

An Isolable Bis-Silylene Oxide (“Disilylenoxane”) and Its Metal Coordination

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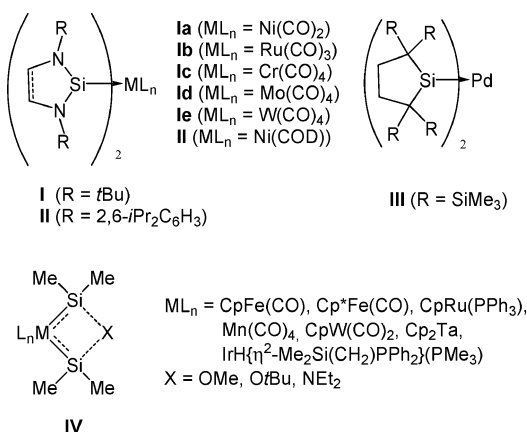
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Abstract: The first isolable oxygen-bridged bis-silylene **1** has been synthesized by facile dehydrochlorination of the corresponding disiloxane [LSiH(Cl)–O–SiH(Cl)L] precursor [L = PhC(N^tBu)₂] with LiN(SiMe₃)₂. Compound **1** contains three-coordinate, pyramidal Si(II) atoms in a bent disiloxane-like moiety and reacts readily with [Ni(COD)₂] to afford the unique bis-silylene oxide unique nickel complex **3**.

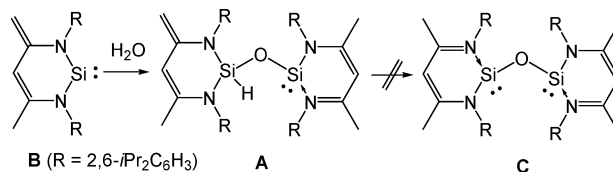
The chemistry of transition-metal complexes with silylene ligands has received significant attention in the past quarter century, because their properties are quite different from those of carbene complexes, and owing to their important role in numerous catalytic processes.¹ For example, silylene complexes are postulated intermediates in a number of transition-metal-mediated transformations, including Müller–Rochow’s direct process,² catalytic redistribution of silanes,³ and various silylene-transfer reactions.⁴ Since the isolation of two base-stabilized silylene complexes in 1987,⁵ a wide variety of transition-metal silylene complexes have been isolated and characterized.¹ However, bis-silylene complexes are still limited to the cyclic diaminosilylene complexes **I**⁶ and **II**,⁷ cyclic dialkyl-silylene complex **III**,⁸ and base-stabilized silyl(silylene) complexes **IV**⁹ (Chart 1). To the best of our knowledge, transition-metal complexes containing a bidentate bis-silylene oxide ligand have not been reported as yet.

Chart 1

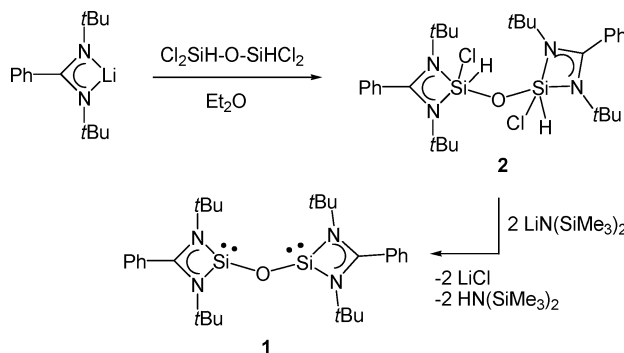


Herein, we report the synthesis and structural features of the first oxygen-bridged bis-silylene [LSi–O–SiL] (L = PhC(N^tBu)₂) **1** as well as its coordination to nickel(0) to give the corresponding bis-silylene oxide chelate complex **3**.

Recently, we reported the synthesis and isolation of the stable siloxysilylene **A** (a mixed-valent disiloxane) by addition of water

Scheme 1. Synthesis of Siloxysilylene **A**

to the stable silylene **B** (Scheme 1).¹⁰ However, attempts to synthesize a stable bis-silylene oxide **C** from siloxysilylene **A** and **B** have been unsuccessful. Recently, Roesky et al. proposed the formation of bis-silylene oxide **1** as a reactive intermediate in the reaction of the bis-silylene [LSi–SiL] with N₂O.¹¹ However, **1** could be neither detected nor chemically trapped. In the present work we report the isolation and characterization of the heteroatom bridged bis-silylene **1** by a facile synthetic protocol.

