Selective [2 + 1 + 1] Fragmentation of P₄ by Heteroleptic Metallasilylenes

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Abstract: Small-molecule activation by low-valent main-group element compounds is of general interest. We here report the synthesis and characterization ([H, ¹³C, ³²Si NMR, IR, sc-XRD) of heteroleptic metallasilylenes L¹(Cl)MSiL² (M = Al 1, Ga 2, L¹ = H(C(Me)NDipp)₂, Dipp = 2,6-Pr₂C₆H₃; L² = PhC(NBu)₃). Their electronic nature was analyzed by quantum chemical computations, while their promising potential in small-molecule activation was demonstrated in reactions with P₄, which occurred with unprecedented [2 + 1 + 1] fragmentation of the P₄ tetrahedron and formation of L¹(Cl)MPSi(L¹)PPSi(L²)PM(CI)L¹ (M = Al 3, Ga 4).

Small-molecule activation plays a central role in catalysis.[1] In recent years, the use of main-group-element compounds that exhibit transition-metal-like behavior have become increasingly popular.[2] Carbone-type divalent tetrylenes, in particular silylenes, with low-lying (unoccupied) acceptor and high-lying (occupied) donor orbitals have been demonstrated to be suitable candidates for the activation of small molecules such as H₂, CO or CO₂[3] and in catalytic transformations.[4,5] The activation of white phosphorus is also of fundamental interest in order to further convert P₄ into valuable organophosphorus compounds. In addition, activation as well as fragmentation of P₄ was reported in reactions with cyclic and acyclic (alkyl)(amino)carbenes as well as with anionic dicarbenes and mesoionic carbenes,[6] as well as disilenes, tetrylenes,[7] and group 13 carbenoids (Figure 1).[8] Cyclic and acyclic silylenes reacted with P₄ to Si₄P₄ cages (n = 1 (I), 2 (II)),[9] whereas amidinato-substituted silylenes (PhC(NBu)₃SiCl) and PhNC(NBu)₂Si(N(SiMe)₂)₂ yielded a Si₄P₄ four-membered ring (III) and an acyclic P₄ chain (IV), respectively.[10] Driess et al. recently reported on the degradation of P₄, yielding an NHSi-stabilized zero-valent P₄ complex (V) and its functionalization by small molecules.[11]

We recently reported the first room temperature stable silylene carbonyl complex [L¹(Br)Ga]ClCO.[12] Homoleptic [L¹(Br)Ga]SiCl cannot be isolated and was only proposed as reaction intermediate. To further elucidate the electronic effect of the L¹(Br)M ligand, we became interested in heteroleptic metallasilylenes and herein report on the synthesis of L¹(Cl)MPSi(L¹)PPSi(L²)PM(CI)L¹ (M = Al 1, Ga 2). Their electronic structures were analyzed by quantum chemical computations, and their reactions with white phosphorus, which proceeded with unforeseen [2 + 1 + 1] fragmentation of the P₄ tetrahedron, are reported.

Group 13 diyls L¹M (M = Al, Ga)[13] react with silylene L¹SiCl[14] in benzene or toluene at ambient temperature with oxidative addition and formation of L¹SiM(CI)L¹ (M = Al 1, Ga 2, Scheme 1). Complexes 1 and 2 are soluble in benzene and toluene, but readily decompose in polar solvents such as CH₂Cl₂ at ambient temperature. ¹H and ¹³C NMR spectra of 1 and 2 (Tables S1 and S2 in the Supporting Information) show the characteristic resonances of the β-diketiminato (L¹) and the amidinate (L²)
ligands; the $^{29}$Si NMR spectra show singlets at 93.0 ppm for 1 and 65.1 ppm for 2.

Single crystals of 1 and 2, which crystallize in the triclinic space group $P\overline{1}$, were obtained from toluene solutions upon storage at $-18^\circ$C for 12 h (Figure 2). The four-membered SINCN rings are planar, whereas the six-membered MN$_2$C$_2$ rings ($M = Al, Ga$) adopt boat-type conformations. The Si–M bond lengths (2.5620(6) Å) are shorter than the Al–Cl bond (2.5170(4) Å) and both are in the range of typical M–Cl bond lengths.$^{[21]}$ The N–Si–N bond angles ($1 \, 69.1(1)^\circ$, $2 \, 69.4(1)^\circ$) are fairly identical with those in $L^2$SiCl$_2$A (68.35(8)°)$^{[18]}$ and silylenes $B\cdots H$ (Figure 3),$^{[18]}$ whereas the M–Si–N bond angles (1 100.5(1)$^\circ$, 103.9(1)$^\circ$, 2 99.0(1)$^\circ$, 101.9(1)$^\circ$) are wider than the Cl–Si–N bond angles in $L^2$SiCl (95.82(6)$^\circ$; 96.56(6)$^\circ$) due to the sterically more demanding $L^1(Cl)$M ligands.

