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Main Group Elements

Reversible Isomerization Between Silacyclopropyl Cation and Cyclic (Alkyl)(Amino)Silylene

Raphaël Nougué, Shintaro Takahashi, Antoine Baceiredo, Nathalie Saffon-Merceron,
Vicenç Branchadell, and Tsuyoshi Kato*

Abstract: A phosphine-stabilized silacyclopropyl cation **2** has been synthesized and fully characterized. Of particular interest, **2** reversibly isomerizes into the corresponding seven-membered cyclic (alkyl)-(amino)silylene **3** at room temperature via a formal migratory ethylene insertion into the Si–P bond. Although silylene **3** has not been spectroscopically detected, its transient formation has been evidenced by the isolation of the corresponding disilene dimer **5** as well as by trapping reactions.
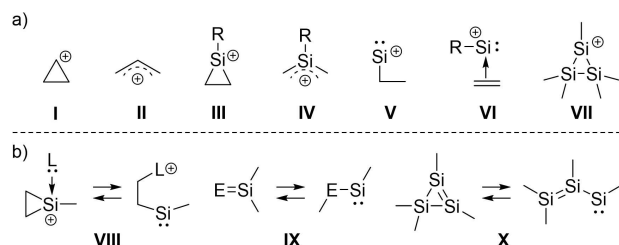
Figure 1. a) Cyclopropenium cation **I** and allyl cation isomer **II** and related silicon-containing species (**III–VII**). b) Known reversible silylene isomerizations (**VIII–X**).

Introduction

Highly strained small cyclic molecules often present unusual stability and properties. Particularly, in marked contrast to the stable aromatic cylopropenium ions,[1] cyclopropyl cations **I** are extremely fragile molecules (Figure 1). Indeed, theoretical[2] and experimental[3] studies indicate that the parent molecule is not a minimum on the potential energy surface[2c,d] and readily undergoes a ring opening reaction to afford the significantly more stable allyl cation isomer **II** ($\Delta E_{\text{II–I}} = -35 \text{ kcal mol}^{-1}$).[2] Only a cyclopropyl cation with a bicyclic structure which, hampers the pericyclic isomerization, was characterized as a persistent molecule.[4] Although cyclopropyl cations **I** have been extensively studied since 1960s, the chemistry of the heavier silacyclopropyl cations **III** is far less investigated. Indeed, to the best of our knowledge, there has been any experimental report on their

synthesis, even though silylium ions have been of growing interest for many years.[5] A few theoretical investigations predict that silacyclopropyl cations **III** and cyclopropyl cation **I** are quite different, and that sila-allyl cation **IV** is a less stable isomer of **III**.[6] It was also predicted that silacyclopropyl cation **III** (R = H) readily isomerizes to the more stable silyliumylidene ion **V** ($\Delta E_{\text{III→V}} = -25 \text{ kcal mol}^{-1}$) via a formal migratory insertion of ethylene fragment into the Si–H bond.[5a] More recently, Müller reported computational investigations predicting that the π-ethylene complex of silyliumylidene ion **VI** (R = Me) is very close in energy to the silacyclopropyl cation **III** ($\Delta E_{\text{III→VI}} = 1.0 \text{ kcal mol}^{-1}$) and the facile interconversion between them due to a small energy barrier ($\Delta E^{\ddagger}_{\text{III→VI}} = 13.5 \text{ kcal mol}^{-1}$).[5c] Although stable silicon analogues **VII** have already been synthesized,[7,8] such a interconversion (**III→VI**) was not observed probably due to the unfavored formation of less stable disilene. The bicyclic derivative of trisilacyclopropyl cation, stabilized by homoconjugation, similarly to the carbon analogues,[9] has been described by Sekiguchi.[7a] Here we report the synthesis of the first isolable monosilacyclopropyl cation **2** stabilized by intramolecular phosphine coordination. Of particular interest, **2** reversibly isomerizes at room temperature to give a transient seven-membered cyclic (alkyl)(amino) silylene **3** by a formal migratory insertion of ethylene into the Si–P bond proceeding through a transient formation of a π-ethylene complex of silyliumylidene ion (type **VI**) as an intermediate. This is a rare inter-conversion involving the formation of a silylene (type **VIII**) other than the previously described thermal and photochemical interconversions between Si=E double bond species (**IX**, E = R$_2$Si, RN) and silylene (type **IX**)[10] or reversible cyclotrisilene-disilenyl silylene interconversion (type **X**) reported by Scheschkewitz and co-workers.[11]

