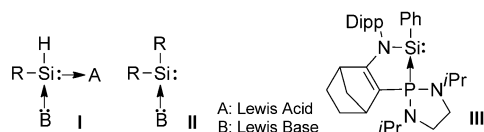


Synthesis of a Phosphine-Stabilized Silicon(II) Hydride and Its Addition to Olefins: A Catalyst-Free Hydrosilylation Reaction**

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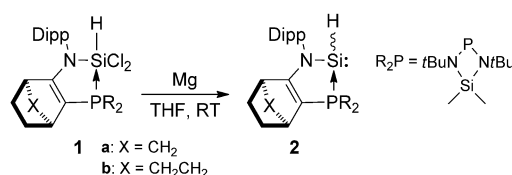
Hydrosilanes (R_3Si-H) are powerful chemical tools and are often used as hydride donors or as reducing agents owing to the labile silicon–hydrogen bond, which has a significant negative polarization toward the hydrogen atom ($Si^{\delta+}-H^{\delta-}$).^[1] Particularly, transition-metal-catalyzed addition of silicon hydrides to unsaturated substrates such as olefins or ketones—the hydrosilylation reaction—is one of the most important reactions in synthetic chemistry.^[2] Furthermore, the versatile reactivity of hydrosilanes also allows for their use as precursors of various highly reactive intermediates, such as silylium cations,^[3–5] silyl radicals,^[6] and silylenes.^[7]

Although a broad range of tetravalent hydrosilanes are known, divalent species (silylenes) with a terminal hydride are highly reactive, and their chemistry is very poorly developed. Indeed, only a few stable and isolable silicon(II) hydride species are known, and most of them are stabilized transition-metal complexes.^[8] Very recently stable bis-adducts (Lewis acid)(Lewis base) $Si^{II}H$ **I**, have also been reported.^[9]



Base-stabilized silylenes **II** have attracted much attention because they are thermally stable and they keep their reactivity as Si^{II} species.^[10–15] The efficiency of this methodology has been well demonstrated by the isolation of silicon(II) halides (SiX_2 , $X = Cl, Br$) as N-heterocyclic carbene complexes and their use in molecular silicon(II) chemistry.^[15a,16] We also recently reported the synthesis of a stable phosphine-stabilized silylene **III** (Dipp = 2,6-*i*Pr₂C₆H₃),^[17] which displays a unique ability to reversibly react with ethylene gas.^[18] However, the synthesis of isolable

base-stabilized three-coordinate silicon(II) hydride remains elusive,^[19] although the corresponding heavier germanium and tin analogues have already been synthesized.^[20] Herein, we present the synthesis and reactivity of the first stable and isolable phosphine-stabilized silicon(II) hydrides **2** (Scheme 1).



Scheme 1. The synthesis of phosphine-stabilized silicon(II) hydride **2**.

The phosphine-stabilized silicon(II) hydrides **2** were readily prepared by reduction of the corresponding dichlorosilane derivatives **1** using magnesium metal and were isolated as pale yellow crystals (70 % (**2a**), 79 % (**2b**)). The silicon(II) hydride **2a** appeared to be highly reactive, but it is thermally robust. Indeed, no degradation of **2a** was observed after heating a toluene solution under argon at 110 °C for several hours. In the ³¹P NMR spectrum, derivative **2a** displays two singlet signals ($\delta = 91.2$ and 90.4 ppm), in agreement with the presence of two diastereomers (60:40), as expected for this type of phosphonium silaylide.^[17] In the ²⁹Si NMR spectrum two doublets were observed in the same ratio, both having a typically large phosphorus–silicon coupling constant ($\delta = -44.8$ ppm ($^1J_{SiP} = 143.2$ Hz) and -38.0 ppm ($^1J_{SiP} = 140.1$ Hz)), thus indicating a direct silicon–phosphorus interaction. The signals corresponding to the terminal hydride appear as doublets in the ¹H NMR spectrum at a somewhat lower field ($\delta = 5.99$ ppm ($^2J_{PH} = 3.3$ Hz) and 5.76 ppm ($^2J_{PH} = 2.9$ Hz)). The ²⁹Si satellites (ca. 4.7 %) for the terminal hydrogen atoms appear as a doublet of doublets with a large silicon–hydrogen coupling constant ($^1J_{H-Si} = 85.1$ and 85.7 Hz), which indicates a direct silicon–hydrogen bond in **2a**. However, this value is much smaller than those observed for tetravalent silicon hydrides (150–380 Hz)^[21] or for silicon(II) species stabilized by the push–pull complexation system **I** (235 Hz).^[9]

