



A Stable Compound Containing a Silicon-Silicon Triple Bond

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 - For an example of Lewis base-catalyzed aldol reactions using trichlorosilylenoethers, see (20).
 - It should be noted that both the labeled enolsilane and TIPS dimer precursor were available in gram quantities from only 1.00 g of ethylene glycol (\$31/mmol).
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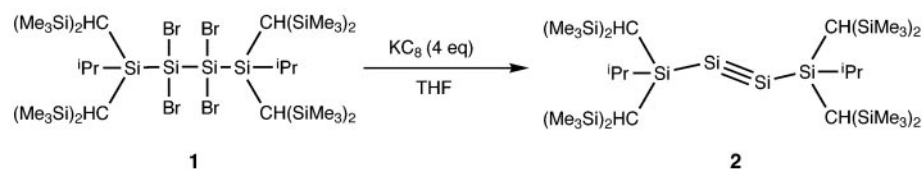
A Stable Compound Containing a Silicon-Silicon Triple Bond

Akira Sekiguchi,* Rei Kinjo, Masaaki Ichinohe

The reaction of 2,2,3,3-tetrabromo-1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyltetrasilane with four equivalents of potassium graphite (KC_8) in tetrahydrofuran produces 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyl-2-tetrasilene, a stable compound with a silicon-silicon triple bond, which can be isolated as emerald green crystals stable up to 100°C in the absence of air. The $Si\equiv Si$ triple-bond length (and its estimated standard deviation) is 2.0622(9) angstroms, which shows half the magnitude of the bond shortening of alkynes compared with that of alkenes. Unlike alkynes, the substituents at the $Si\equiv Si$ group are not arranged in a linear fashion, but are trans-bent with a bond angle of 137.44(4)°.

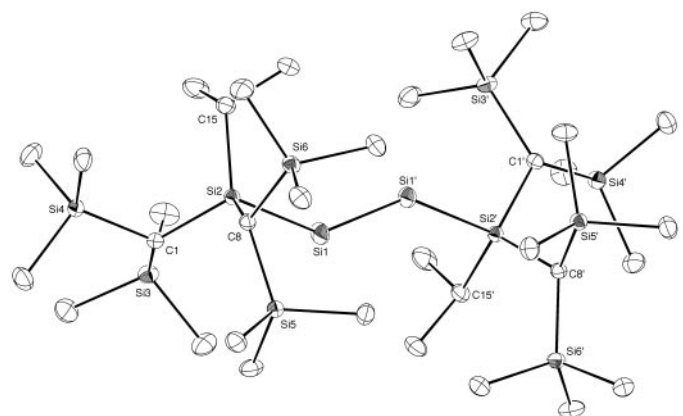
Hydrocarbons containing $C=C$ double bonds (alkenes) and $C\equiv C$ triple bonds (alkynes) form an abundant and structurally diverse class of organic compounds. However, the ability of heavier congeners of carbon (where element E is Si, Ge, Sn, and Pb) to form double bond of the type $>E=E<$ and triple bond of the type $-E\equiv E-$ was for a long time doubted (1–4). The first attempts to generate such species were unsuccessful, resulting in the formation of polymeric substances. This led to the oft-cited “double-bond rule”: Those elements with a principal quantum number equal to or greater than three are not capable of forming multiple bonds because of the considerable Pauli repulsion between the electrons of the inner shells (5–7). Such a viewpoint prevailed despite the accumulation of a vast amount of experimental data supporting the existence of multiply bonded species as reactive intermediates (1–4). This conflict was resolved nearly 30 years ago, when Lappert and Davidson report-

ed the synthesis of the stable distannene $[(Me_3Si)_2CH]_2Sn=Sn[CH(SiMe_3)_2]_2$, where Me is methyl, which has a $Sn=Sn$



Reaction 1.

