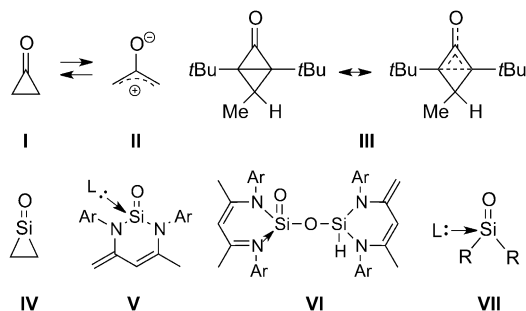


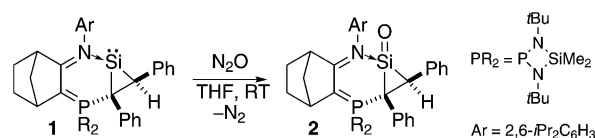
Synthesis of a Donor-Stabilized Silacyclopropan-1-one**

Ricardo Rodriguez, Thibault Troadec, David Gau, Nathalie Saffon-Merceron, Daisuke Hashizume, Karinne Miquieu, Jean-Marc Sotiropoulos, Antoine Baceiredo,* and Tsuyoshi Kato*

Cyclopropanones **I** are highly reactive ketones that display unusual properties due to the incorporation of a carbonyl group in a strained three-membered ring. In particular, substituted cyclopropanones may undergo ring opening to form oxyallyl zwitterions **II**,^[1] which can behave as 1,3-dipoles.^[2] Inherently reactive, oxyallyl zwitterions **II** have been implicated as intermediates in a number of organic reactions,^[3] although there have been very few reports of the direct experimental observation of oxyallyl intermediates.^[4] The bicyclobutanone **III**, with increased ring strain, has a unique hybrid structure between a cyclopropanone and an oxyallyl zwitterion, with a long endocyclic C–C bond.^[5]



The synthesis of the silicon analogue of **I**, silacyclopropan-1-one **IV**, remained elusive. Indeed, in contrast to stable organic carbonyl compounds, silanones are highly reactive intermediates owing to a weak and strongly polarized Si–O π bond.^[6] Therefore, they readily oligomerize to give polysiloxanes.^[7,8] The stabilization of such species is possible by the coordination of electron-donating ligands to the silicon center. This approach enabled the isolation of the first examples of base-stabilized silaureas **V**^[9] and silacarbamates **VI**.^[10] Several donor/acceptor-stabilized silacarbonyl compounds have been reported.^[11] However, no silicon analogue of ketones (a silaketone or silanone **VII**) has previously been reported, and only one example of a transition-metal–silanone complex has been described.^[12] Herein, we report the synthesis of the first donor-stabilized silacyclopropan-1-one **2** (Scheme 1), which has a hybrid structure with an



Scheme 1. Synthesis of the base-stabilized silacyclopropan-1-one **2**.

important oxyallyl character, and its unprecedented isomerization to a stable silenol derivative.

We recently reported the synthesis of the first stable base-supported silacycloprop-1-ylidene **1**.^[13] Silylene **1** readily reacts at room temperature with nitrous oxide (N_2O) to afford the corresponding silacyclopropan-1-one **2**, with the elimination of N_2 (Scheme 1). Colorless crystals of the silanone **2** were obtained in 85% yield from a solution in $CHCl_3/Et_2O$ (1:5). The diastereoselectivity of the reaction was indicated by the presence of a singlet in the ^{31}P NMR spectrum ($\delta = 46.6$ ppm). The ^{29}Si NMR spectrum revealed a doublet ($\delta = -69.1$ ppm, $^2J_{PSi} = 6.8$ Hz) at a lower field than that at which the doublet for **1** appeared ($\delta = -87.5$ ppm, $^2J_{PSi} = 2.9$ Hz), but approximately in the range observed for previously reported Lewis base stabilized silacarbonyl compounds **V** and **VI** ($\delta = -71$ to -86 ppm).^[9,10] The signal for the hydrogen atom on the cyclopropanone ring appeared in the 1H NMR spectrum as a doublet at $\delta = 3.02$ ppm with a relatively large phosphorus–proton coupling constant ($^3J_{PH} = 29.1$ Hz).

