

# Reversible Dimerization of Phosphine-Stabilized Silylenes by Silylene Insertion into Si<sup>II</sup>–H and Si<sup>II</sup>–Cl $\sigma$ -Bonds at Room Temperature

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**Abstract:** Contrary to the classical silylene dimerization leading to a disilene structure, phosphine stabilized hydro- and chloro-silylenes (**2a,b**) undergo an unique dimerization via silylene insertion into Si–X  $\sigma$ -bonds (X = H, Cl), which is reversible at room temperature. DFT calculations indicate that the insertion reaction proceeds in one step in a concerted manner.

The dimerization of silylenes to the corresponding disilene is one of the most common reactions of these low-coordinate silicon species (type **A**). Since the synthesis of the first stable

species **III**,<sup>[6]</sup> **IV**,<sup>[7]</sup> and **V**.<sup>[8]</sup> Particularly, in the case of **V**, its dimer is stable only in the solid state.

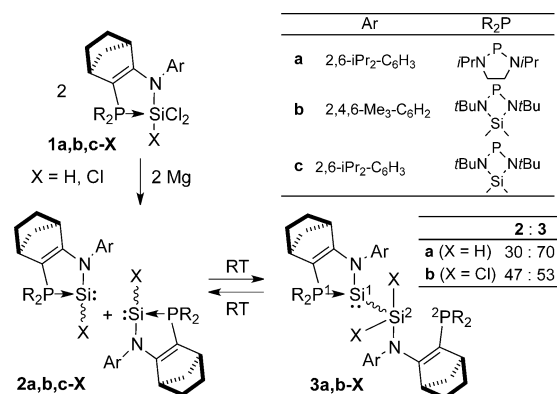
Theoretical calculations predicted that silylenes with a large singlet–triplet energy gap ( $\Delta E_{ST}$ ) and featuring an electronegative group with a lone pair dimerize by the interaction between the substituent lone pair and the silylene empty orbital, leading to a four-membered ring structures (type **B**).<sup>[9,7b]</sup> It is interesting to note that in the case of bis-diisopropylamino silylene **IV**, both types of dimerization processes (Si=Si bonded **A**, and N-bridged **B**) were observed, spectroscopically in solution, depending on the temperature.<sup>[7,10]</sup> In contrast, the stable cyclic diaminosilylene **VI** does not dimerize to the corresponding tetraaminodisilene, or N-bridged dimer, but instead undergoes the insertion reaction of another silylene into a Si–N bond to generate the transient amino-silyl silylene **VII** (inserted dimer, type **C**), which readily dimerizes to the diaminodisilyl disilene **VIII**.<sup>[11]</sup> Interestingly, both steps are reversible at room temperature, and such a dimerization process (type **C**), involving a reversible silylene insertion into a  $\sigma$ -bond, in mild conditions, is extremely rare, although non-reversible insertion reactions are typical for transient silylenes. Herein we report the reversible dimerization of phosphine-stabilized silylenes **2**, leading to inserted dimers **3** (type **C**), which can be isolated and fully characterized in the solid state.

Recently, we have reported the synthesis of the first stable phosphine-supported Si<sup>II</sup> hydride **2c-H** and chloride **2c-Cl** (Scheme 1)<sup>[12,15]</sup> by reduction of the corresponding chlorosilane derivatives **1c-X** (X = H, Cl), and the unique reactivity of **2c-H** with olefins as well as with diphenylacetylene.<sup>[13]</sup> In the present study, we have investigated the relationship between

silylene by West et al.,<sup>[1]</sup> a significant number of disilenes were synthesized by this method.<sup>[2]</sup> It has been experimentally and theoretically shown that the bonding situation in disilenes and their stability strongly depend on the nature of the substituents.<sup>[3]</sup> Indeed, a reversible disilene–silylene equilibrium has been observed for some sterically overcrowded silylenes **I**<sup>[4]</sup> and **II**,<sup>[5]</sup> and  $\pi$ -donor (Br, amino) substituted

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**Scheme 1.** Synthesis of hydro- and chlorosilylenes (**2a,b,c-X**) and their reversible dimerization by silylene insertion into a  $\sigma$ -Si–X bond (X = H, Cl).

