Silylene Dimerization

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Reversible Dimerization of Phosphine-Stabilized Silylenes by Silylene Insertion into Si^{II}–H and Si^{II}–Cl σ-Bonds at Room Temperature

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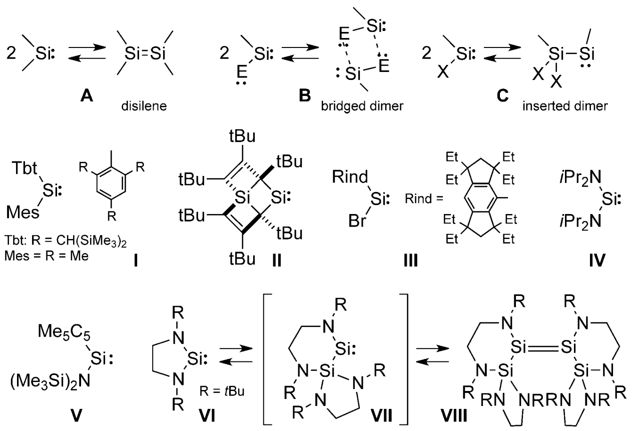
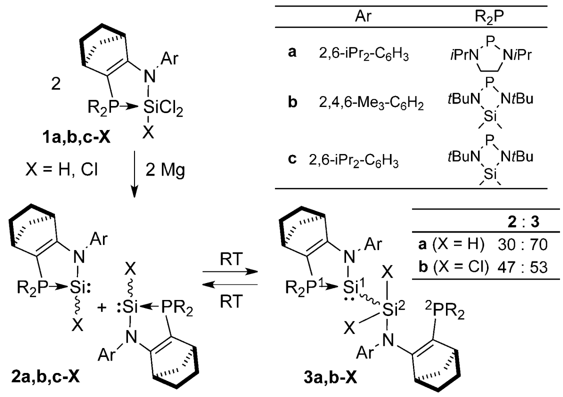
***Abstract:** Contrary to the classical silylene dimerization leading to a disilene structure, phosphine stabilized hydro- and chloro-silylenes (**2 a**,**b**) undergo an unique dimerization via silylene insertion into Si–X σ-bonds (X = H, Cl), which is reversible at room temperature. DFT calculations 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 silylene by West et al.,[1] a significant number of disilenes were synthesized by this method.[2] It has been experimentally and theoretically shown that the bonding situation in disilenes and their stability strongly depend on the nature of the substituents.[3] Indeed, a reversible disilene–silylene equilibrium has been observed for some sterically overcrowded silylenes **I**[4] and **II**,[5] and π-donor (Br, amino) substituted species **III**,[6] **IV**,[7] and **V**.[8] 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 (ΔE_{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**).[9,7b] 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.[7,10] 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**.[11] Interestingly, both steps are reversible at room temperature, and such a dimerization process (type **C**), involving a reversible silylene insertion into a σ-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^{II} hydride **2c-H** and chloride **2c-Cl** (Scheme 1)[12,15] by reduction of the corresponding chlorosilane derivatives **1 c-X** (X = H, Cl), and the unique reactivity of **2c-H** with olefins as well as with diphenylacetylene.[13] In the present study, we have investigated the relationship between



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

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stability and steric hindrance (phosphine ligand and nitrogen substituent). The reduction of dichlorosilane **1a-H**, featuring the less sterically hindered five-membered cyclic diaminophosphine ligand, affords a mixture of hydrosilylene **2a-H** and its Si^{II}–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.[12,15] 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 ^{31}P NMR spectrum. The signals corresponding to the terminal hydride appear as doublets, in the ^{1}H NMR spectrum, at $\delta = 4.75$ ($^{2}J_{PH} = 4.6$ Hz) and 4.95 ppm ($^{2}J_{PH} = 5.0$ Hz). The ^{29}Si NMR spectrum displays two doublets at $\delta = -66.9$ ($^{1}J_{SiP} = 127.0$ Hz) and -61.9 ppm ($^{1}J_{SiP} = 121.4$ 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 ^{31}P NMR spectrum ($\delta = 72.1$(P^{1}) and 86.7(P^{2}) ppm, $J_{PP} = 22.3$ Hz) showing the presence of two different phosphorus atoms in the molecule. The ^{29}Si NMR spectrum presents a broad doublet for the tetravalent silicon atom ($\delta = -13.1$ ppm, $J_{PSi} = 6.9$ Hz, Si2) and a doublet of doublets in the typical region of phosphine-complexed-Si^{II}-atoms ($\delta = -69.3$ ppm, $J_{SiP} = 153.2$ Hz, $J_{SiP} = 162.1$ Hz, Si1). The two large phosphorus–silicon coupling constants for the latter signal suggest that both phosphine ligands interact only with the Si^{II} atom (Si1). In the ^{1}H NMR spectrum, the two diastereotopic protons on the Si^{IV} atom appear as a doublet at $\delta = 5.55$ ($J_{PH} = 37.4$ Hz) and as a doublet of doublets at $\delta = 6.00$ ppm ($J_{PH} = 36.3$ and 5.7 Hz), and both signals present ^{29}Si satellites (ca 4.7%) with large silicon–hydrogen coupling constants ($^{1}J_{Si\text{-}H} = 200.0$ and 178.0 Hz, respectively).

