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Silicon Complexes

Carbene-Stabilized Disilicon as a Silicon-Transfer Agent: Synthesis of a Dianionic Silicon Tris(dithiolene) Complex

*Yuzhong Wang, Cynthia A. Tope, Yaoming Xie, Pingrong Wei, Jeffrey L. Urbauer, Henry F. Schaefer III, and Gregory H. Robinson**

Abstract: *Reaction of carbene-stabilized disilicon (**1**) with the lithium-based dithiolene radical (**2˙**) affords the first dianionic silicon tris(dithiolene) complex (**3**). Notably, the formation of **3** represents the unprecedented utilization of carbene-stabilized disilicon (**1**) as a silicon-transfer agent. The nature of **3** was probed by multinuclear NMR spectroscopy, single-crystal X-ray diffraction, and DFT computations.*

As a result of their unique optical, conductive, and magnetic properties, bis(dithiolene) complexes have substantially bolstered the development of transition-metal dithiolene chemistry.[1] Although reports date to the early 1960s,[1a,2] the chemistry of transition-metal-based tris(dithiolene) complexes[2] has not developed in parallel with that of bis(dithiolene) complexes. Correspondingly, there is a paucity of reports of tris(dithiolene) complexes of main-group metals, the literature revealing only (dithiolene)$_3$ complexes of indium,[3] tin,[4] and antimony.[5] While bis(dithiolene) complexes containing four- and five-coordinate silicon atoms (Figure 1) were first reported nearly two decades ago,[6] six-coordinate silicon tris(dithiolene) complexes have not been reported. Nonetheless, complexes containing silicon atoms in high-coordination environments are attracting considerable attention due to their intriguing structural motifs and their capacity as novel reaction intermediates.[7] Indeed, pyridine-based ligands containing a six-coordinate silicon atom have garnered interest from disparate fields of photo- and electroluminescent materials to biological systems.[8]

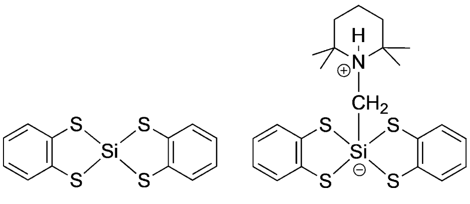
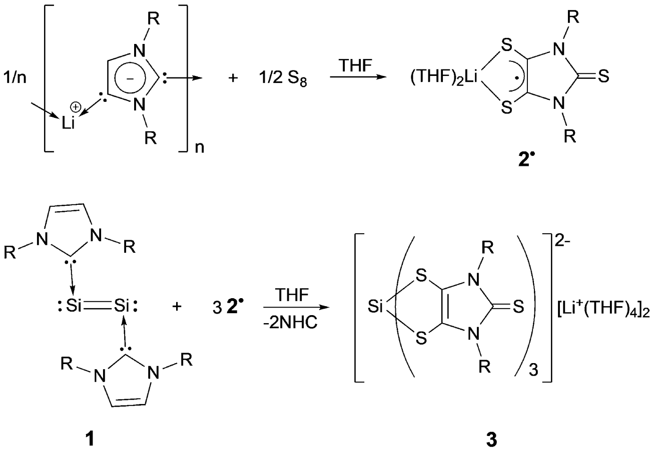


Figure 1. Representative a) four- and b) five-coordinate silicon bis(dithiolene) complexes.

The ability of carbenes to stabilize a wide range of low-oxidation state main group species has been well-documented.[9] The series of carbene-stabilized diatomics, L:EE:L (L: = carbene; E = p-block elements), with E having the formal oxidation state of zero, are noteworthy.[9c,h] Although the strong σ-donor capabilities of carbenes have largely been touted as the predominant factor in the stabilization of these compounds, it has recently been suggested that London dispersion forces[10] may also play an important role. Carbene-stabilized disilicon, L:Si=Si:L,[11] (L: = 2,6-diisopropylphenyl-substituted NHC; **1** in Scheme 1) has demonstrated unique reactivity toward a variety of substrates including Group 13 Lewis acids, transition-metal species, small electrophiles, elemental tellurium, and small gas molecules (i.e., O_2, N_2O, and CO_2).[9b,c] Notably, the thermal extrusion of diphosphorus (P_2) from niobium diphosphaazide complexes, as reported by Cummins, provided a novel synthetic route to organodiphosphorus compounds.[12] The intriguing proposition of L:Si=Si:L serving as a "soluble allotrope"[13] of silicon, however, has not been experimentally realized. Indeed, **1** would possess particular synthetic utility if the disilicon core of **1** could be liberated from the two carbenes. Herein, we report the synthesis,[14] structure,[14] and computations[14] of the first dianionic silicon tris(dithiolene) complex (**3**), prepared by utilizing carbene-stabilized disilicon (**1**) as a silicon-transfer agent.



Scheme 1. Synthesis of **3** (*R* = 2,6-diisopropylphenyl).