The molecular structure of **2b** was unambiguously determined by X-ray crystallography,^[22] which reveals that the molecule is monomeric in the solid state (Figure 1). Although the geometric features of **2b** are quite similar to those of the reported phosphine-stabilized silylene **III**, which bears a phenyl group on the silicon atom, the tricoordinate Si^{II} center ($\Sigma\sigma_{Si\alpha} = 275^\circ$) is much more pyramidalized and has a more

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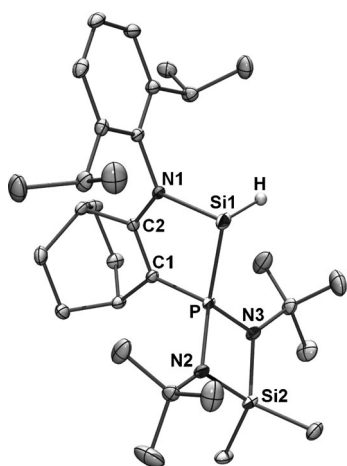


Figure 1. Molecular structure of **2b**. Thermal ellipsoids represent 30% probability. H atoms (Except for that on Si1) are omitted for clarity. The Si–H unit in **2b** was disordered over two positions, and only one molecular arrangement is shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–H 1.44(5), N1–Si1 1.840(13), P–Si1 2.318(15), P–C1 1.7344(13), C1–C2 1.3776(18), C2–N1 1.3593(17); N1–Si1–H 98.7(19), P–Si1–H 90.0(19), N1–Si1–P 86.8(6), Si1–P–C1 96.0(3), P–C1–C2 114.90(10), C1–C2–N1 122.84(12), C2–N1–Si1 119.2(5).

acute silylene angle (N1–Si1–H = 98.7°) than other silylene phosphine complexes ($\Sigma^\circ_{\text{Si}} = 297^\circ$, N1–Si1–C3 = 104.78° for **3**, Figure 2). This difference is probably caused by a decrease of the steric hindrance around the silicon center induced by the small hydrogen substituent. The Si^{II}-containing five-membered ring is quasi-planar, as indicated by the sum of the interior angles (597.5°).

We have recently reported the reversible [2+1] cycloaddition reaction of the silicon(II)-phosphine complex **III** with ethylene gas to form a pentacoordinate silirane.^[18] The silicon(II) hydride **2a** also reacts with olefins such as cyclopentene at 110°C, but in this case, instead of a cycloadduct,

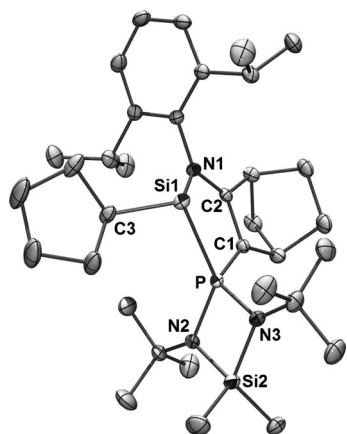
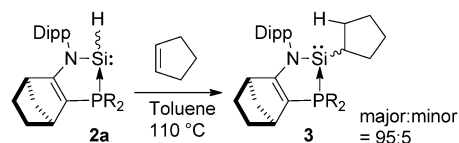


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: P–Si1 2.3272(6), P–C1 1.7245(17), Si1–N1 1.8458(14), Si1–C3 1.921(2), N1–C2 1.346(2), C1–C2 1.388(2); N1–Si1–C3 104.78(7), P–Si1–C3 105.14(6), C1–P–Si1 93.52(6), N1–Si1–P 87.67(5), C2–N1–Si1 115.52(11), N1–C2–C1 124.06(15).

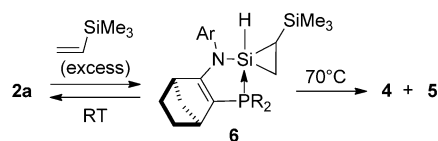
the cyclopentane substituted silicon(II)-phosphine complex **3** was obtained as a mixture of two diastereomers (40% yield of isolated product, Scheme 2). Formally, this result can be



Scheme 2. The olefin insertion reaction into the Si–H bond of **2a**.

rationalized by the addition of the silicon(II) hydride **2a** to the alkene functionality. The formation of **3** was unambiguously established by NMR spectroscopy as well as by an X-ray diffraction analysis (Figure 2). To our knowledge, this is the first example of a hydrosilylation reaction of an alkene involving a stable silicon hydride derivative without any catalyst. This type of reactivity has been postulated for the parent molecule (SiH_2) at much higher temperatures (ca. 600–1000 K).^[23]