[*]   Dr. R. Nougué, Dr. S. Takahashi, Dr. A. Baceiredo, Dr. T. Kato
      Université de Toulouse, UPS, and CNRS, LHFA UMR 5069
      31062 Toulouse (France)
      E-mail: tsuyoshi.kato@univ-tlse3.fr
   Homepage: http://hfa.ups-tlse.fr

      Dr. N. Saffon-Merceron
      Université de Toulouse, UPS, and CNRS, ICT FR2599
      118 route de Narbonne, 31062 Toulouse (France)

      Prof. V. Branchadell
      Departament de Química, Universitat Autònoma de Barcelona
      08193 Bellaterra (Spain)

Results and Discussion

Previously, we have reported the synthesis of silyliumylidene ion complex **1** stabilized by a phosphine- and a dimethylsulfide-ligand, which presents a high reactivity due to the labile character of both ligands.[12] Thus, silyliumylidene ion **1** immediately reacts with ethylene at room temperature to afford the corresponding phosphine-stabilized silacycloprop-
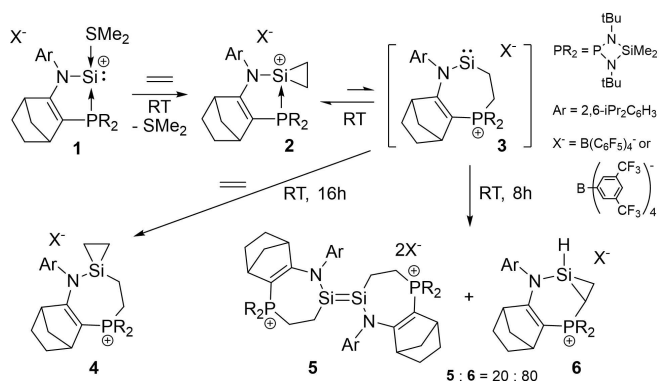
Scheme 1. The synthesis of silacyclopropyl cation **2**, its reversible isomerization to cyclic silylene **3** and the trapping reaction of **3** with ethylene as well as its evolution by dimerization and C–H insertion.
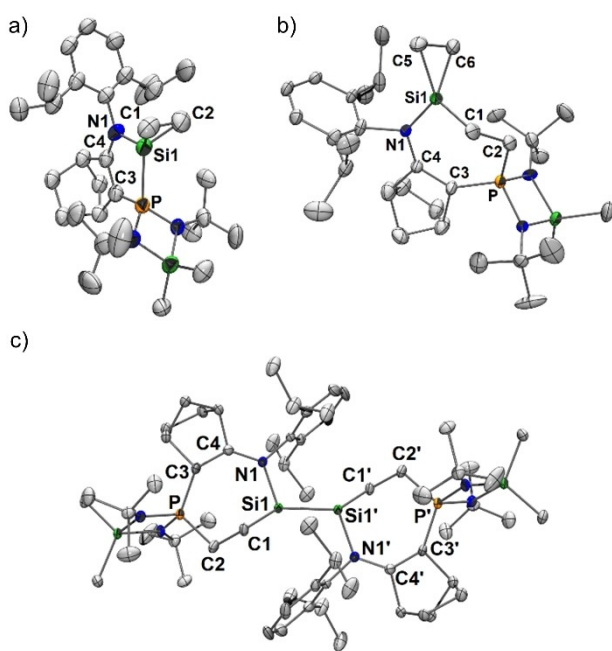

