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Distinctly different reactivity of bis(silylenyl)- versus phosphanyl-silylenyl-substituted *o*-dicarborane towards O₂, N₂O and CO₂†

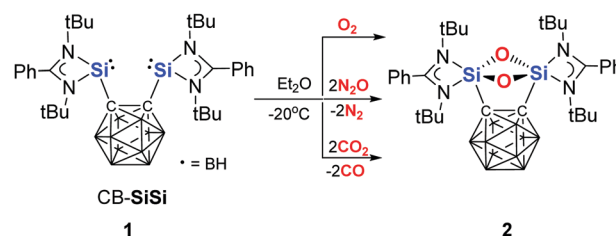
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In stark contrast to the reactivity of the bis-silylenyl dicarborane CB–Si₂ (**1**) [CB = *ortho*-C,C′-C₂B₁₀H₁₀, Si = PhC(tBuN)₂Si] towards O₂, N₂O, and CO₂, yielding the same dioxygenation product CB–Si₂O₂ (**2**) with a four-membered 1,3,2,4-disiladioxetane ring, the activation of the latter small molecules with the phosphanyl-silylenyl-functionalised CB–SiP (**3**) {P=[N(tBu)CH₂]₂} affords with O₂ the CB–Si(=O)P(=O) silanone-phosphine oxide (**4**), with N₂O the CB–Si(=O)P silanone-phosphine (**5**), and with CO₂ the CB–Si(O₂C=O)P silicon carbonate-phosphine (**6**) and CB–C(=O)OSiOP ester (**7**), respectively.

For many decades, the activation of ubiquitous small molecules such as H₂, N₂, O₂, CO, CO₂, N₂O, *etc.* has been considered to be a domain of transition-metal chemistry and metalloenzymes, including their low molecular-weight functional models. However, recent advances in low-valent non- and semi-metal chemistry have provided a plethora of impressive evidence with transition-metal-like reactivity of main-group elements in small molecule activation.^{1–6} This is in part due to the availability of reactive lone pair electrons and relatively low-lying empty acceptor orbitals of main-group elements in unusual low oxidation states, which can mimic the electronic situation of transition-metal centres and even mediate chemical bond cleavage of unactivated small molecules. Striking examples comprise the activation of dihydrogen by acyclic silylenes with a highly reactive silicon(II) centre^{7–10} and the fixation of dinitrogen by a borylene as a carbene analogue.^{11,12} In recent years,

we have been interested in the chemistry of chelating N-heterocyclic silylenes (NHSis) that feature two adjacent divalent silicon atoms as highly reactive sites.^{13–15} Such bis-NHSis not only can serve as steering ligands for coordination of main-group elements in unusual low oxidation states and transition metals for catalysis,^{13–15} they can also mediate cooperative small molecule activation through sufficiently close proximity of the two silicon(II) centres.^{16,17} For instance, the bis-NHSis with a Si···Si distances between 2.6 and 4.5 Å are capable reacting with CO at ambient temperature, affording disilaketenes.^{16–18} Featuring a Si···Si distance of about 3.3 Å, the two Si(II) centres in the *ortho*-dicarborane-based bis-NHSis CB–SiSi (**1**)¹⁹ (Scheme 1) are in a predestinate position to coordinate and subsequently activate CO.¹⁷ Moreover, the bis-NHSis **1** has been employed to stabilise a single zero-valent Si atom,²⁰ monovalent boron,²¹ and serves in nickel-mediated catalytic transformations.¹⁹ More recently we succeeded in the synthesis of the isolobal phosphanyl-silylenyl-functionalised *o*-dicarborane CB–SiP (**3**) where one silylenyl group in **1** is replaced by a phosphanyl moiety.²² Compound **3** enabled the formation of new classes of C,C′-dicarborandiyl-silylene supported Ge₂ and Ge₄ species which could not be realised with **1**.²² Herein, we wish to report the markedly different reactivity of **1** and **3** towards O₂, N₂O, and CO₂, respectively.

Exposure of solutions of **1** in diethyl ether at –20 °C to O₂ gas leads to immediate disappearance of the yellow color and formation of the 1,3,2,4-disiladioxetane **2** (Scheme 1).



Scheme 1 Reactions of **1** with O₂, N₂O, and CO₂ to yield **2**.

