

Reactive Intermediates

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Reversible Silylene Insertion Reactions into Si–H and P–H σ -Bonds at Room Temperature

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Abstract: Phosphine-stabilized silylenes react with silanes and a phosphine by silylene insertion into $E-H \sigma$ -bonds (E = Si, P) at room temperature to give the corresponding silanes. Of special interest, the process occurs reversibly at room temperature. These results demonstrate that both the oxidative addition (typical reaction for transient silylenes) and the reductive elimination processes can proceed at the silicon center under mild reaction conditions. DFT calculations provide insight into the importance of the coordination of the silicon center to achieve the reductive elimination step.

Oxidative addition and reductive elimination are exceedingly important processes in organometallic chemistry. The transition metal mediated bond activation is closely related to the oxidative addition step, while the reductive elimination is a crucial step for the formation of new bonds, and both processes are essential in many catalytic reactions.

Although for many years it was believed that only transition-metal centers could activate enthalpically stable bonds, several nonmetallic systems are known to be capable of performing these tasks.^[1] Notably, frustrated Lewis pairs^[2] are able to reversibly cleave H_2 .^[3] and therefore are active catalysts for hydrogenation reactions.^[4] Stable divalent species such as singlet carbenes and their heavier analogues can also activate small molecules at the nonmetal metallylene center by an oxidative addition.^[1b,4,5] Indeed, stable silylenes react with H_2 ,^[7] NH₃,^[8,9] and silicon hydrides under mild reaction conditions, thus leading to the corresponding Si^{IV}

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201606728. species.^[10] However, such oxidative addition reactions are not reversible since the reverse process (reductive elimination), which generates the less stable divalent silylenes, usually requires a thermal activation.^[11] Nevertheless, Tobita et al.^[12] recently reported the reversible reaction of NHC-supported (NHC = N-heterocyclic carbene) cationic metallogermylene with silanes, and Aldridge, Jones, and co-workers reported that diborylstannylene can undergo oxidative additions with both N–H and O–H bonds, with subsequent reductive eliminations.^[9] Recently, we reported that phosphine-supported Si^{II}

Recently, we reported that phosphine-supported Si^{II} complexes exhibit unusual stability, which is comparable to that of Si^{IV} derivatives, in spite of their enhanced silylenoid character. This peculiarity of Si^{II} complexes was highlighted by the reversible [2+1] cycloaddition reaction with ethylene at room temperature.^[13] With stannyl/Si^{II} and hydride/Si^{II} complexes, the activated alkene readily inserts into Si–H (-Sn) bonds, thus generating new Si^{II} complexes.^[14] Of particular interest, the ethylene insertion reaction is perfectly reversible at room temperature in the case of the Si^{II}–Sn complex.^[15] Herein we report an unprecedented reversible oxidative addition/reductive elimination of silanes and phosphines at the silylene center of the Si^{II}–H complexes **1**.

The Si^{II}-H complex **1A** readily reacts with phenylsilane (a) at room temperature to give the corresponding disilane **2A-a**, which was isolated as colorless crystals in 49% yield (Scheme 1). The presence of a disilane fragment is clearly



Scheme 1. The synthesis of the Si^{IV} hydrides **2**.

indicated by resonances at $\delta = -34.1$ ($J_{\text{Si-P}} = 7.3$ Hz, NSiH₂) and $\delta = -60.4$ ppm ($J_{\text{Si-P}} = 44.8$ Hz, PhSiH₂) in the ²⁹Si NMR spectrum, and they are within the typical shift range for amino-^[16] and phenyl-substituted^[17] disilanes. These chemical shifts, as well as, the moderate J_{SiP} coupling constants suggest a weak phosphine–silane interaction in solution. However, the two hydrogen atoms of the NSiH₂ fragment are not magnetically equivalent. Indeed, the ¹H NMR spectrum displays two signals with large J_{HP} coupling constants [$\delta =$ 5.23 (d-pseudo-t, $J_{\text{PH}} = 39.3$ Hz, $J_{\text{HH}} = 4.1$ Hz) and $\delta =$ 5.74 ppm (ddd, $J_{\text{PH}} = 22.1$ Hz, $J_{\text{HH}} = 5.2$ and 4.1 Hz)], thus

