

Stabilization of elusive silicon oxides

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Molecular SiO₂ and other simple silicon oxides have remained elusive despite the indispensable use of silicon dioxide materials in advanced electronic devices. Owing to the great reactivity of silicon–oxygen double bonds, as well as the low oxidation state of silicon atoms, the chemistry of simple silicon oxides is essentially unknown. We now report that the soluble disilicon compound, L:Si=Si:L (where L = :C{N(2,6-*i*-Pr₂C₆H₃)CH₂})₂, can be directly oxidized by N₂O and O₂ to give the carbene-stabilized Si₂O₃ and Si₂O₄ moieties, respectively. The nature of the silicon oxide units in these compounds is probed by spectroscopic methods, complementary computations and single-crystal X-ray diffraction.

Although carbon and silicon share a number of similar chemical properties, there are also significant differences between these first two of the group 14 elements in the periodic table. This remarkable disparity is perhaps most evident in the respective oxides of carbon and silicon. Carbon monoxide and carbon dioxide, for example, are ubiquitous, each with an extensively developed chemistry¹. Furthermore, the atmospheric levels of carbon dioxide, a principal hydrocarbon combustion product, are of considerable concern and vigorous debate². In contrast, the chemistry of simple silicon oxides (Fig. 1) has remained elusive because of the great reactivity of silicon–oxygen double bonds coupled with the highly reactive silicon atoms that have a low oxidation state^{3–9}. Silicon monoxide (SiO) has been described as the most common oxide of silicon in the universe; however, terrestrially it is only persistent as a monomer at high temperatures (about 1,200 °C)⁹. Transition-metal (that is, Pd and Ag) derivatives of SiO have been explored using a matrix-isolation technique^{10–12}. Unlike bulk silicon dioxide (SiO₂), molecular SiO₂ has been detected in solid noble-gas matrices^{9,13} and gas-phase reactions¹⁴, and probed by photoelectron spectroscopy⁵. Naturally occurring silica (SiO₂) is stable as it consists of a covalent network in which each silicon atom is singly bonded to four neighbouring oxygen atoms¹. Owing to the abundance of silicon and oxygen in the Earth's crust, the chemistry of silica has, arguably, been studied nearly as extensively as that of water. Among its myriad applications, SiO₂ is obviously an indispensable material in advanced electronic devices¹⁵.

Silicon–oxide clusters have fascinated scientists for decades owing to their remarkable roles in many technological areas, which include the formation of silicon-based nanowires^{16,17} and as an aid to understanding the dynamics of silicon-etching processes^{6,18}. Moreover, investigations of the electronic and structural properties of silicon–oxide clusters may help to model microscopic aspects of the bulk materials. Although spectroscopic methods have provided some information on these molecules, the literature reveals a paucity of reliable structural determinations (for example, single-crystal X-ray diffraction) of silicon–oxide clusters¹⁹. Thus, developing a convenient means to stabilize elusive silicon–oxide clusters (Fig. 1) remains a significant challenge.

The study of silicon-surface oxidation is not only pivotal for the semiconductor industry¹⁵, but it is also relevant to spacecraft safety^{20,21}. The recently reported carbene-stabilized disilicon,

L:Si=Si:L (where L = :C{N(2,6-*i*-Pr₂C₆H₃)CH₂})₂ (**1**)²², wherein the silicon atoms are in the formal oxidation state of zero²³, presents a unique platform to mimic the silicon surface from which the formation of a silicon–oxide cluster may be examined. Herein we report the syntheses, computations and X-ray structures of carbene-stabilized Si₂O₃ (**2**) and Si₂O₄ (**3**), which were obtained by nitrous oxide (N₂O) and oxygen (O₂) oxidation of **1**, respectively. We are not aware of other examples of simple silicon oxides being incorporated into molecular compounds. Indeed, compound **3** may be considered as a carbene-stabilized dimeric silicon dioxide.