The structure of **2** was confirmed unambiguously by X-ray diffraction analysis (Figure 1).^[14] The short Si1–O distance (1.547 Å) is very similar to those in the previously reported base-stabilized silanones (1.532–1.579 Å).^[9,10] As a result of

[*] Dr. R. Rodriguez, Dr. T. Troadec, Dr. D. Gau, Dr. A. Baceiredo, Dr. T. Kato

Université de Toulouse, UPS, and CNRS
LHFA UMR 5069, 31062 Toulouse (France)
E-mail: baceired@chimie.ups-tlse.fr

kato@chimie.ups-tlse.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)

Dr. R. Rodriguez, Dr. D. Hashizume
Advanced Technology Support Division, RIKEN Advanced Science
Institute, 2-1 Hirosawa, Wako, Saitama 351-0198 (Japan)

Dr. K. Miquieu, Dr. J.-M. Sotiropoulos
Université de Pau et des Pays de l'Adour and CNRS IPREM UMR
5254, Technopôle Hélioparc
2 avenue du Président Angot, 64053 Pau (France)

[**] We are grateful to the CNRS and the ANR (NOPROBLEM, LEGO) for financial support of this research. R.R. acknowledges the JSPS for a postdoctoral fellowship. For the theoretical studies, access to the HPC resources of Idris was granted by GENCI (Grand Equipement National de Calcul Intensif) under allocation 2012 (i2012080045).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201210010>.

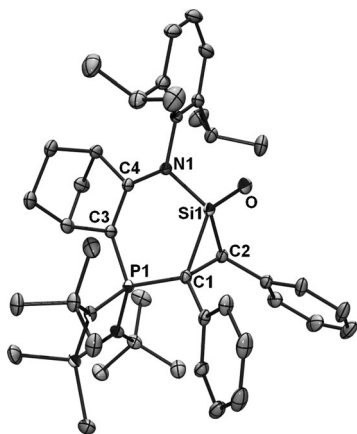


Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O 1.5467(6), Si1–C1 1.9177(7), Si1–C2 1.8358(6), C1–C2 1.6671(9), Si1–N1 1.7641(6), C1–P1 1.7777(6), P1–C3 1.7351(7), C3–C4 1.3799(9), C4–N1 1.3658(8); C1–Si1–C2 52.68(3), Si1–C1–C2 61.13(3), Si1–C2–C1 66.18(3), C1–P1–C3 107.16(3), O–Si1–C1 127.76(3), O–Si1–C2 127.48(3), O–Si1–N1 114.97(3), N1–Si1–C1 109.01(3), N1–Si1–C2 110.38(3).

the oxidation of the Si atom, a significant shortening of the bonds around the silicon atom was observed (Si1–C1 1.918, Si1–C2 1.836, Si1–N1 1.764 Å for **2**; Si1–C1 1.996, Si1–C2 1.929, Si1–N1 1.8525 Å for **1**). The most striking feature of **2** is the very long endocyclic C1–C2 bond (1.667 Å), which is significantly longer than the corresponding C–C bond in the starting silacycloprop-1-ylidene **1** (1.568 Å). This bond is considerably longer than the corresponding σ C–C bond in cyclopropanones (1.592 Å)^[15] and is similar in length to that observed in the more highly strained bicyclobutanone **III** (1.69 Å).^[4] In fact, this value is close to the lengths of the longest C(sp³)–C(sp³) single bonds known to date (1.72–1.78 Å).^[16]