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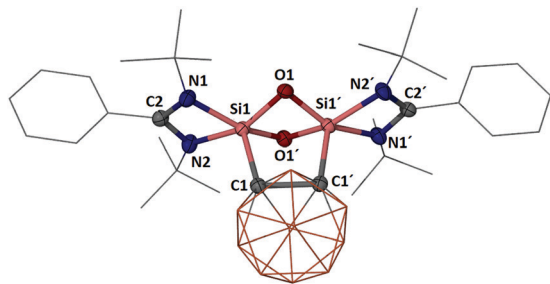
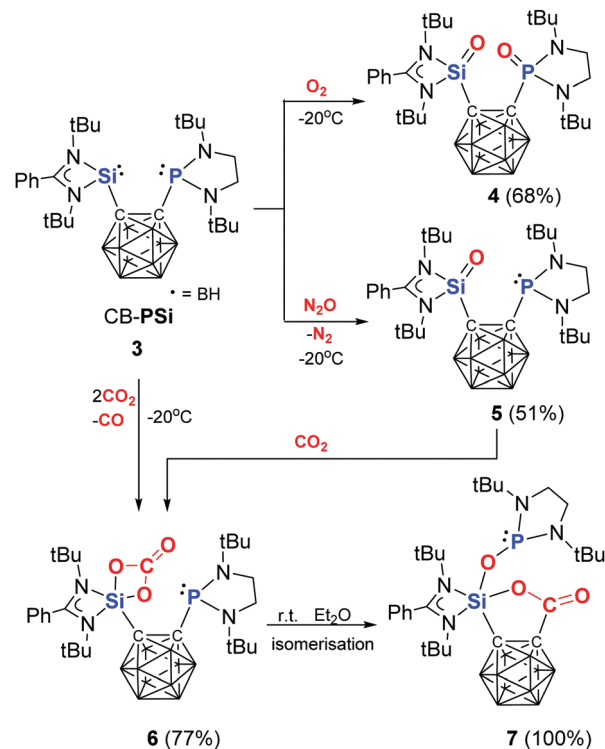


Fig. 1 Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and one toluene molecule are omitted for clarity. Selected bond distances (Å) and angles (°): Si1–O1 1.695(1), Si1–O1' 1.708(1), Si1–C1 1.961(2), Si1–N1 1.861(1), Si1–N2 1.884(1), Si1–Si1' 2.403(1); O1–Si1–O1' 83.4(1), Si1–O1–Si1' 89.8(1), O1–Si1–C1 96.6(1), O1'–Si1–C1 96.1(1).

Interestingly, **2** is also formed as single product through exposure of **1** towards N_2O and CO_2 under the same reaction conditions. After workup, **2** has been isolated as a colorless solid; it crystallises in the monoclinic space group $C2/c$. The two Si centres are five-coordinated and bridged by two oxygen atoms (Fig. 1). The Si atoms adopt a distorted square-pyramidal coordination geometry with the carborane–C atom at the apical position. The Si1–O1 [1.695(1) Å] and Si1–O1' [1.708(1) Å] distances in **2** are slightly longer than the Si–O length in octamethyl cyclotetrasiloxane (*ca.* 1.65 Å).²³ As expected, the five-coordinate ^{29}Si nuclei exhibit a drastic up-field shift in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum ($\delta = -98.6$ ppm) when compared with the precursor **1** ($\delta = 18.9$ ppm).¹⁹

The reactions of O_2 , N_2O , and CO_2 with various stable silylenes to give $\text{Si}=\text{O}$ -containing compounds or further oxygenated Si–O-containing species are well-documented.^{5,9,24–30} We wondered whether a transient or even isolable $\text{Si}=\text{O}$ species could be detected if one silylenyl moiety in **1** is replaced by a isoelectronic phosphanyl group; thus we employed the phosphanyl-silylenyl-functionalised carborane CB–SiP (**3**). Indeed, under the same reaction conditions, exposure of **3** to dioxygen gas at -20°C resulted in the formation of the CB–Si(=O)P(=O) silanone-phosphine oxide (**4**) (Scheme 2 and Fig. 2), in which both P and Si atoms are mono-oxygenated. Compound **4** was isolated at -20°C as a colorless solid in 68% yields. It is sparingly soluble in Et_2O , but well soluble in THF. Solutions of **4** in ethereal solvents are only stable below -20°C ; its decomposition affords a mixture of unidentified products. In the solid state, however, **4** is stable at room temperature and decomposes above 153°C .

