A Stable Compound Containing a Silicon-Silicon Triple Bond

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The reaction of 2,2,3,3-tetramethylenesilane and 2,2,3,3-tetrabromo-1,1,4,4-tetakis[bis(trimethylsilyl)methyl]-1,4-disopropyltetrasilane with potassium graphite produces a stable compound with a silicon-silicon triple bond, which can be isolated as green crystals stable up to 100°C in the absence of air. The Si–Si triple-bond length (and its estimated standard deviation) is 2.0622(9) Å, which shows half the magnitude of the bond shortening compared with that of alkynes. Unlike alkynes, the substituents at the Si=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≡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=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 oftencited "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 reported the synthesis of the stable distannene [(MeMeSi)2CH]3Sn–Sn[(CH2)2Me2]2, where Me is methyl, which has a Sn–Sn double bond in the solid state (8). The next important discoveries came from two research groups in 1981: West and colleagues reported the synthesis of a stable compound with a Si=Si double bond, tetramesityldisilene (9), and Brook et al. synthesized a compound with a Si=C double bond (10). As for triple bonds, Power and co-workers recently prepared alkyne analogs of the heavier group 14 elements: germanium, tin, and lead (11–13). However, despite bearing nominal triple bonds, these compounds actually exhibited a highly pronounced nonbonding electron density character at the central atoms, resulting in a decrease in the bond order on descending group 14 (14, 15). In light of these results, isolation of the silicon analog of alkynes has been a compelling goal. Although the theoretical analysis predicted the experimental accessibility of disilanes with a silicon-silicon triple bond.
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-tetrasilyne, a stable disilene 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-tetraphenyl-1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyltetrasilane 1 with four equivalents of potassium graphite (KC8) in dry tetrahydrofuran (THF) produces a dark green mixture, from which disilene 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 disilene 2 was purified by recrystallization from pentane at −30°C; it has a decomposition point of 127°C to 128°C. No evidence for the isomerization of 2 to RRSi=Si or dissociation into the two RSi fragments (where R is SiPr[(CH(SiMe3)]2 and Pr is isopropyl) was observed, indicating that the two central Si atoms are strongly bonded.

The disilene 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 δ = −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 (δ = 142.1 to 154.5 ppm) (22), as was observed in the case of 13C NMR chemical shifts of silyl-substituted alkynes (δ = 188 to 197 ppm) and alkynes (δ = 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 SiPr[(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=CC triple bond, whereas disilenes 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 electronegative silyl groups leads to a less trans-bent disilene structure (25). The structure of 2 presented here is close to that predicted by a recent density functional (DFT) calculation on (Bu3Si)3MeSi=SiMe3(SiBu3)2, where 1Bu 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 disilene yields a dimerization product instead, bearing a tetrasilatetrahedrane core (27).

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 disilene 2 at the B3LYP/6-31G(d) level of theory 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_x-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.

References and Notes
A Linear, O-Coordination $\eta^1$-CO$_2$ Bound to Uranium

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The electron-rich, six-coordinate tris-aryloxide uranium(II) complex ($[\text{AdArO}_3\text{tacn}]\text{UIV}$) where $[\text{AdArOH}_3\text{tacn}]$ is linearly coordinated to the metal through its oxygen atom ($\eta^1$-CO$_2$). The latter complex has been crystallographically and spectroscopically characterized. The inequivalent O–C–O bond lengths [1.122 Å (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: $\text{UV}^2=\text{O}^=\text{C}^=\text{O}^=\text{C}^=\text{O}$. In these charge-separated resonance structures, the uranium center is oxidized to uranium(V) and the CO$_2$ 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, CO$_2$ also represents an abundant renewable resource for the production of fine chemicals and clean fuels. Interest in metal-mediated multielectron reduction of CO$_2$ therefore requires the development of metal catalysts that achieve CO$_2$ activation and functionalization.

Particularly intriguing for synthetic chemists is the discovery of relatively simple coordination complexes that bind CO$_2$ and facilitate its reduction (2). Chemists have isolated and structurally characterized several synthetic metal complexes of CO$_2$, such as Aresta’s archetypal [Cu$\text{L}_2$Ni(CO$_2$)] (Cu = cyclohexyl) (3, 4) and Herskowitz’s [Cu$_2$(CO$_3$)$_2$] (5) where $\eta^1$-phenylenebis(dimethylarsine); M = Ir, Rh (5)], featuring the bidentate $\eta^1$-CO$_2$ and carbon-bound $\eta^1$-CO$_2$ binding modes, respectively. Activation of CO$_2$ 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 CO$_2$ with a variety of transition (8) and actinide (9) metal atoms generated via laser ablation. Although O–C bond cleavage of a proposed intermediate $\eta^1$-COO complex is predominant in these surface-adsorbed systems, there also is spectral evidence for $\eta^1$-COO adsorption in low-temperature matrices (Scheme 1) (8). The most important CO$_2$ activation process occurs naturally during photosynthesis. It was proposed that during photosynthetic CO$_2$ fixation, an oxygen-coordinated CO$_2$ ligand ($\eta^1$-COO) 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 $\eta^1$-COO coordination mode for biological systems was fueled by a cryocrystallographic study on a deacetoxycycloartenol 3,18-synthsase (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 CO$_2$ molecule (11). However, definitive structural characterization of inorganic coordination complexes with a linear oxygen-bound $\eta^1$-COO coordination mode has remained elusive (2).

**Scheme 1.**

**Supporting Online Material**

www.sciencemag.org/cgi/content/full/305/5691/1755/DC1

Tables S1 to S5

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**References**


3. An emerald green crystal (approximate dimensions of 0.30 by 0.15 by 0.15 mm) of $\text{Zn}$ was used for the x-ray diffraction data collection on a Mac Science DIP2030K image plate diffractometer with graphite-monochromatized Mo-$\text{K}$$\alpha$ radiation ($\lambda = 0.71070$ Å). Cell constants and a orientation matrix for data collection corresponded to the monoclinic space group $\text{C}2/c$, with $a = 16.929$ Å, $b = 20.906$ Å, $c = 11.170$ Å, $\alpha = 90$, $\beta = 118.995$, $\gamma = 90$, $V = 3530$ Å$^3$. Four molecules per unit cell, formular weight 836.14, and calculated density 1.038 Mg/m$^3$. Data were collected at 120 K, $\theta$ range from 2.18$^\circ$ to 28.01$^\circ$. There were 26,993 collected reflections (6412 unique, $R_{	ext{int}} = 0.0020$, $R_{	ext{free}} = 0.031$, $R_{	ext{free}} = 0.038$, $R_{	ext{free}} = 0.037$ for 5479 reflections with $1 > 2\sigma(I)$). Weak peaks were 0.1096 for all reflections. More crystallographic data are available at the Cambridge Crystallographic database, accession code and deposition no. CCDC 242573.

