Hydrosilylation

DOI: 10.1002/anie.201105639

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

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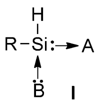
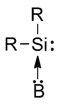
Hydrosilanes (R_3Si–H) are powerful chemical tools and are often used as hydride donors or as reducing agents owing to the labile silicon–hydrogen bond, which has a significant negative polarization toward the hydrogen atom ($Si^{\delta+}$–$H^{\delta-}$).[1] Particularly, transition-metal-catalyzed addition 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]

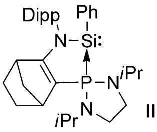


I



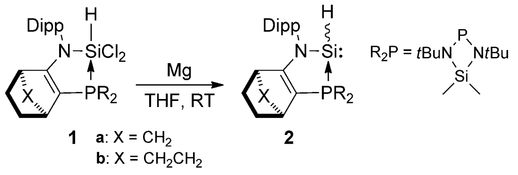
II

A: Lewis Acid
B: Lewis Base



III

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-$iPr_2C_6H_3$),[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 ^{31}P 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 ^{29}Si NMR spectrum two doublets were observed in the same ratio, both having a typically large phosphorus–silicon coupling constant ($\delta = -44.8$ ppm ($^1J_{\mathrm{SiP}} = 143.2$ Hz) and -38.0 ppm ($^1J_{\mathrm{SiP}} = 140.1$ Hz)), thus indicating a direct silicon–phosphorus interaction. The signals corresponding to the terminal hydride appear as doublets in the ^{1}H NMR spectrum at a somewhat lower field ($\delta = 5.99$ ppm ($^2J_{\mathrm{PH}} = 3.3$ Hz) and 5.76 ppm ($^2J_{\mathrm{PH}} = 2.9$ Hz)). The ^{29}Si satellites (ca. 4.7%) for the terminal hydrogen atoms appear as a doublet of doublets with a large silicon–hydrogen coupling constant ($^1J_{\mathrm{H\text{-}Si}} = 85.1$ 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 ($\Sigma°_{\mathrm{Si}\alpha} = 275°$) is much more pyramidalized and has a more

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[**] We are grateful to the CNRS and the ANR (NOPROBLEM) for support of this work. R.R. acknowledges the Ministerio de Educación (MEC, Spain) for a postdoctoral fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105639.

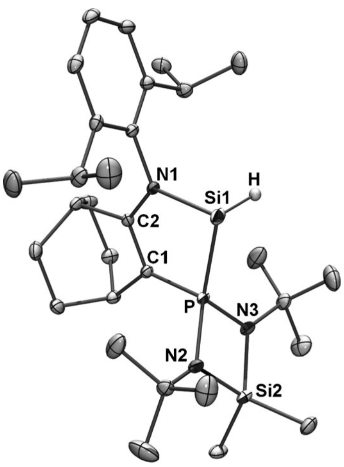


Figure 1. Molecular structure of **2b**. Thermal ellipsoids represent 30% probability. H atoms (Except for that on Si1) are omitted for clarity. The Si–H unit in **2b** was disordered over two positions, and only one molecular arrangement is shown for clarity. Selected bond lengths [Å] and angles [°]: 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 ($\Sigma°_{\text{Si}\alpha} = 297°$, 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, 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 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]

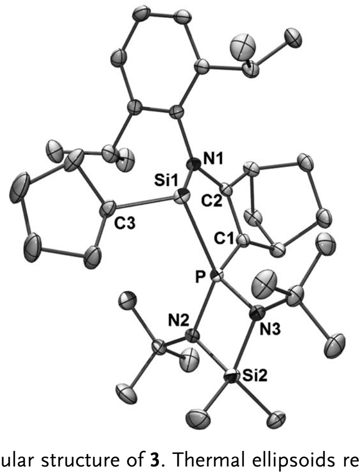
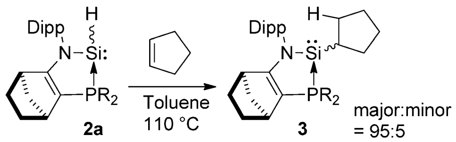
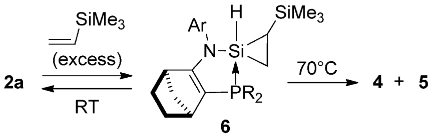


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: P–Si1 2.3272(6), P–C1 1.7245(17), Si1–N1 1.8458(14), Si1–C3 1.921(2), N1–C2 1.346(2), C1–C2 1.388(2); N1-Si1-C3 104.78(7), P-Si1-C3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



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

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 solution by the characteristic upfield ^{29}Si NMR chemical shifts for pentacoordinate siliranes[18] ($\delta = -72.3$ and -70.2 ppm, $^{1}J_{\text{Si-P}} = 40.7$ 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 ($\Delta G_{20°\text{C}}$) 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 ($\mathbf{4}_{\text{TMS}}$ and $\mathbf{5}_{\text{TMS}}$), suggesting that silirane **6** is an intermediate of the hydrosilylation reaction.

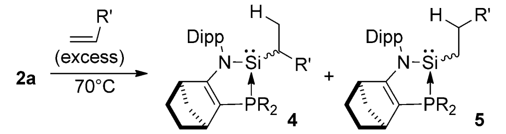


Scheme 3. Reaction of **2a** with vinyltrimethylsilane.

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).

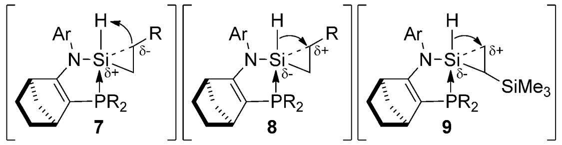
The hydrosilylation reactions involving **2a** mainly give anti-Markovnikov selectivity, suggesting that the reaction

Table 1: Regioselectivity in hydrosilylation reactions of different monosubstituted 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 center (**7**). Indeed, the best regioselectivity was obtained in the case of allyltrimethylsilane ($\mathbf{4}_{\mathrm{CH_2TMS}}:\mathbf{5}_{\mathrm{CH_2TMS}} = 2:98$), 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 ($\mathbf{4}_{\mathrm{Bn}}:\mathbf{5}_{\mathrm{Bn}} = 20:80$). Furthermore, in the case of the vinyltrimethylsilane, the same electronic effect increases the relative amount of the Markovnikov adduct $\mathbf{4}_{\mathrm{TMS}}$. 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 ($\mathbf{4}_{\mathrm{TMS}}:\mathbf{5}_{\mathrm{TMS}} = 50:50$, Table 1). In fact, the observed regioselectivity is very similar to that obtained in the case of hydroboration reactions.[25]



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

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.

Received: August 9, 2011

Keywords: hydrides · hydrosilylation · phosphorus · silicon · silylenes

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