Fig. 1. Molecular structure of 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyl-2-tetrasilene (**2**) (30% probability ellipsoids for Si and C). Selected bond lengths (Å): $Si1-Si1' = 2.0622(9)$, $Si1-Si2 = 2.3698(6)$, $Si2-C1 = 1.9119(15)$, $Si2-C8 = 1.9120(15)$, and $Si2-C15 = 1.9180(16)$. Selected bond angles (°): $Si1'-Si1-Si2 = 137.44(4)$, $Si1-Si2-C1 = 108.97(5)$, $Si1-Si2-C8 = 108.38(5)$, $Si1-Si2-C15 = 106.47(5)$, $C1-Si2-C8 = 106.83(6)$, $C8-Si2-C15 = 114.77(7)$, and $C1-Si2-C15 = 111.30(7)$. Estimated standard deviations are in parentheses.



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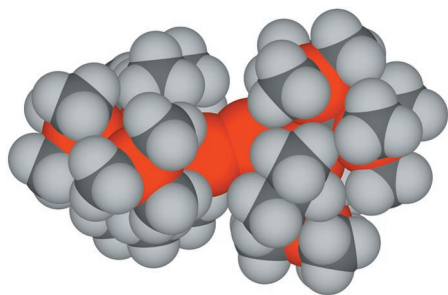


Fig. 2. Space-filling model of **2**. Si, red; C, gray; H, white.

bond (16), all attempts to isolate such postulated molecules have been unsuccessful (17–19). The difficulty in synthesizing disilynes is due in large part to their high reactivities, especially toward isomerization and dimerization.

We report the isolation and full characterization of 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyl-2-tetrasilene **2**, a stable disilyne R-Si≡Si-R, which is the Si analog of an alkyne. In this compound, the Si≡Si triple bond is kinetically and thermodynamically stabilized by two large silyl substituents, each bearing one isopropyl and two bis(trimethylsilyl)methyl groups. The compound is accessed by reduction of a tetrabrominated precursor. Thus, the reaction of 2,2,3,3-tetrabromo-1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyltetrasilane **1** with four equivalents of potassium graphite (K_{C₈}) in dry tetrahydrofuran (THF) produces a dark green mixture, from which disilyne **2** can be isolated as extremely air- and moisture-sensitive emerald green crystals in 73% isolated yield (Reaction 1) (20, 21). Despite the large steric congestion, the debromination reaction proceeds rapidly and cleanly. The disilyne **2** was purified by recrystallization from pentane at –30°C; it has a decomposition point of 127° to 128°C. No evidence for the isomerization of **2** to RRSi=Si or dissociation into the two RSi fragments (where R is SiⁱPr[(CH(SiMe₃))₂] and ⁱPr is isopropyl) was observed, indicating that the two central Si atoms are strongly bonded.

The disilyne **2** was fully characterized spectroscopically; the most informative data came from ²⁹Si nuclear magnetic resonance (NMR) studies. Four equal-intensity resonance signals at the chemical shifts $\delta = -0.3, 0.0, 20.7,$ and 89.9 parts per million (ppm) were observed in the ²⁹Si NMR spectrum, assigned as follows: The peak at 89.9 ppm corresponds to a triply bonded Si atom, the peak at 20.7 ppm corresponds to Si atoms bonded to the Si≡Si group, and peaks at –0.3 and 0.0 ppm correspond to the four CH(SiMe₃)₂ groups (21). The resonance of the sp-hybridized Si atoms is shifted upfield compared with that of silyl-substituted disilenes ($\delta = 142.1$ to 154.5 ppm) (22), as was observed in the case of ¹³C NMR chemical shifts of silyl-substi-

