

Stabilization of Silicon–Carbon Mixed Oxides

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S Supporting Information

ABSTRACT: The first carbene-stabilized silicon–carbon mixed oxide, $(\text{SiO}_2)_2\text{CO}_2$ (**4**), was synthesized by CO_2 oxidation of either carbene-stabilized disilicon, $\text{L}:\text{Si}=\text{Si}:\text{L}$ ($\text{L} = :\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$) (**1**), or carbene-stabilized Si_2O_3 (**2**) (which can be obtained via N_2O oxidation of **1**). The structure and bonding of **4** was probed by both experimental and computational methods.

The chemistry of the two simplest oxides of carbon, carbon monoxide and carbon dioxide, is exceedingly well developed.¹ Considering the pejorative environmental impact of carbon dioxide, a principal hydrocarbon combustion product,² the chemical utilization of CO_2 as a renewable carbon resource is attracting increasing attention.^{3,4} The oligomerization of CO_2 , a unimolecular gas, to form dimers [1,3-dioxetanedione (Figure 1a) and 1,2-dioxetanedione

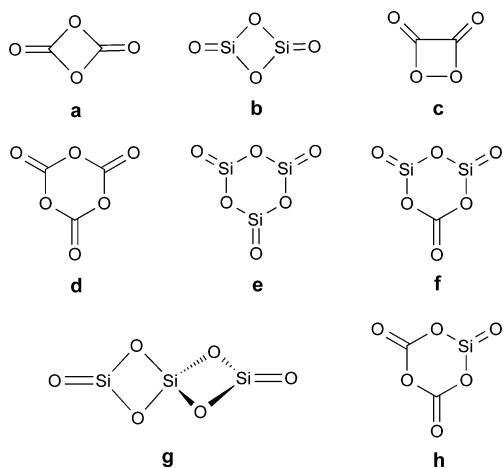


Figure 1. Oligomers of CO_2 and SiO_2 (a–e and g), $(\text{SiO}_2)_2\text{CO}_2$ (f), and $\text{SiO}_2(\text{CO}_2)_2$ (h).

(Figure 1c)] and a cyclic trimer [1,3,5-trioxanetrione (Figure 1d)] are energetically costly.⁵ Notably, oligomers of carbon dioxide (a, c, and d in Figure 1) have been proposed as intermediates in the formation of an extended CO_2 solid.^{6,7}

In contrast to molecular CO_2 , naturally occurring silica (SiO_2) is a network solid wherein each tetrahedrally coordinated silicon atom is bound to four oxygen atoms.⁸ Due to highly reactive silicon–oxygen double bonds, as well as low-oxidation state silicon atoms, molecular SiO_2 and other

simple silicon oxides have remained elusive.^{9–15} Recently, this laboratory synthesized a carbene-stabilized Si_2O_3 complex [$\text{L}:(\text{O})\text{Si}(\mu\text{-O})\text{Si}(\text{O}):\text{L}$ (**2**)] and a carbene-stabilized Si_2O_4 complex [$\text{L}:(\text{O})\text{Si}(\mu\text{-O})_2\text{Si}(\text{O}):\text{L}$ (**3**)] via N_2O (Scheme 2) and O_2 oxidation of the soluble $\text{L}:\text{Si}=\text{Si}:\text{L}$ complex ($\text{L} = :\text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$) (**1**), respectively.¹⁶ While Si_2O_4 , the dimer of SiO_2 , was experimentally realized in **3**, the cyclic isomer of trimeric SiO_2 (Figure 1e) has only been computationally studied. Significantly, the cyclic isomer of $(\text{SiO}_2)_3$ (Figure 1e) is energetically less favored than the isomer with a double-oxygen bridged structure (Figure 1g).¹⁷

