An Isolable Silicon Analogue of a Ketone that Contains an Unperturbed Si=O Double Bond

COMMUNICATION

An Isolable Silicon Analogue of a Ketone that Contains an Unperturbed Si=O Double Bond

Ryo Kobayashi[a], Shintaro Ishida[a], and Takeaki Iwamoto* [a]

Abstract: Despite tremendous efforts to synthesize isolable compounds with an Si=O bond, silicon analogues of ketones that contain an unperturbed Si=O bond have remained elusive for more than 150 years. Herein, we report the synthesis of an isolable silicon analogue of a ketone that exhibits a three-coordinate silicon center and an unperturbed Si=O bond, thus representing the first example of a genuine silanone. Most importantly, this silanone does not require coordination of Lewis bases and acids and/or the introduction of electron-donating groups to stabilize the Si=O bond. The structure and properties of this unperturbed Si=O bond were examined by a single-crystal X-ray diffraction analysis, nuclear magnetic resonance spectroscopy, and theoretical calculations. Bimolecular reactions revealed high electrophilicity on the Si atom and high nucleophilicity on the O atom of this genuine Si=O bond.
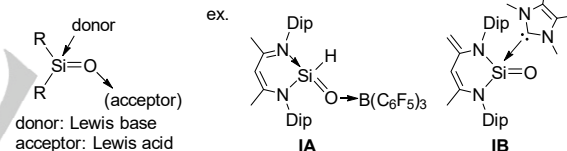
Ever since the pioneering synthetic studies on Si=O species by Friedel and Crafts in the mid-19th century,[1] as well as those by Kipping[2] and Dilthey in the early 20th century,[3] silicon analogues of carbonyls with a Si=O double bond have attracted substantial attention as heavier-group-14-element analogues of carbonyl compounds. Theoretical calculations have predicted a substantial polarization of the Si=O bond (Si$^{\delta+}$–O$^{\delta-}$) due to the large difference in electronegativity between Si and O [Si: 1.7; O: 3.5; Allred–Rochow scale] and a remarkably weak π(Si–O) bond (58.5 kJ/mol) compared to the σ(Si–O) bond (119.7 kJ/mol).[4] Indeed, compounds with a Si=O double bond are intrinsically susceptible to auto-oligomerization, and compounds with an Si=O double bond have so far only been postulated as fleeting intermediates during the formation of the corresponding oligomers (polysiloxanes, silicones), and been detected as short-lived species in low-temperature matrices.[5-15]

To elicit the intrinsic features of the Si=O bond, a substantial number of studies have been devoted to the synthesis of isolable compounds containing an Si=O bond. But despite tremendous efforts, the electronic stabilization of the Si atom by additional electron donation, i.e., via coordination of Lewis bases to the Si atom, or via introduction of strong electron-donating groups at the Si atom, are still indispensable to isolate such Si=O species. Following the seminal study on the synthesis of an isolable silicon analogue of formamide **IA** (Figure 1a) by Driess et al. in 2007, [16] several isolable Si=O species that are either coordinated by an electron donor on the Si atom and an acceptor on the O atom, or
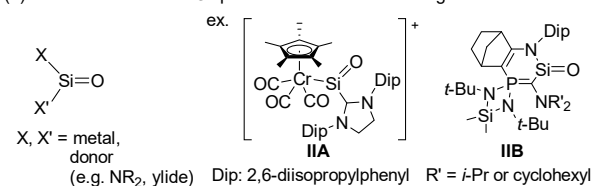
coordinated only by a donor on the Si atom (**IB**) to stabilize the polar Si=O bond, have been reported.[17-38] Recently, the synthesis of isolable Si=O species containing a three-coordinate unsaturated silicon atom such as silaacylium complex **IIA** and silaamide **IIB**, has been reported by the introduction of a transition-metal fragment and an N-heterocyclic carbene or by electron-donating groups (e.g. amido, imino, and ylide) on the Si=O bond (Figure 1b).[39-42]

However, to elucidate the intrinsic nature of an unperturbed Si=O bond, isolable compounds containing an Si=O bond without the aforementioned electronic stabilization such as a silicon analogue of ketone (silanone) with an unperturbed Si=O moiety (Figure 1c) are required, and the thermodynamic stabilization approach used for **I** and **II** cannot be applied. The synthetic difficulties associated with the isolation of such compounds is not least reflected in the fact that these have remained elusive for more than 150 years. Accordingly, an alternative approach is required to synthesize isolable silanones with an unperturbed Si=O moiety.
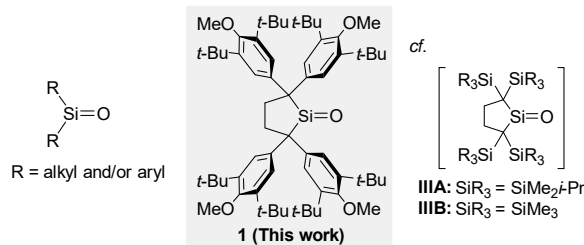