To gain more insight into the electronic situation in **2**, we derived the experimental electron-density distribution from the X-ray diffraction data.^[18] The double-bond character of the Si1–O bond is indicated by a significantly large density at the bond critical point (BCP; 0.213 e au^{−3}); for comparison, a Si–O single bond has a density of 0.135 e au^{−3} at the BCP.^[19] As suggested by the unusual length observed in the X-ray crystal structure, the bond density of the endocyclic C1–C2 σ bond is highly deformed towards the Si1 atom (the BCP is located inside the three-membered ring), in contrast to the Si–C bonds, for which the BCP is found outside the ring, as is typical for strained σ bonds in three-membered rings (Figure 2).^[20] These results strongly suggest an electron delocalization of the C–C σ bond towards the silicon atom. Furthermore, as a result of this delocalization, the electron density at the BCP (C1–C2) is significantly lower (0.164 e au^{−3}) than that of classical C–C single bonds (0.262 e au^{−3}). The C–C σ -bond electrons probably interact through negative hyperconjugation by an in-plane π interaction with low-lying vacant orbitals on the silicon atom. Indeed, the significantly increased electron densities at the BCPs of the Si–C bonds (0.113 for Si1–C1 and 0.138 e au^{−3}

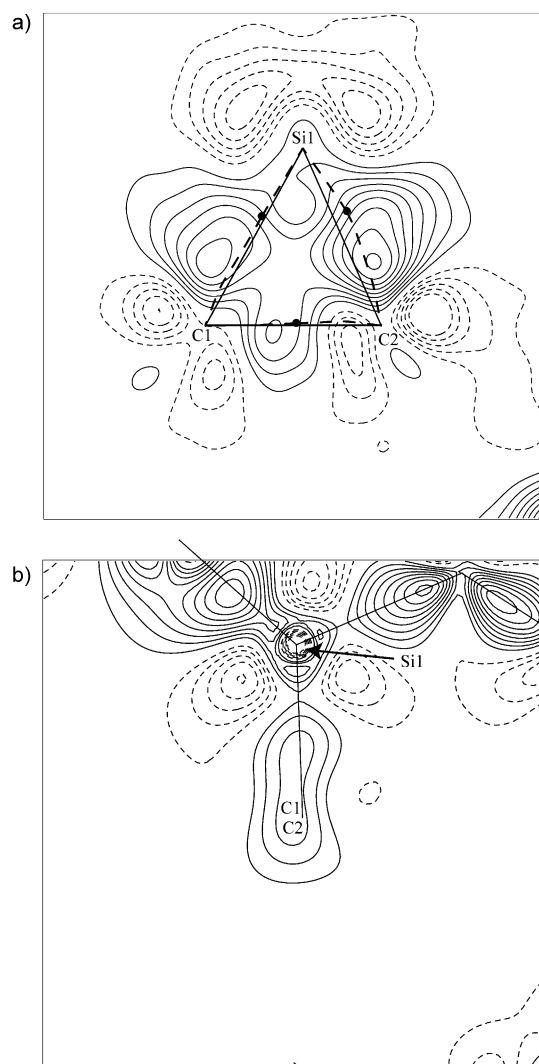
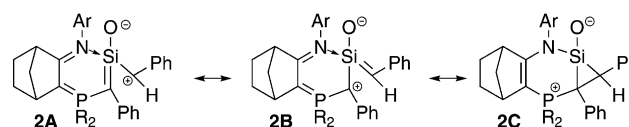


Figure 2. Static model maps^[17] for the silacyclopropanone ring: a) map in the Si1–C1–C2 plane with bond paths and bond critical points; b) map on the cross-section at the bond critical point of the C1–C2 bond. Contours drawn with unbroken and dashed lines indicate positive and negative densities, respectively. The interval is 0.05 e Å³. Bold dashed lines and points indicate bond paths and bond critical points, respectively.

for Si1–C2)^[21] relative to those for the starting material **1** (0.093 for Si1–C1 and 0.097 e au^{−3} for Si1–C2) clearly indicate their enhanced multiple-bonding character. The higher electron density of the Si1–C2 bond relative to that of the Si1–C1 bond suggests a greater contribution of the canonical structure **2B** (Scheme 2).