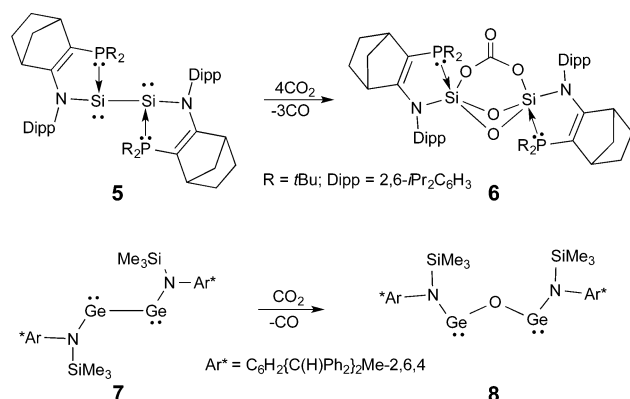
Silicon carbide (SiC), possessing native silicon dioxide (SiO_2), is regarded as a wide-band gap (WBG) semiconductor.¹⁸ However, its utility in electronic devices has been impeded by the poor $\text{SiC}\text{--}\text{SiO}_2$ interface quality.^{19–21} Consequently, investigations of the structural properties of the $\text{SiC}\text{--}\text{SiO}_2$ interfaces have been increasing. The possibility of the formation of crystalline phases for silicon oxycarbide (i.e., Si_2CO_6) near the $\text{SiC}\text{--}\text{SiO}_2$ interfaces has been theoretically studied.²¹ It is noteworthy that the chemical properties of molecular $(\text{SiO}_2)_2\text{CO}_2$ (Figure 1f) and $\text{SiO}_2(\text{CO}_2)_2$ (Figure 1h), valence isoelectronic with $(\text{CO}_2)_3$ (Figure 1d) and $(\text{SiO}_2)_3$ (Figure 1e), remain unexplored owing to their high reactivity. Although bulk SiO_2 is quite inert relative to CO_2 under ambient conditions, the pressure-induced reaction between CO_2 and silicalite, a microporous SiO_2 zeolite, has been observed (at 18–26 GPa), giving a silicon carbonate phase.²² We were curious if *molecular silicon oxides* would react with gaseous CO_2 under ambient conditions, possibly forming a new type of silicon–carbon mixed oxides. Carbene-stabilized silicon oxides (**2** and **3**)¹⁶ provide a unique platform from which this chemistry may be approached. Herein, we report the molecular structure²³ and computational²³ analysis of carbene-stabilized $(\text{SiO}_2)_2\text{CO}_2$ (**4**), which was synthesized via CO_2 oxidation of either **1** or **2**.²³ To the best of our knowledge, compound **4** represents the first compound containing a carbon–silicon mixed oxide core, prepared under ambient conditions.

Since the discovery of carbon dioxide oxidation of decamethylsilicocene nearly two decades ago,²⁴ CO_2 has been utilized as an oxidant for various low oxidation state group 14 compounds [i.e., disilenes,²⁵ coordinated disilyne (**5** in Scheme 1),²⁶ amido-digermyne (**7** in Scheme 1),²⁷ and silylenes^{28,29}].

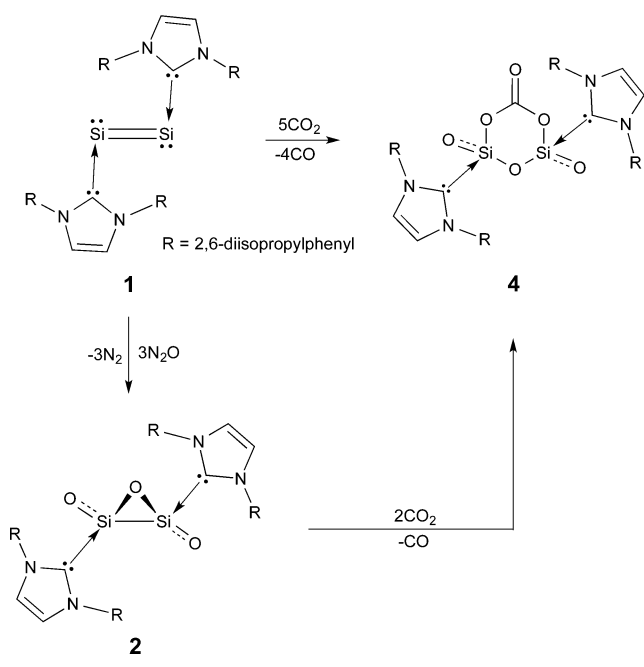
This laboratory synthesized the first carbene-stabilized disilicon(0) complex (**1** in Scheme 2)³⁰ and subsequently

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Scheme 1. CO₂ Oxidation of Base-Stabilized Disilyne and Amido-digermyne