Figure 1. Thermodynamically stabilized (a) donor- and/or acceptor-coordinated Si=O species and (b) Si=O species with a three-coordinate silicon atom containing electron-donating N-heterocyclic carbene, transition-metal, and heteroatom substituents. Kinetically stabilized (c) silicon analogues of ketones containing an unperturbed three-coordinate Si=O moiety.

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Herein, we report the synthesis and isolation of such a kinetically stabilized silicon analogue of a ketone with the unperturbed Si=O moiety (**1**; Figure 1c), which does not contain any coordinating Lewis bases and/or acids on the Si=O moiety, thus representing the first example of the isolable genuine silanone. Bimolecular reactions of **1** confirm the intrinsic high electrophilicity on the Si atom and the high nucleophilicity on the O atom as the unperturbed Si=O moiety.

We have previously generated **IIIA** (Figure 1c), which persists for several hours at –80 °C and was characterized by multinuclear NMR and IR spectroscopy.[15] Although the large protecting groups substantially increase the thermal stability of **IIIA** compared to that of other silanones that have only been observed in low-temperature argon matrices (e.g. **IIIB**),[14] **IIIA** readily undergoes isomerization via 1,3-migration of the i-PrMe$_2$Si group from the carbon to the oxygen atom at room temperature. To further improve the thermal stability of silanones, we designed a more robust substituent that contains bulky carbon-based protecting groups with a diminished migratory propensity relative to that of the i-PrMe$_2$Si group. This feature should prevent oligo-/polymerization and isomerization, and thus preserve the intrinsic electronic structure of the Si=O bond.

The synthesis of **1** was achieved by oxidation of cyclic dialkylsilylene **2** (Scheme 1; for synthetic details, see the Supporting Information). Treatment of solid **2** with gaseous N_2O at room temperature provided **1** in 100% yield as a white solid. The generation of **1** was confirmed by multinuclear NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis (EA). The ^{29}Si NMR resonance of the three-coordinate silicon nucleus in C_6D_6 appears in the low-field region (90.0 ppm), similar to that of metastable silanone **IIIA** (128.7 ppm),[15] and substantially downfield-shifted compared to those of the donor- and/or acceptor-coordinated neutral Si=O species (**I**; –14 to –91.5 ppm)[16-38] and a neutral Si=O species stabilized by electron donation (**II**; 28.8 to 71.3 ppm).[40-42] The IR spectrum of **1** was recorded in C_6H_6 to gain further insight into the structure of the Si=O moiety; however, the band potentially assignable to the Si–O vibration was difficult to discern. Using DFT calculations, the calculated Si–O vibration frequency for the optimized structure of **1** (**1$_{opt}$**; ~1168 cm^{-1}) would overlap with the strong bands of the aryl groups (Figure S2). The UV-vis absorption spectrum of **1** in C_6H_6 exhibits strong π→π* transitions from the aryl moieties (~300 nm), thus preventing the observation of the n(O)→π*(Si=O) transition band, which was predicted by DFT calculations to appear at ~260 nm (Figure S3 and Table S6).