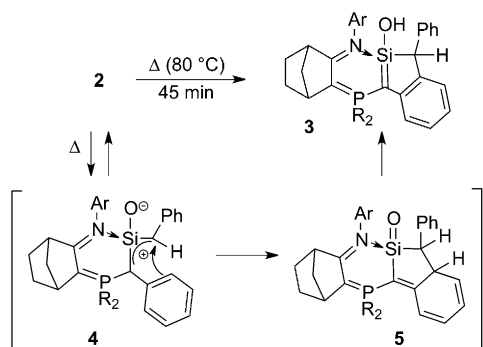
These experimental observations were supported by theoretical calculations performed at the M06/6-31G** level of theory. Indeed, the optimized structure of **2** agrees quite



Scheme 2. Canonical structures of **2**.

well with the experimental data, particularly the calculated C–C endocyclic bond length (1.655 Å).^[22] Furthermore, AIM (“atoms in molecules”) calculations revealed a very small electron density $\rho(r)$ at the BCP of the long endocyclic C–C bond (0.185 e a.u.^{−3}). This value is much smaller than the typical value for a classical σ bond, such as that in **1** (0.217 e a.u.^{−3}). More interestingly, natural bonding orbital (NBO) analysis indeed revealed an interaction between the endocyclic C–C σ bond and the antibonding orbitals at the silicon center of **2** of considerable strength (33 kcal mol^{−1}).

As expected, the very long C1–C2 bond in **2** is thermally labile. This property was demonstrated by the facile isomerization of **2** under mild conditions (80 °C) with the quantitative formation of an unprecedented Lewis base supported 1-silenol derivative **3** (Scheme 3). The ²⁹Si NMR spectrum of **3** exhibited a lower-field chemical shift ($\delta = -7.1$ ppm, ²*J*_{PSi} =



Scheme 3. Synthesis of **3** by the thermolysis of **2**.

23.9 Hz) relative to that observed for **2** ($\delta = -69.1$ ppm), close to the region for silene–Lewis base adducts ($\delta = -18$ to -39 ppm).^[23] In the ¹³C NMR spectrum, the signal for the Si=C atom appeared as a doublet at $\delta = 48.3$ ppm (²*J*_{PC} = 127.8 Hz), in the chemical-shift range typical for carbon atoms in base-stabilized silenes ($\delta = 40$ –52 ppm).^[23] The ¹H NMR spectrum revealed a singlet for the SiCH atom ($\delta = 3.82$ ppm), in agreement with C–C bond cleavage of the three-membered ring. The structure of **3** was confirmed by X-ray diffraction analysis (Figure 3),^[14] which showed a relatively short Si–C1 bond (1.794 Å), intermediate between typical single and double Si–C bonds.^[24] The elongation of the Si=C bond is probably due to Lewis base coordination of the silicon center as well as π -electron delocalization to the adjacent phosphonio fragment. On the other hand, the Si1–O bond length (1.644 Å) is typical for a single bond. To the best of our knowledge, **3** is the first stable 1-silenol derivative to be reported. There have only been a few studies on 1-silenols and their derivatives, and only one stable 1-silenol ether has been reported.^[25] Nevertheless, several related compounds, such as 2-silenolates^[26] and Brook-type silenes,^[27] have been synthesized and fully characterized.^[24,28]

Calculations demonstrated that the silenol **3** is considerably more stable than the corresponding keto tautomer, silanone **3_{keto}**, by 23 kcal mol^{−1}, probably as a result of the efficient stabilization of the silene moiety by the adjacent phosphonio center (Scheme 4). Indeed, in marked contrast,

