

ORGANOMETALLICS

Volume 24, Number 12, June 6, 2005

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American Chemical Society

Communications

Disilanes Containing Two High-Coordinate Silicon Atoms Bridged by Carboxylate Ligands: Synthesis, Structure, and Dynamic Behavior

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Received April 22, 2005

Summary: Disilanes bearing four carboxylate ligands have a trigonal bipyramidal geometry around each silicon atom with two bridging carboxylate ligands with the apical Si–O axes, which are parallel to each other, in the crystalline state, while such a structure is in equilibrium with a tetrahedral structure in solution.

Hypervalent silicon compounds play an important role in organosilicon chemistry and have been studied extensively in view of their structures, reactivity, and synthetic applications.¹ In particular, disilanes and oligosilanes in which two hypervalent silicon atoms are directly connected to each other recently have become a subject of interest as components of high-coordinate polysilanes, which are expected to show unique electronic and optical properties.² Since the silyl groups are electropositive and bulky, they are usually poor at

stabilization of hypervalent silicon species.³ Only a few examples of such disilanes that take advantage of the stabilizing effect of an intramolecularly coordinated tether containing an oxygen or nitrogen donor atom have been reported.⁴ For example, a tetrasilane bearing amide tethers has two pentacoordinate silicon atoms that are connected to each other (Chart 1).^{4a} In such disilanes, the donor site of the tether interacts with the silicon atom (type I).⁴ The conformation of the Si–Si chain in tetracoordinate polysilanes and oligosilanes influences their electronic and optical properties. While this is difficult to control, the conformation in such hypervalent oligosilanes is expected to be fixed due to steric and electronic effects. A μ^2 -bridging ligand is expected to be useful for coordination to the adjacent silicon atom to fix a nearly eclipsed conformation with parallel apical bonds, in which two hypercoordinate silicon atoms and all the equatorial ligands on the

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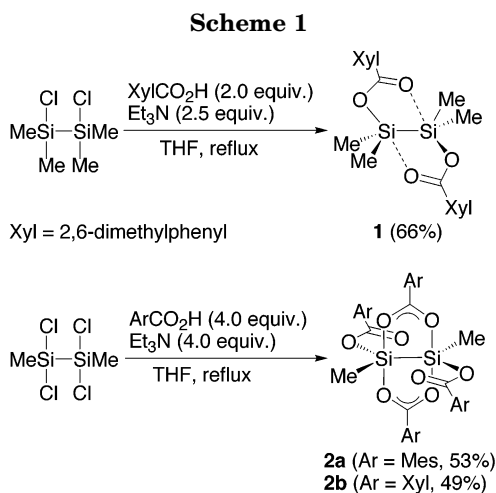
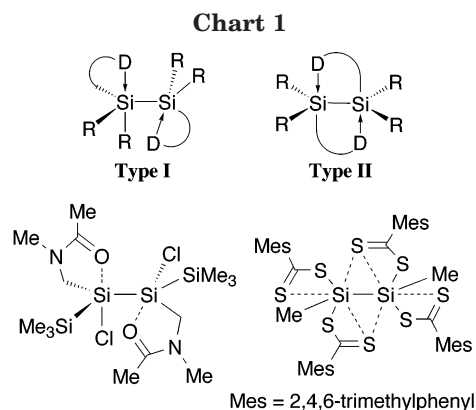
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silicon atoms are on the same two-dimensional plane (type II). However, only few examples of such high-coordinate disilanes with bridging ligands have been reported. We previously described a disilane bearing four dithiocarboxylate ligands with weak intramolecular Si–S interactions.^{5,6} Considering the high affinity of oxygen toward silicon, strong intramolecular interactions, which may enable μ^2 -bridging of two adjacent silicon atoms by the ligand, are expected in a disilane bearing adjacent carboxylate ligands. We report here the synthesis and structural analysis of disilanes bearing two and four carboxylate ligands, respectively.

Disilane **1**, bearing two 2,6-dimethylbenzoyloxy ligands, was synthesized in 66% yield by the reaction of 1,2-dichloro-1,1,2,2-tetramethyldisilane with 2,6-dimethylbenzoic acid (2.0 equiv) and triethylamine (2.5 equiv) in refluxing THF (Scheme 1).⁷ Disilanes **2a** and **2b**, bearing four carboxylate ligands, were similarly synthesized in 53% and 49% yield, respectively, by reacting 1,1,2,2-tetrachloro-1,2-dimethyldisilane with the respective benzoic acids and triethylamine (4.0 equiv). Disilanes **1**, **2a**, and **2b** are highly moisture-sensitive.

