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Communication

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Highly Selective Substitution and Insertion Reactions of Silylenes in a Metal Coordinated Polyphosphide

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Supporting Information Placeholder

ABSTRACT: Selective substitution and insertion reactions of silylenes into the *cyclo*-P₅ ring of $[Cp^*Fe(\eta^{5}-P_5)]$ are reported. The selective substitution of one P atom by an isoelectronic [LSi] fragment (L=PhC(N'Bu)₂) leads to $[(\eta^4-P_4SiL)FeCp^*]$ and [LSi(Cl)=P-SiL(Cl)₂] as a byproduct. To elucidate the reaction mechanism, [{LSi(N(SiMe_3)_2)}{(\eta^4-P_5)FeCp^*}], in which the silicon atom binds to the *cyclo*-P₅ ring, was synthesized as a model compound for the reaction intermediate. The insertion of [LSi-SiL] into the *cyclo*-P₅ ring of [Cp*Fe(η^{5} -P₅)] resulted in [{(η^4 -P_5(SiL)_2}FeCp*] featuring a *cyclo*-P₅(SiL)₂ ring and corresponds to the largest silicon-polyphosphorus ring known in a complex.

Selective substitution of ring atoms or ring expansions are valuable tools in synthetic organic and organometallic chemistry. Established ring-expansion reactions include, e.g. the rearrangements of carbocations¹ such as the Demjanov and Tiffeneau-Demjanov reactions or the Beckmann rearrangement,² radical reactions¹ and oxidation reactions such as the Baeyer-Villiger oxidation.³ In contrast, the selective expansion of phosphorus rings by other elements is not well explored.⁴ The most common reaction in this area is the insertion of heteroatoms into white phosphorus (P₄).⁵ Recently, significant efforts have been devoted to selectively functionalizing P₄ with low-valent main group complexes.^{5a, 5b,} ⁶ For example, a stepwise P-P bond activation of white phosphorus using a divalent silicon compound was reported.^{5g}

In contrast to such insertion reactions involving the very reactive strained P_4 cage, we were challenged by selective substitution and insertion reactions in the non-strained *cyclo*- P_5 ring of the air-stable [Cp*Fe(η^5 -P₅)] (Cp*=C₅Me₅).⁷ Considering the isolobal analogy between Cp⁻ and *cyclo*- P_5^- , [Cp*Fe(η^5 -P₅)] forms a metallocene structure similar to that of ferrocene.⁸ [Cp*Fe(η^5 -P₅)] has been employed as a very useful tool in coordination chemistry due to the presence of five free lone-pairs on the *cyclo*- P_5 ring.⁹ Scheer *et al.* engaged in a systematic study of the coordination behavior of [Cp*Fe(η^5 - P_5)] with various transition and main-group metals.¹⁰ The synthesis of the first inorganic fullerene-like molecule from [Cp*Fe(η^5 - P_5)] and CuCl is a significant breakthrough.¹¹

The selective replacement of P atoms in transition metal polyphosphides such as $[Cp*Fe(\eta^5-P_5)]$ by other heteroatoms is still a major challenge.¹² In addition, since such a replacement would disturb the five-fold symmetry of [Cp*Fe(η^5 -P₅)], the corresponding products can open new avenues in the coordination chemistry of polyphosphorus complexes. The reactivity of $[Cp^*Fe(\eta^5-P_5)]$ with singleelectron reductants usually involves the cyclo-P5 ring in the reduction process without alteration of the ring itself.13 Interestingly, by using NHCs as reactive donor molecules in the reactions with different cyclo-Pn ligand complexes, an extrusion of one P atom is observed, followed by a ring contraction.¹⁴ Therefore, the question arises as to what would happen if a highly reactive low-valent silicon complex is used in the reaction with $[Cp^*Fe(\eta^5-P_5)]$, a similar reaction behavior or a cleavage of a P-P bond in the cyclo-P₅ ring and a unique insertion of heteroatoms in the *cyclo*-P₅ ring or both, P atom elimination and heteroatom insertion. Herein, we report the reaction of $[Cp^*Fe(\eta^5-P_5)]$ with low-valent silicon compounds, resulting in the synthesis of the first sila-phosphaferrocene. Moreover, experimental investigations of the corresponding mechanism are reported.