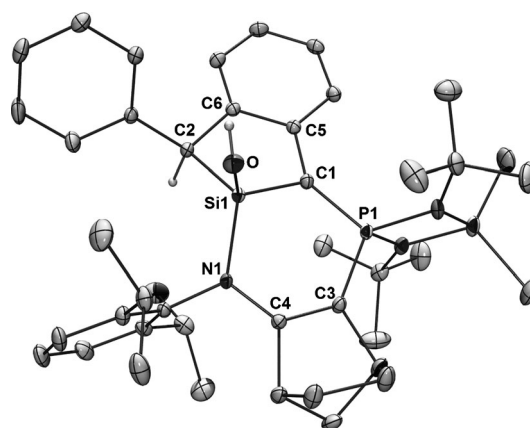
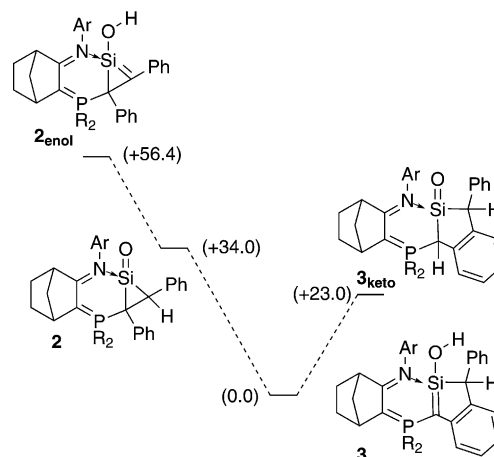


Figure 3. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Only hydrogen atoms on the O and C2 atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–O 1.644(11), Si1–N1 1.747(12), Si1–C2 1.890(14), Si1–C1 1.794(14), C1–P1 1.677(14), P1–C3 1.764(14), C3–C4 1.371(18), C4–N1 1.381(17), C1–C5 1.466(19), C2–C6 1.529(19), C5–C6 1.427(19); C5–C1–P1 132.12(10), Si1–C1–C5 106.47(9), Si1–C1–P1 121.21(8).

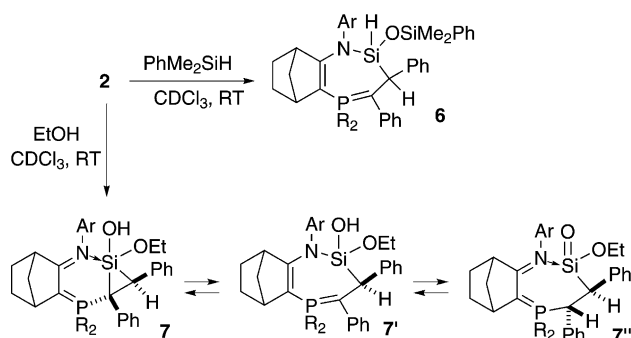


Scheme 4. Relative energies of the silacyclopropan-1-one **2** and its isomers.

the silacyclopropan-1-one **2** is more stable than its silenol tautomer **2_{enol}** ($\Delta E = +22.4$ kcal mol^{−1}). Moreover, the isomerization of silacyclopropanone **2** to form the five-membered-ring cyclic silenol **3** is strongly exothermic ($\Delta E = -34.0$ kcal mol^{−1}).

The rearrangement reaction of **2** probably starts with C–C bond cleavage to form the silaoxyallyl isomer **4** (Scheme 3). Intermediate **4** then undergoes cyclization through an intramolecular Friedel–Crafts reaction between the oxyallyl fragment and one of the phenyl substituents to give a transient α,β -unsaturated silanone **5**.^[29] Finally, the rearomatization of **5** by a 1,4-proton migration affords the isolated silenol derivative **3**.