Scheme 1. Synthesis of **1**
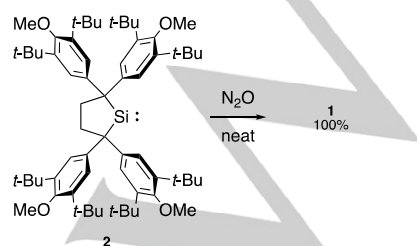
The molecular structure of **1** in the solid state was unequivocally determined by a single-crystal XRD analysis (Figure 2). Colorless platelets of **1** suitable for XRD analysis were obtained from a recrystallization from benzene. The asymmetric unit contains one molecule of **1** and 3.5 molecules of C_6H_6. The distances between the silanone Si and O atoms of the closest neighboring molecules [10.336 (2) Å] (Figure 2b) is much larger than the sum of the van der Waals radii of the Si and O atoms [Si+O: 3.40 Å].[43] The atoms intermolecularly closest to the Si1 and O1 atoms are carbon atoms in the t-Bu groups of a neighboring molecule, with distances [Si1···C: 4.494 (3) Å; O1···C: 3.472 (4) Å] that are significantly longer than the sum of the van der Waals radii [Si+C: 3.85 Å; O+C: 3.25 Å].[43] These results suggest that in the crystal, significant intermolecular interactions are absent between the Si=O moiety of **1** and its nearest neighbor or a molecule of C_6H_6. Accordingly, it is feasible to consider **1** as an isolated Si=O species. The angle sum around the three-coordinate silicon atom [359.99(14)°] indicates that the Si atom adopts a virtually ideal trigonal-planar structure. The Si–O distance [1.518 (2) Å] is much shorter than that in Si–O single bonds (1.63 Å)[44] and represents the shortest hitherto reported Si–O bond for crystalline Si=O species with a three-coordinate silicon atom (1.526–1.543 Å).[39-42] It is also very close to the Si–O bond length in $H_2Si=O$ (1.515 Å), which has been estimated based on rotational spectroscopy.[10]
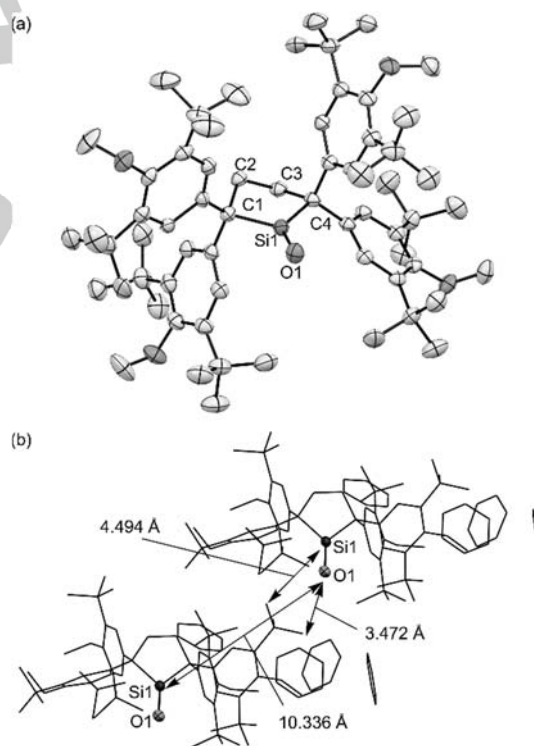
Figure 2. Molecular structure of **1** in the solid state. (a) Molecular structure of **1** with thermal ellipsoids at 50% probability. (b) Closest intermolecular contacts between the three-coordinate silicon atom and the terminal oxygen atom in the crystal. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): O1–Si1, 1.518(2); Si1–C1, 1.887(3); Si1–C4, 1.892(3); C1–C2, 1.548(4); C2–C3, 1.536(4); C3–C4, 1.562(4); O1–Si1–C1, 129.55(14); O1–Si1–C4, 129.95(14); C1–Si1–C4, 100.50(14); C2–C1–Si1, 99.46(19); C3–C2–C1, 110.3(2); C2–C3–C4, 109.8(2); C3–C4–Si1, 98.99(19).

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To obtain further insight into the nature of the Si=O bond in **1**, DFT calculations were carried out on the optimized structure of **1** (**1opt**) at the B3LYP-D3/6-31G(d) level of theory. In **1opt**, the Si=O bond length (1.537 Å) and the angle sum around the three-coordinate silicon atom (359.9°) are in good agreement with those observed in the solid state [1.518(2) Å; 359.99(14)°]. The ^{29}Si NMR chemical shift of **1** (90.0 ppm) was also reproduced well by gauge independent atomic orbital (GIAO) calculations on **1opt** at the B3LYP/6-311+G(2df,p) level of theory (79.9 ppm). The HOMO-13, LUMO, and HOMO-8 orbitals correspond to the π- and π*-orbitals of the Si=O bond, as well as the non-bonding orbital of the terminal oxygen atom, respectively (Figure S8). The natural population analysis of the charges at the silicon (2.08 e) and oxygen (−1.10 e) atoms of **1opt** confirm a substantially polarized $Si^{\delta+}-O^{\delta-}$ bond, similar to those previously predicted for other Si=O species. The results of these DFT calculations thus support the presence of a polar Si=O double bond in **1**.