Figure 2. Molecular structures of **2** (a), **4** (b) and **5** (c). Thermal ellipsoids represent 30% probability. H and disordered atoms, counter anions and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Si1–C1 1.802(7), C1–C2 1.594(10), C2–Si1 1.814(6), N1–Si1 1.739(4), Si1–P 2.260(2), Si1–C1–C2 64.2(3), C1–C2–Si1 63.5(3), C2–Si1–C1 52.3(3), N1–Si1–P 94.8(2). **4**: Si1–C5 1.787(9), C5–C6 1.553(11), C6–Si1 1.821(7), N1–Si1 1.755(5), Si1–C1 1.830(8), Si1–C5–C6 63.4(4), C5–C6–Si1 65.6(4), C6–Si1–C5 51.0(4), N1–Si1–C1 111.8(3). **5**: Si1–Si1′ 2.261(3), N1–Si1 1.787(2), Si1–C1 1.867(3), N1–Si1–Si1′ 113.6(2), C1–Si1–Si1′ 120.1(2), N1–Si1–C1 106.6(2).

yl cation **2** with the release of SMe$_2$ (Scheme 1). In the ^{31}P NMR spectrum of **2**, a signal appears at higher field (32.9 ppm) compared to the chemical shift of silyliumylidene ion **1** (66.9 ppm).[11] A similar upfield shift has already been observed in the analogous reactions of **1** with silanes or alkynes to give the corresponding phosphine-stabilized silylium cations (24–45 ppm).[11] The ^{29}Si NMR spectrum displays a high-field doublet signal at −51.9 ppm with a large coupling constant ($^{1}J_{SiP} = 175.4$ Hz), within the range observed for silacyclopropanes (−42.2 to −81.9 ppm).[13,14] In addition, ^{13}C NMR resonances for the two carbon atoms in the three-membered ring appear as doublets at 2.4 ppm ($J_{CP} = 3.2$ Hz) and 3.0 ppm ($J_{CP} < 1.0$ Hz) in the characteristic region of silacyclopropanes (−2.1 to 4.1 ppm).[13,14] The structure of **2** was confirmed by X-ray diffraction analysis (Figure 2a).[15]

Notably, if excess ethylene gas is not removed under vacuum immediately after the reaction, silacyclopropyl cation **2** reacts further with a second equivalent of ethylene (16 h at room temperature) to give silacyclopropane **4** with an additional ethylene fragment inserted into the Si–P bond. Silacyclopropane **4** was fully characterized in solution by NMR spectroscopy and in the solid state by single crystal X-ray diffraction analysis (Figure 2b).[15] The ^{31}P NMR spectrum of **4** displays a relatively downfield shifted signal at 54.5 ppm compared to that of silacyclopropyl cation **2** (32.9 ppm). The inserted ethylene fragment between Si and P atoms was confirmed by the ^{13}C NMR spectrum which shows two characteristic doublet signals at 2.1 ppm ($^{2}J_{CP} = 2.1$ Hz, SiCH$_2$) and at 31.7 ppm ($^{1}J_{CP} = 61.9$ Hz, CH$_2$P). This result could suggest the in situ-formation of a seven-membered cyclic (alkyl)(amino)-silylene **3**, via an isomerization of **2**, which then undergoes a [2+1]-cycloaddition with ethylene to give **4** (Scheme 1).[16] However, since silylene **3** cannot be detected in solution by NMR spectroscopy, both isomers silacyclopropyl cation **2** and silylene **3** should be in equilibrium at room temperature with a low concentration of **3**.

All attempts to isolate **3** by crystallization failed, however, its dimer, dicationic disilene **5**, was obtained as highly air-sensitive red crystals (20% yield) from a concentrated C$_6$H$_5$F solution of **2** at room temperature. The X-ray diffraction analysis of **5** (Figure 2c) shows a trans-bent arrangement of disilene fragment with strongly pyramidalized silicon centers ($\Sigma°_{Si}$: 340.39°, bent angle: 40.79°) and an elongated Si=Si bond (Si1–Si1′: 2.261(3) Å) compared to the typical values reported for disilenes (2.15–2.20 Å).[17] This Si=Si-bond length is similar to those observed for disilenes substituted by strongly π-donating groups such as 1,2-diamino-1,2-disilyldisilene (2.2890(14) Å)[18] or 1,2-diimino-disilyl-disilene (2.3124(7) Å).[19] Disilene **5** could be detected in solution only as a reaction mixture by ^{31}P NMR ($\delta = 49.4$ ppm) and ^{29}Si NMR ($\delta = 100.9$ ppm) spectroscopies, due to its precipitation/crystallization and its insolubility in common organic solvents. However, the solid-state CP/MAS ^{29}Si NMR spectroscopy of **5** shows the same signal appearing at 100.9 ppm. This chemical shift is in the range of typical values reported for disilenes (50–155 ppm) and is in-between those observed for 1,2-diaminodisilenes (15.1–119.5 ppm).[18]

