ which we expected to be useful for stabilization of unstable and/or unknown types of silyl transition-metal complexes such as tris(silyl)(hydrido)-⁷ and hexasilyl^{5e} transition-metal complexes.



The reaction of **1** with $\text{Ni}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)(\text{PEt}_3)_2$ **2**^{5d} in toluene at 0 °C for 10 min afforded complex **3** in 77% isolated yield. The structure of **3** was determined by single-crystal X-ray analysis at 113 K to be a bis(silyl)[$\eta^2-(\text{Si}-\text{H})$]nickel complex (Figure 1). The structure of **3** can be described to be distorted trigonal-bipyramidal (DTBP) with Si1, $\eta^2-(\text{Si}2-\text{H})$, and P2 ligands at equatorial positions. The Ni–Si2 distance (2.3480(8) Å) is longer than the known Ni–Si bonds (2.14–2.30 Å)^{5c,d,8} and reflects the $\eta^2-(\text{Si}-\text{H})\text{Ni}$ character, while Ni–Si1 and Ni–Si3 distances are within the range of the known Ni–Si bond distances. IR spectrum of the crystal showed a broad absorption around 1600 cm^{-1} that is assignable to the $\text{Ni}\cdots\text{H}\cdots\text{Si}$ moiety.³

¹H NMR spectrum of **3** at 20 °C (Figure 2a) showed the signal for Si2–H at normal position (5.67 ppm), and it showed the signal for five hydrogens (two SiH₂ and one bridged hydrogen) at 2.61

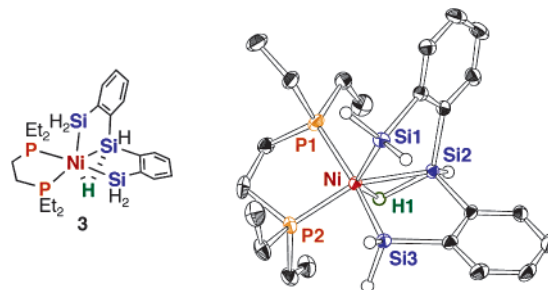


Figure 1. Molecular structures of complex **3** (50% probability level). Selected bond distances (Å) and angles (deg): Ni–H1, 1.47(3); Ni–Si1, 2.2552(6); Ni–Si2, 2.3480(8); Ni–Si3, 2.2445(6); Ni–P1, 2.2156(6); Ni–P2, 2.1978(6); Si2–H1, 1.75(3); Si1–Ni–H1, 130(1); Si1–Ni–Si2, 82.61(2); Si1–Ni–Si3, 79.96(2); Si1–Ni–P1, 91.99(3); Si1–Ni–P2, 129.20(3); Si2–Ni–H1, 48(1); Si2–Ni–Si3, 88.05(3); Si2–Ni–P1, 102.97(2); Si2–Ni–P2, 146.32(3); Si3–Ni–P1, 165.49(4); Si3–Ni–P2, 87.50(2); P1–Ni–P2, 88.34(2); Ni–Si2–H1, 38.8(9); Ni–H1–Si2, 92(1).

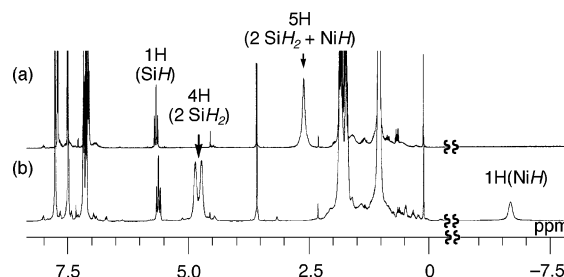


Figure 2. ¹H NMR spectra of complex **3** in THF-*d*₈ at (a) 20 °C and (b) –80 °C.

ppm as a broad singlet. The latter signal indicates that rapid exchange of the five hydrogens takes place at 20 °C, which is further supported by ²⁹Si NMR spectroscopy. ²⁹Si{¹H} NMR spectrum at 20 °C showed two triplets: one at 34.4 ppm (²J(P,Si) = 40 Hz) for Si2 and the other at –2.3 ppm (²J(P,Si) = 22 Hz) for Si1 and Si3 (Figure 3a). In ¹H-nondecoupled ²⁹Si NMR spectrum (Figure 3b), the former signal further splits into two by coupling with one hydrogen with a normal ¹J(H,Si) (173 Hz), while the latter signal coupled with *five* hydrogens with a smaller ¹J(H,Si) (80 Hz). At –80 °C, the broad ¹H NMR signal of five hydrogens splits into two signals: one at 4.79 ppm for four hydrogens on Si1 and Si3 and the other at –6.70 ppm for one hydrogen on the nickel (Figure 2b). The ²⁹Si NMR signal of Si1 and Si3, upon cooling, disappeared at –50 °C (too broad to be observed) but reappeared at –80 °C as a broad triplet coupled with *two* hydrogens with a normal ¹J(H,Si) (173 Hz), while that of Si2 showed virtually no change between 20 and –80 °C (Figure 3d). The NMR data at –80 °C suggest the exchange of hydrogens is frozen at this temperature, although the

