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A Stable Cation of a CSi_3P Five-Membered Ring with a Weakly Coordinating Chloride Anion**

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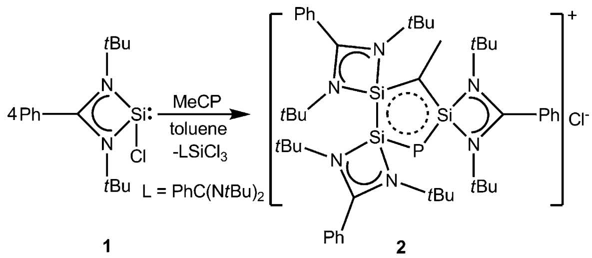
Dedicated to Professor K. Barry Sharpless on the occasion of his 70th birthday

In 2002,[1] Bertrand et al. described that the previously reported pentamethylcyclopentadienyl cation (Cp^{*+}) is actually the pentamethylcyclopentenyl cation and concluded that the stable Cp^+/Cp^{*+} remains unknown ($Cp = C_5H_5$).[2] Single crystal X-ray determination by Cowley et al.[3a] and quantum chemical calculations by Müller[3b] further supported the conclusion drawn by Bertrand et al. The instability of the cyclopentadienyl cation is presumably due to its antiaromatic properties. It is known that the incorporation of heteroatoms from the third row, such as Si and P in the ring can contribute to compensate this instability. In a seminal paper, Schleyer et al.[4] concluded that the inherent π-donor capability of phosphorus is larger than that of its second row counterpart nitrogen and new chemical bricks can indeed be furnished utilizing phosphorus.[5] Very recently we described the synthesis of a four-membered CSi_2P ring (LSi-C(Ad)-Si(L)-P, L = PhC(N*t*Bu)$_2$) (**A**)[6] which can be deemed as an analogue of cyclobutadiene by the reaction of chlorosilylene LSiCl (**1**)[7,8] with adamantyl phosphaalkyne. The fascinating features of this four-membered ring (**A**) are 1) a two-coordinate phosphorus atom,[6,9] 2) a three-coordinate carbon atom, and 3) a cyclic architecture where all Si, C, and P atoms are formally present in low oxidation states. The synthesis of this CSi_2P ring under mild conditions opens up a new avenue to Si, C, and P containing heterocycles. On the basis of our results, it seems obvious to examine the reaction of **1** with less bulky and unhindered phosphaalkynes because alteration of the alkyl group could enable the synthesis of different ring systems. Herein we report the reaction of **1** with methyl phosphaalkyne, which afforded a stable silicon, carbon, and phosphorus containing five-membered heterocycle cation **2** (see Scheme 1).

Hallmark studies by Lambert,[10] Reed,[11] Corriu,[12] Müller,[13] and Belzner[14] brought acyclic silylium cations to the fore which emerged as potential Lewis acids for catalysis.[13a,15] Very recently Oestreich et al. reported a unique transition metal stabilized silicon cation.[16] However, the examples with silylium cation in which the positively charged silicon is embedded into a π-system are still very scant.[17,18] The first cyclic silylium ion, silatropylium ion was reported by Komatsu et al. although without a single-crystal structure.[17] The first structurally characterized cyclic silylium cation, namely cyclotetrasilenylium ion [(tBu$_2$MeSiSi)$_3$SitBu$_2$)]$^+$ was reported by Sekiguchi et al.[18a] Following this, cyclotrisilenylium tetraarylborates (Ar = C_6F_5, 2,3,5,6-F_4-C_6H, 4-tBuMe$_2$Si-2,3,5,6-F_4C_6) and a 1,3,4,4-tetra-*tert*-butyl-2-(di-*tert*-butylmethylsilyl) cyclotetrasilenylium cation were also prepared by the same group.[18b,c] Inoue and Driess reported on a tetrasilacyclobutadiene dication supported with a benzamidinato ligand.[18e] Nevertheless, the quest for isolable derivatives of silylium ions is still very high and in this respect our present finding is important for organosilicon chemistry. Moreover, a phosphorus atom is an isolobal equivalent to a CH group,[19a] so the number of π-electrons in **2** is 4 which is the same for the cyclopentadienyl cation (Cp^+). Therefore, it is feasible to state that **2** is a formal analogue of Cp^+. Note that similar carbon–phosphorus cage cations which are also isolobal to Cp^+ have recently been reported by Russell and co-workers.[19b]

