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P_4 Activation

Consecutive Insertion of a Silylene into the P_4 Tetrahedron: Facile Access to Strained SiP_4 and Si_2P_4 Cage Compounds**

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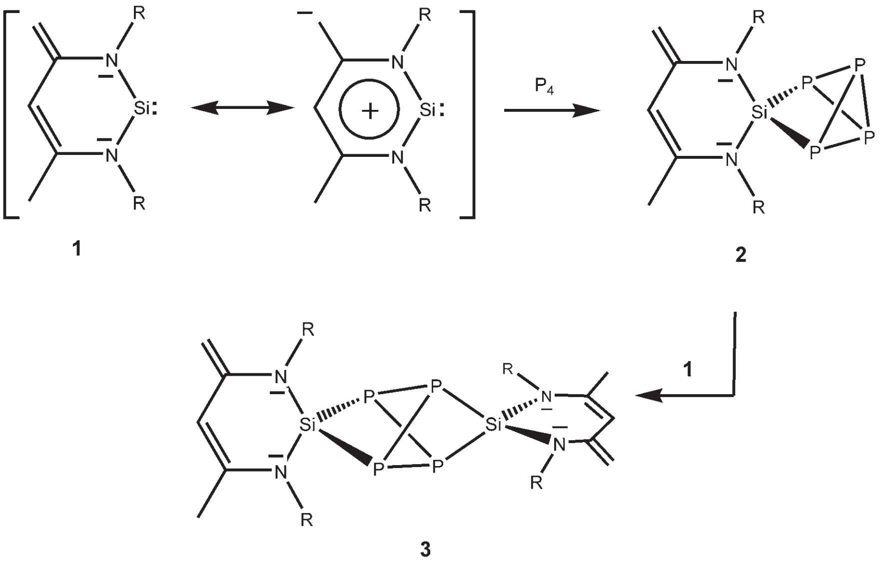
Dedicated to Professor Michael F. Lappert

Organosilicon–phosphorus compounds are versatile building blocks in contemporary organophosphorus chemistry[1] and for the synthesis of metal phosphide semiconducting materials or respective molecular clusters.[2] Likewise, cyclic silicon–phosphorus compounds can serve as chelating electron-rich ligands in transition-metal complexes, modeling unusual coordination modes of metal centers in catalysts.[3] The formation of silicon–phosphorus compounds is commonly achieved by salt metathesis reactions using silicon halides and main-group-metal phosphides (for example, lithium phosphides).[1,4] However, the latter method is hardly suitable for the synthesis of strained silicon–phosphorus cycles and cages because of facile skeletal rearrangement reactions (for example, intermolecular ring enlargement) under the reaction conditions.[5] Hence, other synthetic methods are desirable to gain access to well-defined, strained silicon–phosphorus cycles and cages. A promising alternative strategy represents the utilization of unsaturated silicon compounds and white phosphorus (P_4) as shown by the gentle reaction of disilenes ($R_2Si{=}SiR_2$) and phosphasilenes ($R_2Si{=}PR'$) with P_4 at 40°C, leading to the unusual butterfly-shaped Si_2P_2 and SiP_3 heterobicyclo[1.1.0]butanes,[6a,7] respectively. The mechanism of this remarkably mild P_4 activation and degradation process, initiated by low-valent silicon, is not clearly understood as yet.[6b] The latter results prompted us to investigate whether stable silylenes ($R_2Si{:}$) are also capable of P_4 activation to give novel strained silicon–phosphorus cycles. Herein we report the first SiP_4 and Si_2P_4 cage compounds which result from consecutive P_4 activation with the stable silylene **1** (Scheme 1).



Scheme 1. Synthesis of **2** and **3** from **1** and P_4. $R = 2,6\text{-}i\text{Pr}_2C_6H_3$.

