Si=O Bonds

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A Stable Silanone with a Three-Coordinate Silicon Atom: A Century-Long Wait is Over[**]

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Silanones ($R_2Si{=}O$), the silicon analogues of ketones, are one of the most sought-after compounds in main-group chemistry. More than 100 years ago, Kipping and Lloyd first attempted to synthesize silanones, although physical and chemical studies showed that they did not obtain silanones, but single-bonded siloxanes, $(R_2SiO)_n$.[1] Unlike ketones, silanones are extremely reactive, and this enhanced reactivity stems from 1) a weak π-bond with a small HOMO–LUMO energy gap that is due to unfavorable overlapping between the $p_\pi(Si)$ and $p_\pi(O)$ orbitals and 2) a strongly polarized $Si^{\delta+}{-}O^{\delta-}$ bond. As a result, the Si=O bond has an extreme propensity towards oligomerization even under ambient conditions. Until very recently, the Si=O bond had only been detected either in the gas phase or in an argon matrix at 77 K, and the presence of such species as intermediates had been confirmed by trapping reactions or kinetic studies. However, the isolation and characterization of a species with a Si=O double bond ("Kipping's Dream")[2] had not been reported.

A significant breakthrough in the field of heavy-element ketone analogues has recently been achieved by Tamao et al., who synthesized the first genuine germanone (**A**; Scheme 1) using a very bulky ligand, 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind).[3] The Ge=O double bond was prepared through the oxygenation of the corresponding germylene (R_2Ge) with trimethyl-*N*-oxide. However, until now, such oxygenation reactions with stable silylenes have never rendered silanones; instead, four-membered cyclodisiloxane derivatives were usually obtained, presumably through dimerization of the Si=O bond. To prevent the dimerization, Driess et al. devised a donor–acceptor concept and isolated a handful of compounds, including **B** and **C**, that feature a Si=O bond[4a] and an additional donor ligand, such as an N-heterocyclic carbene (NHC) or 4-(dimethylamino)pyridine (DMAP), is coordinated to the silicon atom. Subsequently, the donor–acceptor approach became popular[4b] and was exploited by the groups of Driess, Baceiredo, Roesky, and others for the isolation of several compounds, including base-supported sila-urea **D**,[4c] silanoic silyl ester **E**,[4d] silaformyl chloride **F**,[4e] sila-acid anhydride **G**,[4f] and silacyclopropan-1-one **H**.[4g] However, unlike a ketonic carbon atom, the silicon atoms in these compounds are four-coordinate, and a Si=O bond with a three-coordinate silicon atom has remained synthetically elusive.

Another strategy that has often been used in organometallic chemistry for the synthesis of reactive species entails the coordination of these species to transition metals. Following this strategy, Filippou and co-workers isolated silylidyne (Si≡Mo) and germylidyne (Ge≡Re) fragments in the coordination sphere of late transition metals.[5] Similarly, in boron chemistry, Braunschweig and co-workers exploited the coordination sphere of $[Pt(PR_3)_2]$ (R = cyclohexyl, *i*Pr) to isolate a number of complexes that feature B≡N, B≡O, B≡C, or B≡B bonds.[6] Ueno et al. sought to implement this approach for the isolation of silanones and reported the base-stabilized silanone complex **I**.[7]

In a recent study, Filippou et al.[8] reported the first isolation of a compound that features a Si=O bond between a three-coordinate silicon atom and an oxygen atom (Scheme 2). A salt elimination reaction between bromosilylidene complex **1** and $Na[B(Ar^F)_4]$ ($Ar^F = 3{,}5\text{-}(CF_3)_2\text{-}C_6H_3$) afforded the ionic chromium silylidyne complex **2**, which gave chromiosilylene complex **3** upon exposing to CO. Oxygenation of silylene **3** with N_2O resulted in the formation of complex **4**. The ^{29}Si NMR signal of **4** was found at $\delta = 169.6$ ppm, far downfield of the signals for base-stabilized silanones (−61 to −86 ppm).[4] X-ray diffraction studies confirmed the presence of a Si=O double bond (1.526(3) Å), which was marginally shorter than the base-stabilized Si=O double bonds (1.531–1.579 Å).[4] The Si atom displayed a trigonal planar geometry with a sum of the bond angles around the Si atom of 359.9°. The increase in the Cr-Si-C bond angle from **3** to **4** (**3**: 116.2(1)°; **4**: 125.1(1)°) indicated the redistribution of electron density from the silicon to the oxygen atom.

The interpretation of bonding in **4** is not very straightforward. More precisely, one would expect silanones to be neutral compounds with two organic substituents at the silicon atom, similar to germanone **A**. Complex **4** can either be described as a cationic chromiosilanone complex (considering the C−Si bond to be a covalent bond) or an NHC silicon monoxide complex (considering the C→Si bond to be a dative bond). Taking into account the rather short Si−C bond

