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Stabilization of Silicon−Carbon Mixed Oxides

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Supporting Information

ABSTRACT: The first carbene-stabilized silicon−carbon mixed oxide, $(SiO_2)_2CO_2$ (**4**), was synthesized by CO_2 oxidation of either carbene-stabilized disilicon, L:Si═Si:L (L: = :C{N(2,6-$Pr^i_2C_6H_3$)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 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]

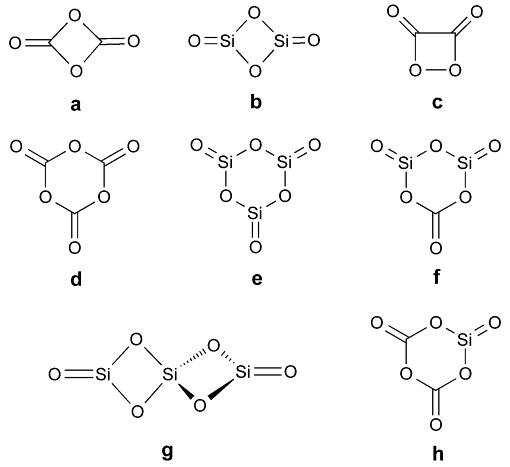

Figure 1. Oligomers of CO_2 and SiO_2 (a−e and g), $(SiO_2)_2CO_2$ (f), and $SiO_2(CO_2)_2$ (h).

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 [L:(O)Si(μ-O)Si(O):L (**2**)] and a carbene-stabilized Si_2O_4 complex [L:(O)Si(μ-O)$_2$Si(O):L (**3**)] via N_2O (Scheme 2) and O_2 oxidation of the soluble L:Si═Si:L complex (L: = :C{N(2,6-$Pr^i_2C_6H_3$)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 $(SiO_2)_3$ (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 SiC−SiO_2 interface quality.[19−21] Consequently, investigations of the structural properties of the SiC−SiO_2 interfaces have been increasing. The possibility of the formation of crystalline phases for silicon oxycarbide (i.e., Si_2CO_6) near the SiC−SiO_2 interfaces has been theoretically studied.[21] It is noteworthy that the chemical properties of molecular $(SiO_2)_2CO_2$ (Figure 1f) and $SiO_2(CO_2)_2$ (Figure 1h), valence isoelectronic with $(CO_2)_3$ (Figure 1d) and $(SiO_2)_3$ (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 structure[23] and computational[23] analysis of carbene-stabilized $(SiO_2)_2CO_2$ (**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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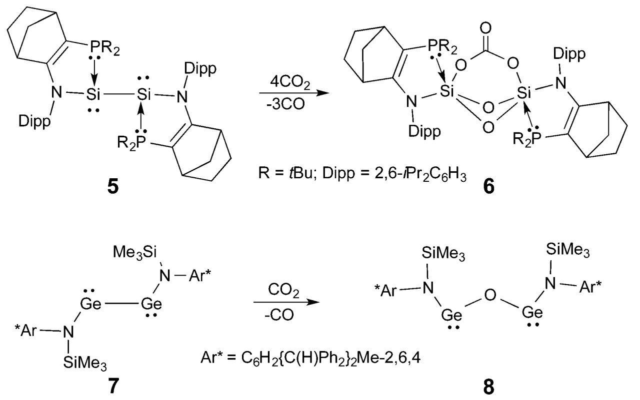
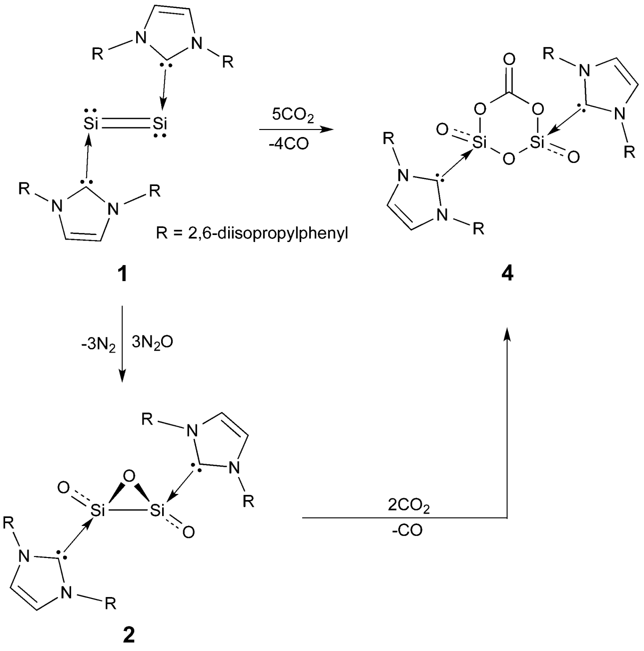
Scheme 1. CO_2 Oxidation of Base-Stabilized Disilyne and Amido-digermyne