The electronic structures of 1 and 2 were analyzed with ORCA (version 5.0)$^{[19]}$ and the NBO program package (version 7.0.10)$^{[20]}$ at the 6-311G(d,p)$^{[21]}$ level of theory (def2-TZVP for E $> Ne$)$^{[22]}$ using the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)$^{[23]}$ with the B3LYP$^{[24]}$ functional. The HOMOs of 1 and 2 are almost exclusively reflected by the electron lone pair of the silicon atom and the Si–M bonds, while the LUMOs are located at the β-diketiminate ligands (Figure 2). The smaller HOMO–LUMO gap of 1 (2.81 eV) compared to 2 (3.52 eV) reflects the more electropositive nature of Al versus Ga, indicating a higher reactivity of 1 compared to 2. Natural bond orbital (NBO) analyses (Table S5) showed that the M–Si bond in 1 (Si: 59.6%; Al: 40.4%) is more polarized than in 2 (Si: 48.7%; Ga: 51.3%), resulting from the more electropositive character of Al. This also agrees with the observed natural charges for the Si (±0.33 1, ±0.50 2) and the group 13 metals M (Al: +1.47 1, Ga: +1.17 2).

Heteroleptic metallasilylenes 1 and 2 are expected to be reactive species due to the presence of a Lewis basic (Si) and Lewis acidic (M) center. To evaluate the influence of the L(X)M ligand on the electronic nature of 1 and 2, we compared both silylenes with structurally related heteroleptic and homoleptic acyclic silylenes $A\cdots H$ (Figure 3). Replacing the L(Cl)M ligand in 1 and 2 by $E$SiMe$_3$$_2$ ligands ($E = C, Si$) increases the natural partial charge of Si, following the trend of electronegativity (E = +1.10e, F = +0.73e), and polarizes the Si–E bond, whereas introduction of a second $L^1(X)$M ligand results in a reversed polarity of the silicon center in the homoleptic metallasilylenes $L^2(X)M_i$Si: (M = Ga, −0.13e; G, −0.45e; H), with marginal changes in bond polarity. In addition, the partial charge of the Si atom increases significantly upon replacement of the Ga atom by a more electropositive Al atom. Wiberg bond indices (WBI) and Mayer bond orders (MBO) are in good agreement and point to rather covalent Si–M bonds in $G$ and $H$. Replacing the L(Cl)M ligand in 1 and 2 by electronegative halide (Cl $A, Br$ B) and $E$SiMe$_3$$_2$ ligands ($E = N, C, P$ D) results in an increase of the natural partial charges on the Si atom and further polarizes the Si–E bond to a comparable value as observed for E. Furthermore, the HOMO–LUMO gaps increase, with $A$ and $B$ showing the largest energy gap of the investigated compounds.

Figure 2. Molecular structure and frontier orbitals (isovalue 0.05) of metallasilylenes 1 (left) and 2 (right). Displacement ellipsoids are at 50% probability; hydrogen atoms are omitted for clarity; Pr groups are omitted, and $^t$Bu groups are reduced to C for clarity in calculated structures. Selected bond lengths [Å] and angles [°]: 1: Si1–Al1 2.5620(6), Al1–Cl1 2.2043(6), Si1–N1 1.8760(12), Si1–N4 1.8888(13), Al1–N1 1.9176(13), Al1–N2 1.9505(13), N3–Si1–N4 69.10(6), N1–Al1–N2 94.39(5), Si1–Al1–Cl1 117.81(2); 2: Si1–Ga1 2.5170(4), Ga1–Cl1 2.2837(4), Si1–N3 1.8686(9), Si1–N4 1.859(9), Ga1–N1 1.9810(9), Ga1–N2 2.0183(9), N3–Si1–N4 69.38(4), N1–Ga1–N2 92.65(4), Si1–Ga1–Cl1 119.13(11).

Figure 3. Silylenes 1, 2 and A–H selected for comparison.