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** (measured at -20°C in d_8 -THF) exhibits a singlet at $\delta = 26.4$ ppm, which is significantly up-field shifted relative to that of the precursor **3** ($\delta = 102.9$ ppm).²² A similar up-field shift is observed for the $^{29}\text{Si}\{^1\text{H}\}$ NMR resonance of **4** ($\delta = -52.8$ vs. 17.5 ppm for **3**).²² The IR spectrum of **4** shows a very strong stretching vibration mode at $\nu = 1193\text{ cm}^{-1}$ for the $\text{Si}=\text{O}$ bond, which is slightly larger than the value observed for the $\text{Si}=\text{O}$ bond in a C=O-supported silanone (1153 cm^{-1}).²⁷ A single-crystal X-ray diffraction analysis confirmed the presence of $\text{Si}=\text{O}$ and $\text{P}=\text{O}$



Scheme 2 Reactions of CB–Psi **3** with N_2O , O_2 , and CO_2 to give **4**, **5**, **6** and **7**.

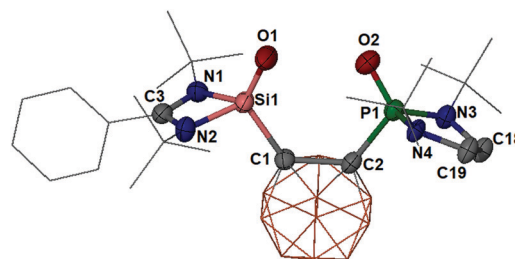


Fig. 2 Molecular structure of **4** (There are two molecules in the asymmetric unit, only one is depicted). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for molecule 1: Si1–O1 1.524(3), Si1–C1 1.943(4), Si1–N1 1.820(3), Si1–N2 1.814(3), P1–O2 1.456(3), P1–C2 1.899(4), P1–N3 1.638(3), P1–N4 1.656(3); O1–Si1–C1 122.5(2), O2–P1–C2 109.2(2).

bonds in **4** with a O1–Si1–P1–O2 torsion angle of 36.8° (Fig. 2). In **4** both silicon and phosphorus atoms adopt a distorted tetrahedral coordination environment. In line with the IR spectroscopic data, the Si–O distance of 1.524(3) Å in **4** is slightly shorter than that in the aforementioned keto-supported silanone adduct [1.532(2) Å],²⁷ indicating a more pronounced $\text{Si}=\text{O}$ bond character.

As mentioned above, the reaction of silylenes with dioxygen usually affords disiladioxetanes or related Si–O single bond containing products. The formation of **4** as an isolable $\text{Si}=\text{O}$ species is apparently due to the presence of the phosphanyl



moiety, acting as an oxygen atom acceptor in close proximity to the silicon atom. In order to figure out whether **3** is capable of N_2O activation to furnish a $\text{Si}=\text{O}$ -(and/or $\text{P}=\text{O}$)-containing product, we exposed solutions of **3** in Et_2O to N_2O gas at -20°C . To our surprise, the oxygenation took place only at the silicon centre to form the CB-($\text{Si}=\text{O}$)P silanone-phosphine (**5**), which could be isolated in 51% yields (Scheme 2). This is consistent with the fact, that such substituted phosphines are inert toward N_2O . Akin to **4**, compound **5** is labile in Et_2O and THF solutions above -20°C and decomposes to an unidentified mixture of products. However, **5** is indefinitely stable in the solid state at ambient temperature and decomposes above 176°C .

The molecular structure of **5** established by a single-crystal X-ray diffraction analysis revealed a four-coordinate silicon atom with a distorted tetrahedral coordination geometry (Fig. 3), while the phosphorus atom remains unchanged with respect to the precursor **3**. The $\text{Si}=\text{O}$ distance of $1.524(1)\text{ \AA}$ in **5** is identical to that in **4**. In line with that, the IR spectrum of **5** exhibits a $\text{Si}=\text{O}$ stretching frequency of 1187 cm^{-1} , which is very close to the value observed for **4** ($\nu = 1193\text{ cm}^{-1}$). The four-coordinate Si atom in **5** shows a resonance at $\delta = -51.9\text{ ppm}$ in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (measured at -30°C in $d_8\text{-THF}$), matching well with that for **4** ($\delta = -52.8\text{ ppm}$). In contrast, the marginally different chemical shift at $\delta = 114.2\text{ ppm}$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** (vs. $\delta = 102.9\text{ ppm}$ of its precursor **3**)²² confirms the presence of the unchanged phosphine moiety.