Compound **2** was synthesized by the reaction of **1** with methyl phosphaalkyne. Typically, treatment of **1** with MeCP in a 4:1 ratio in toluene at −30 °C immediately afforded a yellow solution (Scheme 1). Removal of the solvent under



1 **2**

Scheme 1. Preparation of compound **2**.

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vacuum and recrystallization from toluene gave extremely air and moisture sensitive yellow crystals of **2** in 33.5% yield at room temperature. Compound **2** is stable in the solid state under an inert atmosphere and soluble in toluene, diethyl ether, and THF and partially soluble in benzene. Melting associated with decomposition was observed at 210°C. The molecular ion in the EI-mass spectrum of **2** is observed at m/z 835 for $C_{47}H_{72}N_6PSi_3$ although with very low intensity.

An X-ray diffraction study on a single crystal of **2** shows that it crystallizes in the trigonal space group $P3_212$ (Figure 1).[20] The molecular structure of **2** is unique and is the first crystallographic example of a cation bearing a novel five-membered CSi_3P cycle which exists as 1:1 salt with chloride as the counteranion. The molecule is located on a crystallographic twofold axis bisecting the central five-membered ring through the Si–Si bond and the tertiary amidinate carbon atom C33. This results in a disordered model in which the phosphorus atom and the CCH_3 group share the same sites and the Si3 atom is not located on the twofold axis but on a general position close to it. The crystal has solvent channels passing through it exhibiting excessive disorder and generally causing slight flexibility in the arrangement of the molecules of **2**. The absolute values for the bond lengths might therefore be not as reliable as their standard deviations indicate and should be considered cautiously.

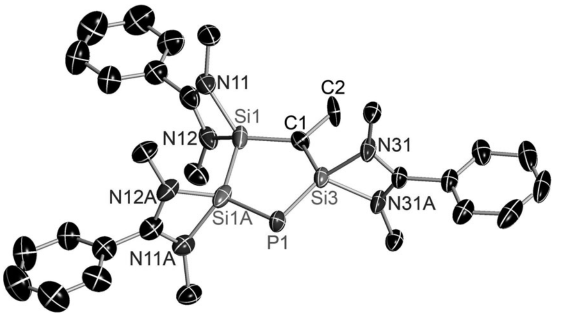


Figure 1. Molecular structure of the cation of **2**. Hydrogen atoms and methyl groups of *t*Bu substituents are not shown. Anisotropic displacement parameters are set at 50% probability. Selected bond lengths [Å] and bond angles [°], calculated values from geometry optimization (B3LYP/def2-TZVP level of theory) given in square brackets: Si1–C1 1.784(5) [1.752], Si3–C1 1.769(7) [1.793], Si1–Si1A 2.371(2) [2.418], Si1A–P1 2.169(2) [2.137], Si3–P1 2.175(5) [2.199]; Si1A-P1-Si3 84.9(1) [91.9], P1-Si1A-Si1 117.85(5) [108.6], C2-C1-Si1 118.7(4) [124.4], C2-C1-Si3 120.4(4) [120.5], Si1-C1-Si3 121.0(3) [115.1], C1-Si1-Si1A 92.58(19) [102.3], C1-Si3-P1 123.2(2) [121.7].