The scarcity of molecular Si₂O₃ and Si₂O₄ moieties may largely be attributed to the presence of formal Si=O double bonds in these two species, which, like those in silanones (R₂Si=O)^{24,25}, have pronounced zwitterionic character (Si⁺–O[−])²⁶. Consequently, these species are inclined to undergo oligomerization reactions. Lewis-base coordination, especially carbene coordination, is an effective strategy to stabilize highly reactive main-group molecules^{27–32}. Lewis-base-stabilized silanone³³ and silanoic silylester³⁴ were first synthesized by the oxygenation of silylenes. Subsequently, a number of Lewis-base-stabilized formal Si=O bonds have been reported^{24,35–38}. Both aerial and N₂O oxidation of L':Si:L' (L' = cyclic (alkyl)(amino)carbenes) have recently been reported to yield the corresponding decomposition products (*N*-aryl amides and SiO₂)³⁹.

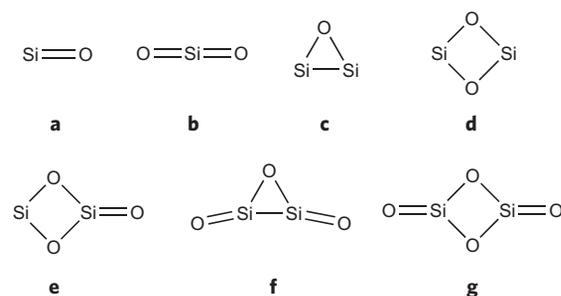


Figure 1 | Elusive silicon–oxide clusters. **a**, SiO. **b**, SiO₂. **c**, Si₂O. **d**, Si₂O₂. **e, f**, Si₂O₃. **g**, Si₂O₄. Isomer **e** represents the global minimum, which in the gas phase is much lower in energy than isomer **f**. However, isomer **f** is stabilized by two carbene ligands in compound **2** (see Fig. 2 for its structure).

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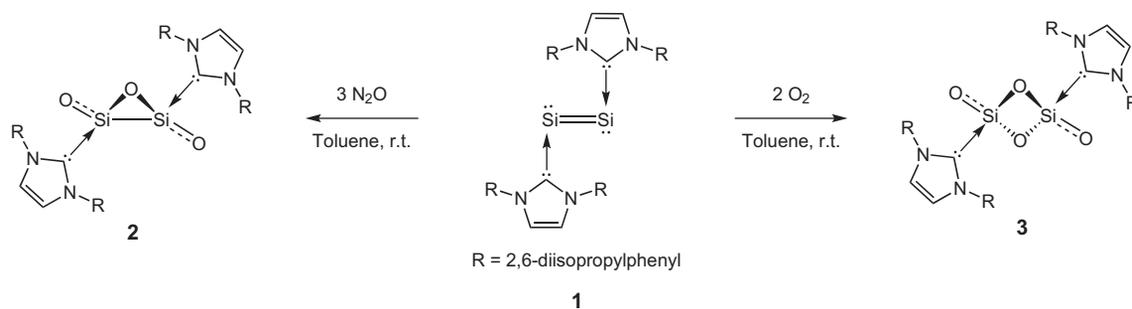


Figure 2 | Synthetic scheme for 2 and 3. Compound **2** was obtained by the N_2O oxidation of **1**, whereas compound **3** was obtained by the oxidation of **1** with O_2 . r.t., room temperature.

Results and discussion

As an oxygen atom donor, N_2O has been utilized extensively in silicon chemistry^{24,40}. The reaction of **1** (red colour) with N_2O resulted in **2** (50.0% yield) (Fig. 2), a yellow crystalline powder. In contrast, the reaction of **1** with O_2 afforded **3** (38.7% yield) (Fig. 2) as a colourless crystalline powder. Careful control of the amount of the oxidants added in the reaction system is critical in the preparation of **2** and **3**. The reaction of **1** with excess oxidant (that is, N_2O or O_2) results in free *N*-heterocyclic carbene and an uncharacterized white silicon oxide powder. Indeed, unlike the recently reported air-stable carbene- P_2O_4 complex⁴¹, compounds **2** and **3** immediately decompose when exposed to additional oxidant. The Si_2O_3 species, in a laser vaporization source, has been proposed as an intermediate in the formation of Si_2O_4 (ref. 5). The conversion of **2** into **3** was not observed when combining **2** with N_2O (which only led to the by-products mentioned above).