The reaction of [LSiCl]¹⁵ (L=PhC(N^{*i*}Bu)₂) with [Cp*Fe(η^{5} -P₅)] in toluene at room temperature resulted in the formation of [(η^{4} -P₄SiL)FeCp*] (**1**) in 40 % yield, consisting of a unique silatetraphospha-cyclopentadienyl ring, and [LSi(Cl)=P-SiL(Cl)₂] (**2**) (Route A, Scheme 1). This result reveals that with silylenes both processes, extraction and insertion, occur. The isolation of both species was enabled by their slightly different solubilities in hydrocarbons. Compound **2** can be extracted with *n*-hexane while complex **1** is less soluble in this solvent and can subsequently be extracted using toluene. In a different approach, complex **1** was synthesized in high yield (80%) by reacting [K(dme)]₂[Cp*Fe(η^{4} -P₅)]^{13b} with an excess of [LSiCl] (Route B, Scheme 1). In this case, the recently reported [L₂Si₂P₂]¹⁶ is formed as a by-product.

The solid-state structure of **1** shows the formation of a fivemembered [*cyclo*-**L**SiP₄]⁻ ring η^4 -coordinated to the [Cp*Fe]⁺ moiety (Figure 1). The Si-P1 (2.1707(13) Å) and Si-P4 (2.1729(12) Å) bond distances are almost equal and lie inbetween single (2.24-2.27 Å) and double bonds (2.06-2.09 Å).^{16a, 17} Also, the P-P bond lengths (P1-P2 2.1391(13), P2-P3 2.1597(15), and P3-P4 2.1444(13) Å) show a substantial

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double-bond character as observed in the previously reported K₂[Cp*Fe(η^4 -P₅)] (2.133(1)-2.153(1) Å).^{13b}

Scheme 1. Synthesis of 1 and 2.



Figure 1. Molecular structure of **1.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si-P1 2.1707(13), Si-P4 2.1729(12), P1-P2 2.1391(13), P2-P3 2.1597(15), P3-P4 2.1444(13).



Figure 2. ³¹P{¹H} NMR spectrum at 298 K of **1** with nuclei assigned to an AA'XX' spin system; insets: extended signals (upwards) and simulations (downwards).

Figure 3. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1-Si2 2.1093(8), P1-Si1 2.1925(8).

The ³¹P{¹H} NMR spectrum of **1** shows an AA'XX' spin system with two sets of multiplets at δ -194.4 and 50 ppm (Figures 2, S25). Such an AA'XX' spin system is typical for an open-chain P_4 unit.¹⁸ The multiplet at δ -194.4 ppm can be unambiguously assigned to the P1 and P4 atoms $(P_{AA'})$ due to the presence of well-defined Si satellite peaks with a ${}^{1}J_{Si-P}$ coupling constant of 145.5 Hz (Table S1). Accordingly, the ²⁹Si{¹H} NMR spectrum showed a triplet at δ 42.3 ppm (${}^{1}J_{\text{Si-P}}$ =145.4 Hz). The formation of complex 1 (Route A) can be rationalized by the insertion of a formal [LSi] moiety in the cyclo-P₅ ring of [Cp*Fe(η^5 -P₅)], accompanied by the elimination of one P atom from the cyclo-P₅ ring and one Cl atom from [LSiCl]. The eliminated P and Cl atoms are scavenged by two other molecules of [LSiCl], forming a base-stabilized phosphasilene (2). The solid-state structure of 2 confirmed the formation of the functionalized phosphasilene (Figure 3). The Si2-P bond length (2.1093(8) Å) is in the range of the reported Si=P bonds.^{16a, 17a, 19} Interestingly, the Si1-P bond distance (2.1925(8) Å) is in-between the distances for Si-P single and double bonds, suggesting a partially double-bond character. The ³¹P{¹H} NMR spectrum showed a singlet at δ -182.7 ppm with two Si satellites (${}^{1}J_{\text{Si}}$ -

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 $_{\rm P}$ =167 Hz). In solution, complex 2 slowly decomposes into two known species, [LSiCl₃]¹⁵ and [L₂Si₂P₂]¹⁶ (Figure S11).

Scheme 2. Synthesis of complex 3.