As aforementioned, previous studies on CO_2 activation toward silylenes revealed mono-oxygen transfer and liberation of CO to form either $\text{Si}=\text{O}$ ^{26,28–30} or dimeric disiladioxetane species.^{29,31} In less cases, silicon carbonates^{31–34} could be isolated which resulted from trapping reaction of $\text{Si}=\text{O}$ intermediate with CO_2 . Similar to the reactivity of **3** towards N_2O , **3** reacts with CO_2 in diethyl ether at -20°C only at the Si(III) site to yield the CB-($\text{SiO}_2\text{C}=\text{O}$)P silicon carbonate-phosphine (**6**) (Scheme 2). The latter product was isolated in 77% yields after workup at low temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** shows a signal at $\delta = 115.5\text{ ppm}$ (measured at -10°C in $d_8\text{-THF}$), indicating the presence of the unchanged phosphine

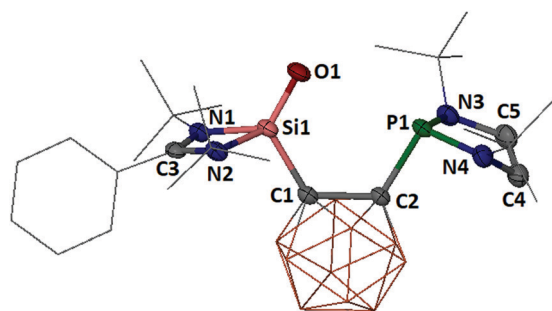


Fig. 3 Molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): $\text{Si1}-\text{O1}$ $1.524(1)$, $\text{Si1}-\text{C1}$ $1.930(2)$, $\text{Si1}-\text{N1}$ $1.827(2)$, $\text{Si1}-\text{N2}$ $1.814(2)$, $\text{P1}-\text{C2}$ $1.949(1)$, $\text{P1}-\text{N3}$ $1.717(2)$, $\text{P1}-\text{N4}$ $1.677(2)$; $\text{O1}-\text{Si1}-\text{C1}$ $120.2(1)$.

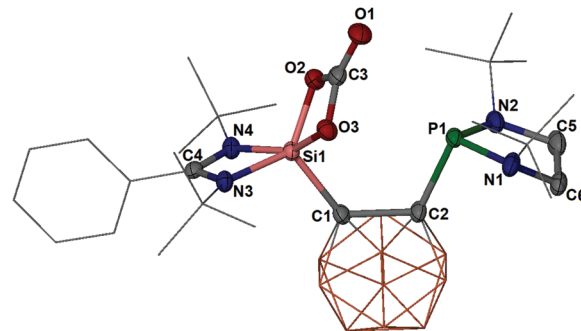


Fig. 4 Molecular structure of **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): $\text{Si1}-\text{O2}$ $1.718(1)$, $\text{Si1}-\text{O3}$ $1.770(1)$, $\text{Si1}-\text{C1}$ $1.939(2)$, $\text{Si1}-\text{N3}$ $1.811(2)$, $\text{Si1}-\text{N4}$ $1.874(2)$, $\text{P1}-\text{C2}$ $1.932(2)$, $\text{P1}-\text{N1}$ $1.684(2)$, $\text{P1}-\text{N2}$ $1.708(2)$, $\text{C3}-\text{O1}$ $1.194(2)$, $\text{C3}-\text{O2}$ $1.362(2)$, $\text{C3}-\text{O3}$ $1.340(2)$, $\text{C1}-\text{C2}$ $1.738(3)$; $\text{O2}-\text{Si1}-\text{C1}$ $117.5(1)$, $\text{O3}-\text{Si1}-\text{C1}$ $102.1(1)$, $\text{N3}-\text{Si1}-\text{C1}$ $109.8(1)$, $\text{N4}-\text{Si1}-\text{C1}$ $103.2(1)$, $\text{O2}-\text{Si1}-\text{O3}$ $75.0(1)$, $\text{O1}-\text{C3}-\text{O2}$ $126.9(2)$, $\text{O1}-\text{C3}-\text{O3}$ $129.3(2)$, $\text{O2}-\text{C3}-\text{O3}$ $103.7(2)$.