The imidazole ^1H NMR resonances (in C_6D_6) of **2** (6.30 ppm) and **3** (6.32 ppm) are quite similar. The ^{29}Si NMR singlet resonances of **2** (-49.1 ppm) and **3** (-76.3 ppm) in d_8 -THF are shifted dramatically upfield as compared to that of **1** (224.5 ppm in C_6D_6)²². The infrared spectrum of **2** contains three characteristic absorption bands ($\nu(\text{Si}=\text{O}) = 1,092 \text{ cm}^{-1}$; $\nu(\text{Si}-\text{O}) = 799$ and 621 cm^{-1}), comparing well to the computed results ($\nu(\text{Si}=\text{O}) = 1,094 \text{ cm}^{-1}$; $\nu(\text{Si}-\text{O}) = 797$ and 598 cm^{-1}) of the **2-Ph** model ($\text{L} = \text{:C}\{\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\}$). Four characteristic infrared absorption bands were observed

for **3** ($\nu(\text{Si}=\text{O}) = 1,147 \text{ cm}^{-1}$; $\nu(\text{Si}-\text{O}) = 837$, 772 and 519 cm^{-1}). These are consistent with the theoretical values ($\nu(\text{S}=\text{O}) = 1,156 \text{ cm}^{-1}$; $\nu(\text{Si}-\text{O}) = 824$, 759 and 515 cm^{-1}) of the **3-Ph** model (where $\text{L} = \text{:C}\{\text{N}(\text{C}_6\text{H}_5)\text{CH}_2\}$), but are red-shifted compared to the data reported for matrix-trapped Si_2O_4 ($\nu(\text{Si}=\text{O}) = 1,293 \text{ cm}^{-1}$; $\nu(\text{Si}-\text{O}) = 889$ and 786 cm^{-1})⁴.

Recrystallization of **2** in a THF/hexane mixed solvent gave X-ray-quality crystals of both **2** and **2**·(THF)₂. Considering the similarity of the structural data of **2** and **2**·(THF)₂ (see the Supplementary Information), only the metrical values of **2** are discussed herein (Fig. 3a). The Si_2O_3 core (with C_2 symmetry) in **2**, which features a Si_2O three-membered ring and two terminal oxygen atoms (Fig. 1f), is intriguing because it is energetically less favoured than the Si_2O_3 isomer that contains a cyclic Si_2O_2 ring and a terminal oxygen (Fig. 1e)⁴². Each silicon in **2** is four coordinated. The formal oxidation state of +3 for the silicon atoms in **2** results from the N_2O partial oxidation of **1**. The two terminal oxygen atoms are coplanar with the C-Si-Si-C backbone, as the bridging oxygen atom is disordered and perches above and below the C_2Si_2 plane. The structural data of the Si_2O_3 core of **2** ($d_{\text{Si}-\text{O}} = 1.5347(18) \text{ \AA}$; $d_{\text{Si}-\text{O}} = 1.646(3)$ and $1.672(3) \text{ \AA}$; $d_{\text{Si}-\text{Si}} = 2.2405(14) \text{ \AA}$) are similar to the computed values ($d_{\text{Si}-\text{O}} = 1.536 \text{ \AA}$; $d_{\text{Si}-\text{O}} = 1.714 \text{ \AA}$ and $d_{\text{Si}-\text{Si}} = 2.221 \text{ \AA}$) for the symmetric Si_2O_3 isomer (Fig. 1f)⁴². In addition, the formal Si=O bond distance of **2** ($1.5347(18) \text{ \AA}$) also compares well to those for Lewis-base-stabilized Si=O double bonds