In spite of the efficient stabilization of **2** by complexation of the imine fragment, the silanone functionality remains highly reactive. Indeed, the silacyclopropan-1-one **2** reacted readily with dimethylphenylsilane at room temperature



Scheme 5. Reactions of **2** with an alcohol and a silane.

through Si=O insertion into the Si–H σ bond to afford the siloxane **6** with a seven-membered heterocyclic ring (Scheme 5). A similar ring-opening reaction of the three-membered silacyclopropane fragment was observed in the reaction of the silacycloprop-1-ylidene **1** with ethyl vinyl ketone.^[13] Similarly, **2** reacted with ethanol to give the silaester derivative **7''**, which was isolated in the solid state and characterized by X-ray diffraction analysis (Figure 4).^[14] The bonding situation around the silicon center in **7''** is very

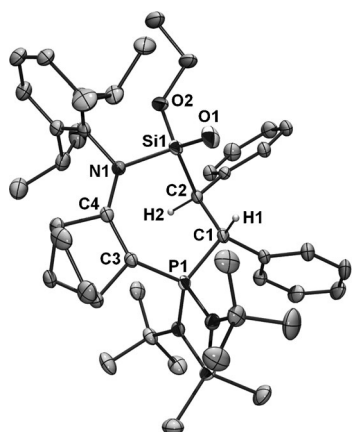


Figure 4. Molecular structure of **7''**. Thermal ellipsoids represent 30% probability. Only hydrogen atoms on the C1 and C2 atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.5422(16), Si1–O2 1.6312(16), Si1–N1 1.8062(16), Si1–C2 1.8915(18), C1–C2 1.560(3), C1–P1 1.8235(18), P1–C3 1.7357(18), C3–C4 1.393(3), N1–C4 1.347(2); O1–Si1–O2 119.81(9), O1–Si1–N1 114.54(9), O1–Si1–C2 111.57(9), O2–Si1–C2 106.20(8), O2–Si1–N1 98.28(8).

similar to that observed in related silacarbamates **VI**,^[10] in particular, the two Si–O bonds have different lengths (Si1–O1: 1.542 Å, Si1–O2: 1.631 Å). In solution, the silaester **7''** exists in equilibrium with a silanol tautomer. The interconversion of the two compounds involves a 1,4-proton migration. This silanol isomer could be either the sila-hemiacetal **7** or its ring-opened derivative **7'**. However, owing to its highly fluxional character, the complete characterization of **7/7'** is quite difficult. The equilibrium is strongly solvent-dependent, as indicated by the signals observed in the ¹H and ¹³C NMR

spectra of the two isomers **7/7'** and **7''** (**7/7'**:**7''** = 80:20 in C₆D₆ and 0:100 in CDCl₃).

In conclusion, we have successfully synthesized the first stable and isolable sila analogue of ketones, the Lewis base stabilized silacyclopropan-1-one **2**, which presents a novel silacyclopropanone–oxyallyl hybrid structure. This feature is mainly due to negative hyperconjugation involving the strong Lewis acidity of the silanone functionality, in spite of the coordination of the imine fragment. Indeed, the silacyclopropan-1-one **2** remains highly reactive, and its unique reactivity also enabled the first synthesis of an isolable base-stabilized 1-silenol, **3**. Further investigations on the reactivity of these new species are under way.

Received: December 14, 2012

Published online: March 12, 2013

Keywords: reactive intermediates · silanones · silicon · silylenes · small ring systems