Although several stable silylenes have been described thus far, to our knowledge, both the highly electrophilic silylene $(CH_2)_2[C(SiMe_3)_2]_2Si{:}$[8] and the silicon analogues of nucleophilic Arduengo-type carbenes[9] seemed to be unsuitable for P_4 activation. In contrast, the zwitterionic silylene **1**[10a] reacts gently with P_4 in the molar ratio of 1:1 at ambient temperature to give solely the compound **2**. Remarkably, the germylene analogue of **1**,[10b] in turn, is resistant towards P_4 even in boiling toluene owing to the lower reduction potential of Ge^{II} versus Si^{II} (inert-pair effect). Compound **2** can be isolated in the form of colorless crystals in 60% yield.[11]

According to EI-MS spectra and combustion analysis, **2** is a 1:1 adduct of **1** and P_4. Its ^1H NMR spectrum proves the integrity of the C_3N_2 chelate ligand at the silicon atom. As shown by ^{31}P NMR spectroscopy, **2** bears three chemically different sorts of ^{31}P nuclei (A, B, and X), giving rise to temperature-invariant resonance signals at $\delta_X = 131.9$, $\delta_A = -342.4$, and $\delta_B = -348.0$ ppm. The low-field resonance signal at δ_X splits into a doublet of doublets ($^1J(P_X,P_A) = 146.8$, $^1J(P_X,P_B) = 144.7$ Hz) while each of the two high-field signals exhibits a doublet of triplets ($^1J(P_X,P_A) = 144.7$, $^1J(P_A,P_B) = 188.0$ Hz), indicating an ABX_2 splitting pattern.[11] The

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unusual low-field shift of P_X is similar to values observed for M–P-bonded P atoms in isovalent $[L_nMP_4]$ complexes with a tricyclo[3.1.0]pentane-like core ($\{L_nM\}$ = diamagnetic transition-metal complex fragment[12a–c] and PI_2^+ [12d]). Likewise, the high-field shifts of P_A and P_B in **2** signalize similar electronic features as observed for bridgehead P atoms in $[L_nMP_4]$ complexes[12] and related butterfly-shaped Si,P compounds (Scheme 1).[6,7] The ^{29}Si NMR spectrum of **2** displays a broadened triplet resonance at $\delta = -40.4$ ppm ($^1J(^{29}Si,^{31}P) = 32.0$ Hz), which is in the typical range of related cyclosilaphosphanes with silicon–phosphorus single bonds.[13] The molecular structure of **2** deduced from ^{1}H, ^{31}P, and ^{29}Si NMR spectroscopy was confirmed by a single-crystal X-ray diffraction analysis.[11] Compound **2** consists of a tricyclic SiP_4 core with pyramidally coordinated phosphorus atoms and silicon atoms in a tetrahedral environment (Figure 1). The six-membered C_3N_2Si skeleton is almost planar and possesses endocyclic C–N and C–C bond lengths typical for its π-conjugated C_3N_2 backbone.[10] The exocyclic C1–C2 and C4–C5 bond lengths are identical owing to orientation disorder. As expected, both the Si–P (av. 224.7 pm) and P–P bond lengths (av. 222.9 pm) are similar to those observed in related strained silaphosphanes[13] and isostructural η^2-P_4 transition-metal complexes,[12a–c] respectively, except for the P3–P4 bridgehead bond length of 215.9(2) pm, which is even shorter than that in P_4 (220 pm). This result is reminiscent of the situation in related bicyclo[1.1.0]tetraphosphanes, R_2P_4 (R = organyl), which have relatively short P–P bridgehead bonds (212 pm) owing to partial P–P π-bond character.[14] Apparently, this bonding situation favors the insertion of a Si^{II} atom into the P3–P4 bond in **2**. Thus, **1** reacts slowly with **2** in toluene at 25 °C to give the insertion product **3** (Scheme 1), which was isolated in 27 % yield in the form of colorless crystals.[11] The reaction progress for the second insertion step of **1** into a P–P bond of the P_4 core is kinetically hampered because of steric congestion.