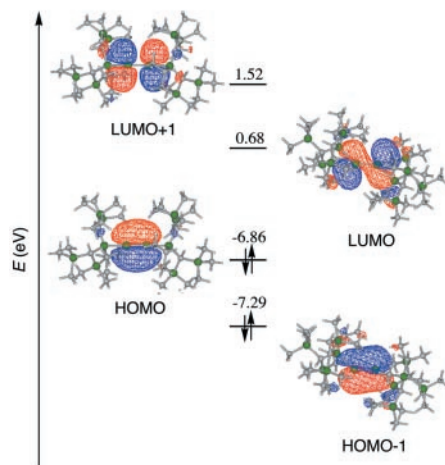


Fig. 3. The π MOs of **2** calculated at the HF/6-311G(d)//B3LYP/6-31G(d) level (HOMO-1, HOMO, LUMO, and LUMO+1). E is the energy level of the orbitals. The large vertical arrow indicates the energy level. The two small arrows indicate two electrons of opposing spin, referred to as paired electrons.

tuted alkenes ($\delta = 188$ to 197 ppm) and alkynes ($\delta = 112$ to 114 ppm) (23).

The solid state structure of **2** was confirmed by x-ray crystallographic analysis (Fig. 1). Full metrical parameters are listed in table S3 (24). The four Si atoms (Si2, Si1, Si1', and Si2') are perfectly coplanar and the bulky SiⁱPr[(CH(SiMe₃))₂] groups protect the central Si≡Si triple bond. The most significant result is the Si≡Si triple-bond length of 2.0622(9) Å. This value is 3.8% shorter than typical Si=Si double-bond length (2.14 Å) and 13.5% shorter than the average Si-Si single-bond length of 2.34 Å (4). This shortening is half the magnitude of that in the carbon counterparts. Moreover, alkynes have a linear geometry around the C≡C triple bond, whereas disilynes have been predicted to have a highly pronounced trans-bent geometry around the Si≡Si triple bond (14, 16). The structure confirms this prediction: The substituents at the Si≡Si are not arranged in a linear fashion, but are trans-bent with a bond angle of 137.44(4)°, as determined by the Si2-Si1-Si1' angle. This bond angle is 12.5° smaller than that calculated for HSi≡SiH (124.9°). According to theoretical investigations, substitution by electropositive silyl groups leads to a less trans-bent disilyne structure (25). The structure of **2** presented here is close to that predicted by a recent density functional (DFT) calculation on (t-Bu₃Si)₂MeSiSi≡SiSiMe(SiⁱBu₃)₂, where ⁱBu is *tert*-butyl (26).

The space-filling model of **2** shown in Fig. 2 highlights the steric protection of the Si≡Si group by the isopropyl and bis(trimethylsilyl)methyl substituents. Upon replacement of the isopropyl groups in precursor with methyls, the reaction to produce the disilyne yields a dimerization product instead, bearing a tetrasilatetrahedrane core (27).

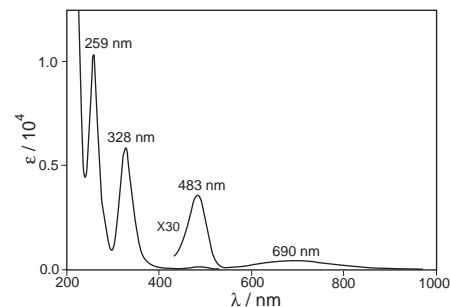


Fig. 4. Ultraviolet-visible absorption spectrum of **2** in hexane at room temperature; ϵ is the molar extinction coefficient ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

Despite the steric protection, the Si≡Si triple bond in **2** does undergo addition reactions with a halogen. Thus, **2** readily reacted with two equivalents of bromine at room temperature in hexane to form **1** in 94% yield by cleavage of the two π (Si≡Si) bonds.