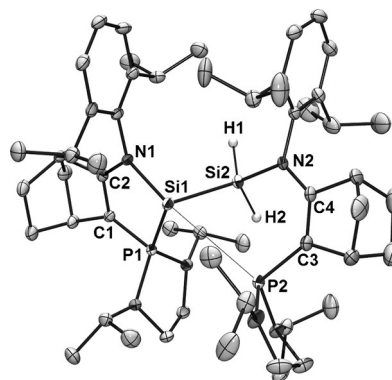
stability and steric hindrance (phosphine ligand and nitrogen substituent). The reduction of dichlorosilane **1a-H**, featuring the less sterically hindered five-membered cyclic diamino-phosphine ligand, affords a mixture of hydrosilylene **2a-H** and its Si<sup>II</sup>-H-inserted dimer **3a-H** in a ratio of 70:30 at room temperature (Scheme 1). The amount of dimer **3a-H** slowly increases, and after 7–10 h at RT the equilibrium was reached leading to a 30:70 molar ratio. Silylene **2a-H** was characterized in solution, and it presents spectroscopic data very similar to those already reported for similar compounds.<sup>[12,15]</sup> Particularly, **2a-H** was obtained as a mixture of two diastereomers (60:40) as indicated by the presence of two singlet signals ( $\delta = 91.1$  and 89.0 ppm) in the <sup>31</sup>P NMR spectrum. The signals corresponding to the terminal hydride appear as doublets, in the <sup>1</sup>H NMR spectrum, at  $\delta = 4.75$  ( $^2J_{\text{PH}} = 4.6$  Hz) and 4.95 ppm ( $^2J_{\text{PH}} = 5.0$  Hz). The <sup>29</sup>Si NMR spectrum displays two doublets at  $\delta = -66.9$  ( $^1J_{\text{SiP}} = 127.0$  Hz) and  $-61.9$  ppm ( $^1J_{\text{SiP}} = 121.4$  Hz), in agreement with the presence of diastereomers.

Dimer **3a-H** was isolated as pale yellow crystals from a concentrated pentane solution of a mixture of **2a-H**/**3a-H** in 62% yield. It exhibits a non-symmetric structure, which is completely different compare to the other known dimer structures (Si=Si bonded, and bridged). This is clearly indicated by an AB system in the <sup>31</sup>P NMR spectrum ( $\delta = 72.1(\text{P}^1)$  and 86.7( $\text{P}^2$ ) ppm,  $J_{\text{PP}} = 22.3$  Hz) showing the presence of two different phosphorus atoms in the molecule. The <sup>29</sup>Si NMR spectrum presents a broad doublet for the tetravalent silicon atom ( $\delta = -13.1$  ppm,  $J_{\text{PSi}} = 6.9$  Hz, Si2) and a doublet of doublets in the typical region of phosphine-complexed-Si<sup>II</sup>-atoms ( $\delta = -69.3$  ppm,  $J_{\text{SiP}} = 153.2$  Hz,  $J_{\text{SiP}} = 162.1$  Hz, Si1). The two large phosphorus–silicon coupling constants for the latter signal suggest that both phosphine ligands interact only with the Si<sup>II</sup> atom (Si1). In the <sup>1</sup>H NMR spectrum, the two diastereotopic protons on the Si<sup>IV</sup> atom appear as a doublet at  $\delta = 5.55$  ( $J_{\text{PH}} = 37.4$  Hz) and as a doublet of doublets at  $\delta = 6.00$  ppm ( $J_{\text{PH}} = 36.3$  and 5.7 Hz), and both signals present <sup>29</sup>Si satellites (ca 4.7%) with large silicon–hydrogen coupling constants ( $^1J_{\text{Si-H}} = 200.0$  and 178.0 Hz, respectively).

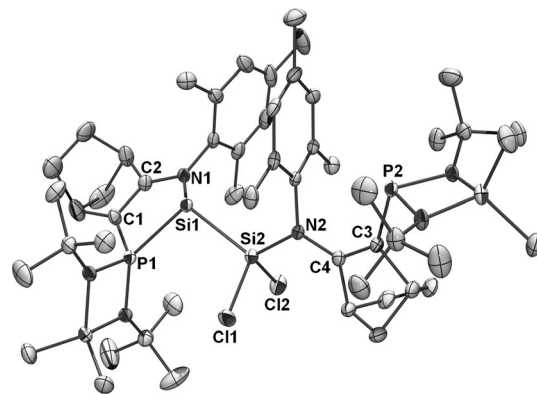
The structure of **3a-H** was unambiguously confirmed by X-ray crystallography (Figure 1),<sup>[14]</sup> which reveals the presence of two units of monomer **2a-H** connected by a Si–Si single bond (2.377 Å). The two silicon atoms present different coordination numbers, with tetrahedral geometry around Si2, whereas the low-valent silicon center Si1 adopts a distorted seesaw geometry with N1 and P2 atoms at the apical position (N1–Si1–P2: 170.3°). The short Si1–P1 bond (2.310 Å) confirms a strong silicon–phosphorus interaction. Furthermore, the orientation of the second phosphine (P2) suggests a weak interaction between P2 and divalent silicon centre (Si1). These two Si1–P interactions are in good agreement with the two large coupling constants  $J_{\text{SiP}}$  observed in the NMR spectra.