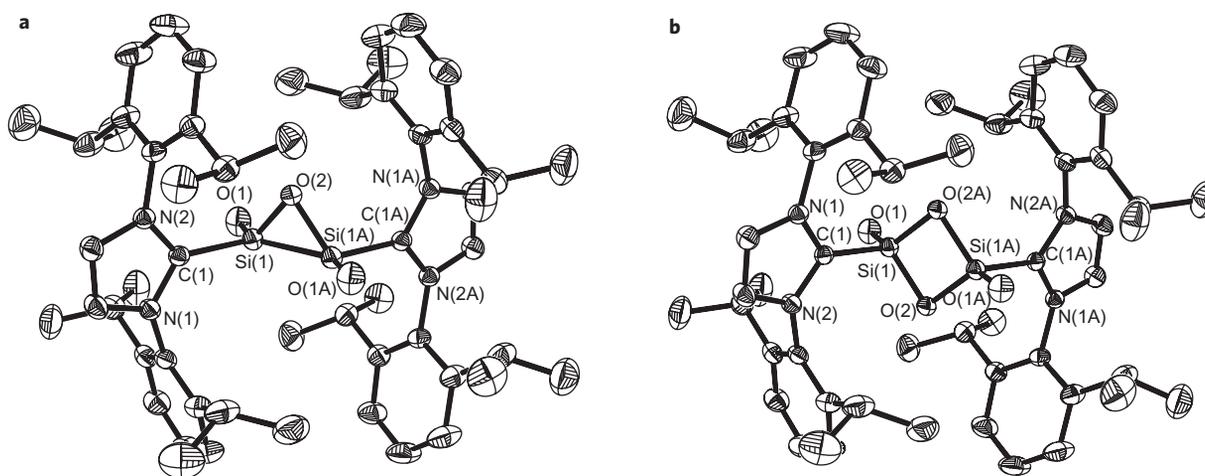


Figure 3 | Molecular structures of the carbene-stabilized Si_2O_3 and Si_2O_4 species. **a, b**, Structures of compounds **2** (**a**) and **3** (**b**). Thermal ellipsoids represent a 30% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (\AA) for **2**: Si(1)-Si(1A) 2.2405(14), Si(1)-O(1) 1.5347(18), Si(1)-O(2) 1.646(3), Si(1A)-O(2) 1.672(3), Si(1)-C(1) 1.940(2). Selected angles ($^\circ$) for **2**: C(1)-Si(1)-Si(1A) 108.34(8), O(1)-Si(1)-Si(1A) 142.06(9), C(1)-Si(1)-O(1) 109.56(10), Si(1)-O(2)-Si(1A) 84.95(14). Selected bond distances (\AA) for **3**: Si...Si 2.3980(11), Si(1)-O(1) 1.5260(14), Si(1)-O(2) 1.6763(13), Si(1)-O(2A) 1.6735(13), Si(1)-C(1) 1.9259(17). Selected angles ($^\circ$) for **3**: O(1)-Si(1)-C(1) 110.41(8), C(1)-Si(1)-O(2) 102.18(7), C(1)-Si(1)-O(2A) 103.82(7), Si(1)-O(2)-Si(1A) 91.43(6). See discussion of the bonding in the text.