Scheme 2. Synthesis of Compound 4



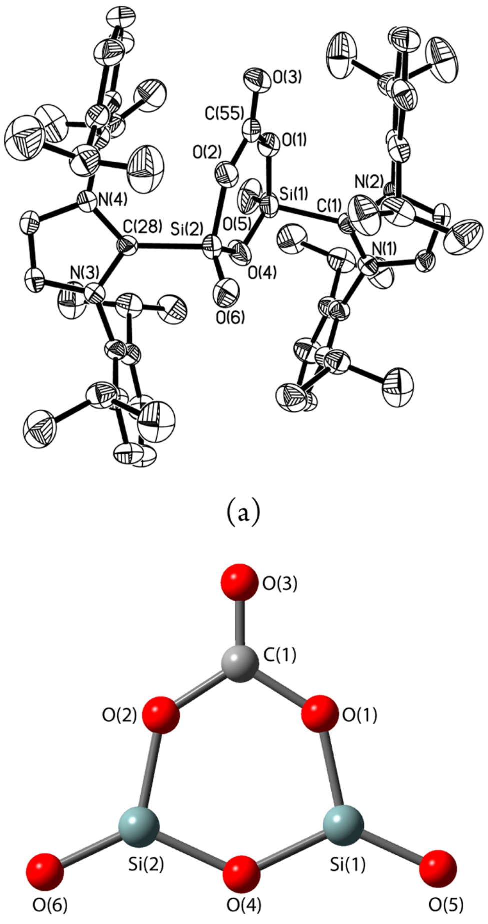
explored its reactivity toward main group (BH_3)[31] and transition metal (CuCl)[32] moieties. Encouraged by our recent synthesis of carbene-stabilized P_2O_4[33] through O_2 oxidation of carbene-stabilized P_2,[34] we investigated the O_2 and N_2O oxidation of **1**.[16] Considering its dual reactive sites, the $Si{=}Si$ double bond and the silicon-based lone pair, **1** was also expected to exhibit unusual reactivity toward CO_2. Indeed, in contrast to the CO_2-mediated transformation of disilene to oxadisiletane,[25] reaction of **1** (red color) with CO_2 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 CO_3 unit between two silicon atoms (Scheme 2). In addition to the direct transformation of **1** to **4**, we discovered that the CO_2 oxidation of carbene-stabilized Si_2O_3 (**2**) also afforded **4** (54.2% yield) (Scheme 2) via the insertion of the CO_3 unit into the Si−Si σ-bond in **2**. Notably, the CO_2-mediated insertions of oxygen (and CO_3) 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 Si_2O_4 (**3**) with CO_2 only resulted in immediate decomposition, giving L:CO_2 as the only characterized byproduct. Moreover, reaction of either **1** or **2** with excess CO_2, or combining **4** with CO_2, only gave the L:CO_2 adduct and uncharacterized silicon−carbon-based oxide powder, suggesting the importance of controlling the amount of CO_2 added to the reaction system.

The imidazole ^{1}H NMR resonance (in C_6D_6) 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 ^{29}Si NMR resonance (in THF-d8) 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 ^{29}Si NMR resonance of **4** is comparable to those for **6** (−100.7 and −101.6 ppm).[26] The carbonyl ^{13}C NMR resonance (142.5 ppm, in THF-d_8) of **4** is similar to that for $[(Me_5C_5)_2SiO_2CO]_2$ (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 $(SiO_2)_2CO_2$ 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 CO_2 adsorption on the surfaces of metal oxide catalysts.[35]

Monomeric $(SiO_2)_2CO_2$ 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 $(SiO_2)_2CO_2$ core in **4** adopts C_2 symmetry with the terminal oxygen atom at each silicon atom residing at each side of the almost planar six-membered Si_2CO_3 ring (Figure 2a). The $Si-O_{terminal}$ bonds in **4** [1.521(4) Å, av], comparing well to those for $(SiO_2)_2CO_2$ (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 $(SiO_2)_2CO_2$ 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 C_2 symmetry), L: = :$C\{N(C_6H_5)CH\}_2$] was performed using the B3LYP/6-311+G** level of theory.[23] In contrast to the almost planar Si_2CO_3 ring in **4** [O(4)−Si(1)−O(1)−C(55) torsion angle = 2.1°], the Si_2CO_3 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 Si_2CO_3 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



(a)

(b)

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 $(SiO_2)_2CO_2$ 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.

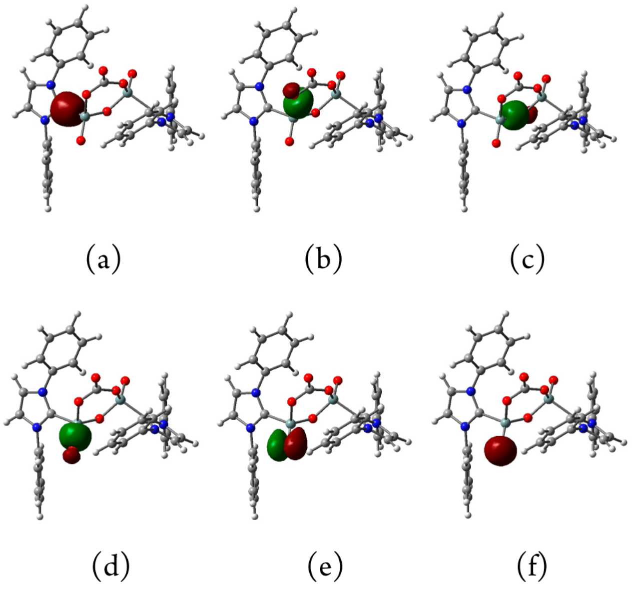


Figure 3. Selected localized molecular orbitals (LMOs) of **4-Ph**. (a) Si−C σ-bonding orbital; (b and c) Si−O_{ring} σ-bonding orbitals; (d) Si−$O_{terminal}$ σ-bonding orbital; (e and f) lone pair orbitals of $O_{terminal}$.

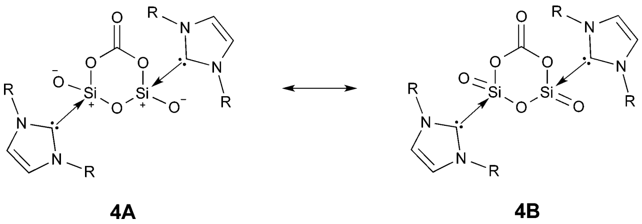


Figure 4. Resonance contributors of **4**. Zwitterionic **4A** represents the major resonance structure.

(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 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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