As a possible reaction pathway, we suggest the formation of an intermediate, A (Route A, Scheme 1), which further reacts with [LSiCl], resulting in the formation of 1 and 2. VT-NMR studies show that the reaction is more complex than indicated in Scheme 1, explaining the moderate yields of 1 and 2 (Figures S2-3). To isolate an analog of the possible intermediate A, a relatively bulkier silylene, [LSi(N(SiMe₃)₂)],²⁰ was selected as an analog of [LSiCl]. Reaction of [LSi(N(SiMe₃)₂)] with $[Cp*Fe(\eta^5-P_5)]$ in toluene at room temperature resulted in the formation of $[{LSi(N(SiMe_3)_2)}{(\eta^4-P_5)FeCp^*}]$ (3) (Scheme 2). The solid-state structure of **3** (Figure 4) resembles that of the suggested intermediate **A**. At room temperature, the ${}^{31}P{}^{1}H$ NMR spectrum of **3** shows a broad signal at δ 35.3 ppm. A wellresolved spectrum with an AA'MXX' spin system could be observed at 193 K, with signals at δ -29.9 (P_{AA'}), 28.4 (P_M), and 30.7 (P_{xx'}) ppm (Figures S17, S26-S27). The ²⁹Si{¹H} NMR spectrum exhibits three resonances at δ =-34.9 (SiMe₃), 6.0 (SiMe₃) and 10.8 (Si1) ppm (Figures S12). No ¹/_{Si-P} coupling could be identified at room temperature, indicating a possible lability of the Si1-P bond.



Figure 4. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1-P1 2.2722(5), P1-P2 2.1725(6), P1-P5 2.1654(6), P2-P3 2.1483(8), P3-P4 2.1252(10), P4-P5 2.1533(9).

To gain insight into the formation process and the electronic properties of **1**, density functional theory (DFT) calculations (RI-BP86 level, basis sets of each atom of def-SV(P)-quality) were carried out. Especially, the formation of the suggested elusive intermediate **A**, which may be structurally similar to **3**, was investigated theoretically to confirm the process proposed in Scheme 1. The formation of **A** is exothermic by -5.2 kJ mol⁻¹, the further reaction with two more silylenes forming **1** and **2** is exothermic by -136.8 kJ mol⁻¹. In comparison, complex **3** formed by using [LSi(N(SiMe₃)₂] is much more stable than the educts (by -26.2 kJ mol⁻¹). According to an Ahlrichs-Heinzmann population analysis²¹ of intermediate **A**, the Si-P bond formed in the intermediate after the reduction of the P_5 system is of a polarized strong single-bond character.

The electronic properties of **1** are not immediately obvious. It could be described as either: a) an aromatic 6π -electron system, b) a P_4^{2-} ligand sandwiched between [Cp*Fe]⁺ and [LSi]⁺ or c) a P_4^{4-} ligand between [Cp*Fe]⁺ and a [LSi]³⁺ cation. The classification of the SiP₄ ligand as an aromatic 6π -electron system may be ruled out because of the strong bending of the positively charged Si from the P₄ plane. To decide whether to consider silicon formally as silvlene or as Si (+IV), the partial atomic charges Q(Si) from Ahlrichs-Heinzmann population analyses and the bond distances r(Si-N) can help. The comparison of the partial charges Q(Si) of the silylenes [LSiCl] and [LSi(N(SiMe₃)₂] with those of the molecules with Si in the formal oxidation state +IV like in 2 shows that, in the former group, the values are about +0.1, while, in the reference system 2, with Si(+IV) it is about +0.4 to +0.5. Furthermore, in both silylenes, the Si-N distances to the amidinate ligand are significantly prolonged. This is also found, e.g., in the comparison of AlF and AlF₃: in the sub-valent compound, the Al-F distance is significantly longer due to the partial s character of the lone pair on the central atom.²² Therefore, in 1, 2, A and 3, the silicon atoms are considered to be of the formal oxidation state +IV (Table S5). On the basis of these findings, the formal explanation of the bonding situation as a P_4^{4-} ligand between [Cp*Fe]⁺ and a [LSi]³⁺ cation would be justified. The bending of Si out of the expected SiP₄ plane is explained by the repelling positive charges.