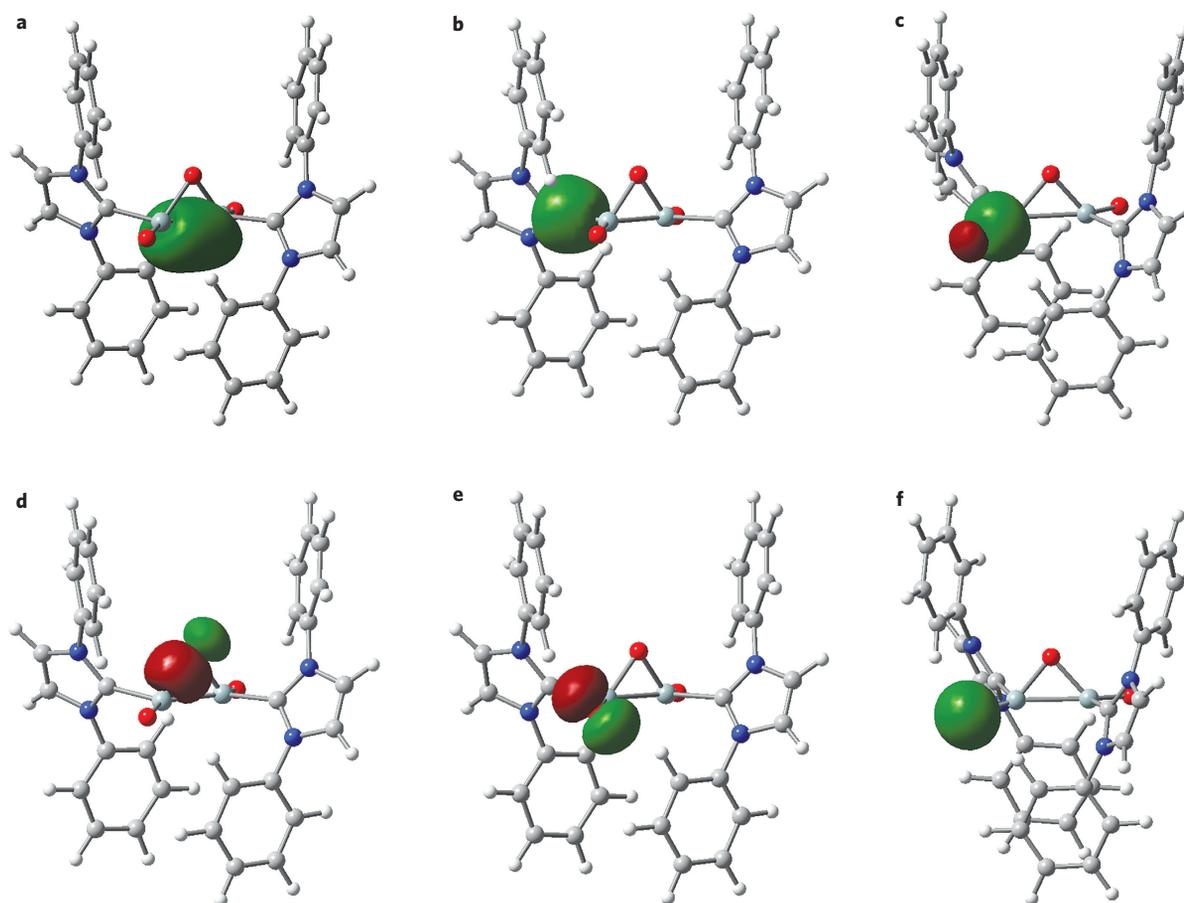


Figure 4 | LMOs of the 2-Ph model. **a**, Si-Si σ -bonding orbital. **b**, Si-C σ -bonding orbital. **c**, Si-O_{terminal} σ -bonding orbital. **d**, Si-O_{bridging} σ -bonding orbital. **e,f**, Lone-pair orbitals of the O_{terminal}. **e** represents one of the two degenerate lone-pair orbitals (with an almost pure p character) of the terminal oxygen, which are obviously distorted towards silicon.

(1.526–1.579 Å)^{24,34,38}. Interestingly, the Si-Si (2.2405(14) Å) and Si-C (1.940(2) Å) bond distances of **2** are similar to those of **1** ($d_{\text{Si-Si}} = 2.2294(11)$ Å; $d_{\text{Si-C}} = 1.9271(15)$ Å)²².

In contrast to the partial oxidation of **1** with N₂O to give **2**, O₂ not only caps the lone-pair electrons of both silicon atoms in **1** with oxygen atoms, but also cleaves the Si=Si double bond by O₂ insertion, which renders the Si₂O₄ core in **3** (Fig. 3b). Although Si₂O₄, the silicon dioxide dimer, favours D_{2h} geometry in the gas phase (Fig. 1g)⁴ (also see Supplementary Table 4), the Si₂O₄ core of **3** adopts C_{2h} symmetry because of the coordination of the two carbene ligands. The central four-membered Si₂O₂ ring is perpendicular to the C-Si=O plane. Each four-coordinated silicon centre in **3** is in the formal oxidation state of +4. Although comparable to that in **2** (1.940(2) Å), the Si-C bond distance in **3** (1.9259(17) Å) is almost the same as that in **1** (1.9271(15) Å)²². The formal Si=O (1.5260(14) Å) and Si-O (1.6763(13) and 1.6735(13) Å) bond distances in **3** are similar to those in **2** ($d_{\text{Si=O}} = 1.5347(18)$ Å; $d_{\text{Si-O}} = 1.646(3)$ and 1.672(3) Å) and the computed values for those in free Si₂O₄ ($d_{\text{Si=O}} = 1.512$ Å and $d_{\text{Si-O}} = 1.680$ Å) (see Supplementary Table 4).