The closest distance between the cationic Si atom and Cl^- is 6.32 Å, which is beyond the range of any significant interaction. The planar five-membered ring of **2** consists of three Si atoms, one C, and one P atom. All Si atoms are four-coordinated each and exhibit distorted tetrahedral geometry. The Si–Si bond length in **2** (2.371(2) Å) is consistent with a single bond, only 0.03 Å longer than the sum of the covalent radii of the Si atoms[21] and very close to that in the recently reported 1,2-disilacyclobutene (2.3659(4) Å).[8] The two Si–C bonds, Si1–C1 and Si3–C1 show bond lengths of 1.784(5) and 1.769(7) Å, respectively, which are intermediate between the Si–C double and single bonds (ca. 1.70[22] and 1.89 Å[23]). The Si–C bond lengths in **2** are in the same range as those of LSi-C(Ad)-Si(L)-P, L = PhC(N*t*Bu)$_2$ (1.7808(18) and 1.7834(18) Å)[6] and the recently published 1,4-disilabenzene derivative [LSi(μ-C_2Ph_2)$_2$SiL] (1.800(3) Å).[24] The geometry of the three-coordinate C1 can best be described as trigonal planar with the sum of the bond angles around C1 of 360°. Another predominant structural feature of **2** is the "naked" phosphorus atom (P1), which connects Si1A and Si3. The question arises of how many valence charge concentrations are present at that divalent P1.[25] The bond lengths of the phosphorus atom to the atoms Si1A and Si3 are 2.169(2) and 2.175(5) Å, respectively, with a Si-P-Si angle of 84.9(1)°. This would also be consistent with a populated non-hybridized *p*-orbital and a lone-pair in a stereochemically non-active s-orbital. The bond lengths lie between the average Si–P single bond length of 2.25 Å[26] and Si = P double bond length of 2.09 Å.[27,28]

A multinuclear NMR spectroscopy study of **2** supports the features deduced from the single crystal X-ray diffraction studies. In the ^{1}H NMR spectrum of **2** a broad resonance appeared at $\delta = 1.41$ ppm for the 54 *t*Bu protons, which is shifted significantly downfield compared to that of **1** ($\delta = 1.08$ ppm). In the ^{31}P NMR there is a sharp resonance displayed at $\delta = -272.06$ ppm, which corresponds to the dicoordinate phosphorus atom and is shifted slightly upfield when compared with that of **A** ($\delta = -243$ ppm).[6] In the ^{29}Si NMR spectrum of **2** there are three resonances at $\delta = 19.25$, 22.03, and 63.88 ppm which are assigned to the three different Si atoms in **2** and they are shifted downfield compared to that in **1** ($\delta = 14.6$ ppm). ^{31}P and ^{29}Si NMR show that neither Si nor P atom in **2** is protonated. The cyclic voltammogram of a THF solution of **2** exhibits a non-reversible reduction at 2.224 V versus Fc^+/Fc ($Fc = [Cp_2Fe]$).

To confirm the structure of compound **2**, as well as its cationic state, a series of quantum chemical calculations were carried out. Starting from the X-ray diffraction coordinates, the structure of the cation was optimized at the B3LYP/def2-TZVP level of theory.[29] To exclude any further protonation of the ring, hydrogen atoms were deliberately added at the P and C ring atoms to the optimized cation, followed by full geometry optimizations (given the large number of tentative structures, a smaller basis set was used, see Supporting Information). We find that any such changes lead to a strong destabilization of the ring. Double protonation at the P atom leads to breaking of a P–Si bond. Single protonation at both P and C breaks the ring at the Si–Si bond. Besides these results, one should note that protonation at the C atom would lead to a tetrahedral arrangement as in the pentamethylcyclopentenyl cation[2] which is incompatible with the structural information available. Therefore, we rule out the possibility of additional bonded hydrogen atoms at the ring. The optimized cation structure agrees well with the X-ray information. In another series of calculations, we investigated the stability of the cation relative to the anionic species. As anticipated, we found the aromatic anion significantly more stable than the cation **2**. Single point energy calculations at the DF-LCCSD(T0)/cc-pVTZ level[30] reveal a 24 kcal mol^{-1} difference (using the cation optimized geometry). However, relaxing the anion geometry, there is a significant rotation of the two phenyl rings connected to the Si1- and Si3-benzamidinate ligands (see Figure 2). They are tilted out of the heterocyclic plane by about 40°, in clear disagreement with