Scheme 3. Synthesis of complex 4.



To examine the possibility of ring expansion reactions, we studied the reaction between [LSi-SiL]²³, a formal Si(I) compound, and $[Cp*Fe(\eta^5-P_5)]$ (Scheme 3). The ³¹P{¹H} NMR spectrum of the crude reaction mixture showed the formation of **1**, $[L_2Si_2P_2]$ and $[\{(\eta^4-P_5(SiL)_2\}FeCp^*]$ (**4**) as a new product (Figure S22). Compound 4 was isolated after work-up as yellow-orange colored crystals. The analysis of the solid-state structure of **4** (Figure 5) revealed the insertion of two [LSi] silicon moieties into two P-P bonds of the cyclo-P₅ ring. In a similar approach as for the synthesis of **1**, we also tried to access **4** from a reduced anionic form of $[Cp^*Fe(\eta^5-P_5)]$ $([K(dme)_2K(dme)][{Cp*Fe}_2(\eta^{4:4}-P_{10})]^{13b})$ and [LSiCl]. In situ NMR studies showed that 4 is formed in low yields. As byproducts, $[(LSi)_2P_2]$, $[Cp^*Fe(\eta^5-P_5)]$, **1** and two unstable intermediates were observed by VT-NMR studies (Figure S23). No further attempts were made to explore this reaction on a preparative scale.

The ³¹P{¹H} NMR spectrum of **4** reveals an AMM'XX' spin system. Simulations using an iterative fitting procedure revealed two sets of multiplets for the four P atoms coordinated to the [Cp*Fe]⁺ moiety at δ =-47.6 (P_{MM}) and 80.8 (P_{xx'}) ppm (Figure S28). The P atom between the two Si atoms (P_A) in the ring is upfield shifted to δ -163.5 ppm (¹/_{Si-P}=118.3 Hz). The multiplet at δ -47.6 ppm is unambiguously assigned to P2 and P5 on the basis of the well-defined Si satellite signals (${}^{1}J_{Si-P}$ =169.3 Hz). Accordingly, the ${}^{29}Si{}^{1}H$ NMR spectrum showed a doublet of doublets at δ 31.9 ppm with the same ${}^{1}J_{\text{Si-P}}$ coupling constants. The ring-expanded complex 4 also represents the largest structurally characterized siliconpolyphosphorus ring in a coordination sphere.²⁴ The Si1-P2 (2.2151(8) Å) and Si2-P5 (2.2126(9) Å) bond lengths are slightly shorter than Si-P single bonds (2.24-2.27 Å).^{16a, 17a, 19} In contrast, the Si1-P1 (2.1419(8) Å) and Si2-P1 (2.1407(9) Å) distances are in-between single (2.24-2.27 Å) and double bonds (2.06-2.09 Å).^{16a, 17a, 19} The P-P bond lengths (2.1416(9)-2.1612(9) Å) in **4** are also in the same range as in $\mathbf{1}$ (2.1391(13)-2.1597(15) Å), indicating a partially double bond character.^{17a} Interestingly, the Si-P seven-membered ring is isolobal to the tropylium anion. Therefore, the expansion of the cyclo-P5 ring to a cyclo-Si2P5 ring is a significant advancement in the silicon and phosphorus chemistry.

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Figure 5. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1-P1 2.1419(8), Si2-P1 2.1407(9), Si1-P2 2.2151(8), Si2-P5 2.2126(9), P2-P3 2.1416(9), P3-P4 2.1612(9), P4-P5 2.1454(9).

In summary, we have shown that (i) the P atoms in P-cycles can be removed and selectively substituted by isoelectronic [LSi] fragments and (ii) that the [LSi] fragment can be inserted via a ring expansion into phosphorus cycles. As a result, we have synthesized the first example of a sila-phosphaferrocene (1) by substituting one P atom in the cyclo-P₅ ring of $[Cp^*Fe(\eta^5 -$ P₅)]. In addition, the by-product of the reaction, an amidinatedichlorosilyl group-functionalized phosphasilene (2), was isolated, allowing a better understanding of the reaction pathway between silvlene and $[Cp^*Fe(n^5-P_5)]$. The isolation of the possible analog of the reaction intermediate (3) was achieved by using a silylene bearing a bulkier group. To examine further ring expansions, the insertion of a basestabilized di-silvlene into the cyclo-P₅ ring of $[Cp^*Fe(\eta^5-P_5)]$ was studied. The resulting complex 4 possesses the largest silicon-polyphosphorus ring as a ligand known to date. This work bridges a gap between the low-valent silicon chemistry and transition metal polyphosphides, both of which are important parts of the current research in the field of organometallic and heterocyclic chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization details, NMR, IR, computational and structural information (PDF).