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gave the four-membered \( \text{Si}_2\text{P}_2 \) ring (III) and the acyclic \( \text{Si}_4\text{P}_4 \) chain (IV), 1 and 2 reacted with \( \text{P}_2 \) in 2:1 molar ratio. After short heating to reflux, dark green solutions were formed, which according to \( \text{H} \) and \( ^{31}\text{P} \) NMR spectroscopy studies only contained a single species, which was finally identified as the unique \( [2 + 1 + 1] \) fragmentation products \( \text{L}^1(\text{Cl})\text{MPSiL}^2(\text{L}^3)\text{PPSiL}^3(\text{L}^4)\text{PMCL}^4(\text{L}^1) \) (M = Al 3, Ga 4) containing two \( \text{P}_2 \) and one \( \text{P}_2 \) unit.

### Table 1. Natural partial charge of Si, HOMO-LUMO (\( \Delta E_{\text{HOMO-LUMO}} \)) and singlet-triplet energy gaps (\( \Delta E_{\text{ST}} \)) of acyclic silylenes 1, 2 and A–H.

|   | Q(Si) | \( \sigma(\text{Si–E}) \) contribution | \( \Delta E_{\text{HOMO-LUMO}} \) [eV] | \( \Delta E_{\text{ST}} \) [kcal mol\(^{-1}\)] |
|---|---|---|---|---|
| A\(^{[4]} \) | +0.97 | Si(20.4\%)–Cl(79.6\%) | 4.37 | -51.78 |
| B\(^{[8]} \) | +0.93 | Si(22.5\%)–Br(77.5\%) | 4.39 | -50.50 |
| C\(^{[26]} \) | +1.15 | Si(12.5\%)–N(87.5\%) | 3.88 | -38.93 |
| D\(^{[17]} \) | +0.83 | Si(31.2\%)–P(68.8\%) | 3.82 | -40.28 |
| E\(^{[8]} \) | +1.10 | Si(20.0\%)–Cl(80.0\%) | 3.74 | -29.51 |
| F\(^{[39]} \) | +0.73 | Si(39.0\%)–Si(61.0\%) | 3.61 | -42.43 |
| 1 | +0.33 | Si(59.6\%)–Al(40.4\%) | 2.81 | -36.36 |
| 2 | +0.50 | Si(48.7\%)–Ga(51.3\%) | 3.52 | -49.14 |
| G\(^{[29]} \) | -0.13 | Si(53.4\%)–Ga(46.6\%) | 2.17 | -1.77 |
| H | -0.45 | Si(62.6\%)–Al(37.4\%) | 1.93 | +4.81 |

Compounds 3 and 4 were isolated in good yields after storage at ambient temperature for 12 h (Scheme 2). Their \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra show the expected resonances of the ligands (\( \text{L}^1, \text{L}^2 \)), whereas no \( ^{29}\text{Si} \) NMR signal could be recorded. The \( ^{31}\text{P} \) NMR spectra each show two signals for the \( \text{P}_2 \) unit (3 641.7 ppm; 4 629.4 ppm), and the chemical shifts agree to values previously reported for diphosphenes\(^{[30]} \) including silyl-substituted diphosphenes \( \text{R}_2\text{SiPPSiR}_2 \) (\( \text{R} = \text{Bu}_3\text{Si}, \delta = 818.1 \text{ppm} \)\(^{[31]} \)). In addition, the single phosphorus atoms gave resonances at \(-262.7 \text{ppm} \) (3) and \(-253.6 \text{ppm} \) (4), which are in a comparable region observed for compounds with monophosphide anions such as \( \text{L}^2\text{Si}[\text{N}(2\text{-py})\text{Me}]\text{P}(\text{SiL}^3)\text{P}(\text{SiL}^4)\text{P}[\text{N}(2\text{-py})\text{Me}] \) \(-261.4 \text{ppm} \).\(^{[30]} \)