A DFT calculation on disilyne **2** at the B3LYP/6-31G(d) level of theory well reproduces the experimental geometry and the structural parameters (calculated value: 2.093 Å for the Si≡Si bond length, 136.1° for the trans-bending angle). The molecular orbitals (MOs) of **2** calculated at the HF/6-311G(d)//B3LYP/6-31G(d) level presented in Fig. 3 show two nondegenerate highest occupied π MOs (HOMO-1 and HOMO) and two lowest unoccupied antibonding π^* MOs (LUMO and LUMO+1). The out-of-plane HOMO and LUMO+1 are represented by the pure (p_z - p_z) π MOs, whereas the in-plane HOMO-1 and LUMO are represented mainly by (p_y - p_y) π MOs with a slight contribution from the antibonding σ^* (Si-Si) orbital of the central bond. In accordance with the triple-bond structure, natural bond orbital analysis of **2** shows electron occupation of the two π (Si≡Si) orbitals (1.934 and 1.897 electron), indicating their bonding character. The bond order (Wiberg bond index) of Si1-Si1' is 2.618, which agrees with the real Si≡Si triple bond. The presence of the two nondegenerate π and two π^* MOs in **2** is reflected in the ultraviolet-visible absorption of **2**, as shown in Fig. 4. The strong absorption bands at wavelengths (λ) of 259 and 328 nm are due to the two allowed π - π^* transitions. The weak absorption bands with maxima of 483 and 690 nm are probably a result of forbidden transitions, and the latter very weak one (HOMO-LUMO transition) is responsible for the emerald green color of **2**.

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- The reduction of (t-Bu₃Si)₂MeSiClSi=SiClSiMe(Si^tBu₃)₂ with lithium naphthalene in THF has recently been reported (28). This contains an unstable product with a low field ²⁹Si NMR signal at δ = 91.5 ppm, which was ascribed to a Si=Si triple-bond resonance.
- Crystals of **1** (100 mg, 0.087 mmol) and K₂C (50 mg, 0.370 mmol) were placed in a glass tube and degassed. Dry oxygen-free THF (2 mL) was introduced by vacuum transfer and the mixture was allowed to warm from -78°C to room temperature overnight with stirring. The solution turned an intense green color. The solvent was replaced by hexane, and then the resulting potassium salt and graphite were filtered off in a glove box (a box equipped with gloves in which air- and moisture-sensitive compounds can be handled). After evaporation of the solvent, pentane was added and the solution was cooled at -30°C to give emerald green crystals of **2** (53 mg, 73%).
- NMR of **2** ([D₆]benzene solution, 1H) δ values (ppm): -0.01 (singlet, 4H), CH protons; 0.39 (singlet, 36H), SiMe₃ protons; 0.57 (singlet, 36H), SiMe₃ protons, 1.44 (doublet, 12H, spin-spin coupling constant *J* = 6.0 Hz, 12H), isopropyl methyl protons, 1.49 (septet, spin-spin coupling constant *J* = 6.0 Hz, 2H), isopropyl methyne proton. NMR (¹³C) δ values: 5.1, 5.7, 8.9, 17.8, and 22.3. NMR (²⁹Si) δ values: -0.3, 0.0, 20.7, and 89.9. High-resolution mass spectrum: mass-to-charge ratio (*m/z*) calculated for C₃₄H₅₀Si₁₂ to be 834.4274, experimentally found to be 834.4275. Ultraviolet-visible spectrum (in hexane solution): λ_{max} [wavelength, molar extinction coefficient (ε)/dm³ mol⁻¹ cm⁻¹] 259, 10300; 328, 5800; 483, 120; and 690, 14.
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- An emerald green crystal (approximate dimensions, 0.30 by 0.15 by 0.15 mm) of **2** was used for the x-ray diffraction data collection on a Mac Science DIP2030K Image Plate Diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71070 Å). Cell constants and an orientation matrix for data collection corresponded to the monoclinic space group C2/c, with *a* = 30.9620(11) Å, *b* = 10.9060(2) Å, *c* = 18.1170(7) Å, β = 118.995(2)°, *V* = 5350.8(3) Å³, four molecules per unit cell, formula weight 836.14, and calculated density 1.038 Mg/m³. Data were collected at 120 K, θ range from 2.18° to 28.01°. There were 26,993 collected reflections (6412 unique, *R*_{int} = 0.0290); *R*₁ = 0.0373 for 5479 reflections with *I* > 2σ(*I*), *wR*₂ = 0.1096 for all reflections. More crystallographic data are available