X-ray crystallographic data CCDC 1919229-1919231 and 1919233 (CIF).

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) Carey, F. A.; Sundberg, R. J., *Advanced Organic Chemistry : Part B: Reactions and Synthesis.* Fifth Edition ed.; Springer US: Boston, MA, 2007.

(2) (a) Smith, M. B.; March, J., Marchs advanced organic chemistry : reactions, mechanisms, and structure. 7. ed. ed.; Wiley: Hoboken, NJ, 2013. (b) Smith, P. A. S.; Baer, D. R., The Demjanov and Tiffeneau-Demjanov Ring Expansions. In *Organic Reactions*, 1960; Vol. 11, pp 157–188.

(3) ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A., The Baeyer–Villiger Reaction: New Developments toward Greener Procedures. *Chem. Rev.* **2004**, *104* (9), 4105-4124.

(4) (a) Goicoechea, J. M.; Grützmacher, H., The Chemistry of the 2-Phosphaethynolate Anion. *Angew. Chem. Int. Ed.* **2018**, *57* (52), 16968-16994. (b) Coburger, P.; Grützmacher, H.; Hey-Hawkins, E., Molecular doping: accessing the first carborane-substituted 1,2,3triphospholanide via insertion of P- into a P-P bond. *Chem. Commun.* **2019**, *55* (22), 3187-3190.

(5) (a) Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S., NHCs in Main Group Chemistry. *Chem. Rev.* **2018**, *118* (19), 9678-9842. (b) Khan, S.; Sen, S. S.; Roesky, H. W., Activation of phosphorus by group 14 elements in low oxidation states. *Chem. Commun.* **2012**, *48* (16), 2169-2179. (c) Weigand, J. J.; Holthausen, M.; Fröhlich, R., Formation of $[Ph_2P_5]^*$, $[Ph_4P_6]^{2*}$, and $[Ph_6P_7]^{3*}$ Cationic Clusters by Consecutive Insertions of $[Ph_2P]^*$ into P-P Bonds of the P₄ Tetrahedron. *Angew. Chem. Int. Ed.* **2009**, *48* (2), 295-298. (d) Krossing, I.; Raabe, I., P₅X₂* (X=Br, I), a Phosphorus-Rich Binary P–X Cation with a C_{2v}-Symmetric P₅ Cage. *Angew. Chem. Int. Ed.* **2001**, *40* (23), 4406-4409. (e) Dube, J. W.; Graham, C. M. E.; Macdonald, C. L. B.; Brown, Z. D.; Power, P. P.; Ragogna, P. J., Reversible, Photoinduced Activation of P₄ 1