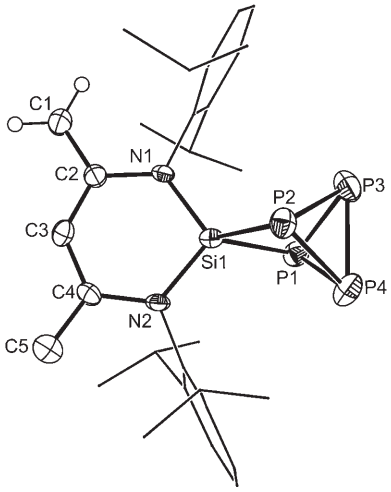

Figure 1. Molecular structure of **2**. Thermal ellipsoids (C1 through C5, P atoms, N1, N2, Si1) are drawn at the 50% probability level. Hydrogen atoms (except for those at C1) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1-N1 172.8(3), Si1-N2 172.4(3), Si1-P2 225.0(1), Si1-P1 224.6(1), P3-P2 223.2(1), P1-P3 223.5(2), P3-P4 215.9(2), P2-P4 222.7(1), P1-P4 222.1(2), N1-C2 141.2(4), N2-C4 142.2(4), C1-C2 141.8(4), C2-C3 139.7(5), C3-C4 139.2(4), C4-C5 141.6(5); N1-Si1-N2 104.1(1), P1-Si1-P2 87.32(5), P4-P3-P2 60.94(5), P4-P3-P1 60.70(5), P2-P3-P1 88.03(5), P4-P2-P3 57.91(5), P4-P2-Si1 84.82(5), P3-P2-Si1 83.85(5).

This reaction sequence is in contrast to the spontaneous multiple insertions of subvalent main-group-metal centers into the P_4 cage. For example, a related β-diketiminato Al^I complex reacts with P_4 to give a double-insertion product with a Al_2P_4 core.[15a] Likewise, the tetrameric Al^I compound $[(Cp^*Al)_4]$ reacts with P_4 in a 1.5:1 ratio to give $[(Cp^*Al)_6P_4]$,[15b] whereas the isovalent Ga^I atom in $[(Me_3Si)_3CGa\!:]$ affords an insertion product with a Ga_3P_4 core.[15c]

The composition of **3** is proven by EI-MS (molecular ion *m*/*z* 1013) and a correct combustion analysis while its constitution is evident by NMR spectroscopy. As expected, the $^{31}P\{^1H\}$ NMR spectrum displays two multiplets at $\delta_A = 153$ and $\delta_B = 158$ ppm, representing a AA′BB′ splitting pattern of higher order with unusually small magnitudes of the respective $^1J(^{31}P,^{31}P)$ coupling constants.[11] The ^{29}Si NMR spectrum displays a multiplet at $\delta = -15.9$ ppm, about 24 ppm to lower field in comparison with **2**. The molecular structure of **3** was confirmed by an X-ray diffraction analysis (Figure 2).[11] The P–P bond lengths in the asterane-shaped P_4 core in **3** are similar (av. 228.5(1) pm) but somewhat longer than those in **2**, presumably because of the steric congestion from the substituents at the silane moieties. The same is true for the Si–P bond lengths (av. 228.5(1) pm), which are slightly longer than those in **2**. Both C_3N_2Si moieties are practically planar