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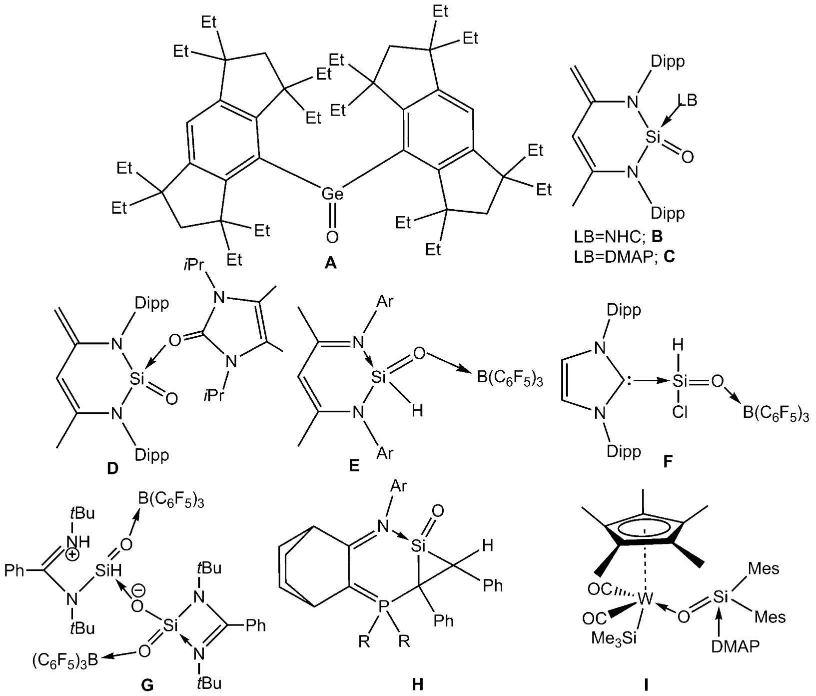
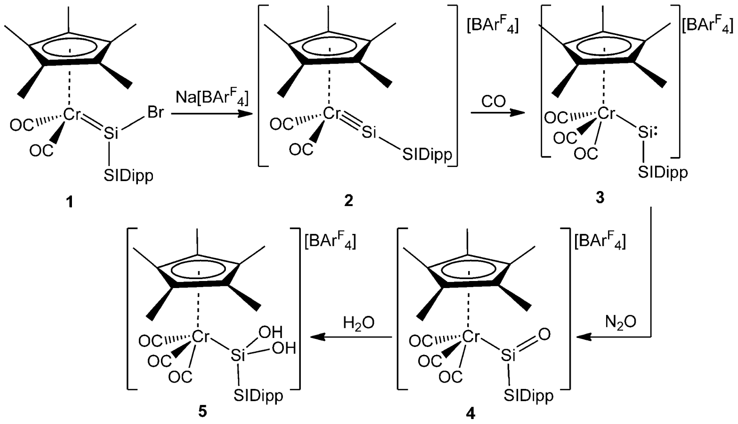


Scheme 1. Germanone **A** and selected examples of compounds with base-stabilized Si=O double bonds. Dipp = 2,6-*i*Pr_2-C_6H_3, LB = Lewis base.



Scheme 2. Synthetic route to silanone **4**. SIDipp = 1,3-bis(2,6-*i*Pr_2-C_6H_3)imidazolidin-2-ylidene.

[1.947(4) Å; C→Si bonds in NHC→SiX_2 (X = Cl or Br): ca. 1.98 Å), the similar energy requirements for homolytic (408.9 kJ mol^{-1}) and heterolytic (392 kJ mol^{-1}) bond cleavage, and the bond dissociation enthalpy (BDE) of **4** (269 kJ mol^{-1}), which is larger than those of NHC→SiX_2 species (121–124 kJ mol^{-1}), the description as a cationic metallosilanone complex would be more reasonable. The short Cr–Si bond (2.314(1) Å) indicates multiple-bond character, and a natural resonance theoretical (NRT) analysis of **4** revealed that the contributions of the canonical structures with a Cr=Si bond and a Si–O bond to the overall resonance structure amount to 11.8 % and 14.1 %, respectively. These results suggest a small contribution from a silylidene-type complex, $[LnCr{=}Si(SIDipp){-}O]^+$.

The nature of the Si=O double bond in **4** is also intriguing. In line with previous theoretical calculations on $H_2Si{=}O$,[9] the Si=O bond in **4** was found to be highly polarized ($Si^{\delta+}$–$O^{\delta-}$). This was indicated by the Wiberg bond index (WBI; for Si=O: 1.12), the partial charges obtained by natural population analysis (NPA; 1.77 for Si and −1.21 for O), and an ionic bond order (1.30) that was greater than that obtained for the covalently bound complex by NRT analysis. Because of this strong polarization and the low-lying π* orbitals, silanones have been predicted to be extremely reactive towards polar and nucleophilic reagents, such as water. This was apparent from the instantaneous conversion of **4** into dihydroxysilyl complex **5**, which occurred even in the argon atmosphere of a glove box containing 1 ppm of H_2O. The reaction is in agreement with theoretical findings by Kudo and Nagase,[9a] who determined that the bimolecular reaction of the parent silanone ($H_2Si{=}O$) with water proceeded with no overall barrier. It is noteworthy that germanone **A** also underwent an addition reaction with H_2O to form the analogous dihydroxygermanium derivative.[3]

The synthesis of **4** completed a century-long search for isolable silanones, from siloxanes to matrix-detected species to base-stabilized Si=O compounds and ultimately to a stable metallosilanone with a three-coordinate silicon atom, and will have a significant impact on main-group chemistry. Future work might be directed towards investigating the reactivity of such silanones, which could react through frontier-orbital-controlled as well as charge-controlled pathways.[9a]

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