X-ray crystallographic analysis of **1** showed a slightly distorted tetrahedral structure, as indicated by the bond angles (100.53(9)–116.36(9)°) around the silicon atoms (Figure 1).⁸ This is in contrast to certain pentacoordinate digermanes⁹ and distannanes¹⁰ bearing two bridging carboxylate ligands, which exhibit trigonal bipyra-

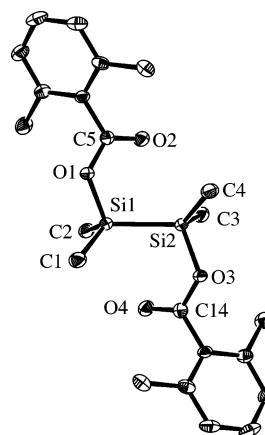


Figure 1. ORTEP drawing of **1** (50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 = 2.3238(9), Si1–C1 = 1.847(2), Si1–C2 = 1.851(2), Si2–C3 = 1.845(2), Si2–C4 = 1.848(2), Si1–O1 = 1.7235(16), Si2–O3 = 1.7239(16), C5–O1 = 1.332(3), C5–O2 = 1.204(3), C14–O3 = 1.330(3), C14–O4 = 1.212(3), O1–Si1–C1 = 100.70(10), C1–Si1–C2 = 112.93(12), C2–Si1–O1 = 104.99(9), O3–Si2–C3 = 105.10(10), C3–Si2–C4 = 113.17(12), C4–Si2–O3 = 100.53(9), O1–Si1–Si2 = 109.71(6), C1–Si1–Si2 = 116.24(9), C2–Si1–Si2 = 111.11(9).

midal (TBP) geometry around group 14 atoms. The carbonyl oxygen atoms O2 and O4 of **1** are located on the opposite sides of the Si2–O3 and Si1–O1 bonds, respectively. The interatomic distances O2...Si2 and O4...Si1, both of which are 2.9868(18) Å, are considerably shorter than the sum of the van der Waals radii (3.62

(7) Synthesis of **2b**: To a THF solution (10 mL) of 2,6-dimethylbenzoic acid (341 mg, 2.27 mmol) were added triethylamine (337 μ L, 2.43 mmol) and 1,1,2,2-tetrachloro-1,2-dimethyldisilane (100 μ L, 556 μ mol) at room temperature. After refluxing for 6 h, the solvent was evaporated under reduced pressure. Benzene was added to the residue, and the material insoluble in benzene was removed by filtration. After the filtrate was evaporated, the remaining crude solid was recrystallized from benzene and washed with hexane to give colorless crystals of **2b** (186 mg, 49%). **2b**: colorless crystals, mp 127–128 °C (dec); ¹H NMR (400 MHz, C₆D₆) δ 1.27 (s, 6H), 2.47 (s, 24H), 6.80 (d, ³J_{HH} = 7.6 Hz, 8H), 6.97 (t, ³J_{HH} = 7.7 Hz, 4H); ¹³C NMR (100 MHz, C₆D₆) δ -0.32 (q), 20.58 (q), 128.54 (d), 129.85 (d), 133.82 (s), 136.26 (s), 171.37 (s); ²⁹Si NMR (99 MHz, C₆D₆) δ -20.7 (s); UV/vis (hexane) λ_{max} (ϵ) = 275 (300), 400 (4300) nm; IR (KBr) 1693 (vs), 1597 (w), 1522 (w), 1467 (m), 1432 (m), 1381 (w), 1301 (vs), 1259 (m), 1171 (w), 1126 (m), 1079 (m) cm⁻¹. Anal. Calcd for C₃₈H₄₂O₈Si₂: C, 66.83; H, 6.20. Found: C, 66.71; H, 6.43. Compounds **1** and **2a** were synthesized similarly.¹⁴ **1**: colorless crystals, mp 96–98 °C; ¹H NMR (500 MHz, C₆D₆) δ 0.73 (s, 12H), 2.38 (s, 12H), 6.86 (d, ³J_{HH} = 7.6 Hz, 4H), 7.01 (t, ³J_{HH} = 7.6 Hz, 2H); ¹³C NMR (126 MHz, C₆D₆) δ -1.26 (q), 20.51 (q), 128.14 (d), 129.44 (d), 134.90 (s), 135.47 (s), 171.74 (s); ²⁹Si NMR (99 MHz, C₆D₆) δ 13.4 (s); IR (KBr) 1685 (vs), 1653 (m), 1636 (w), 1507 (w), 1457 (m), 1431 (s), 1397 (w), 1303 (vs), 1250 (s), 1123 (s), 1078 (s) cm⁻¹. Anal. Calcd for C₂₂H₃₀O₄Si₂: C, 63.73; H, 7.29. Found: C, 63.70; H, 7.33. **2a**: colorless crystals, mp 206–207 °C; ¹H NMR (500 MHz, C₆D₆) δ 1.32 (s, 6H), 2.03 (s, 12H), 2.53 (s, 24H), 6.63 (s, 8H); ¹³C NMR (126 MHz, C₆D₆) δ -0.51 (q), 20.72 (q), 20.98 (q), 129.18 (d), 130.86 (s), 136.76 (s), 139.71 (s), 171.51 (s); ²⁹Si NMR (99 MHz, C₆D₆) δ -20.7 (s); IR (KBr) 1690 (vs), 1611 (s), 1516 (m), 1489 (m), 1452 (s), 1408 (m), 1384 (m), 1290 (vs), 1259 (s), 1186 (m), 1174 (s), 1095 (s) cm⁻¹. Anal. Calcd for C₄₂H₅₀O₈Si₂: C, 68.26; H, 6.82. Found: C, 68.10; H, 6.84.