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by Low-Coordinate Main Group Compounds. Chem. Eur. J. 2014, 20 (22), 6739-6744. (f) Scheer, M.; Schindler, A.; Bai, J.; Johnson, B. P.; Merkle, R.; Winter, R.; Virovets, A. V.; Peresypkina, E. V.; Blatov, V. A.; Sierka, M.; Eckert, H., Structures and Properties of Spherical 90-Vertex Fullerene-Like Nanoballs. Chem. Eur. J. 2010, 16 (7), 2092-2107. (g) Xiong, Y.; Yao, S.; Brym, M.; Driess, M., Consecutive Insertion of a Silylene into the P4 Tetrahedron: Facile Access to Strained SiP4 and Si₂P₄ Cage Compounds. Angew. Chem. Int. Ed. 2007, 46 (24), 4511-4513. (h) Peng, Y.; Fan, H.; Zhu, H.; Roesky, H. W.; Magull, J.; Hughes, C. E., [{HC(CMeNAr)₂}₂Al₂P₄] (Ar=2,6-iPr₂C₆H₃): A Reduction to a Formal {P₄}⁴⁻ Charged Species. Angew. Chem. Int. Ed. 2004, 43 (26), 3443-3445. (i) Prabusankar, G.; Doddi, A.; Gemel, C.; Winter, M.; Fischer, R. A., P-P Bond Activation of P4 Tetrahedron by Group 13 Carbenoid and its Bis 10 Molybdenum Pentacarbonyl Adduct. Inorg. Chem. 2010, 49 (17), 7976-11 7980. (j) Fox, A. R.; Wright, R. J.; Rivard, E.; Power, P. P., Tl₂[Aryl₂P₄]: A Thallium Complexed Diaryltetraphosphabutadienediide and its Two-12 Electron Oxidation to a Diaryltetraphosphabicyclobutane, Aryl₂P₄. 13 Angew. Chem. Int. Ed. 2005, 44 (47), 7729-7733. For related insertion 14 into P-P or As-As bonds see for example: (k) di Vaira, M.; Stoppioni, P.; Peruzzini, M., Polyhedron report number 19: Naked phosphorus atoms 15 and units in transition-metal compounds. Polyhedron 1987, 6 (3), 351-16 382 and references therein. (I) Caporali, M.; Barbaro, P.; Gonsalvi, L.; 17 Ienco, A.; Yakhvarov, D.; Peruzzini, M., Heterobimetallic Cooperation 18 Mediates the Transformation of White Phosphorus into Zwitterionic catena-Phosphonium(+)diphosphenide(-) Ligands. Angew. Chem. Int. 19 Ed. 2008, 47 (20), 3766-3768. (m) Di Vaira, M.; Niccolai, L.; Peruzzini, 20 M.; Stoppioni, P., Generation and stabilization of the 3,3-diphenyl-1,2,4-21 thiadiarsete unit at a transition metal. Organometallics 1985, 4 (10), 22 1888-1890.

(6) Scheer, M.; Balázs, G.; Seitz, A., P4 Activation by Main Group 23 Elements and Compounds. Chem. Rev. 2010, 110 (7), 4236-4256. 24

(7)Scherer, O. J.; Brück, T., $[(\eta^{5}-P_{5})Fe(\eta^{5}-C_{5}Me_{5})]$ 25 Pentaphosphaferrocene Derivative. Angew. Chem. Int. Ed. 1987, 26 (1), 59-59. 26

(8) (a) Baudler, M., Chain and Ring Phosphorus Compounds-27 Analogies between Phosphorus and Carbon Chemistry. Angew. Chem. 28 Int. Ed. 1982, 21 (7), 492-512. (b) Grützmacher, H., The Power of 29 Experiment and Imagination: The Discovery of Pentaphosphacyclopentadienide, [P5]-. Z. Anorg. Allg. Chem. 2012, 638 30 (12-13), 1877-1879.

31 (9) (a) Scheer, M., The coordination chemistry of group 15 element 32 ligand complexes—a developing area. Dalton Trans. 2008. (33), 4372-33 4386. (b) Scheer, M.; Schindler, A.; Gröger, C.; Virovets, A. V.; Peresypkina, E. V., A Spherical Molecule with a Carbon-Free Ih-C80 34 Topological Framework. Angew. Chem. Int. Ed. 2009, 48 (27), 5046-35 5049. (c) Dielmann, F.; Schindler, A.; Scheuermayer, S.; Bai, J.; Merkle, 36 R.; Zabel, M.; Virovets, A. V.; Peresypkina, E. V.; Brunklaus, G.; Eckert, 37 H.; Scheer, M., Coordination Polymers Based on [Cp*Fe(n⁵-P₅)]: Solid-State Structure and MAS NMR Studies. Chem. Eur. J. 2012, 18 (4), 1168-38 1179. (d) Fleischmann, M.; Welsch, S.; Krauss, H.; Schmidt, M.; 39 Bodensteiner, M.; Peresypkina, E. V.; Sierka, M.; Gröger, C.; Scheer, M., 40 Complexes of Monocationic Group 13 Elements with Pentaphosphaand Pentaarsaferrocene. Chem. Eur. J. 2014, 20 (13), 3759-3768. 41

(10) Dielmann, F.; Fleischmann, M.; Heindl, C.; Peresypkina, E. V.; 42 Virovets, A. V.; Gschwind, R. M.; Scheer, M., Tunable Porosities and 43 Shapes of Fullerene-Like Spheres. Chem. Eur. J. 2015, 21 (16), 6208-44 6214.