The structure of **3a-H** was unambiguously confirmed by X-ray crystallography (Figure 1),[14] 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_{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.

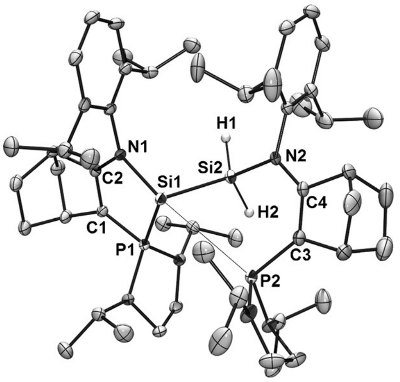


Figure 1. Molecular structure of **3a-H**. Ellipsoids are set at 30% probability; H atoms (Except for that on Si2) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.377(1), Si1–N1 1.885(2), P1–Si1 2.310(1), P1–C1 1.726(2), C1–C2 1.378(3), C2–N1 1.345(3), P2–C3 1.802(3), Si2–P2 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).

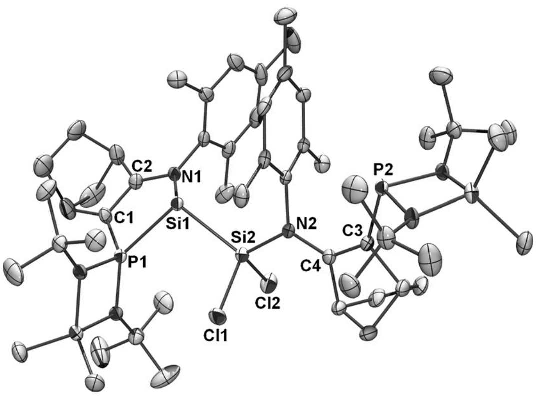


Figure 2. Molecular structure of **3b-Cl**. Ellipsoids are set at 30% probability; only one of the two independent molecules in the asymmetric unit is represented. H atoms (except for that on Si2) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] : Si1–Si2 2.368(2), 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–Cl1 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).

In the second case studied, **1b-X** features a more bulky phosphine fragment and a less sterically demanding N-aryl 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.[15] 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}P NMR spectrum, and two doublets at $\delta = -8.4$ ($J_{\mathrm{SiP}} = 212.1$ Hz) and -1.4 ppm ($J_{\mathrm{SiP}} = 212.6$ Hz), in the ^{29}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}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}Si satellites with large Si-P-coupling constants ($^{1}J_{\mathrm{Si\text{-}P}} = 178.6$ 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.