The CP/MAS ^{31}P NMR also shows a signal at 49.0 ppm, which is consistent with the result observed in solution. The dimerization of **3** in C_6H_5F (**3**+**3**→**5**) is calculated to be exergonic ($\Delta G = -15.5$ kcal mol^{-1}, $\Delta G^{\ddagger} = 16.2$ kcal mol^{-1}).[20] In addition to the formation of silylene dimer **5**, the isomerization of **2**, via a silylene insertion into the C–H bond at the β-position of Si^{II} center to afford a silirane derivative **6**,[21] was observed (Scheme 1). The structure of **6** was also confirmed by X-ray diffraction analysis. (See the Supporting Information.) The reaction completed in 8 h at room temperature to give a mixture of **5** and **6** in a 20:80 ratio. This result is in good agreement with DFT-calculations indicating that the formation of **6** from **3** via a C–H activation by the silylene in C_6H_5F proceeds with a slightly smaller energy barrier ($\Delta G^{\ddagger} = 15.5$ kcal mol^{-1}) and is a less exergonic process ($\Delta G = -14.6$ kcal mol^{-1}).[22,23] This result also confirms the in situ-generation of silylene **3** via the isomerization of silacyclopropyl cation **2**.

The DFT calculations indicate that the formation of silylene **3** from silacyclopropyl cation **2** is only slightly endergonic ($\Delta G_{2\rightarrow3} = +2.5$ kcal mol^{-1}) and the energy barrier for the reaction is reasonably small ($\Delta G^{\ddagger}_{2\rightarrow3} = 22.5$ kcal mol^{-1}), which is in good agreement with the experimental results suggesting the presence of an equilibrium between silacyclopropyl cation **2** and silylene **3** at room temperature (Figure 3). Calculations also indicate that the reaction starts with the formation of a π-ethylene complex of silyliumylidene ion **INT1** rather than a direct isomerization from **2** to **3** via a formal reductive elimination of phosphonium fragment from the cationic tetra-coordinate silicon center or via a nucleophilic attack of phosphine on the carbon atom of the three-membered ring. The nature of π-ethylene complex of **INT1** was indicated by the ethylene coordinating on the Si atom from the top of P–Si–N molecular plane in **INT1** as well as by the significantly shortened C–C bond (1.402 Å) and elongated Si–C bonds (2.016 and 2.512 Å) in the three-membered ring relative to those calculated for **2** (C–C: 1.559 Å, Si–C: 1.841 and 1.839 Å). Then, the **INT1** isomerizes via a migratory

insertion of ethylene into the Si–P bond to generate a phosphonioenamine adduct of silylene **INT2** as second intermediate, which isomerizes further via a ring-opening reaction to give the base-free cyclic (alkyl)(amino)silylene **3** ($\Delta G_{\mathbf{INT2}\rightarrow3} = -5.0$ kcal mol^{-1}, $\Delta G^{\ddagger}_{\mathbf{INT2}\rightarrow3} = 6.5$ kcal mol^{-1}).