The non-bonded silicon-silicon distance in **3** (2.398 Å), comparable to those in 1,3-cyclodisiloxanes [2.382(2)–2.431(2) Å]^{43,44}, is longer than the sum of the silicon covalent radii (2.34 Å)⁴⁵, but marginally shorter than that computed for Si₂O₄ (2.406 Å) (see Supplementary Table 4).

The nature of the bonding in **2** and **3** was further probed by density functional theory computations at the B3LYP/6-311+G** level on the simplified models **2-Ph** (optimized in C₂ symmetry) and **3-Ph** (optimized in C_{2h} symmetry), respectively (where

L: =:C{N(C₆H₅)CH₂})₂). Natural bond orbital (NBO) analysis shows that the Si₂O ring in **2-Ph** involves a σ Si-Si single bond (Wiberg bond index (WBI) = 0.812), with a 27.5% s , 71.6% p and 0.9% d character (Fig. 4a). Both the Si-C bond polarizations (for **2-Ph**, 78.3% towards C and 21.7% towards Si (Fig. 4b); for **3-Ph**, 79.5% towards C and 20.5% towards Si (see Supplementary Fig. 1a)) and the silicon-carbon WBIs of **2-Ph** (0.59) and **3-Ph** (0.57) are consistent with the lability of the Si-C bonds in **2** and **3**. All the Si-O σ bonds in both **2-Ph** (Fig. 4c,d) and **3-Ph** (see Supplementary Fig. 1b,c) are significantly polarized towards the oxygen atoms (that is, 82–85% of the NBO electron densities reside at the oxygen atoms). The two degenerate lone-pair orbitals for each terminal oxygen atom in **2-Ph** (one is shown as Fig. 4e) and in **3-Ph** (see Supplementary Fig. 1d,e), with an almost pure p character, are obviously distorted towards silicon. Consequently, the WBI values of the Si-O_{terminal} bonds in **2-Ph** (1.05) and **3-Ph** (1.11) are almost double those of the corresponding Si-O_{bridging} bonds (0.59 for **2-Ph** and 0.57 for **3-Ph**), which suggests that the terminal Si-O bonds in **2** and **3** have a modest double-bond character (as shown in the resonance structures **2A** and **3A** in Fig. 5). In addition, the Si-O WBI values of **2-Ph** and **3-Ph** compare to those for Si₂O₃ (Fig. 1f, Si-O_{terminal} = 1.42, Si-O_{bridging} = 0.68) and Si₂O₄ (Fig. 1g, Si-O_{terminal} = 1.45, Si-O_{bridging} = 0.64) (see Supplementary Tables 3 and 4), respectively. Also, each silicon atom bears a positive charge of +1.52 (for **2-Ph**) or of +2.14 (for **3-Ph**), whereas each oxygen atom has a negative charge of –1.22 (average, for **2-Ph**) or of –1.23 (for **3-Ph**). In summary, NBO analyses, coupled with the localized molecular orbitals (LMOs) of

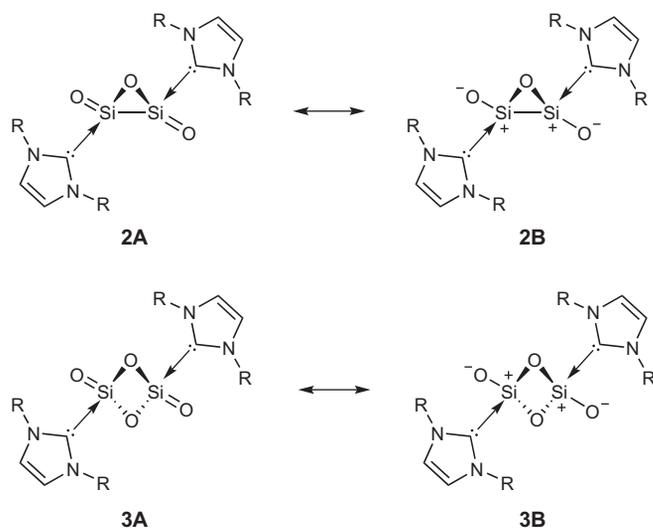


Figure 5 | Resonance contributors of 2 and 3. In the resonance structures **2A** and **3A**, the Si-O_{terminal} bonds are double bonds. In the major resonance structures **2B** and **3B**, the Si-O_{terminal} bonds are zwitterionic.