We recently synthesized an anionic dithiolene radical **2˙**,[15] via trisulfurization of the corresponding anionic N-heterocyclic dicarbene (Scheme 1).[16] Compound **2˙** may well serve

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as a convenient synthetic platform from which various main group-based dithiolenes could be synthetically approached. For example, both boron dithiolene radicals[17] and magnesium dithiolene complexes[18] have recently been synthesized by utilizing **2**˙. Reaction of **1** with **2**˙ (ca. 1:3 molar ratio) in THF at room temperature produced an orange-red solution, from which **3** may be isolated as yellow-orange crystals in 18.0% yield (Scheme 1). While the mechanism remains obscured, the formation of **3** involves cleavage of both the Si=Si double bond and Si−C_{NHC} bond. Although cleavage of the Si=Si double bond in **1** has been well documented,[19] reports of the Si−C_{NHC} bond cleavage are rare.[20] Due to the non-innocent character of the dithiolene ligands, the mono-anionic dithiolene radical ligand **2**˙ is readily reduced to the corresponding dithiolate by the $Si_2(0)$ core of **1** during the formation of **3** (correspondingly, the silicon atom is oxidized in this process). The parent solution, from which **3** is crystallized, is extremely oxygen-sensitive (immediately changing color from orange to purple upon exposure to trace amounts of O_2). Such reactivity suggests the presence of highly redox-active dithiolate by-products in the parent solution. Multiple attempts to isolate the corresponding by-products were unsuccessful. Although insoluble in both toluene and THF, **3** is readily soluble in acetonitrile (however, it gradually decomposes overnight).

Compounds containing five- and six-coordinate silicon atoms usually have ^{29}Si chemical shifts at high field (−50 to −150 ppm for five-coordinate silicon compounds; −130 to −200 ppm for six-coordinate silicon compounds).[21] The ^{29}Si NMR resonance of −150.8 ppm for **3** (in CD_3CN) is comparable to that of −148.3 ppm (in [D$_6$]DMSO) reported for $[Si(Tm^{Ph})_2]^{2+}$ dications (Tm^{Ph} = hydro-tris(phenylthioimidazolyl)borate), supporting the presence of a six-coordinate silicon atom in **3**.[22] In contrast, ^{29}Si NMR resonances of the four-coordinate (Figure 1 a)[6a] and five-coordinate (Figure 1 b)[6b] silicon bis(dithiolene)s were reported at +45.4 ppm and −57.2 ppm, respectively. Five-coordinate ^{29}Si resonances were not observed in variable-temperature (VT) ^{29}Si NMR experiments (Figures S4–S7 in the Supporting Information), which does not support an equilibrium between **3** and the five-coordinate silicon species (which could possibly be produced through partial dissociation of a dithiolene ligand in solution). Indeed, over the 40 °C to −35 °C temperature range the ^{29}Si NMR resonances of **3** only shift slightly from −150.3 ppm to −153.4 ppm.

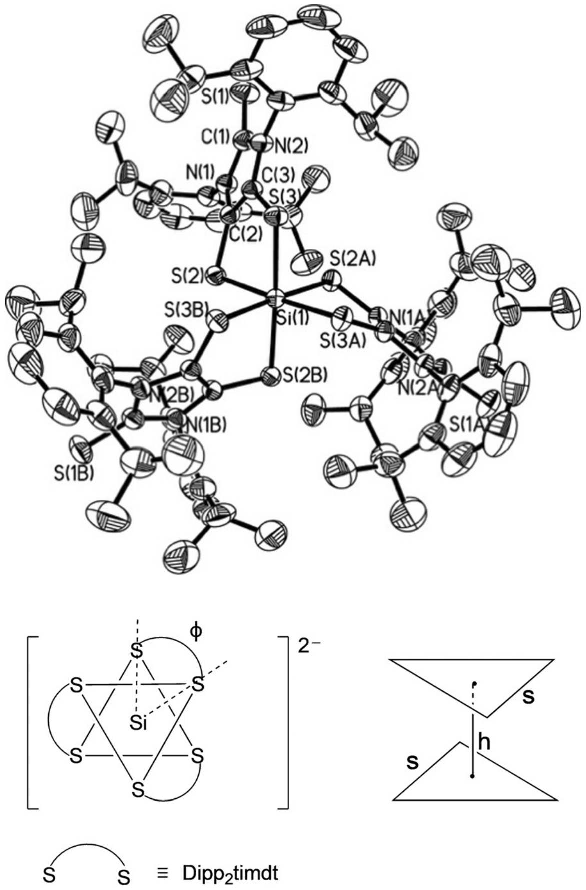

Figure 2. a) Molecular structure of silicon tris(dithiolene) dianion (**[3]**$^{2-}$; thermal ellipsoids set at 30% probability; hydrogen atoms bound to carbon atoms are omitted for clarity).[25] Selected bond lengths [Å] and angles (°): C(1)–S(1) 1.680(4), C(2)–C(3) 1.342(4), C(2)–S(2) 1.729(3), C(3)–S(3) 1.725(3), S(2)–Si(1) 2.3195(12), S(3)–Si(1) 2.3374(12); S(2)-C(2)-C(3) 124.9(3), C(2)-S(2)-Si(1) 95.10(11), S(2)-Si(1)-S(3) 94.71(3), S(2)-Si(1)-S(3A) 177.19(3). b) Schematic representation of **[3]**$^{2-}$ (trigonal twist angle ϕ, triangle side s, intertriangle distance h, $Dipp_2timdt$ = diisopropylphenyl-substituted imidazolidine-2,4,5-trithione).[1a, 23]