The calculated structure of **3** shows a relatively short N–Si bond (1.783 Å in Figure 4), indicating a π-donation of amino group to the divalent silicon atom (canonical structure **3-B** in Figure 5). However, it is longer than those observed for other mono-amino silylenes (1.715–1.730 Å). In addition, the C4–N (1.384 Å) and P–C3 (1.750 Å) bonds are shorter than the corresponding single bonds (N–C5 1.465 Å, C2–P 1.812 Å). These results suggest a significant delocalization of *N*-lone pair to the phosphonio fragments (**3-C**, Figure 4), Indeed, the NBO analysis of **3** indicates a Lewis structure with a C3–C4 double bond and lone pairs on Si and N atoms, with a total non-Lewis occupancy of only 1.6%, showing that **3-A** is the most representative canonical structure of **3**. The second order perturbation analysis of donor-acceptor interactions, assessing electron delocalization, shows that the most significant interactions in the P–C3–C4–N–Si fragment are LP(N)→π*(C3–C4) (54.9 kcal mol^{-1}), LP(N)→empty 3p (Si) (32.6 kcal mol^{-1}) and π(C3–C4)→σ*(P–N) (13.0 kcal mol^{-1}). This indicates an important contribution of canonical structure **3-C** which should reduce the electronic compensation of divalent silicon center by the amino group (**3-B**). Indeed, the LUMO of **3** (-3.6 eV), mainly localized on the silicon atom ($p_{\pi Si}$) (Figure 3b), is the considerably lower than that calculated for the Iwamoto's neutral five-membered cyclic (amino)-(alkyl)silylene **XI** (-0.1 eV, Figure 5).[24] Furthermore, probably due to such a reduced π-electron donation of amino group as well as the increased silylene bond angle (100.9° for **3**, 92.6° for **XI**), the singlet/triplet gap of **3** (36.7 kcal mol^{-1}) is significantly smaller than that calculated for **XI** (50.0 kcal mol^{-1}) and thus silylene **3** presents a greater
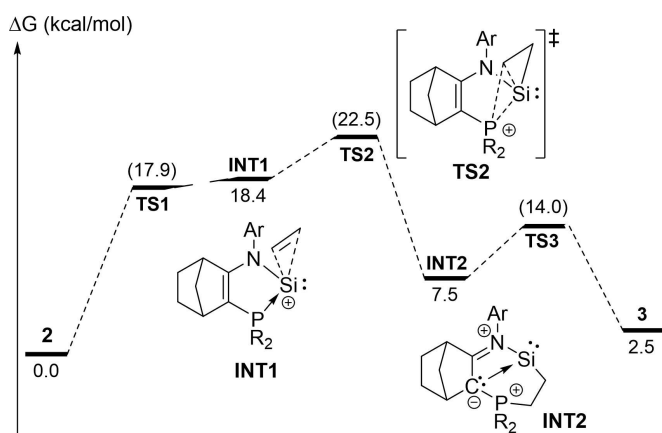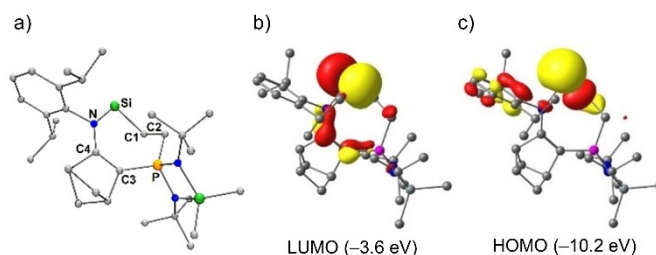

Figure 4. Calculated structure of **3** (a) and its frontier orbitals (b: LUMO and c: HOMO, Isosurface level: 0.05). Selected bond lengths [Å] and angles [°]: N–Si 1.783, Si–C1 1.926, C1–C2 1.540, C2–P 1.812, P–C3 1.750, C3–C4, 1.374, C4–N 1.384, N–Si–C1 100.91.
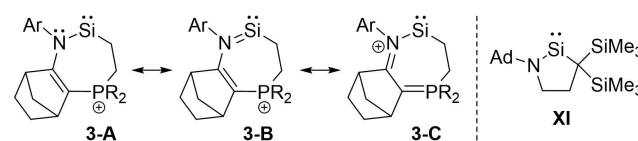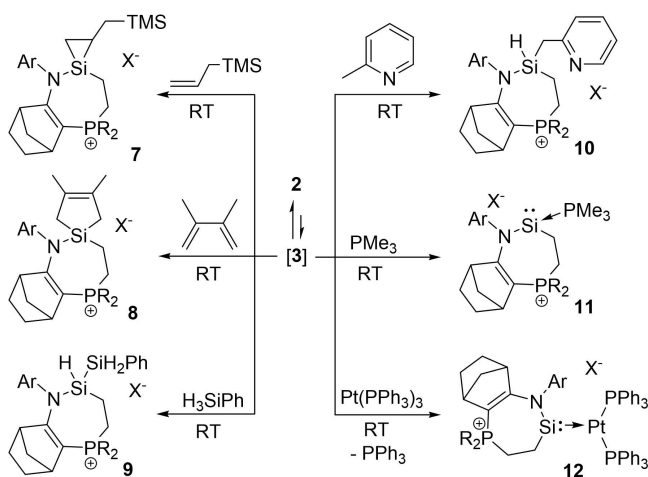

Figure 5. Some canonical structures of **3A–C**.