(8) Crystal data for **1**: C₂₂H₃₀O₄Si₂, triclinic, space group P $\bar{1}$, $Z = 2$, $a = 8.577(2)$ Å, $b = 8.5990(19)$ Å, $c = 17.598(4)$ Å, $\alpha = 97.626(6)^\circ$, $\beta = 98.156(6)^\circ$, $\gamma = 115.882(7)^\circ$, $V = 1128.0(5)$ Å³, MW = 414.64, $D_{\text{calcd}} = 1.221$ g·cm⁻³, $T = 120$ K, GOF(F^2) = 1.098. R1[$I > 2\sigma(I)$] = 0.040, wR2(all data) = 0.101. For **2b**·C₆H₆: C₄₄H₄₈O₈Si₂, orthorhombic, space group P2₁/n, $Z = 2$, $a = 13.236(5)$ Å, $b = 10.745(5)$ Å, $c = 14.515(5)$ Å, $\beta = 104.961(5)^\circ$, $V = 1994.4(14)$ Å³, MW = 761.00, $D_{\text{calcd}} = 1.267$ g·cm⁻³, $T = 120$ K, GOF(F^2) = 0.899. R1[$I > 2\sigma(I)$] = 0.044, wR2(all data) = 0.081.

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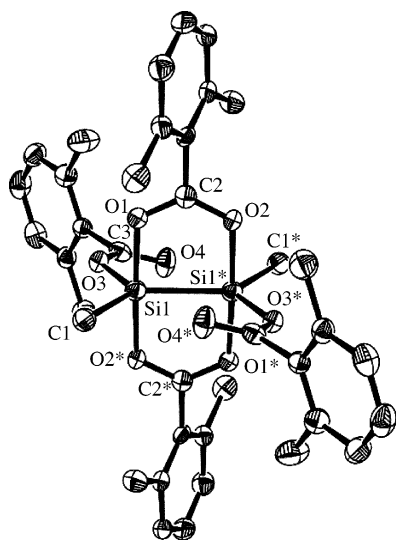
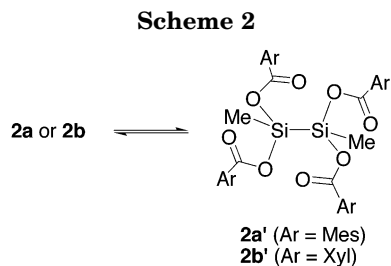


Figure 2. ORTEP drawing of **2b**·C₆H₆ (50% probability). Benzene in **2b**·C₆H₆ and hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si1* = 2.324(2), Si1–C1 = 1.850(3), Si1–O1 = 1.895(2), Si1–O2* = 1.939(2), Si1–O3 = 1.706(2), C2–O1 = 1.271(4), C2–O2 = 1.262(4), C3–O3 = 1.333(4), C3–O4 = 1.211(4), O1–Si1–O2* = 175.10(10), O1–Si1–Si1* = 89.70(9), O1–Si1–C1 = 93.01(12), O1–Si1–O3 = 88.45(10), C1–Si1–Si1* = 131.51(13), C1–Si1–O3 = 107.57(14), O3–Si1–Si1* = 120.90(10), C1–Si1–O2* = 91.80(12), O3–Si1–O2* = 89.18(10), Si1–Si1*–O2 = 87.84(9).