Dark green crystals of 3 (Figure 4A) and 4 (Figure S17A), which crystallize in the triclinic space group \( \text{P}1 \) with one molecule in the unit cell, were grown from benzene solutions upon storage at ambient temperature. Central structural motif in both compounds is the unique eight-membered chain with planar \( \text{M} = \text{P} \) and \( \text{Si} \) units and rather localized alternating single (\( \text{M} = \text{P}, \text{Si} \)) and double bonds (\( \text{P} = \text{Si} \)). The P2–P2 bond lengths (2.0270(10) \text{Å}; 2.0323(7) \text{Å}) are at the upper range of P-P double bonds (1.985–2.050 \text{Å})\(^{[32]} \) and slightly shorter than the P–P double bond in \( \text{L}^3\text{Si} = \text{P} = \text{P} = \text{P} = \text{Si} = \text{L}^4 \text{IV} \) (2.0559(7) \text{Å})\(^{[33]} \) and in \( \text{L}^5\text{Si}[\text{N}(2\text{-py})\text{Me}]\text{P}(\text{SiL}^3)\text{P}(\text{SiL}^4)\text{P}[\text{N}(2\text{-py})\text{Me}] \) (2.0775(4) \text{Å})\(^{[40]} \) whereas the P–P bond in zero-valent \( \text{P} \) complex \( \text{V} \) is substantially elongated (2.2369(8) \text{Å})\(^{[40]} \). The Si1–P2 bond lengths (2.3091(7) \text{Å}; 2.3018(3) \text{Å}) are in the range of typical Si–P single bonds and agree with the calculated single bond value of 2.27 \text{Å} \(^{[19]} \) whereas the Si1–P1 bonds (2.1010(4) \text{Å}; 2.1127(4) \text{Å}) which perfectly fit to the calculated sum of covalent radii for a Si–P double bond (2.09 \text{Å})\(^{[12]} \) to that identified for reported phosphasilene \( (\text{Bu}_3\text{MeSi})_2\text{SiPMe}_2(2.1114(7) \text{Å}; \text{Mes}^* = 2.4,6\text{-Me}_3\text{C}_6\text{H}_2) \)\(^{[13]} \) and in

![Figure 4. A) Molecular structure and B) frontier orbitals (isovalue 0.05) of compound 3. Displacement ellipsoids are at 50% probability; hydrogen atoms, disorders and solvent molecules (benzene) are omitted for clarity. Selected bond lengths [Å] and angles [°]: 3: P2–P2a 2.0270(10), Si1–P1 2.1010(4), Si1–P2 2.3091(7), A1–P1 2.2622(4), P1–Si1–P2 125.65(2), P2a–P2–Si1 100.38(4), Si1–P1–A1 107.17(2); 4: P2–P2a 2.0323(7), Si1–P1 2.1127(4), Si1–P2 2.3018(7), Ga1–P1 2.2510(3), P1–Si1–P2 125.763(17), P2a–P2–Si1 99.36(2), Si1–P1–Ga1 104.770(4).](image-url)
The first step in the nucleophilic activation of \( P_4 \) by silylenes typically occurs with cleavage of one \( P-P \) bond by \( \alpha \)-bond metathesis.\(^{[36]} \) However, understanding the fragmentation process of the subsequent \( P-P \) bond cleavage reactions by trapping \( \alpha \)-FORMED \( P_4 \) and \( P_3 \)-containing species is challenging due to their high reactivity.\(^{[37]} \) For \( P_4 \), the fragmentation can be achieved by the step-by-step process of three \( P-P \) bond cleavages and four \( P-C \) bond formation, as well as with a diboraallene.\(^{[38]} \) While this work was under revision, Roesky et al. reported \([3 + 1]\)-type fragmentation of white phosphorus, which was previously reported for reactions with lutetacyclopentadienes,\(^{[39]} \) which occurred by a step-by-step process of three \( P-P \) bond cleavages, and four \( P-C \) bond formation, as well as with a diboraallene.\(^{[40]} \) This work was under revision, Roesky et al. reported \([3 + 1]\)-type fragmentation of the \( P_4 \) tetrahedron by treating the \( \text{amido}(\text{pyridyl})\)-functionalized silylene \( \text{L}^3\text{Si}[\text{N}(2-\text{py})\text{Me}]\text{P}[\text{SiL}(\text{Dipp})]_2 \) with \( \text{L}^3\text{Si}[\text{N}(2-\text{py})\text{Me}] \) and \( \text{P} \) to form the hexatriene-type chains in complexes \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \). The formation of the hexatriene-type chains in complexes \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) probably follows a similar reaction mechanism as described by Roesky et al., even though we finally isolated the \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \), \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) and \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \). The resulting frontier orbitals of both calculations agreed well with each other, with the HOMOs being reflected by the \( P_1 \) electron lone pair, while the LUMOs are represented by the antibonding \( P_2-P_2a \) \( \pi \)-orbital. However, \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) and \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) show rotation about the \( \text{Si}-P \) bond, resulting in \( \text{L}^3 \text{M} \) being nearly perpendicular to the \( \text{SiP}_2 \text{Si} \) plane (Figures 4B and S17B).