Scheme 2. Synthesis of Compound 4



explored its reactivity toward main group (BH₃)³¹ and transition metal (CuCl)³² moieties. Encouraged by our recent synthesis of carbene-stabilized P₂O₄³³ through O₂ oxidation of carbene-stabilized P₂,³⁴ we investigated the O₂ and N₂O oxidation of **1**.¹⁶ Considering its dual reactive sites, the Si=Si double bond and the silicon-based lone pair, **1** was also expected to exhibit unusual reactivity toward CO₂. Indeed, in contrast to the CO₂-mediated transformation of disilene to oxadisiletane,²⁵ reaction of **1** (red color) with CO₂ resulted in colorless **4** (49.3% yield), which involved the cleavage of a Si=Si double bond as a result of the insertions of an oxygen atom and a CO₃ unit between two silicon atoms (Scheme 2). In addition to the direct transformation of **1** to **4**, we discovered that the CO₂ oxidation of carbene-stabilized Si₂O₃ (**2**) also afforded **4** (54.2% yield) (Scheme 2) via the insertion of the CO₃ unit into the Si–Si σ -bond in **2**. Notably, the CO₂-mediated insertions of oxygen (and CO₃) into the Si–Si and Ge–Ge single bonds have been observed in the synthesis of **6** and **8**, respectively (Scheme 1).^{26,27} In contrast to **2**, reaction of carbene-stabilized Si₂O₄ (**3**) with CO₂ only resulted in immediate decomposition, giving L:CO₂ as the only charac-

terized byproduct. Moreover, reaction of either **1** or **2** with excess CO₂, or combining **4** with CO₂, only gave the L:CO₂ adduct and uncharacterized silicon–carbon-based oxide powder, suggesting the importance of controlling the amount of CO₂ added to the reaction system.

The imidazole ¹H NMR resonance (in C₆D₆) shifts upfield from **1** (6.58 ppm) to **2** (6.30 ppm), **3** (6.32 ppm),^{16,30} and then to **4** (6.20 ppm). Meanwhile, the singlet ²⁹Si NMR resonance (in THF-*d*₈) shifts dramatically upfield from **1** (224.5 ppm) to **2** (–49.1 ppm), **3** (–76.3 ppm),^{16,30} and then to **4** (–91.5 ppm). The –91.5 ppm ²⁹Si NMR resonance of **4** is comparable to those for **6** (–100.7 and –101.6 ppm).²⁶ The carbonyl ¹³C NMR resonance (142.5 ppm, in THF-*d*₈) of **4** is similar to that for [(Me₅C₅)₂SiO₂CO]₂ (143.9 ppm)²⁴ and for **6** (148.8 and 148.9 ppm).²⁶ While the infrared (IR) absorption of the Si=O stretch in **4** (1165 cm^{–1}) is similar to that of the **4-Ph** model (1169 cm^{–1}), the ν (C=O) band is red-shifted from the (SiO₂)₂CO₂ model (1911 cm^{–1}) to the **4-Ph** model (1806 cm^{–1}), and then to **4** (1751 cm^{–1}).²³ Moreover, the C=O stretching mode (1751 cm^{–1}) of **4** compares well to that for a bridged silicon carbonate species (1780 cm^{–1})²² and for metal carbonates (1776 and 1781 cm^{–1}) which were formed via CO₂ adsorption on the surfaces of metal oxide catalysts.³⁵

Monomeric (SiO₂)₂CO₂ in the gas phase (Figure 2b) is planar with C_{2v} symmetry.²³ Due to the coordination of two carbene ligands, however, in the solid state the (SiO₂)₂CO₂ core in **4** adopts C₂ symmetry with the terminal oxygen atom at each silicon atom residing at each side of the almost planar six-membered Si₂CO₃ ring (Figure 2a). The Si–O_{terminal} bonds in **4** [1.521(4) Å, av], comparing well to those for (SiO₂)₂CO₂ (1.512 Å),²³ **2** [1.5347(18) Å], and **3** [1.5260(14) Å],¹⁶ are the shortest among the reported Lewis base stabilized Si=O double bonds [1.526(3)–1.579(3) Å].^{28,36,37} The Si–O_{ring} bonds in **4** (1.651 Å, av), similar to that in the (SiO₂)₂CO₂ model (1.647 Å, av),²³ are significantly longer than the Si–O_{terminal} bonds in **4** [1.521(4) Å, av]. The nonbonded silicon–silicon distance in **4** (2.944 Å) is much longer than that in **6** (2.4151 Å)²⁶ and the sum of silicon covalent radii (2.34 Å).³⁸ While the five-coordinate silicon atoms in **6** adopt a distorted trigonal bipyramidal geometry,²⁶ the four-coordinate silicon atoms in **4** have a distorted tetrahedral geometry. The Si–C bond distances in **4** (1.929 Å, av) correspond to the usual Si–C_{NHC} bond distances. The C=O bond distance in **4** [1.185(5) Å] is similar to that in a bis(silyl) carbonate [1.198(5) Å]²⁹ and in **6** [1.201(2) Å].²⁶