Six-coordinate silicon atoms residing in an S_6 coordination environment are rare, the literature only revealing bis(tridentate) $[Si(Tm^{Ph})_2]X_2$ (Tm^{Ph} = hydro-tris(phenylthioimidazolyl)borate, X = I^- and I_3^-).[22] By comparison, **3** is the first tris(bidentate ligand) complexes containing a SiS_6 core. In the solid-state the six-coordinate silicon atom of **3** adopts a distorted octahedral geometry (Figure 2 a). Both trigonal twist angle (ϕ) and s/h ratio (Figure 2 b) have been utilized in evaluating the structural distortion from the regular octahedron ($\phi = 60.0°$ and s/h = 1.22) for tris(bidentate ligand) complexes.[1a,23] Both **3** and its simplified model **[3-H]**$^{2-}$ (in D_3 symmetry, optimized at the B3LYP/6–311G** DFT level)[14] have a trigonal twist angle (ϕ) of 60.0° based on the view in Figure 2 b. The 1.14 s/h ratio of **3** is smaller than that of the regular octahedron (1.22), indicating the presence of somewhat elongated distortion in **3**.[23] The s/h ratio of the simplified model **[3-H]**$^{2-}$ (1.12) is even marginally smaller than that of **3** (1.14). It is noteworthy that the SiS_6 cores in $[Si(Tm^{Ph})_2]^{2+}$ dications exhibit the slightly flattened octahedral structures, with 83.45(4)–84.54(3)° intra-ligand S-Si-S angles and 95.46(3)–96.55(4)° inter-ligand S-Si-S angles.[22] In contrast to the planar C_2S_2Si rings in **[3-H]**$^{2-}$ and in $Si[S_2(o\text{-}C_6H_4)]_2$[6a] (Figure 1 a), the C_2S_2Si rings in **3** are bent [bend angle[1a] (η) between the SiS_2 plane and the S_2C_2 plane = 29.7°, av], which may be due to the steric repulsion between the bulky ligands and the packing effects. The olefinic C−C bonds [1.342(4) Å] and C−S bonds [1.727(3) Å, av] in the C_2S_2 units of **3** are comparable with those in various reported dithiolates, such as $(NMe_4)_2(C_3S_5)$ [$d_{C-C} = 1.371(8)$ Å, $d_{C-S} = 1.716(4)$ Å].[24] Considering the dianionic character of **3**, the central silicon atom has the formal oxidation state of +4. While being similar to those in $[Si(Tm^{Ph})_2]^{2+}$ dications (2.3176 Å, av),[22] the Si−S bonds of **3** [2.3195(12)–2.3374(12) Å] are somewhat shorter than that in **[3-H]**$^{2-}$ (2.3894 Å), and considerably longer than that [2.1381(6) Å] in four-coordinate silicon bis(dithiolene), Si[$S_2(o\text{-}C_6H_4)$]$_2$ (Figure 1 a).[6a] The zwitterionic pentacoordinate silicon bis(dithiolene) (Figure 1 b) contains both [2.1590(9) Å, av] equatorial and [2.3076(7) Å, av] axial Si−S bonds.[6b]

While the LUMO of the simplified model **[3-H]**$^{2-}$ is a silicon–sulfur σ-antibonding orbital, the corresponding HOMO is almost entirely ligand-based, involving C−C π-bonding and C–S π-antibonding character (Figure 3). The 0.630 Wiberg bond index of the Si−S bond in **[3-H]**$^{2-}$ supports its single-bond character. The central silicon atom bears a positive natural charge of +0.72 while each sulfur atom (adjacent to the silicon atom) bears a negative charge of −0.16.

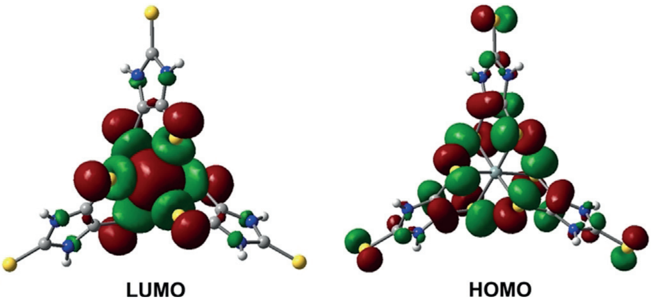

Figure 3. Frontier molecular orbitals of **[3-H]**$^{2-}$ model.

In conclusion, the first six-coordinate silicon tris(dithiolene) dianion (**3**) has been synthesized by employing carbene-stabilized disilicon (**1**) as a silicon-transfer agent. The application of **1** as a silicon-transfer agent may be extended to a broad group of inorganic and organometallic substrates in the future. The redox reactivity of **3** is being explored.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbenes · dithiolenes · hypervalent compounds · radicals · silicon

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[25] CCDC 1966399 (**3·THF**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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