(11) Bai, J.; Virovets, A. V.; Scheer, M., Synthesis of Inorganic Fullerene-45 Like Molecules. Science 2003, 300 (5620), 781-783.

46 (12) (a) Caporali, M.; Gonsalvi, L.; Rossin, A.; Peruzzini, M., P4 Activation 47 by Late-Transition Metal Complexes. Chem. Rev. 2010, 110 (7), 4178-4235. (b) Cossairt, B. M.; Piro, N. A.; Cummins, C. C., Early-Transition-48 Metal-Mediated Activation and Transformation of White Phosphorus. 49 Chem. Rev. 2010, 110 (7), 4164-4177. (c) For the substitution of three 50 P atoms by three (PhC) in NaP₅ see: Miluykov, V.; Kataev, A.; Sinyashin, 51 O.; Lönnecke, P.; Hey-Hawkins, E., Reaction of NaP5 with Half-Sandwich Complexes of Nickel: The First Example of an Ni-Promoted 52 Transformation of the P5⁻ Anion. Organometallics 2005, 24 (9), 2233-53 2236.

54 (13) (a) Li, T.; Wiecko, J.; Pushkarevsky, N. A.; Gamer, M. T.; Köppe, R.; Konchenko, S. N.; Scheer, M.; Roesky, P. W., Mixed-Metal Lanthanide-55 Iron Triple-Decker Complexes with a cyclo-P5 Building Block. Angew. 56 Chem. Int. Ed. 2011, 50 (40), 9491-9495. (b) Butovskiy, M. V.; Balázs, 57 G.; Bodensteiner, M.; Peresypkina, E. V.; Virovets, A. V.; Sutter, J.; Scheer,

M., Ferrocene and Pentaphosphaferrocene: A Comparative Study Regarding Redox Chemistry. Angew. Chem. Int. Ed. 2013, 52 (10), 2972-2976. (c) Li, T.; Gamer, M. T.; Scheer, M.; Konchenko, S. N.; Roesky, P. W., P-P bond formation via reductive dimerization of $[Cp^*Fe(n^5-P_5)]$ by divalent samarocenes. Chem. Commun. 2013, 49 (22), 2183-2185. (d) Schoo, C.; Bestgen, S.; Schmidt, M.; Konchenko, S. N.; Scheer, M.; Roesky, P. W., Sterically induced reductive linkage of iron polypnictides with bulky lanthanide complexes by ring-opening of THF. Chem. Commun. **2016**, *52* (90), 13217-13220.

(14) Piesch, M.; Reichl, S.; Seidl, M.; Balázs, G.; Scheer, M., Ring Contraction by NHC-Induced Pnictogen Abstraction Angew. Chem. Int. Ed. 2019, 58 (46), 16563-16568.

(15) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B., Synthesis and Characterization of [PhC(NtBu)₂]SiCl: A Stable Monomeric Chlorosilylene. Angew. Chem. Int. Ed. 2006, 45 (24), 3948-3950.

(16) (a) Inoue, S.; Wang, W.; Präsang, C.; Asay, M.; Irran, E.; Driess, M., An Ylide-like Phosphasilene and Striking Formation of a 4π -Electron, Resonance-Stabilized 2,4-Disila-1,3-diphosphacyclobutadiene. J. Am. Chem. Soc. 2011, 133 (9), 2868-2871. (b) Sen, S. S.; Hey, J.; Eckhardt, M.; Herbst-Irmer, R.; Maedl, E.; Mata, R. A.; Roesky, H. W.; Scheer, M.; Stalke, D., A Stable Cation of a CSi₃P Five-Membered Ring with a Weakly Coordinating Chloride Anion. Angew. Chem. Int. Ed. 2011, 50 (52), 12510-12513. (c) Seitz, A. E.; Eckhardt, M.; Erlebach, A.; Peresypkina, E. V.; Sierka, M.; Scheer, M., Pnictogen-Silicon Analogues of Benzene. J. Am. Chem. Soc. 2016, 138 (33), 10433-10436.