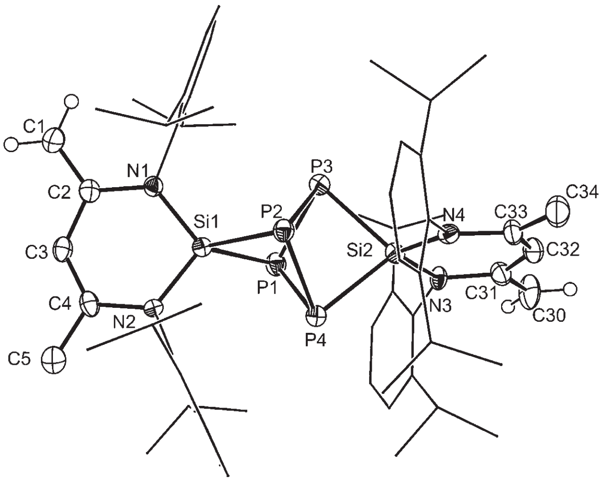

Figure 2. Molecular structure of **3**. Thermal ellipsoids (C1 through C5, C30 through C34, P atoms, N1 through N4, Si1, Si2) are drawn at the 50% probability level. Hydrogen atoms (except for those at C1 and C30) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1-N1 172.6(3), Si1-N2 172.9(3), Si2-N3 172.5(3), Si2-N4 173.4(3), Si1-P1 229.1(1), Si1-P2 227.5(1), Si2-P3 229.5(1), Si2-P4 227.5(1), P1-P3 228.0(1), P1-P4 229.7(1), P2-P3 229.6(1), P2-P4 228.0(1), C1-C2 138.9(5), C2-C3 142.0(5), C3-C4 136.6(5), C4-C5 145.5(5); N1-Si1-N2 102.9(1), N3-Si2-N4 102.8(1), P2-Si1-P1 82.1°(4), P4-Si2-P3 82.30(5), P3-P1-Si1 82.42(5), P3-P1-P4 82.16(5), Si1-P1-P4 80.00(5), P1-P3-Si2 82.31(5), P1-P3-P2 81.90(5), Si2-P3-P2 79.75(5).

and the endo- and exocyclic C–C bond lengths of the ligand backbone indicate alternating C–C single and double bonds. This situation suggests only little perturbation of the buta-1,3-diene π system by the nitrogen atoms, similar to the situation in other compounds with tetravalent silicon.[10a]

In summary, the novel strained tricyclic silaphosphans **2** and **3** are readily accessible by the first insertion reaction of a stable silylene into the P–P bonds of P_4. Owing to the intrinsic $Si^{\delta+}$–$P^{\delta-}$ σ-bond polarity, the compounds **2** and **3** could serve as nucleophilic reagents for a mild transfer of formally P_4^{2-} (in **2**) and P_4^{4-} moieties (in **3**) to transition metals, leading to phosphorus-rich metal clusters or complexes with "naked" polyphosphorus ligands.[16] Respective investigations are currently underway.

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[1] Reviews: a) G. Fritz, P. Scheer, *Chem. Rev.* **2000**, *100*, 3341–3402; b) D. A. Armitage, *Organosilicon derivatives of phosphorus, arsenic, antimony and bismuth* in *The Silicon-Heteroatom Bond* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1991**, chap. 5, pp. 152–182, and references therein; c) Appendix to "Organosilicon derivatives of phosphorus, arsenic, antimony and bismuth": D. A. Armitage, in *The Silicon-Heteroatom Bond* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1991**, chap. 6, pp. 183–231, and references therein.

[2] III/V materials: a) R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Pardy, S. Safieezad, R. B. Hallock, *Chem. Mater.* **1989**, *1*, 4–6; b) T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, W. E. Buhro, *Science* **1995**, *270*, 1791–1794; metal–phosphorus clusters: c) D. Fenske, J. Ohmer, J. Hachgenie, K. Merzweiler, *Angew. Chem.* **1988**, *100*, 1300–1320; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1277; d) D. Fenske, W. Holstein, *Angew. Chem.* **1994**, *106*, 1311–1312; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1290–1292.

[3] a) G. Fritz, R. Biastoch, *Z. Anorg. Allg. Chem.* **1986**, *535*, 63 and G. Fritz, R. Biastoch, *Z. Anorg. Allg. Chem.* **1986**, *535*, 95; b) G. Fritz, R. Biastoch, W. Hönle, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1986**, *535*, 86; c) M. Driess, M. Faulhaber, H. Pritzkow, *Angew. Chem.* **1997**, *109*, 1980–1982; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1892–1894; d) M. Driess, M. Reisgys, H. Pritzkow, *Angew. Chem.* **1992**, *104*, 1514–1516; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1510–1513; M. Driess, H. Pritzkow, M. Reisgys, *Chem. Ber.* **1996**, *129*, 247–252; e) R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828–845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789–805.

[4] a) R. T. Oakley, D. A. Stanislawski, R. West, *J. Organomet. Chem.* **1978**, *157*, 389; b) G. Fritz, R. Uhlmann, *Z. Anorg. Allg. Chem.* **1978**, *442*, 95; c) U. Winkler, M. Schieck, H. Pritzkow, M. Driess, I. Hyla-Kryspin, H. Lange, R. Gleiter, *Chem. Eur. J.* **1997**, *3*, 874–880.