In contrast to the case of **2a-H**, the corresponding chlorosilylene **2a-Cl** with the same ligand system is stable as monomer and no formation of dimer **3a-Cl** has been detected.

In the second case studied, **1b-X** features a more bulky phosphine fragment and a less sterically demanding N-aryl



**Figure 1.** Molecular structure of **3a-H**. Ellipsoids are set at 30% probability; H atoms (Except for that on Si2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.377(1), Si1–N1 1.885(2), P1–Si1 2.310(1), P1–C1 1.726(2), C1–C2 1.378(3), C2–N1 1.345(3), P2–C3 1.802(3), Si2–P2 3.310(1), C3–C4 1.364(4), C4–N2 1.386(3), N2–Si2 1.785(2); N1–Si1–Si2 105.9(1), P1–Si1–Si2 93.8(1), Si1–P1–C1 94.7(1), C2–N1–Si1 115.6(2), C1–C2–N1 124.0(2), P2–C2–C3 128.7(2), C3–C4–N2 131.1(2), Si1–Si2–N2 118.9(1), N1–Si1–P1 87.9(1), Si1–P2 3.521(1).



**Figure 2.** Molecular structure of **3b-Cl**. Ellipsoids are set at 30% probability; only one of the two independent molecules in the asymmetric unit is represented. H atoms (except for that on Si2) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.368(2), Si1–N1 1.835(3), P1–Si1 2.324(2), P1–C1 1.731(4), N1–C2 1.356(5), C1–C2 1.375(5), P2–C3 1.822(4), Si2–N2 1.743(3), N2–C4 1.410(4), C3–C4 1.360(5), Si2–Cl2 2.088(2), Si2–C1 2.092(1); P1–Si1–Si2 102.6(1), N1–Si1–Si2 111.3(1), N1–Si1–P1 89.6(1), Si1–P1–C1 90.5(1), P1–C1–C2 116.7(3), C1–C2–N1 124.2(3), C2–N1–Si1 112.6(2), Si1–Si2–N2 113.0(1), Si2–N2–C4 126.7(2), N2–C4–C3 131.8(3), C4–C3–P2 134.4(3).

substituent (a mesityl group). Unfortunately, all attempts to synthesize **1b-H** failed. In contrast, **1b-Cl** can be readily synthesized and isolated as colorless crystalline materials in good yield (75%; Figure 2). The reduction of trichlorosilane derivative **1b-Cl**, using magnesium powder, at 50 °C for 12 h, cleanly gives a mixture of chlorosilylene **2b-Cl** and its dimer **3b-Cl** in a ratio of 94:6 (Scheme 1). The relative proportions of monomer **2b-Cl** and dimer **3b-Cl** slowly change, and after 7 days at RT, an almost equal ratio between both compounds was obtained (47:53). It is important to note that with a more sterically demanding Dipp group on the nitrogen atom, the corresponding phosphine-stabilized chlorosilylene is perfectly

stable and no dimer formation was observed.<sup>[15]</sup> Here again, all the NMR data of chlorosilylene **2b-Cl** are very similar to those already reported for a similar compound. Indeed, **2b-Cl** was obtained as a mixture of two diastereomers (22:78, ratio), as indicated by the presence of two singlets at  $\delta = 75.2$  and  $74.0$  ppm, in the  $^{31}\text{P}$  NMR spectrum, and two doublets at  $\delta = -8.4$  ( $J_{\text{SiP}} = 212.1$  Hz) and  $-1.4$  ppm ( $J_{\text{SiP}} = 212.6$  Hz), in the  $^{29}\text{Si}$  NMR spectrum.