To further probe the bonding nature of **4**, the DFT computation of the geometry and electronic structure of the simplified model **4-Ph** [optimized in C₂ symmetry], L: = :C{N(C₆H₅)CH₂}₂ was performed using the B3LYP/6-311+G** level of theory.²³ In contrast to the almost planar Si₂CO₃ ring in **4** [O(4)–Si(1)–O(1)–C(55) torsion angle = 2.1°], the Si₂CO₃ ring in **4-Ph** is somewhat distorted [O(4)–Si(1)–O(1)–C(55) torsion angle = –28.4°]. This suggests that the planar conformation of the Si₂CO₃ ring in **4** may be ascribed to the steric effect of the carbene ligands and crystal packing effects. The bond distances computed for **4-Ph** [*d*_{Si–O(ring)} = 1.683 Å (av); *d*_{Si–O(terminal)} = 1.545 Å (av); *d*_{Si–C} = 1.953 Å (av)] are comparable to those of **4** [*d*_{Si–O(ring)} = 1.651 Å (av); *d*_{Si–O(terminal)} = 1.521(4) Å, (av); *d*_{Si–C} = 1.929 Å (av)].

Natural bond orbital (NBO) analysis shows that the Si–C bonds (Figure 3a) in **4-Ph** [Wiberg bond index (WBI) = 0.59], similar to those of **2-Ph** and **3-Ph**, are strongly polarized (78.7%) toward carbon. For **4-Ph**, the Si–O_{terminal} σ -bond

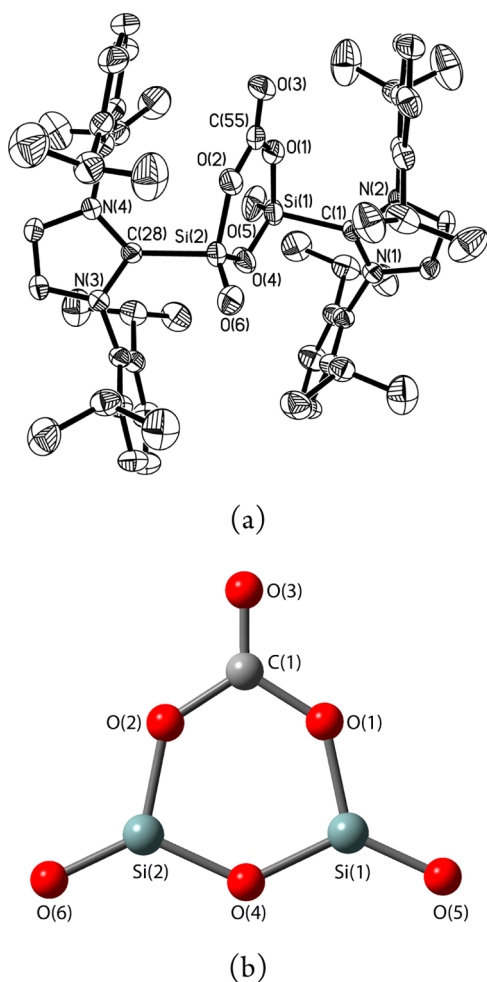


Figure 2. (a) Molecular structure of **4**. Thermal ellipsoids represent 30% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)···Si(2) 2.944, Si(1)–O(1) 1.666(4), Si(1)–O(4) 1.629(4), Si(1)–O(5) 1.515(4), Si(1)–C(1) 1.926(5), C(55)–O(1) 1.329(6), C(55)–O(2) 1.339(6), C(55)–O(3) 1.185(5), C(1)–Si(1)–O(1) 101.80(18), C(1)–Si(1)–O(4) 105.2(2), C(1)–Si(1)–O(5) 108.9(2), Si(1)–O(4)–Si(2) 129.11(19). (b) The $(\text{SiO}_2)_2\text{CO}_2$ model (optimized in C_{2v} symmetry). Selected bond distances (Å) and angles (deg): Si(1)–O(1) 1.653, Si(1)–O(4) 1.641, Si(1)–O(5) 1.512, C(1)–O(1) 1.370, C(1)–O(3) 1.178, Si(1)–O(4)–Si(2) 129.4, O(1)–Si(1)–O(4) 103.8, O(4)–Si(1)–O(5) 129.5, O(1)–Si(1)–O(5) 126.7, O(1)–C(1)–O(2) 114.7, O(1)–C(1)–O(3) 122.6.