Figure 3. Calculated pathway for the silacyclopropyl cation-silylene interconversion in C_6H_5F. Gibbs energies of intermediates (and transition states) are in kcal mol^{-1}.

reactivity, as indicated by the facile dimerization and isomerization (Scheme 1).

As expected, the in situ generated silylene **3** exhibits the typical reactivity of silylenes, even though the very low concentrations of **3** in solution slow down reaction rates (Scheme 2). Thus, **3** reacts slowly with unsaturated compounds such as allytrimethylsilane (8 h) and 2,3-dimethylbutadiene (8 h) at room temperature to give the corresponding [2+1]- and [4+2]-cycloadducts (**7** and **8**), respectively (Scheme 2). It is interesting to note that the intramolecular C–H insertion of **3** to give **6** was not observed upon these reactions. Silylene **3** also reacts with H_3SiPh at room temperature via a silylene insertion into a Si–H bond of the silane to give the corresponding disilane **9**. Interestingly, silylene **3** is able to activate a C–H bond of the methyl group of 2-methylpyridine to give a cyclic silane **10**. The reaction is probably triggered by the coordination of pyridine to the Si^{II} center of **3**, which increases both the

acidity of the methyl group of 2-methylpyridine and the basicity of the Si^{II} center, which promotes the deprotonation of the methyl group by the silylene moiety. Indeed, no reaction was observed with a bulkier, and therefore less coordinating, 2,6-dimethylpyridine.

As expected, silylene **3** possess an ambiphilic character and behaves as Lewis acid as well as Lewis base. Indeed, the addition of an excess of PMe_3 cleanly affords the corresponding phosphine-stabilized silylene **11** as a mixture of two diastereomers (85:15) which have been fully characterized by NMR spectroscopy (^{29}Si NMR: $\delta = 18.4$ ppm, $^1J_{Si\text{-}P} = 193.5$ Hz for the major diastereomer) and X-ray diffraction analysis (Figure 6-left). The structure of **11** confirms the coordination PMe_3 on the Si^{II} atom and a resulting pyramidalized and chiral three-coordinate silicon center ($\Sigma^\circ_{Si} = 295.8^\circ$). In the absence of an excess of PMe_3, **11** is not stable and slowly and cleanly affords silylene dimer **5** certainly due to an easy dissociation of phosphine ligand in solution. It is interesting to note that in this case the isomerization of silylene **3** to give the insertion product **6** was not observed. This suggests that the silylene dimerization process could be promoted by a Lewis base such as PMe_3. In turn, the Lewis basic character of **3** was demonstrated by its reaction with $Pt(PPh_3)_3$ leading to the clean formation of silylene→Pt^0 complex **12**. The ^{29}Si NMR spectrum of **12** displays a low-field shifted triplet signal at 278 ppm ($^2J_{SiP} = 126$ Hz, $^1J_{SiPt} = 3631$ Hz), within the range observed for the Pt^0-complexes with the Iwamoto's (alkyl)-(amino)silylene ligand **XI** ($\delta = 281–285$ ppm, $^1J_{SiPt} = 2335–2250$ Hz).[25] The structure of complex **12** has been also confirmed by X-ray diffraction analysis (Figure 6-right). The structure exhibits a Si1-Pt bond length (2.201(1) Å) which is as short as those observed for the related Pt^0-complexes with a aryl- or alkyl-silylene ligands [silylene→$Pt(PR_3)_2$ complexes (2.2076(15)–2.2123(11) Å)][26] and is shorter than that observed for the complex with a diaminosilylene Si-[(NCH_2^tBu)_2C_6H_4-1,2] (2.261(3) Å).[27] This also confirms the enhanced electrophilic character of silylene **3**.

Scheme 2. The reactions of cyclic (alkyl)(amino)silylene **3**.