The presence of two sets of two singlets ( $\delta = 77.5$ – $114.1$ , and  $77.2$ – $114.2$  ppm,) in the  $^{31}\text{P}$  NMR spectrum suggests the formation of dimer **3b-Cl** as a pair of two diastereomers (1.1:1.0, ratio). The two high field signals ( $77.5$  and  $77.2$  ppm) present  $^{29}\text{Si}$  satellites with large Si-P-coupling constants ( $^1J_{\text{Si-P}} = 178.6$  and  $183.8$  Hz), which confirm a direct interaction between phosphine and silicon. In contrast to dimer **3a-H**, the other two signals appear in the region of free phosphines suggesting the absence of any interaction with silicon.

Dimer **3b-Cl** was isolated as yellow crystals in 83 % yield from a concentrated ether solution of mixture **2b-Cl/3b-Cl**, after 6 days at RT. All the attempts to isolate monomer **2b-Cl** in the solid state were unsuccessful. The molecular structure of **3b-Cl**, determined by X-ray crystallography, clearly shows the presence of a three-coordinate  $\text{Si}^{\text{II}}$  and a four-coordinate  $\text{Si}^{\text{IV}}$  atoms.<sup>[14]</sup> As suggested by the NMR spectroscopy, phosphorous P1 strongly interacts with the  $\text{Si}^{\text{II}}$  atom ( $\text{Si1-P1} = 2.324$  Å), while P2 remains uncoordinated, in contrast to the case of **3a-Cl**.

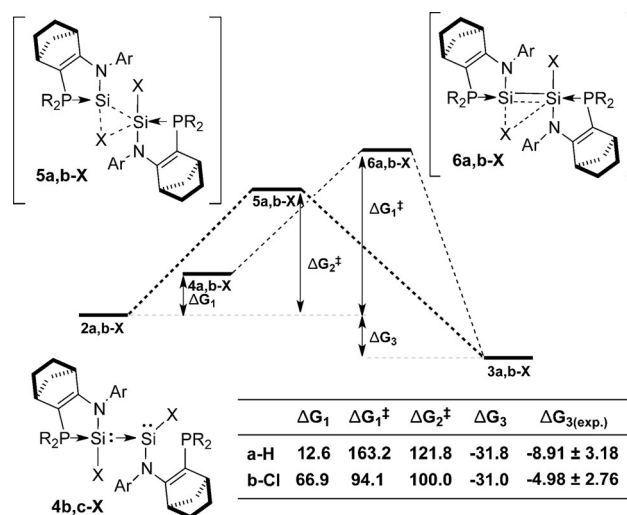
Of particular interest, in both cases dimerization of silylenes **2** is reversible. Indeed, monitoring the dissolution of crystalline pure dimers **3**, in  $\text{C}_6\text{D}_6$  at room temperature, by  $^{31}\text{P}$  NMR spectroscopy indicates a slow release of monomers **2**, leading after 7 days to the initial **3:2** ratio observed during the initial reduction of chlorosilanes **1** (Scheme 1). Furthermore, the ratio **3:2** are temperature-dependent, and the proportions of silylenes **2** increase with temperature (Table 1). These results clearly indicate that the dimerization of silylenes **2** is an equilibrium process, and as expected, the Gibbs free energies are quite small ( $\Delta G_{20^\circ\text{C}} = -2.13$  kcal  $\text{mol}^{-1}$  for **2a-H**,  $\Delta G_{20^\circ\text{C}} = -1.19$  kcal  $\text{mol}^{-1}$  for **2b-Cl**).

**Table 1:** Proportions of phosphine stabilized-silylenes **2** and related dimers **3** in  $\text{C}_6\text{D}_6$  at different temperatures.

|                                 |       |       |       |       |       |       |
|---------------------------------|-------|-------|-------|-------|-------|-------|
| $T$ [ $^\circ\text{C}$ ]        | 25    | 35    | 45    | 55    | 65    | 75    |
| <b>3a-H/2a-H</b> <sup>a</sup>   | 70/30 | 57/43 | 42/58 | 27/73 | 15/85 | 7/93  |
| $T$ [ $^\circ\text{C}$ ]        | 8     | 25    | 35    | 55    | 65    | 80    |
| <b>3b-Cl/3a-Cl</b> <sup>a</sup> | 70/30 | 53/47 | 45/55 | 29/71 | 18/82 | 11/89 |

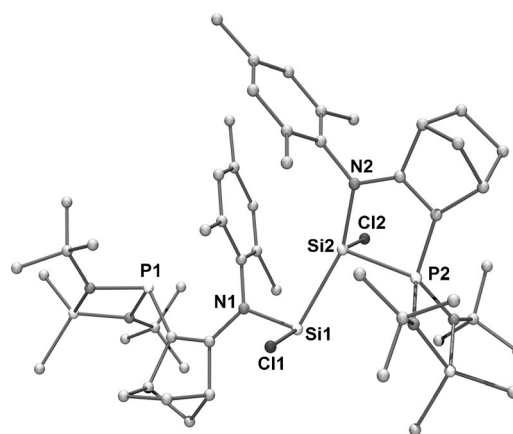
[a] determined by  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy.