In marked contrast, silicon(II) hydride **2a** reacts with an excess of vinyltrimethylsilane (58 equiv) at room temperature in a [2+1] cycloaddition reaction to give the corresponding pentacoordinate silirane **6** as a mixture of two diastereomers (**2a**:**6** = 1:3, 25°C; Scheme 3). Silirane **6** has been identified in

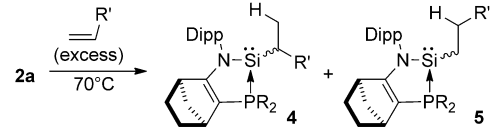


Scheme 3. Reaction of **2a** with vinyltrimethylsilane.

solution by the characteristic upfield ^{29}Si NMR chemical shifts for pentacoordinate siliranes^[18] ($\delta = -72.3$ and -70.2 ppm, $^1\text{J}_{\text{Si-P}} = 40.7$ and 36.2 Hz). At room temperature, cycloadduct **6** appears to be in equilibrium with **2a**, which was quantitatively recovered after removal of the olefin under vacuum. A van't Hoff analysis of the variable-temperature ^{31}P NMR spectroscopy data affords a Gibbs free energy ($\Delta G_{20^\circ\text{C}}$) of (0.803 ± 0.128) kcal mol^{−1} for the olefin addition reaction to **2a**. This small endothermic value explains the reversibility of the reaction as well as the equilibrium preferentially displaced to **2a**. Upon heating the mixture in toluene at 110°C for 2 h, **6** transforms into the corresponding ethylene insertion products (**4**_{TMS} and **5**_{TMS}), suggesting that silirane **6** is an intermediate of the hydrosilylation reaction.

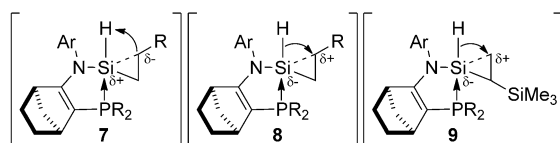
Similarly, hydrosilylation of other monosubstituted olefins has been performed, which leads to the formation of two regioisomers: Markovnikov-type products **4** as well as the anti-Markovnikov-type adducts **5**. The regioselectivity of the reaction appears to be strongly dependent on the nature of the olefin used (Table 1).

The hydrosilylation reactions involving **2a** mainly give anti-Markovnikov selectivity, suggesting that the reaction

Table 1: Regioselectivity in hydrosilylation reactions of different mono-substituted olefins with **2a**.


R	TMS	Bn	CH ₂ TMS
4:5	50:50	20:80	2:98

proceeds by hydride migration from the silicon atom to a carbon atom of the silirane ring (**8**, Scheme 4) rather than by a deprotonation of Si–H by the negatively polarized carbon

**Scheme 4.** Possible transition states for the hydrosilylation reactions of monosubstituted olefins.

center (**7**). Indeed, the best regioselectivity was obtained in the case of allyltrimethylsilane (**4**_{CH₂TMS}:**5**_{CH₂TMS} = 2:98), which can be explained by an energetically favored pathway arising from a transition state of type **8**, in which the positively charged carbon center is well-stabilized by the trimethylsilyl group (β-effect).^[24] Indeed, a decreased regioselectivity has been observed in the case of nonsilylated olefins such as allylbenzene (**4**_{Bn}:**5**_{Bn} = 20:80). Furthermore, in the case of the vinyltrimethylsilane, the same electronic effect increases the relative amount of the Markovnikov adduct **4**_{TMS}. In this case, the less substituted carbon center is at the β-position of the trimethylsilyl group (**9**), which should favor the hydride migration to this carbon atom. Despite these electronic effects, the proportion of the anti-Markovnikov isomer remains significant, probably for steric reasons (**4**_{TMS}:**5**_{TMS} = 50:50, Table 1). In fact, the observed regioselectivity is very similar to that obtained in the case of hydroboration reactions.^[25]

In conclusion, we have successfully synthesized a stable and isolable tricoordinate silicon(II) hydride stabilized by a phosphine ligand. Interestingly, this silicon hydride adds to olefins in an unprecedented catalyst-free hydrosilylation reaction. More detailed mechanistic studies on this hydrosilylation reaction involving silicon(II) hydrides as well as studies on other reactions are under active investigation.

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