Conclusion

In conclusion, we have successfully synthesized the first phosphine-stabilized silacyclopropyl cation **2** and its unprecedented reversible isomerization at room temperature to the corresponding seven-membered cyclic (alkyl)-(amino)silylene **3** (CAASi) via a formal migratory ethylene insertion into the Si–P bond. Although silylene **3** has not been detected in solution by NMR spectroscopy, its formation was evidenced by typical reactions of silylenes such as cycloaddition reactions, insertion reactions into C–H or Si–H bonds, and complexations with a Lewis Base or a Lewis Acid. Therefore, the phosphine-stabilized cyclopropenium ion **2** can be considered as a masked CAASi which is stable and easy-to-manipulate. The applications of this unique molecule is under active investigation.
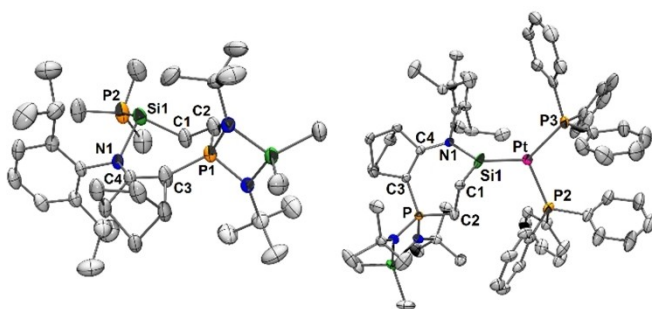

Figure 6. Molecular structures of **11** (left) and **12** (right). Thermal ellipsoids represent 30% probability. H and disordered atoms and counter anions are omitted for clarity. Selected bond lengths [Å] and angles [°]: **11**: Si1–P2 2.339(3), N1–Si1 1.869(4), Si1–C1 1.922(9), C1–C2 1.578(17), C2–P1 1.810(11), P1–C3 1.732(5), C3–C4 1.393(6), C4–N1 1.339(6), N1–Si1–P2 105.2(2), P2–Si1–C1 92.6(3), N1–Si1–C1 98.0(4). **12**: Si1–Pt 2.201(1), Pt–P2 2.298(1), Pt–P3 2.308(1), N1–Si1 1.791(3), Si1–C1 1.849(4), Si1–Pt–P2 113.7(1), P2–Pt–P3 109.2(1), P3–Pt–Si1 135.0(1), N1–Si1–Pt 133.5(2), Pt–Si1–C1 122.9(2), N1–Si1–C1 103.5(2).

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[16] Alternatively, the formation of **4** can also be explained by a direct insertion of ethylene into the Si–P bond of **2**. However, this route was ruled out because it was calculated to proceed with an excessively high energy barrier ($\Delta G^{\ddagger}_{2\rightarrow4} = 54.9 \text{ kcal mol}^{-1}$).

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[21] Product **6** can also be regarded as an imine-stabilized silacyclopropyl cation. We have already reported the related three-membered cyclic silylene stabilized by the same ligand system: R. Rodriguez, T. Troadec, T. Kato, N. Saffon-Merceron, J.-M. Sotiropoulos, A. Baceiredo, *Angew. Chem. Int. Ed.* **2012**, *51*, 7158–7161; *Angew. Chem.* **2012**, *124*, 7270–7273.

[22] Although, unlike the dimerization process, the effect of the counterion on the Gibbs reaction and activation energies for the isomerization of **3** via the C–H insertion is negligible ($\Delta G_{3\to6}$ and G$^+_{3\to6}$: -15.2 and 15.5 kcal mol^{-1} for **3** with a [B(C$_6$F$_5$)$_4$$^-$] counterion, -14.6 and 15.5 kcal mol^{-1} for **3** without a counterion), we use the average values of those calculated for the two models (-14.8 and 15.5 kcal mol^{-1}).

[23] As an alternative pathway for the formation of **6**, we can consider a process starting with a 1,2-hydride migration from the carbon atom of silacyclopropanyl cation to the silicon atom. However, according to DFT calculations, this route requires an exceedingly high energy ($\Delta G^+ = 69.9$ kcal mol^{-1}) and leads to the formation of a different product such as a phosphine-stabilized silylium cation substituted by a H and a vinyl group.

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