The electrophilic and nucleophilic nature of **1** is reflected in the following bimolecular reactions (Scheme 2). While **1** is stable in the solid state and in C_6H_6 at 25 °C, it gradually dimerizes in C_6H_6 at 60 °C to furnish the head-to-tail dimer (**3**) over the course of one day. Similar to other stable Si=O species, **1** reacts with H_2O, ethyldimethylsilane, $LiAlH_4$, and acetone to provide the corresponding hydrolysis, hydrosilylation, reduction, and ene-type reaction products (**4**–**7**).[39-41] Noticeably, **1** also reacts with styrene, which contains a C=C double bond of relatively low polarity, to regioselectively furnish the formal [2+2] adduct **8**. It should be noted here, that such reactions with isolable Si=O species have not yet been investigated so far. The regioselectivity of this reaction suggests that the electrophilic addition of the Si atom to the terminal carbon atom of styrene leads to an intermediate that contains a benzyl cation or to a transition state with a similar structure. More strikingly, the reaction of **1** with $B(C_6F_5)_3$ affords aryl(boryloxy)silane **9**, which is different from the electronically stabilized Si=O species **I** and **II**, as these furnish the corresponding borane complex of the Si=O species $(R_2Si=O\rightarrow B(C_6F_5)_3)$.[16,22,24,25,41] The initial step for the formation of **9** is most likely the formation of a $R_2Si=O\rightarrow B(C_6F_5)_3$ species similar to those previously reported. The strong electron-deficient character of Si in the initial complex obtained from **1** may allow further 1,3-migration of a C_6F_5 substituent from the B to the Si atom. These results clearly indicate that the electron donation of the carbon-based substituents in **1** is substantially lower than that in **I** and **II**. Accordingly, the unperturbed Si=O moiety in **1** exhibits both an intrinsically high electrophilicity on the Si atom and nucleophilicity on the O atom of the genuine Si=O bond.

Scheme 2. Bimolecular reactions of **1** with small molecules in benzene
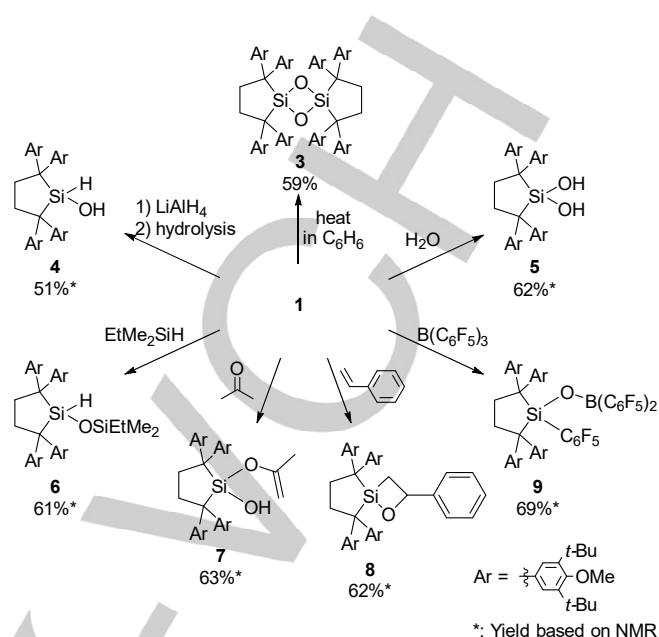
In conclusion, we have synthesized the first example of an isolable silicon analogue of a ketone that contains an unperturbed Si=O double bond and that is thermally stable at room temperature. A single-crystal XRD analysis, DFT calculations, and relevant bimolecular reactions of **1** with small molecules have provided insight into the molecular and electronic structure as well as the properties of the unperturbed Si=O moiety in that silanone, which should open new avenues in the chemistry of silicon analogues of carbonyl species. Moreover, **1** represents the missing member in the family of isolable compounds containing an unperturbed group-14-element-group-16-element double bond (such as Si=S and Ge=O species).[45,46]

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COMMUNICATION

The first example of an isolable genuine silanone, i.e., an isolable silicon analogue of a ketone that contains an unperturbed Si=O bond, was synthesized. The structure and properties of this silanone were examined by a single-crystal XRD analysis, NMR spectroscopy, and theoretical calculations. Bimolecular reactions revealed high electrophilicity on the Si atom and high nucleophilicity on the O atom of the genuine Si=O bond.

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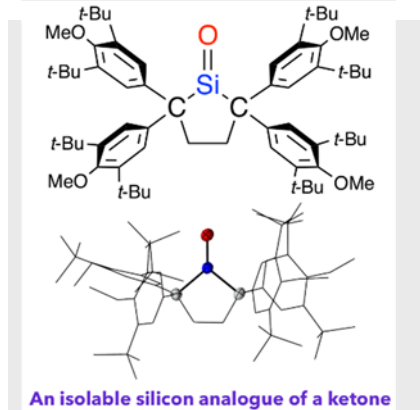
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