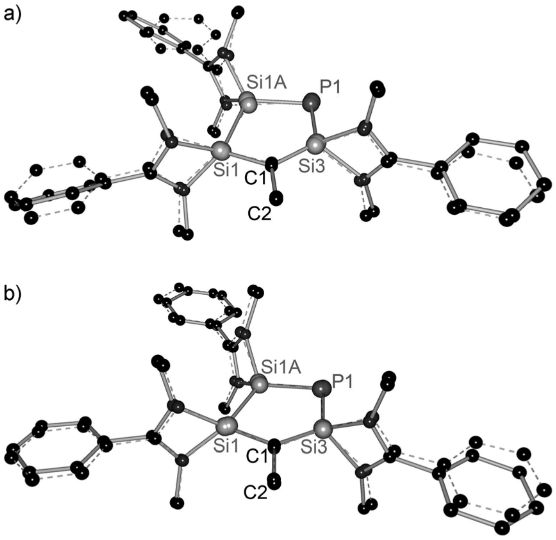


Figure 2. a) Superposition plot of the experimentally derived cation (dashed lines) with the computationally optimized geometry (solid lines) and b) of the experimentally derived cation (dashed) with the optimized geometry of the virtual anion (solid); methyl groups of *t*Bu substituents and hydrogen atoms are omitted for clarity.

the X-ray data. In order to explain this difference in the geometry, the electronic density was computed at the DF-LMP2/cc-pVTZ level of theory, complemented with a Natural Population Analysis (NPA).[31]

In the following, we compare the density for three cases. In a first calculation, we consider the cation at the optimized B3LYP/def2-TZVP geometry. In a second calculation, we kept the geometry, but changed the electronic configuration to the anion. The electronic density difference is shown in Figure 3. As it is visible, the two added electrons are mostly located in the Si1 and Si3 atoms, as well as in the coordinating moieties. The NPA charges agree with this picture, showing a difference in charge of about −1.0 in the two Si atoms, and −0.66 in the coordinated rings. Repeating the calculation in the relaxed anion geometry, the charge in the Si atoms is almost identical to that found in the cation (only a 0.14 variation in the combined atomic charges). The rotation of the benzamidinate phenyl rings accounts for a larger interaction in the π-system, and the added charge is, for the most part, removed from the five-membered heterocyclic ring.

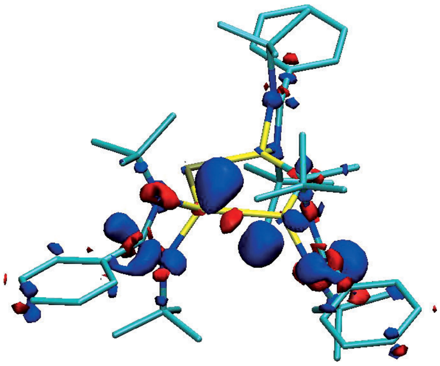
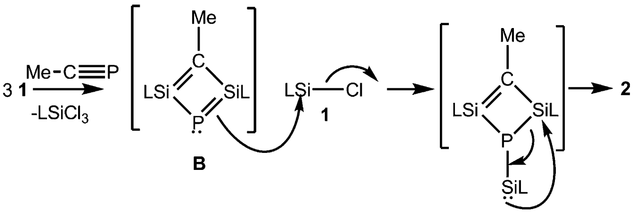


Figure 3. Isosurface plot of the DF-LMP2/cc-pVTZ density difference between the anion and cation of **2**, at the optimized cation structure. The hydrogen atoms were removed for clarity.

The mechanism of the reaction seems to be clear. Initially a four-membered CSi_2P ring (**B**; Scheme 2) was formed by the reaction of MeCP with 2 equivalents of **1**, which is like **A**,[6] along with the formation of 1 equivalent of $LSiCl_3$ for which a third molecule of **1** is required.[6] Due to the instability, **B** further reacts with another molecule of **1** and subsequently rearranges to **2** (Scheme 2).



Scheme 2. Tentative mechanism for the formation of **2**.

In conclusion, we report the reaction of the chlorosilylene **1** with methyl phosphaalkyne, to give a stable cation **2** which can be deemed as a formally heavier analogue of Cp^+. The most surprising property of **2** is the counteranion of the five-membered cationic ring system which is a simple chloride anion, and does not interact with the ring system and therefore does not contribute to its stability.

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