The WBIs for the central chain \( \text{M}(\text{M} \text{P}_2 \text{Si} _2) \) \( \text{M}(\text{M} \text{P}_2 \text{Si} _2) \) and also replaced the \( \text{Pr} \) by smaller \( \text{Me} \) groups \( \text{Pr} \) by smaller \( \text{Me} \) groups. The resulting frontier orbitals of both calculations agreed well with each other, with the HOMOs being reflected by the \( P_1 \) electron lone pair, while the LUMOs are represented by the antibonding \( P_2-P_2a \) \( \pi \)-orbital. However, \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) and \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) show rotation about the \( \text{Si}-P \) bond, resulting in \( \text{L}^3 \text{M} \) being nearly perpendicular to the \( \text{SiP}_2 \text{Si} \) plane (Figures 4B and S17B).

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The WBIs for the central chain \( \text{M}(\text{M} \text{P}_2 \text{Si} _2) \) \( \text{M}(\text{M} \text{P}_2 \text{Si} _2) \) and also replaced the \( \text{Pr} \) by smaller \( \text{Me} \) groups \( \text{Pr} \) by smaller \( \text{Me} \) groups. The resulting frontier orbitals of both calculations agreed well with each other, with the HOMOs being reflected by the \( P_1 \) electron lone pair, while the LUMOs are represented by the antibonding \( P_2-P_2a \) \( \pi \)-orbital. However, \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) and \( \text{SiP}_2 \text{P} \text{Si}(\text{Dipp}) \) \( \text{Si}(\text{Dipp})_2 \) show rotation about the \( \text{Si}-P \) bond, resulting in \( \text{L}^3 \text{M} \) being nearly perpendicular to the \( \text{SiP}_2 \text{Si} \) plane (Figures 4B and S17B).
a) C. Ganesamoorthy, J. Schoening, C. Wölper, L. Song, P. R. Schreiner, S. Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, Z. Zhou, E. Rivard, Frötschel, J. J. Weigand, Angew. Chem. Int. Ed. 2011, 40, 11078–11085.

b) M. Driess, A. D. Fanta, D. R. Powell, R. West, Angew. Chem. Int. Ed. 1989, 28, 1038–1040; Angew. Chem. 1989, 101, 1087–1088; b) S. S. Sen, S. Khan, H. W. Roesky, D. Krätzke, K. Knott, J. Henn, D. Stalke, J.-P. Demers, A. Lange, Angew. Chem. Int. Ed. 2011, 50, 2322–2325; Angew. Chem. 2011, 121, 2370–2373; c) S. Khan, R. Michel, S. S. Sen, H. W. Roesky, D. Stalke, Angew. Chem. Int. Ed. 2011, 50, 11786–11789; Angew. Chem. 2011, 121, 11990–11993; d) J. W. Dube, C. M. E. Graham, C. L. B. Wang, M. L. Brown, P. D. Bureau, P. J. Rigney, Chem. Eur. J. 2014, 20, 6739–6744; e) D. Sarkar, C. Weetman, D. Muniz, S. Inoue, Angew. Chem. Int. Ed. 2021, 60, 3519–3523; Angew. Chem. 2021, 133, 3561–3565.

[37] a) M. Scheer, U. Becker, M. H. Chisholm, J. C. Huffman, F. Lemoigno, O. Szilvási, T. Veszprémi, Inorg. Chem. Commun. 2006, 9, 2662–2666; b) C. Weetman, S. Inoue, Chem. Commun. 2007, 43, 3434–3435; Angew. Chem. 2004, 116, 3525–3527; c) B. Dohme, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, Angew. Chem. Int. Ed. 1994, 33, 199–200; Angew. Chem. 1994, 106, 225–227; c) W. Uhl, M. Bentler, Chem. Commun. 2000, 771–772; d) A. R. Fox, R. J. Wright, E. Rivard, P. P. Power, Angew. Chem. Int. Ed. 2005, 44, 7729; e) S. S. Sen, H. W. Roesky, D. Stalke, Chem. Soc. Rev. 2011, 40, 3744–3750; f) F. H. Allen, Acta Crystallogr. Sect. B 1973, 29, 387–393.