- [1] a) M. H. J. Cordes, J. A. Berson, *J. Am. Chem. Soc.* **1992**, *114*, 11010; b) T. Ichino, S. M. Villano, A. J. Gianola, D. J. Goebbert, L. Velarde, A. Sanov, S. J. Blanksby, X. Zhou, D. A. Hrovat, W. T. Borden, W. C. Lineberger, *Angew. Chem.* **2009**, *121*, 8661; *Angew. Chem. Int. Ed.* **2009**, *48*, 8509.
- [2] a) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, W. B. Hammond, *J. Am. Chem. Soc.* **1969**, *91*, 2283; b) “Recent Aspects of Cyclopropanone Chemistry”: H. H. Wasserman, G. M. Clark, P. C. Turley, *Stereochemistry I, Topics in Current Chemistry*, Vol. 47, Springer, Berlin, **1974**, p. 73; c) N. J. Turro, *Acc. Chem. Res.* **1969**, *2*, 25.
- [3] a) R. Noyori, *Acc. Chem. Res.* **1979**, *12*, 61; b) H. Takaya, S. Makino, Y. Hayakawa, R. Noyori, *J. Am. Chem. Soc.* **1978**, *100*, 1765; c) Y. Hayakawa, K. Yokoyama, R. Noyori, *J. Am. Chem. Soc.* **1978**, *100*, 1791; d) Y. Hayakawa, Y. Baba, S. Makino, R. Noyori, *J. Am. Chem. Soc.* **1978**, *100*, 1786; e) K. Lee, J. K. Cha, *Org. Lett.* **1999**, *1*, 523.
- [4] For the detection of oxyallyl intermediates by UV/Vis spectroscopy, see: T. Hirano, T. Kumagata, T. Miyashi, K. Akiyama, Y. Ikegami, *J. Org. Chem.* **1991**, *56*, 1907.
- [5] S. Bhargava, J. Hou, M. Parvez, T. S. Sorensen, *J. Am. Chem. Soc.* **2005**, *127*, 3704.
- [6] R. C. West, *CRC Handbook of Chemistry and Physics*, 62nd ed., CRC, Boca Raton, FL, **1981**, C-301, E-61.
- [7] C. A. Arrington, R. C. West, J. Michl, *J. Am. Chem. Soc.* **1983**, *105*, 6176.
- [8] G. Raabe, J. Michl, *Chem. Rev.* **1985**, *85*, 419.
- [9] a) Y. Xiong, S. Yao, R. Müller, M. Kaupp, M. Driess, *Nat. Chem.* **2010**, *2*, 577; b) Y. Xiong, S. Yao, R. Müller, M. Kaupp, M. Driess, *J. Am. Chem. Soc.* **2010**, *132*, 6912; c) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562.
- [10] S. Yao, Y. Xiong, M. Brym, M. Driess, *J. Am. Chem. Soc.* **2007**, *129*, 7268.
- [11] a) S. Yao, M. Brym, C. van Wüllen, M. Driess, *Angew. Chem.* **2007**, *119*, 4237; *Angew. Chem. Int. Ed.* **2007**, *46*, 4159; b) Y. Xiong, S. Yao, M. Driess, *Dalton Trans.* **2010**, *39*, 9282; c) R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Pröpper, B. Dittrich, S. Klein, G. Frenking, *J. Am. Chem. Soc.* **2011**, *133*, 17552; d) Y. Xiong, S. Yao, M. Driess, *Angew. Chem.* **2010**, *122*, 6792; *Angew. Chem. Int. Ed.* **2010**, *49*, 6642; e) R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Pröpper, B. Dittrich, C. Goedecke, G. Frenking, *Chem. Commun.* **2012**, *48*, 8186.
- [12] T. Muraoka, K. Abe, Y. Haga, T. Nakamura, K. Ueno, *J. Am. Chem. Soc.* **2011**, *133*, 15365.