[5] a) G. Fritz, R. Uhlmann, R. Uhlmann, W. Hölderich, *Z. Anorg. Allg. Chem.* **1978**, *442*, 86; b) strained Si/P cycles are accessible by employing bulky substituents at the Si and/or P atoms: see cited works in reference [1b]; c) M. Baudler, G. Scholz, K.-F. Tebbe, M. Feher, *Angew. Chem.* **1989**, *101*, 352–354; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 339–341; d) M. Driess, H. Pritzkow, S. Rell, R. Janoschek, *Inorg. Chem.* **1997**, *36*, 5212–5217; e) M. Driess, H. Pritzkow, M. Reisgys, *Chem. Ber.* **1991**, *124*, 1923–1929; f) M. Driess, R. Gleiter, R. Janoschek, M. Reisgys, *Angew. Chem.* **1994**, *106*, 1548–1551; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1484–1487.

[6] a) M. Driess, A. D. Fanta, D. R. Powell, R. West, *Angew. Chem.* **1989**, *101*, 1087–1088; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1038–1040; b) R. Okazaki, R. West, *Chemistry of Stable Disilenes* in *Adv. Organomet. Chem.* (Eds.: F. G. A. Stone, R. West), Academic Press, New York, **1996**, pp. 267–269.

[7] M. Driess, *Angew. Chem.* **1991**, *103*, 979–981; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1022–1024.

[8] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723.

[9] a) M. Denk, R. Lennon, R. Hayashi, R. West, A. Haaland, H. Belyakov, P. Verne, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692; recent reviews: b) N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165–4183; c) B. Gehrhus, P. B. Hitchcock, R. Pongtavornpinyo, L. Zhang, *Dalton Trans.* **2006**, 1847, and references therein.

[10] a) M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz, *J. Am. Chem. Soc.* **2006**, *128*, 9628; b) M. Driess, S. Yao, M. Brym, C. van Wüllen, *Angew. Chem.* **2006**, *118*, 4455–4458; *Angew. Chem. Int. Ed.* **2006**, *45*, 4349–4352.

[11] Experimental details as well as X-ray diffraction data for **2** and **3** are provided as Supporting Information.

[12] a) O. J. Scherer, M. Swarowsky, G. Wolmershäuser, *Angew. Chem.* **1988**, *100*, 738–739; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 694–695; b) O. J. Scherer, M. Swarowsky, G. Wolmershäuser, *Organometallics* **1989**, *8*, 841–842; c) D. Yakhvarov, P. Barbaro, L. Gonsalvi, S. M. Carpio, S. Midollini, A. Orlandini, M. Peruzzini, O. Sinyashin, F. Zanobini, *Angew. Chem.* **2006**, *118*, 4288–4291; *Angew. Chem. Int. Ed.* **2006**, *45*, 4182–4185; d) I. Krossing, *J. Chem. Soc. Dalton Trans.* **2002**, 500–512.

[13] M. Driess, H. Pritzkow, M. Reisgys, *Chem. Ber.* **1991**, *124*, 1931–1939; see also reference [1a].

[14] a) E. Niecke, R. Rüger, B. Krebs, *Angew. Chem.* **1982**, *94*, 553–554; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 544–545; b) R. Riedel, H.-D. Hausen, E. Fluck, *Angew. Chem.* **1985**, *97*, 1050; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1056–1057; c) W. W. Schoeller, V. Staemmler, P. Rademacher, E. Niecke, *Inorg. Chem.* **1986**, *25*, 4382.

[15] a) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chem.* **2004**, *116*, 3525–3527; *Angew. Chem. Int. Ed.* **2004**, *43*, 3443–3445; b) C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem.* **1994**, *106*, 225–227; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 199–200; c) W. Uhl, M. Benter, *Chem. Commun.* **1999**, 771–772.

[16] a) Review: O. J. Scherer, *Acc. Chem. Res.* **1999**, *32*, 751–762; b) M. Scheer, C. Troitzsch, P. G. Jones, *Angew. Chem.* **1992**, *104*, 1395–1397; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1377–1379.