2-Ph and **3-Ph**, indicate that the zwitterionic resonance structures **2B** and **3B** (Fig. 5) may represent the major resonance contributors for **2** and **3**, respectively.

In summary, we isolated carbene-stabilized Si₂O₃ (**2**) and Si₂O₄ (**3**) through N₂O and O₂ oxidation of the carbene–disilicon complex **1** at room temperature, respectively. The Si₂O₃ core in **2** is stabilized in its energetically less favoured form, which consists of a Si₂O ring and two terminal oxygen atoms (Fig. 1f). In **2** and **3**, the sterically demanding carbene ligand (where L = :C{N(2,6-¹Pr₂C₆H₃)CH₂}) can effectively shield the elusive Si₂O_x (x = 3 and 4) cores and thus avoid the oligomerization of the strongly polarized (formal) Si=O bonds in these two silicon–oxide cores. With P₂O₄ (ref. 41), Si₂O₃ and Si₂O₄ now as prominent examples, carbene stabilization^{27,28,30} is demonstrated to be an effective means to approach the elusive main-group oxides.

Methods

All the reactions were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster 130). Chemicals were purchased from commercial sources and used as received. N₂O (AA grade) and O₂ gas (research grade) were purchased from Airgas and passed through molecular sieves before use. Solvents were dried and distilled under argon from Na/benzophenone prior to use. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. ²⁹Si NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. Infrared spectra were recorded using a Shimadzu IRPrestige-21 FTIR spectrophotometer. X-ray intensity data for compounds **2**, **2·(THF)₂** and **3** were collected on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), using the ω -scan technique.

For compound **2**, a 250 ml Schlenk flask was charged with 0.25 g (0.30 mmol) of **1** and 140 ml of toluene. The mixture was stirred at room temperature until it gave a homogeneous dark-red solution. N₂O was then introduced into the reaction system in a controlled manner until the colour of the solution faded to yellow. Immediately, the volatiles were removed *in vacuo*. The residue was rinsed with 40 ml of hexane and then extracted with 30 ml of THF. A pale-yellow powder, **2**, was obtained after removing THF *in vacuo* (0.130 g, 50.0% yield). X-ray-quality yellow crystals of both **2** and **2·(THF)₂** were isolated by diffusion of hexane into the THF solution of **2**.

For compound **3**, a 250 ml Schlenk flask was charged with 0.25 g (0.30 mmol) of **1** and 140 ml of toluene. The mixture was stirred at room temperature until it gave a homogeneous dark-red solution. O₂ was then introduced into the reaction system in a controlled manner until the colour of the solution faded to pale yellow. Immediately, the volatiles were removed *in vacuo*. The residue was rinsed with 40 ml of hexane and then extracted with 30 ml of THF. An off-white powder, **3**, was obtained after removing THF *in vacuo* (0.104 g, 38.7% yield). X-ray-quality colourless crystals of **3** were isolated by diffusion of hexane into the THF solution of **3**.

Accession codes. Coordinates and other crystallographic information for compounds **2·(THF)₂**, **2** and **3** are deposited in the Cambridge Crystallographic Database Centre (CCDC) with deposition numbers CCDC 1030981, 1030982 and 1030983, respectively.

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Author contributions

G.H.R. and Y.W. designed the experiments. Y.W. and M.C. performed all the experiments. P.W. performed the X-ray diffraction studies. Y.X., H.F.S. and P.v.R.S. carried out the computations. Y.W., P.v.R.S. and G.H.R. wrote the paper. All the authors discussed the results and commented on the manuscript.

Additional information

Supplementary information and chemical compound information are available in the [online version](#) of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to G.H.R.

Competing financial interests

The authors declare no competing financial interests.