- [13] R. Rodriguez, T. Troadec, T. Kato, N. Saffon-Merceron, J.-M. Sotiropoulos, A. Baceiredo, *Angew. Chem.* **2012**, *124*, 7270; *Angew. Chem. Int. Ed.* **2012**, *51*, 7158.
- [14] CCDC 913900 (**1**), 914627 (**2**, structure analysis), 912563 (**2**, electron-density-distribution analysis), 913790 (**3**), and 922352 (**7'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [15] M. H. J. Cordes, S. de Gala, J. A. Berson, *J. Am. Chem. Soc.* **1994**, *116*, 11161.
- [16] a) K. K. Baldridge, Y. Kasahara, K. Ogawa, J. S. Siegel, K. Tanaka, F. Toda, *J. Am. Chem. Soc.* **1998**, *120*, 6167; b) H. Kawai, T. Takeda, K. Fujiwara, M. Wakeshima, Y. Hinatsu, T. Suzuki, *Chem. Eur. J.* **2008**, *14*, 5780.
- [17] *International Tables for Crystallography, Vol. C* (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, **1996**, pp. 627–645.
- [18] For some other reports on electron-density analysis on the basis of diffraction data, see: a) E. Espinosa, C. Lecomte, E. Molins, S. Veintemillas, A. Cousson, W. Paulus, *Acta Crystallogr. Sect. B* **1996**, *52*, 519; b) K. Akiba, Y. Moriyama, M. Mizozoe, H. Inohara, T. Nishii, Y. Yamamoto, M. Minoura, D. Hashizume, F. Iwasaki, N. Takagi, K. Ishimura, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 5893.
- [19] V. G. Avakyan, V. F. Sidorkin, E. F. Belogolova, S. L. Guselnikov, L. E. Guselnikov, *Organometallics* **2006**, *25*, 6007.
- [20] G. D. Ruggiero, I. H. Williams, *J. Chem. Soc. Perkin Trans. 2* **2001**, 733.
- [21] The comparatively lower density of the Si1–C1 bond is due to further extended electron delocalization towards the adjacent phosphonio fragment.
- [22] Selected bond lengths [Å] and angles [°] calculated at M06/6-31G** for **2**: Si1–O 1.542, Si1–C1 1.940, Si1–C2 1.839, C1–C2 1.638, Si1–N1 1.793; C1–Si1–C2 51.29, Si1–C1–C2 61.14, Si1–C2–C1 67.57.
- [23] a) D. Gau, T. Kato, N. Saffon-Merceron, F. P. Cossío, A. Baceiredo, *J. Am. Chem. Soc.* **2009**, *131*, 8762; b) N. Wiberg, G. Wagner, G. Reber, J. Riede, G. Müller, *Organometallics* **1987**, *6*, 35; c) M. Mickoleit, K. Schmohl, R. Kempe, H. Oehme, *Angew. Chem.* **2000**, *112*, 1679; *Angew. Chem. Int. Ed.* **2000**, *39*, 1610.
- [24] H. Ottosson, A. M. Eklöf, *Coord. Chem. Rev.* **2008**, *252*, 1287.
- [25] S. Inoue, M. Ichinohe, A. Sekiguchi, *Angew. Chem.* **2007**, *119*, 3410; *Angew. Chem. Int. Ed.* **2007**, *46*, 3346.
- [26] R. Dobrovetsky, L. Zborovsky, D. Sheberla, M. Botoshansky, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chem.* **2010**, *122*, 4178; *Angew. Chem. Int. Ed.* **2010**, *49*, 4084; T. Guliashvili, I. El-Sayed, A. Fischer, H. Ottosson, *Angew. Chem.* **2003**, *115*, 1678; *Angew. Chem. Int. Ed.* **2003**, *42*, 1640.
- [27] a) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc. Chem. Commun.* **1981**, 191; b) K. M. Baines, A. G. Brook, R. R. Ford, P. D. Lickiss, A. K. Saxena, W. J. Chatterton, J. F. Sawyer, B. A. Behnam, *Organometallics* **1989**, *8*, 693; c) A. G. Brook, A. Baumegeger, A. J. Lough, *Organometallics* **1992**, *11*, 3088; d) I. Bejan, D. Güclü, S. Inoue, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Angew. Chem.* **2007**, *119*, 3413; *Angew. Chem. Int. Ed.* **2007**, *46*, 3349.
- [28] a) Y. Apeloig, M. Karni, *J. Am. Chem. Soc.* **1984**, *106*, 6676; b) H. Ottosson, *Chem. Eur. J.* **2003**, *9*, 4144; c) A. M. Eklöf, T. Guliashvili, H. Ottosson, *Organometallics* **2008**, *27*, 5203.
- [29] A similar cyclization reaction was reported previously for cyclopropanones: A. G. Moiseev, M. Abe, E. O. Danilov, D. C. Neckers, *J. Org. Chem.* **2007**, *72*, 2777.