Scheme 2. Synthesis of **1** via Precursor **2**

Reaction of 1,1,3,3-tetrachlorodisiloxane [Cl₂SiH–O–SiHCl₂] with 2 molar equiv of lithium amidinate LLi [L = PhC(N^tBu)₂] in diethylether gives the expected disiloxane [LSiH(Cl)–O–SiH(Cl)L] **2** in 53% yield. The formation of **2** was confirmed by NMR spectroscopy and X-ray crystallography (Scheme 2; see Supporting Information). The ¹H NMR spectrum of **2** reveals two singlets, one for the *t*Bu groups and one corresponding to the Si–H protons as well as one set of resonances for the Ph group of the amidinate ligand L. The ²⁹Si NMR spectrum of **2** shows a singlet resonance at δ –111.0 ppm.

The target bis-silylene oxide [LSi–O–SiL] **1**, which possesses two lone pairs, one at each of the Si centers, was readily available by dehydrochlorination of **2** employing 2 molar equiv of LiN(SiMe₃)₂ in toluene (Scheme 2). Recrystallization in toluene afforded pale yellow crystals of **1** in 76% yield. The molecular structure of **1** was characterized by means of spectroscopy and X-ray crystallography. The ¹H and ¹³C NMR spectra of **1** display one set of resonances that result from the amidinate ligand L. The ²⁹Si NMR signal of **1** (δ –16.1 ppm) appears shifted ca. 95 ppm downfield from the precursor **2** (δ –111.0 ppm). This shift is comparable to

that reported for the monosilylene alkoxides [LSiOrBu] (δ -5.2 ppm) and [LSiOiPr] (δ -13.5 ppm),¹² respectively.

The molecular structure of bis-silylene oxide **1** is shown in Figure 1. The Si–O distances in **1** of 1.641(2) and 1.652(2) Å are comparable to those of siloxysilylene **A** [1.6442(3) Å and 1.6501(2) Å] and, thus, typical for silicon–oxygen single bonds of other disiloxanes.¹³ Moreover, as expected for an disiloxane-like system,¹³ the Si1–O–Si2 angle of **1** is bent 159.88(15)° and larger than that observed for a C–O–C moiety of ethers. Accordingly, DFT calculations of compound **1** revealed that the Si1–O–Si2 angle deformation energy is very small. In fact, the energy difference between the experimental geometry (159.88°) and linear Si–O–Si arrangement is only 0.17 kcal mol⁻¹ (see Supporting Information). The sum of bond angles at Si1 and Si2 are 277.69° and 275.34°, respectively, which is consistent with the presence of a lone pair at each silicon center.

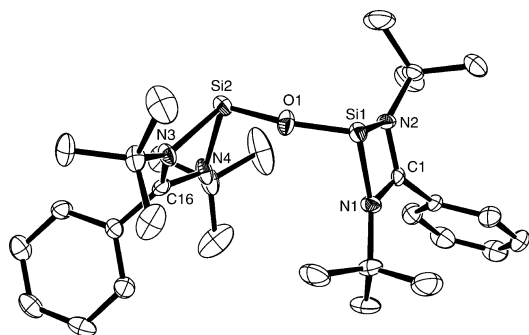
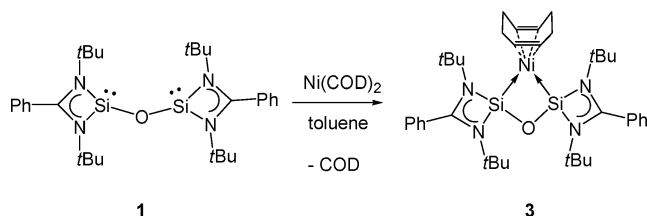


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–O1, 1.641(2); Si1–N1, 1.896(3); Si1–N2, 1.902(3); Si2–O1, 1.652(2); Si2–N3, 1.888(2); Si2–N4, 1.908(3); Si1–O1–Si2, 159.88(15); O1–Si1–N1, 104.17(12); O1–Si1–N2, 105.35(11); O1–Si2–N3, 101.96(11); O1–Si2–N4, 104.81(12); N1–Si1–N2, 68.15(10); N3–Si2–N4, 68.55(11).