[38] a) S. Du, J. Yin, Y. Chi, L. Xu, W.-X. Zhang, Angew. Chem. Int. Ed. 2014, 53, 15404–15408; b) S. S. Sen, J. Hey, H. R. Herbst-Immer, H. W. Roesky, D. Stalke, J. Am. Chem. Soc. 2011, 133, 12311–12316; e) S. Kaufmann, F. Krätschmer, R. Köppe, T. Schon, C. Schoo, P. W. Roesky, Chem. Soc. Rev. 2020, 49, 12446–12452; f) R. Asahkar, H. W. Roesky, J. J. Holstein, B. Dittrich, Eur. J. Inorg. Chem. 2013, 2013, 2777–2781; g) R. Asahkar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, Chem. Commun. 2012, 48, 4561–4563; h) M. K. Bisi, V. S. V. S. N. Swamy, T. Dar, K. Vanka, R. G. Gonade, S. S. Sen, Inorg. Chem. 2019, 58, 10536–10542.

[39] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, Phys. Rev. Lett. 2003, 91, 146401.

[40] X.-Y. Ye, J.-G. Sun, Acta Crystallogr. Sect. B 2004, 60, 2393–2405.

[41] a) M. Driess, F. H. Allen, Angew. Chem. Int. Ed. 2018, 57, 1027–1035; c) V. Cappello, J. Baumgartner, A. Dransfeld, M. Flock, K. Hassler, Eur. J. Inorg. Chem. 2006, 2393–2405.

[42] A search for P=O with the c.n. of P=O of 1.265 Å for bonds ranging from 1.965 to 2.159 Å with a mean of 2.04(3) Å. Cambridge Structural Database, Version 5.4, see also: F. H. Allen, Acta Crystallogr. Sect. B 2002, 58, 380–388.

[43] A search for Si–O single and double bonds in the CSD gave 36 hits ranging from 2.0630 to 2.1800 Å (mean 2.116 Å) for Si–O single bonds and 1052 hits ranging from 2.067 to 2.987 Å (mean 2.253 Å) for Si–O double bonds. C. R. Groom, J. B. Stobbs, S. C. Ward, Acta Crystallogr. Sect. B 2016, 72, 171–177.

[44] Y. V. A. Lee, M. Kawai, A. Sekiguchi, H. Ranaivonjato, J. Escudié, Organometallics 2009, 28, 4262–4265.

[45] M. Driess, S. Rell, H. Pitzkos, R. Janoschek, Angew. Chem. Int. Ed. 1997, 36, 1236–1239; Angew. Chem. 1997, 109, 1384–1387.

[46] M. K. Sharma, C. Wölper, G. Haberhauer, Angew. Chem. Int. Ed. 2021, 60, 6878–6890; Angew. Chem. 2021, 133, 6859–6865.

[47] a) R. Damrauer, S. E. Pusede, Organometallics 2009, 28, 1298–1294; b) T. Szilágyi, T. Veszprémi, Dalton Trans. 2010, 49, 7193–7200; c) M. Scheer, G. Balázs, A. Saitz, Chem. Rev. 2010, 110, 4236–4254.

[48] a) M. Scheer, U. Becker, M. H. Chisholm, J. C. Huffman, F. Lemoigno, M. L. G. E. O. Kelemen, Inorg. Chem. 1995, 34, 3117–3119; b) M. Scheer, U. Becker, J. Magull, Polyhedron 1998, 17, 1983–1993; c) J. Breiner, K. Faust, A. Schultz, Eur. J. Inorg. Chem. 2022, 42, 1–20.

[49] a) S. Du, J. Yin, Y. Chi, L. Xu, W.-X. Zhang, Angew. Chem. Int. Ed. 2017, 56, 15886–15890; Angew. Chem. 2017, 129, 16102–16106; b) G. Luo, S. Du, P. Wang, Lü, W.-X. Zhang, Y. Luo, Chem. Eur. J. 2020, 26, 13282–13287.

[50] W. Lu, K. Xu, Y. H. Hirao, R. Rinjo, Angew. Chem. Int. Ed. 2018, 57, 15691–15695; Angew. Chem. 2018, 130, 15917–15921.

[51] X. Sun, A. Hinz, P. W. Roesky, Chem. Eur. J. 2022, 28, e202001031 (5 of 5)