DFT calculations, at the  $\text{M06/6-311}^{++}\text{G(d,p)}/\text{M06/6-31G(d)}$  level of theory, have been performed to investigate the dimerization of silylenes **2** (Figure 3). Two alternative mechanisms can be considered: 1) the direct silylene insertion into a Si–X bond ( $\text{X} = \text{H}, \text{Cl}$ ) of a second monomer; or 2) a two-step process involving the first formation of disilenes **4** followed by a 1,2-migration of substituent X.<sup>[16,17]</sup> However, all attempts to find a reaction pathway leading to disilenes **4**



**Figure 3.** Calculated reaction profiles (Gibbs energies [ $\text{kJ mol}^{-1}$ ] in THF) for the dimerization of silylene complexes **2a-H** and **2b-Cl** at the  $\text{M06/6-311} + \text{G(d,p)}/\text{M06/6-31G(d)}$  level and experimentally obtained Gibbs free energies ( $\Delta G_{3(\text{exp.})}$ ).

failed, even though dimers **4** are a minimum on the potential energy surface, and the dimerization process is only slightly endergonic in the case of **2a-H** ( $\Delta G_1 = 12.6$   $\text{kJ mol}^{-1}$ ). The formation of **4b-Cl** is more endergonic ( $\Delta G_1 = 66.9$   $\text{kJ mol}^{-1}$ ), which is probably due to steric reasons. It is important to note that the optimized geometries of **4a,b** reveal that they can be regarded as silylenes stabilized by a second silylene ligand, rather than symmetric disilene structures (Figure 4). Indeed, they present extremely long Si–Si bonds (2.456 Å for **4a-H**,



**Figure 4.** Calculated geometry of **4b-Cl**. H atoms are omitted for clarity. Selected bond lengths [Å]: Si1–Si2 2.468, Si1–N1 1.815, Si1–Cl1 2.203, Si2–P2 2.345, Si2–N2 1.848, Si2–Cl2 2.131.

2.468 Å for **4b-Cl**) which are and much longer than Si=Si double bond (2.14–2.27 Å)<sup>[18]</sup> and are even longer than Si–Si single bonds (For comparison, 2.377 Å for **3a-H** and 2.368 Å for **3b-Cl**). Moreover, rearrangement of **4a-H** into inserted dimer **3a-H** requires a considerable activation energy Gibbs of 163.2  $\text{kJ mol}^{-1}$ , which is not consistent with a reversible

process at room temperature. In the case of chlorosilylene **2b-Cl** the energy profiles of both processes are very similar with comparable free energy barriers ( $\Delta G_1^\ddagger = 94.1 \text{ kJ mol}^{-1}$ , and  $\Delta G_2^\ddagger = 100.0 \text{ kJ mol}^{-1}$ ). Nevertheless, the direct pathway by silylene insertion proceeds with a reasonably low energy barrier ( $\Delta G_2^\ddagger = 121.8 \text{ kJ mol}^{-1}$  for **2a-H**, and  $100.0 \text{ kJ mol}^{-1}$  for **2b-Cl**). The dimerization Gibbs free energies was calculated to be around  $-31 \text{ kJ mol}^{-1}$  ( $\Delta G_3$ ), and this is in qualitative agreement with the experimental values ( $\Delta G_{3(\text{exp})}$ ; Figure 3).

In conclusion, we have demonstrated that the stability of phosphine supported hydro- and chlorosilylenes is strongly dependent on the steric hindrance of the substituents. Indeed, a diminution of the kinetic protection of these species results in a non-classical dimerization by an original direct silylene insertion into a  $\text{Si}^{\text{II}}\text{-X}$   $\sigma$ -bond of a second molecule. Of particular interest, this concerted dimerization process is perfectly reversible at room temperature. Although the system is quite particular, this process can be regarded as reversible oxidative addition/reductive elimination reactions at the silicon center at room temperature, which is a typical behavior of transition metals. Generalization of this system to activate other molecules is under active investigation.

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