To probe the chelate coordination ability of **1**, its reactivity toward [Ni(COD)₂] (COD = cycloocta-1,5-diene) was investigated. A solution of the bis-silylene oxide **1** was added to 1 molar equiv of [Ni(COD)₂] in toluene at room temperature to furnish an intensely red-colored reaction solution. Recrystallization of the crude product from a saturated *n*-hexane solution at -30 °C afforded dark red crystals of the Ni complex **3** in 91% yield (Scheme 3). The constitution and composition of **3** could be determined by NMR spectroscopy, elemental analysis, and ESI mass spectrometry. The ¹H NMR spectrum of **3** exhibits one singlet for the *t*Bu groups and one set of resonances for the COD ligand and Ph groups of the amidinate ligands. The ²⁹Si NMR spectrum of **3** exhibits one singlet (δ = 32.8 ppm), which shows a downfield shift relative to that of the “free” ligand **1**. The observed downfield shift for the ²⁹Si(II) nuclei in **3** clearly suggests the presence of a bis-silylene chelate complex.

Scheme 3. Synthesis of **3**



This is confirmed by X-ray diffraction analysis; the molecular structure of **3** is displayed in Figure 2. The two silylene subunits

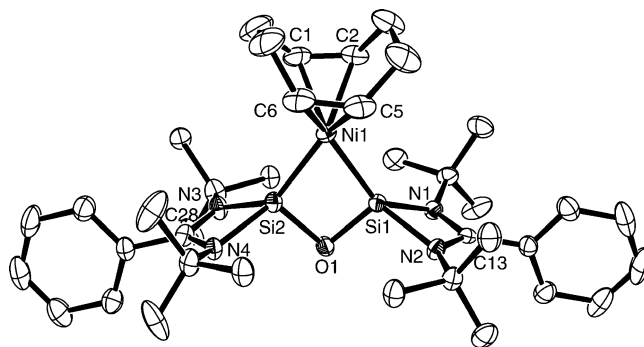


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The *t*Bu group on the N3 atom was disordered over two positions (site occupancies 0.76 and 0.24), but only one is shown. Selected bond lengths (Å) and angles (deg): Si1–Ni1, 2.1969(7); Si2–Ni1, 2.1908(7); Si1–O1, 1.7011(15); Si1–N1, 1.8929(19); Si1–N2, 1.875(2); Si2–O1, 1.7081(17); Si2–N3, 1.8776(19); Si2–N4, 1.893(2); Si1–O1–Si2, 93.44(8); Si1–Ni1–Si2, 68.90(3); N1–Si1–N2, 69.41(9); N3–Si2–N4, 69.54(8).

and one COD ligand are coordinated to the nickel atom with the Si1–Ni1–Si2 angle at 68.90(3)°. The Si–O bond lengths in **3** [1.7011(15) and 1.7081(17) Å] are longer than that in **1** [1.641(2) and 1.652(2) Å], while the Si1–O–Si2 angle of **3** (93.44(8)°) is significantly smaller than that in **1**. The Ni–Si bond lengths [2.1908(7) and 2.1969(7) Å] are slightly shorter than those in bis-silylene nickel complex **Ia** [2.207(2) and 2.216(2) Å]^{6a} but longer than those found in bis-silylene nickel complex **II** (2.1395(8) Å).⁷ Moreover, the Ni–Si bond lengths of bis-silylene nickel complex **1** are longer than those in ylide-like silylene–nickel complexes [2.0369(6) and 2.0597(10)].¹⁴ The Ni–C distances (2.070–2.090 Å) in **2** are shorter than those in Ni(COD)₂ (2.11–2.13 Å)¹⁵ and bis-silylene nickel complex **II** (2.130–2.146 Å),⁷ indicating a somewhat stronger π back-donation from the nickel atom to the chelating bis-silylene ligand.

In conclusion, we have reported a facile method for the preparation of the isolable bis-silylene oxide (“disilylenoxane”) **1** by dehydrochlorination of the corresponding disiloxane with base. The reaction of **1** with [Ni(COD)₂] leads to the first bis-silylene oxide nickel complex **3**, indicating that **1** could serve as a novel bidentate ligand for transition-metal chemistry. Investigations on the reactivity of **1** toward other transition-metal complexes and their use as molecular catalysts are currently underway.

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Supporting Information Available: Experimental details for the synthesis and spectroscopic data of **1**, **2**, and **3**, DFT calculations and Cartesian coordinates of **1** (PDF); crystallographic data for **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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