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suggesting a chiral pentacoordinate geometry around the silicon center resulting from the coordination of the phosphine. The single-crystal X-ray diffraction analysis of **2A-a** reveals a trigonal bipyramidal geometry around the Si1 center with H1 and P1 atoms in the apical positions (H1-Si1-P1 176.5°; Figure 1).^[18] This arrangement was clearly



Figure 1. Molecular structure of **2A-a**. Thermal ellipsoids shown at 30% probability. Disordered and H atoms (except for that on Si1 and Si2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-P1 3.344(1), Si2-P1 3.396(1), Si1-Si2 2.344(1), Si1-N1 1.753(2), Si2-C3 1.880(3), P1-C1 1.793(4), C1-C2 1.361(6), N1-C2 1.388(5); N1-Si1-Si2 121.7(1), Si1-Si2-C3 110.5(1), Si1-N1-C2 126.4(3), N1-C2-C1 131.6-(5), C2-C1-P1 127.8(4).

indicated by the presence of an AIM bond critical point between P1 and Si1 atoms (for more details, see the supporting information). As expected, the phosphine ligand only weakly coordinates to the silicon center as indicated by the long Si1-P1 distance (3.344 Å) as compared to other pentacoordinate phosphine-silicon complexes (2.407–2.987 Å),^[19] even though it is shorter than the sum of van der Waals radii (3.90 Å). The Si1-Si2 bond length (2.344 Å) is slightly longer than those observed for other disilanes (2.329–2.339 Å).^[20]

Of particular interest, monitoring the reaction by sila³¹P NMR spectroscopy shows that the conversion of **1A-a** stops at 97% and an extended reaction time does not change the ratios (Table 1). In fact, the completion of the reaction needs the addition of an excess of silane. In contrast, removal of phenylsilane under vacuum drives the reaction towards the starting **1A-a**. Also, the **1A/2A-a** ratio is temperature dependent, and the proportion of **1A** increases with

Table 1: Reaction of **1** with different E–H reagents (1 equiv, 298 K, C_6D_6): silylene (1)/silane (2) ratio, and equilibrium constants ($k_{ea2.1}$)

1	H-E	1/2 (298 K) ^[a]	К _{еq2-1(298 К)}	$\Delta {\rm G}_{\rm 298K}{}^{\rm [b]}$	$\Delta H_{\rm 298K}{}^{\rm [b]}$	$\Delta S_{_{298K}}^{}^{[b]}$
1A	а	3:97	5561.3	-5.2	-11.4	-21.5
1B	а	61:39	3.0	-0.8	-10.2	-32.0
1A	Ь	18:82	27.1	-1.9	-12.3	-35.3
1B	Ь	100:n.d.				
1A	с	6:94				
1B	с	33:67	53.3	-2.6	-12.8	-35.1

[a] Determined by ³¹P and ¹H NMR spectroscopy. [b] In kcal mol⁻¹.

Table 2: Silylene (1)/silane (2) molar ratio in the reaction of 1 with phenylsilane (1 equiv) in C_6D_6 at different temperatures.

T [°C]	25	40	50	60	70	80
1A/2A-a ^[a]	3:97	6:94	10:90	14:86	19:81	25:75
T [°C]	15	25	35	55	65	75
1B/2B-a ^[a]	61:39	71:29	80:20	90:10	94:6	96:4

[a] Determined by ³¹P and ¹H NMR spectroscopy.

temperature (Table 2). These results taken together clearly indicate that the reaction is an equilibrium process.

The steric congestion around the silicon center has a dramatic effect on the ratio between 1 and 2. Indeed, an increase of the steric hindrance (1B) shifts the equilibrium toward the starting, less-hindered 1B compared to the pentacoordinate disilane 2B-a. The same trend is observed in the reaction of 1A with the more hindered b, which gives an increased 1A/2A-b molar ratio. Furthermore, in the case of the more congested 1B and the more crowded b no traces of the disilane adduct 2B-b could be detected. However, we can unambiguously state that 1B and b do interact since the use of deuterated diphenylsilane (D₂SiPh₂) led to the formation of a deuterated Si^{II}–D complex. Similarly, the Si^{II} complexes 1 undergo reversible oxidative additions with diphenylphosphine (c) at room temperature.

The Si^{II}–Sn complex **3A** reacts with 1 equivalent of phenylsilane at 40 °C to give a mixture of disilanes (**2A-a**,



Scheme 2. Substituent exchange between the Si^{II}-Sn complex **3A** and phenylsilane by a reversible oxidative addition/reductive elimination process.