- at the Cambridge Crystallographic database, accession code and deposition no. CCDC 245523.
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Supporting Online Material

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Tables S1 to S5

30 June 2004; accepted 2 August 2004

A Linear, O-Coordinated η¹-CO₂ Bound to Uranium

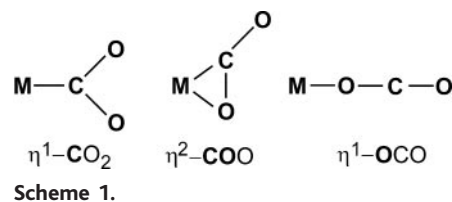
Ingrid Castro-Rodriguez, Hidetaka Nakai, Lev N. Zakharov, Arnold L. Rheingold, Karsten Meyer*

The electron-rich, six-coordinate tris-aryloxide uranium(III) complex [(^{Ad}ArO)₃tacn]U^{III} [where (^{Ad}ArOH)₃tacn = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)1,4,7-triazacyclononane] reacts rapidly with CO₂ to yield [(^{Ad}ArO)₃tacn]U^{IV}(CO₂), a complex in which the CO₂ ligand is linearly coordinated to the metal through its oxygen atom (η¹-OCO). The latter complex has been crystallographically and spectroscopically characterized. The inequivalent O-C-O bond lengths [1.122 angstroms (Å) for the O-C bond adjacent to uranium and 1.277 Å for the other], considered together with magnetization data and electronic and vibrational spectra, support the following bonding model: U^{IV}=O=C-O⁻ ↔ U^{IV}-O≡C-O⁻. In these charge-separated resonance structures, the uranium center is oxidized to uranium(IV) and the CO₂ ligand reduced by one electron.

Carbon dioxide has been implicated as a main contributor to global warming because of its role in radiative forcing (1). However, CO₂ also represents an abundant renewable resource for the production of fine chemicals and clean fuels. Interest in metal-mediated multielectron reduction of CO₂ therefore remains high, but the molecule's inherent thermodynamic stability hinders the development of metal catalysts that achieve CO₂ activation and functionalization.

Particularly intriguing for synthetic chemists is the discovery of relatively simple coordination complexes that bind CO₂ and facilitate its reduction (2). Chemists have isolated and structurally characterized several synthetic metal complexes of CO₂, such as Aresta's archetypal [(Cy₃P)₂Ni(CO₂)] (Cy = cyclohexyl) (3, 4) and Herskowitz's [(diars)₂M(CO₂)(Cl)] [diars = *o*-phenylenebis(dimethylarsine); M = Ir, Rh] (5), featuring the bidentate η²-COO and carbon-bound η¹-CO₂ binding modes, respectively. Activation of CO₂ via its adsorption on metal surfaces is of considerable interest for catalysis at the gas-surface interface (6, 7). Most recently, Andrews and co-workers studied the interaction of CO₂ with a variety of transition (8) and actinide (9) metal atoms gen-

erated via laser ablation. Although C-O bond cleavage of a proposed intermediate η²-COO complex is predominant in these surface-adsorbed systems, there also is spectral evidence for η¹-OCO adsorption in low-temperature matrices (Scheme 1) (8). The most important CO₂ activation process occurs naturally during photosynthesis. It was proposed that during photosynthetic CO₂ fixation, an oxygen-coordinated CO₂ ligand (η¹-OCO) is enzymatically reduced by ribulose-1,5-bisphosphate carboxylase-oxygenase (RuBisCO) (10). Oxygen coordination appears to be an indispensable step for C-functionalization in this system. Recently, the relevance of the η¹-OCO coordination mode for biological systems was fueled by a crystallographic study on a deacetoxycephalosporin C synthase (DAOCS) mutant. The presence of electron density in proximity to the active site's iron center was found to be consistent with a monodentate O-bound CO₂ molecule (11). However, definitive structural characterization of inorganic coordination complexes with a linear oxygen-bound η¹-OCO coordination mode has remained elusive (2).



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