moiety, whereas the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum shows a resonance at $\delta = -93.1\text{ ppm}$, reminiscent of the five-coordinate ^{29}Si nuclei attached to a ferrocene spacer ($\delta = -92.1\text{ ppm}$).²⁹ The IR spectrum of **6** exhibits a stretching vibration mode at $\nu = 1813\text{ cm}^{-1}$ for the $\text{C}=\text{O}$ group, comparable to that observed in a bis-NHC-supported silicon dicarbonate (1746 cm^{-1}).³⁵ A single-crystal X-ray diffraction analysis confirmed the molecular structure of **6** (Fig. 4), which features a five-coordinate silicon atom in a strongly distorted square-pyramidal coordination geometry with the carborane-C atom at the apical position. The $\text{Si}-\text{O}$ distances of $1.718(1)$ and $1.770(1)\text{ \AA}$ in **6** are significantly longer than the $\text{Si}=\text{O}$ lengths in **4** and **5**, respectively, but close to the $\text{Si}-\text{O}$ bonds in **2** [$1.695(1)$, $1.708(1)\text{ \AA}$]. The $\text{C3}-\text{O1}$ distance of $1.194(2)\text{ \AA}$ is considerably shorter than those of $\text{C3}-\text{O2}$ ($1.362(2)\text{ \AA}$) and $\text{C3}-\text{O3}$ ($1.340(2)\text{ \AA}$), implying a $\text{C}=\text{O}$ bond between C3 and O1 .

Although the mechanism of **6** from **3** with CO_2 is still unknown, we propose that the initial step of the reaction is the formation of **5** with a $\text{Si}=\text{O}$ moiety under release of CO. To prove this, we conducted the reaction of **5**, obtained from **3** and N_2O , with CO_2 at -20°C (Scheme 2). Indeed, a clean formation of **6** confirmed this by multinuclear NMR spectroscopy measurements.

While **6** is stable at room temperature in the solid state, it isomerises quantitatively at room temperature in ethereal solvents to give **7** in the course of 24 hours (Scheme 2). Its molecular structure has been established by a single-crystal X-ray diffraction analysis. As depicted in Fig. 5, the silicon atom in **7** is five-coordinate and in a distorted trigonal-bipyramidal coordination environment with the N1 and O2 atoms in the axial positions. Thus, the $\text{Si1}-\text{O2}$ distance of $1.773(2)\text{ \AA}$ is longer than that of $\text{Si1}-\text{O3}$ ($1.624(2)\text{ \AA}$). The driving force of the isomerization of **6** to **7** is attributed to the oxygen affinity of phosphorus that induces CB C-P bond scission and CB C-CO bond formation. In addition, the steric congestion in **6** between the phosphine group and the CB cage is released after migration of the phosphine moiety from the carborane-C2 to the



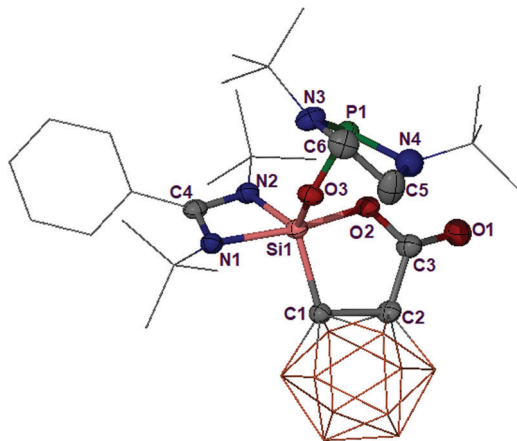


Fig. 5 Molecular structure of **7**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Si1–O2 1.773(2), Si1–O3 1.624(2), Si1–C1 1.937(3), O3–P1 1.666(2), O2–C3 1.314(3), O1–C3 1.200(3), C2–C3 1.515(4), C1–C2 1.652(3); O3–Si1–O2 94.2(1), O3–Si1–N2 120.2(1), N2–Si1–C1 118.3(1), O3–Si1–C1 120.6(1), N1–Si1–O2 167.8(1), Si1–O3–P1 134.7(1), O2–C3–O1 125.5(2), O1–C3–C2 122.4(2), O2–C3–C2 112.1(2).

O3 atom. As a result, the C1–C2 distance of 1.652(3) Å in **7** is significantly shorter than that in **6** (1.738(3) Å). In accordance with the molecular structure of **7**, its $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum shows a doublet at $\delta = -110.4$ ppm ($^2J_{\text{Si,P}} = 9.4$ Hz) comparable to that of **6** ($\delta = -93.1$ ppm), and the ^{31}P nucleus resonates at $\delta = 119.6$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reminiscent of that for **6** ($\delta = 115.5$ ppm).

In summary, we have described the markedly different reactivity of the bis-NHSi dicarborane **1** and its isolobal phosphanyl-NHSi-functionalised dicarborane analogue **3** towards O_2 , N_2O , and CO_2 . While all reactions of **1** with O_2 , N_2O , and CO_2 let to the same dioxygenation product CB–Si($\mu\text{-O}$) $_2$ Si **2**, the activation products with **3** turned out to furnish different products featuring Si=O, P=O, or C=O functionalities.

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Conflicts of interest

There are no conflicts to declare.

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