4A, and 5A) and 3A (Scheme 2). This result can be related to the readily reversible oxidative addition/reductive elimination reactions (Scheme 3). Although 1A was not detected, by extrapolating the already obtained results it is reasonable to suggest its transient formation from 4A by the reductive elimination of trimethylstannyl(phenyl)silane. The silylene 1A can subsequently react either with Ph₃SiH₃ or with Me₃Sn-SiH₂Ph (Si-H or Si-Sn activation) to give a mixture of Si^{IV} derivatives (2A-a, 4A, and 5A). The reversible nature of the reactions is clearly demonstrated by the exclusive formation of 2A-a and Me₃Sn-SiH₂Ph after the addition of an excess amount of phenylsilane (15 equiv) to this complex reaction mixture (Scheme 2). In this case, the excess amount of PhSiH₃, relative to Me₃Sn-SiH₂Ph, displaces the equilibrium to the formation of 2A-a. These results also demonstrate that not only E–H σ -bonds (E = Si, P) but also Si–Sn σ -bonds can be reversibly activated by phosphine-stabilized silvlene complexes.

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Angew. Chem. Int. Ed. 2016, 55, 1-5





Scheme 3. Possible reductive elimination reactions.

Usually reductive eliminations to produce low-valent silicon species from tetravalent silicon derivatives are strongly endothermic processes. For instance, the reductive elimination of hydrosilanes forms disilanes to generate transient silvlenes, and requires high temperatures (225-400 °C).^[11] Thus, in the case of the phosphine-stabilized silvlene complexes 1, the coordination of the silicon center is crucial to realizing readily reversible oxidative addition/reductive elimination reactions. Furthermore, it is well known that the disproportionation of chlorodisilanes to polychlorosilanes is a base-catalyzed reaction in which the nucleophilic catalyst coordinates to the silicon center, thus inducing the elimination of chlorosilanes and the formation of transient chlorosilvlenes.^[21] To better understand the role played by the ligand, we have calculated the Gibbs energies of the reactions between phenylsilane and several silylene complexes (1A and 6A) featuring different ligands.

As expected, the results clearly show that the nucleophilic character of the ligand strongly influences on the energy balance of the reaction (Figure 2). Indeed, a very strong nucleophilic ligand, such as an NHC, clearly disfavors the silylene insertion reaction ($6A \rightarrow 7A$, $\Delta G = +6.3 \text{ kcal mol}^{-1}$) but favors the reductive elimination step ($7A \rightarrow 6A$). For the phosphine-silylene complex **1A**, the oxidative addition is predicted to be slightly exothermic ($\Delta G = -6.5 \text{ kcal mol}^{-1}$), which is in good agreement with the experimental observation ($\Delta G_{298K} = -5.2 \text{ kcal mol}^{-1}$). In the absence of silicon coordination (L=H), the oxidative addition is strongly exergonic ($\Delta G_{298K} = -28.1 \text{ kcal mol}^{-1}$). From these calculations it is clear that the reductive elimination step is favored upon increasing the nucleophilicity of the ligand.



Figure 2. Calculated Gibbs free energy (in kcal mol⁻¹) for the reaction between silylene complexes and phenylsilane at the M06/6-31G(d,p) level of theory.

In conclusion, we have observed the oxidative addition of Si–H and P–H σ -bonds to the silicon center of phosphine-stabilized Si^{II} complexes (1) under very mild reaction conditions. Of particular interest, the reaction is reversible at room temperature, thus demonstrating that a reductive elimination can take place at a nonmetallic silicon center under extremely mild reaction conditions. DFT calculations indicate that the coordination of a nucle-ophilic ligand to the silicon center is crucial for the reductive elimination step. Detailed mechanistic studies and applications of the reaction are currently under active investigation.

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Communications

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reversible oxidative addition/reductive elimination at Si center

New inserts: Phosphine-stabilized silylenes react with silanes (or phosphine) by silylene insertion into E–H σ -bonds (E= Si,P) at room temperature to give the corresponding silanes. Of special interest, the process occurs reversibly at room temperature. These results demonstrate that both the oxidative addition and the reductive elimination processes can proceed at the silicon center under mild reaction conditions.