(17) (a) Pyykkö, P.; Atsumi, M., Molecular Double-Bond Covalent Radii for Elements Li-E112. Chem. Eur. J. 2009, 15 (46), 12770-12779. (b) Sen, S. S.; Khan, S.; Roesky, H. W.; Kratzert, D.; Meindl, K.; Henn, J.; Stalke, D.; Demers, J.-P.; Lange, A., Zwitterionic Si-C-Si-P and Si-P-Si-P Four-Membered Rings with Two-Coordinate Phosphorus Atoms. Angew. Chem. Int. Ed. 2011, 50 (10), 2322-2325.

(18) (a) Ziegler, C. G. P.; Maier, T. M.; Pelties, S.; Taube, C.; Hennersdorf, F.; Ehlers, A. W.; Weigand, J. J.; Wolf, R., Construction of alkylsubstituted pentaphosphido ligands in the coordination sphere of cobalt. Chem. Sci. 2019, 10 (5), 1302-1308. (b) Gómez-Ruiz, S.; Hey-Hawkins, E., Oxidative cleavage of tetraaryltetraphosphane-1,4-diides by nickel(ii) and palladium(ii): formation of unusual Ni0 and Pd0 diaryldiphosphene complexes. Dalton Trans. 2007, (48), 5678-5683. (c) Donath, M.; Hennersdorf, F.; Weigand, J. J., Recent highlights in mixed-coordinate oligophosphorus chemistry. Chem. Soc. Rev. 2016, 45 (4), 1145-1172. (d) Schwedtmann, K.; Haberstroh, J.; Roediger, S.; Bauzá, A.; Frontera, A.; Hennersdorf, F.; Weigand, J. J., Formation of an imidazoliumyl-substituted [(LC)₄P₄]⁴⁺ tetracation and transition metal mediated fragmentation and insertion reaction (LC = NHC). Chem. Sci. 2019, 10 (28), 6868-6875. (e) Conrad, E.; Burford, N.; Werner-Zwanziger. U.: McDonald. R.: Ferguson, Μ. Phosphinopnictinophosphonium frameworks. Chem. Commun. 2010, 46 (14), 2465-2467. (f) Wiesner, A.; Steinhauer, S.; Beckers, H.; Müller, C.; Riedel, S., $[P_4H]^+[Al(OTeF_5)_4]^-$: protonation of white phosphorus with the Brønsted superacid H[Al(OTeF₅)₄](solv). Chem. Sci. 2018, 9 (36), 7169-7173.

(19) Driess, M.; Janoschek, R., A comparison of silylidene-amines, phosphanes and -arsanes: syntheses and quantum chemical calculations. J. Mol. Struct. 1994, 313 (1), 129-139.

(20) Sen, S. S.; Hey, J.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D., Striking Stability of a Substituted Silicon(II) Bis(trimethylsilyl)amide and the Facile Si-Me Bond Cleavage without a Transition Metal Catalyst. J. Am. Chem. Soc. 2011, 133 (31), 12311-12316.

(21) Heinzmann, R.; Ahlrichs, R., Population analysis based on occupation numbers of modified atomic orbitals (MAOs). Theor. Chim. Acta 1976, 42 (1), 33-45.

(22) Ahlrichs, R.; Zhengyan, L.; Schnöckel, H., Zur Struktur der Moleküle (AIF)2, OAIF und (OAIF)2 Matrix-IR-Untersuchungen und ab initio SCF-Rechnungen. Z. Anorg. Allg. Chem. 1984, 519 (12), 155-164.

(23) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C., A Remarkable Base-Stabilized Bis(silylene) with a Silicon(I)-Silicon(I) Bond. Angew. Chem. Int. Ed. 2009, 48 (45), 8536-8538.

(24) Driess, M.; Faulhaber, M.; Pritzkow, H., Multidentate, Cyclic Phosphorus Ligands with a Silicon Phosphorus Backbone: Template Synthesis of a 1,4,7-Triphospha-2,3,5,6,8,9-hexasilacyclononane and a 1,3,5,7,9,11-Hexaphospha-2,4,6,8,10,12-hexasilacyclododecane. Angew. Chem. Int. Ed. 1997, 36 (17), 1892-1894.

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