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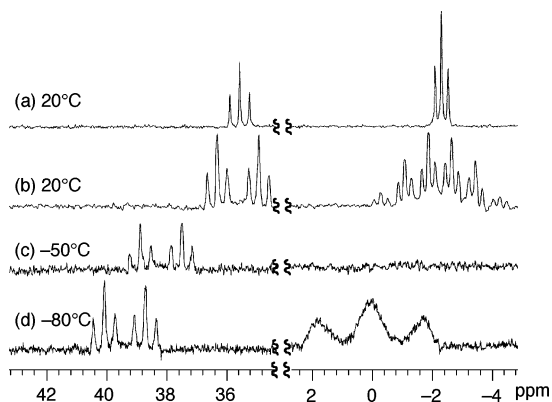


Figure 3. ^{29}Si NMR spectra of complex **3** in $\text{THF-}d_8$. (a) ^1H -decoupled spectrum. (b)–(d) ^1H -nondecoupled spectra.

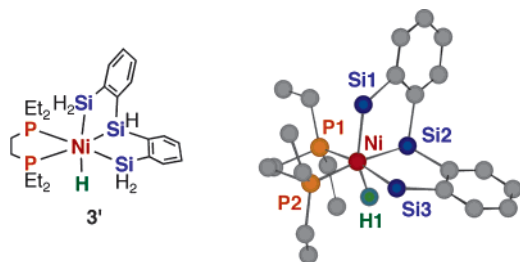


Figure 4. Molecular structure of **3'** optimized with B3LYP/6-31g* (Ni, Si, and P atoms), cc-pVDZ (H1 atom), 3-21G* (C and other H atoms). Only H atom bound to Ni is shown for clarity. Selected bond distances (Å) and angles (deg): Ni–H1, 1.482; Ni–Si1, 2.303; Ni–Si2, 2.266; Ni–Si3, 2.249; Ni–P1, 2.221; Ni–P2, 2.205; Si2···H1, 2.362; Si1–Ni–H1, 153.8; Si1–Ni–Si2, 83.8; Si1–Ni–Si3, 94.9; Si1–Ni–P1, 99.9; Si1–Ni–P2, 101.0; Si2–Ni–H1, 74.9; Si2–Ni–Si3, 85.3; Si2–Ni–P1, 92.9; Si2–Ni–P2, 174.2; Si3–Ni–P1, 164.9; Si3–Ni–P2, 90.7; P1–Ni–P2, 89.5; Ni–Si2–H1, 37.3; Ni–H1–Si2, 67.8.

structure of the complex is still fluxional as judged by the single ^{29}Si NMR signal for Si1 and Si3 as well as a single $^{31}\text{P}\{^1\text{H}\}$ NMR signal (see Supporting Information). Since the ^{29}Si NMR signal of Si2 couples with only one hydrogen even at -80°C , the structure of **3** in solution at -80°C is assumed to be a formally tetravalent tris(silyl)(hydrido)nickel **3'** rather than η^2 -(Si–H) structure, which is supported by the absence of an absorption around 1600 cm^{-1} in the IR spectrum in solution and the following theoretical calculation.

The structure of **3** was fully optimized with density functional theory (DFT) employing Becke's three-parameter exchange and Lee–Yang–Parr's correlation functionals (B3LYP) using 6-31G* basis sets for Ni, Si, and P atoms, cc-pVDZ for H atom bound to Ni, and 3-21G* for C and other H atoms.⁹ The determined geometry is shown in Figure 4, which is envisioned to represent the most stable structure of **3** in solution.¹⁰ The Si2···H1 distance is now 2.362 Å and shows no bonding. The Ni–Si2 distance (2.266 Å) is within the range of the known Ni–Si bond distance.^{5c,d,8} The structure of the complex changed from DTBP in the X-ray structure to distorted octahedral, and it suggests high sensitivity of the structure to the environment. To the best of our knowledge, this is the first example of formally tetravalent nickel hydride complex.¹¹

In summary, the nickel complex obtained by the reaction of **1** with **2** has proved to be the first η^2 -(Si–H)nickel complex **3** in the solid state and the first $\text{Ni}^{\text{IV}}\text{–H}$ complex **3'** in solution at low temperature. Further studies on the reactivity and the detail of the electronic state of **3** are now underway.

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Supporting Information Available: Synthesis and characterization data, VT NMR and IR spectra of **3**, and Cartesian coordinate of **3'** (PDF). X-ray crystallographic file for **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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