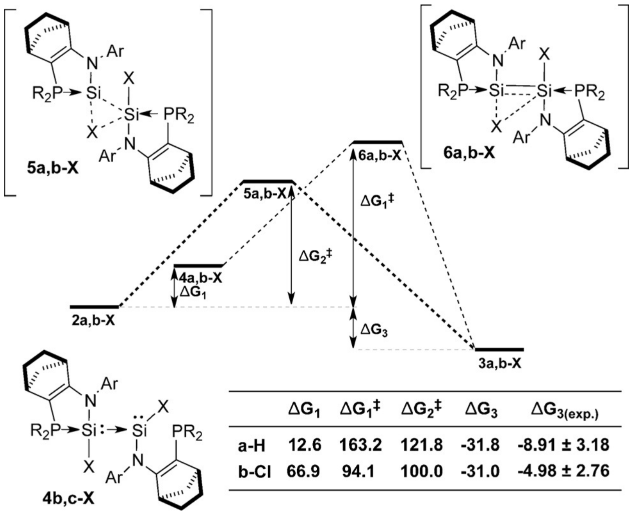
Dimer **3b-Cl** was isolated as yellow crystals in 83 % yield from a concentrated ether solution of mixture **2b-Cl**/**3b-Cl**, after 6 days at RT. All the attempts to isolate monomer **2b-Cl** in the solid state were unsuccessful. The molecular structure of **3b-Cl**, determined by X-ray crystallography, clearly shows the presence of a three-coordinate Si$^{\mathrm{II}}$ and a four-coordinate Si$^{\mathrm{IV}}$ atoms.[14] As suggested by the NMR spectroscopy, phosphorous P1 strongly interacts with the Si$^{\mathrm{II}}$ atom (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 C_6D_6 at room temperature, by ^{31}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 ($\Delta G_{20\,^{\circ}\mathrm{C}} = -2.13$ kcal mol^{-1} for **2a-H**, $\Delta G_{20\,^{\circ}\mathrm{C}} = -1.19$ kcal mol^{-1} for **2b-Cl**).

Table 1: Proportions of phosphine stabilized-silylenes **2** and related dimers **3** in C_6D_6 at different temperatures.

T [°C]	25	35	45	55	65	75
3a-H/2a-H[a]	70/30	57/43	42/58	27/73	15/85	7/93
T [°C]	8	25	35	55	65	80
3b-Cl/3a-Cl[a]	70/30	53/47	45/55	29/71	18/82	11/89

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



	ΔG_1	$\Delta G_1^{\ddagger}$	$\Delta G_2^{\ddagger}$	ΔG_3	$\Delta G_{3(\mathrm{exp.})}$
a-H	12.6	163.2	121.8	-31.8	-8.91 ± 3.18
b-Cl	66.9	94.1	100.0	-31.0	-4.98 ± 2.76

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

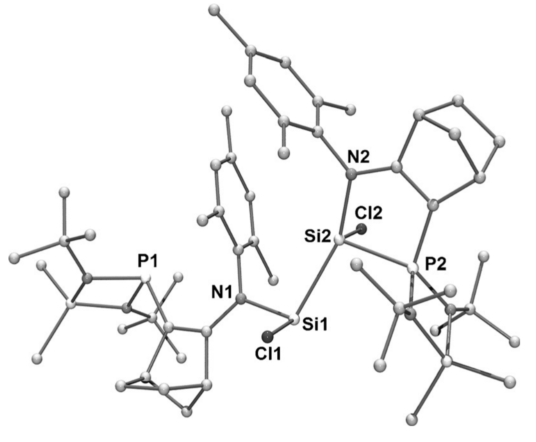


Figure 4. Calculated geometry of **4b-Cl**. H atoms are omitted for clarity. Selected bond lengths [Å] : Si1–Si2 2.468, Si1–N1 1.815, Si1–Cl1 2.203, Si2–P2 2.345, Si2–N2 1.848, Si2–Cl2 2.131.

DFT calculations, at the M06/6-311^{++}G(d,p)//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 (X = H, 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.[16,17] However, all attempts to find a reaction pathway leading to disilenes **4** 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** ($\Delta G_1 = 12.6$ kJ mol^{-1}). The formation of **4b-Cl** is more endergonic ($\Delta G_1 = 66.9$ 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**, 2.468 Å for **4b-Cl**) which are and much longer than Si=Si double bond (2.14–2.27 Å)[18] 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 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 ($\Delta G_1^{\neq}=94.1\ \text{kJ mol}^{-1}$, and $\Delta G_2^{\neq}=100.0\ \text{kJ mol}^{-1}$). Nevertheless, the direct pathway by silylene insertion proceeds with a reasonably low energy barrier ($\Delta G_2^{\neq}=121.8\ \text{kJ mol}^{-1}$ for **2a-H**, and $100.0\ \text{kJ mol}^{-1}$ for **2b-Cl**). The dimerization Gibbs free energies was calculated to be around $-31\ \text{kJ mol}^{-1}$ (ΔG_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 Si^{II}–X σ-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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