(Figure 3d, 81.4% toward O and 18.6% toward Si) is less polarized than the Si–O_{ring} σ -bonds [Figure 3b–c, 86.3% toward O (av) and 13.7% toward Si (av)]. This may be due to the fact that the two degenerate lone pair orbitals for each terminal oxygen atom (residing at silicon) in **4-Ph** (one of them is shown as Figure 3e) are significantly distorted toward silicon. In addition, the 1.10 Si–O_{terminal} WBI value for **4-Ph**, similar to those for **2-Ph** (1.05) and **3-Ph** (1.11), is approximately double those (0.51 and 0.56) for the Si–O_{ring} bonds in **4-Ph**, revealing the modest double bond character of the Si–O_{terminal} bond in **4** (see the resonance structure **4B** in Figure 4). Meanwhile, for **4-Ph**, each silicon has a +2.19 positive charge, whereas the oxygen atoms in the ring and at the terminals of the silicon atoms have a –0.89 to –1.26 negative charge. In terms of both LMOs and NBO analysis of **4-Ph**, the

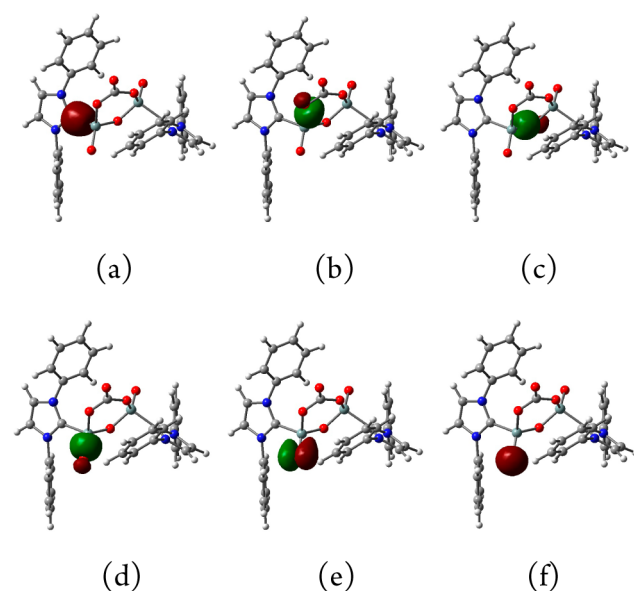


Figure 3. Selected localized molecular orbitals (LMOs) of **4-Ph**. (a) Si–C σ -bonding orbital; (b and c) Si–O_{ring} σ -bonding orbitals; (d) Si–O_{terminal} σ -bonding orbital; (e and f) lone pair orbitals of O_{terminal}.

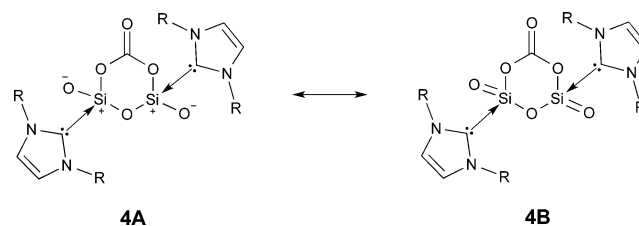


Figure 4. Resonance contributors of **4**. Zwitterionic **4A** represents the major resonance structure.

zwitterionic resonance structure **4A** (Figure 4) may represent the predominate formulation of **4**.

As an extension of our recent work on carbene-stabilized Si_2O_3 , Si_2O_4 , and P_2O_4 ,^{16,33} synthesis of **4**, the first carbene-stabilized silicon–carbon mixed oxide, indicates that carbenes may be also employed in stabilizing highly reactive mixed main group oxide clusters.

■ ASSOCIATED CONTENT

📄 Supporting Information

Complete ref 23, full details of the syntheses, computations, and X-ray crystal determination, including cif files. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05202.

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Notes

The authors declare no competing financial interest.

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