Å). These structural features indicate the existence of weak intramolecular Si···O interactions in the crystal. Furthermore, **1** has a nearly eclipsed conformation around the Si–Si bond axis, as judged by the torsion angle (C2–Si1–Si2–C3: 18.09(11)°). Such coordination of a chalcogen atom to the adjacent silicon atom and a similar eclipsed conformation were observed in a hepta-coordinate disilane, [Me(2,4,6-Me₃C₆H₂CS₂)₂Si]₂ (Chart 1).^{5,6}

In contrast, carboxylate ligands behave differently in the crystal structure of **2b**·C₆H₆ (Figure 2).^{8,11} Two carboxylate ligands including the C2 or C2* atoms of **2b** exhibit little bond alternation, while the other two carboxylate ligands exhibit distinct bond alternation. Each silicon atom has a TBP geometry with high pentacoordination character, %TBP_a (99%) and %TBP_e (98%).¹² The Si1 atom is almost located in the plane defined by the C1, O3, and Si1* atoms. The apical bond lengths are somewhat long (Si1–O1, 1.895(2) Å; Si1–O2*, 1.939(2) Å). The apical axes of the two silicon atoms are parallel to each other; this is in contrast to the gauche-like conformation of the reported disilanes with



TBP geometry around the two silicon atoms.⁴ Furthermore, the carbonyl oxygen atom O4 of the carboxylate ligand that includes the C3 atom is located on the opposite side of the equatorial Si1*–O3* bond (Si1*···O4: 3.187(3) Å). A similar situation was observed for O4*, which indicates potentially weak coordination of these oxygen atoms to each silicon atom. The silicon atoms of **2b** are doubly bridged by the two oxygen atoms of each carboxylate ligand. The high coordination state of silicon in **1** and **2b** can be attributed to the interactions between the nonbonding orbitals (lone pair) of the carbonyl oxygen atoms and the σ^* orbitals of the Si–O bond on their opposite sides, as observed in the hepta-coordinate disilane.^{5,13} The difference between the structures of **1**, **2a**, and **2b** can be ascribed to the electron density of silicon; that is, replacement of the electron-donating methyl group by the electron-withdrawing benzoyloxy group lowers the electron density at silicon in **2b**. Thus, the lone pair of the carbonyl oxygen atom interacts strongly with the σ^* orbital of the Si–O bond, resulting in a bridging structure for **2b**.

In the ¹H and ¹³C NMR spectra, the signals of all methyl groups attached to the silicon atoms as well as those of all carbonyl carbon atoms and all 2,6-dimethylphenyl or mesityl groups were observed equivalently in **1**, **2a**, and **2b**. In the ²⁹Si NMR spectra (C₆D₆), the signals of **2a** (δ_{Si} –19.8) and **2b** (δ_{Si} –20.7) were observed in a high-field region relative to Me(MeO)₂–SiSiMe(OMe)₂ (δ_{Si} 7.5), while the signal of **1** (δ_{Si} 13.0) was observed in a region similar to Me₂(MeO)SiSi(OMe)–Me₂ (δ_{Si} 11.7). The upfield shifts of **2a** and **2b** indicate the contribution of certain intramolecular Si–O coordinations in solution. In the variable-temperature ²⁹Si NMR spectra, the signal of **2a** in THF-*d*₈ shifted to lower field with an increase in the temperature from –103 °C (δ_{Si} –42.9) via rt (δ_{Si} –18.8) to 57 °C (δ_{Si} –17.6). It is certain that these results show the existence of an equilibrium in **2a** between the TBP structure as observed in the crystalline state and the tetrahedral structure. The latter is depicted as **2a'**, in which there is no C=O···Si interactions (Scheme 2). The higher the temperature, the more the equilibrium approaches the tetrahedral structure.

The conformational difference in the disilanes **1** and **2b** is substantiated by theoretical calculation of the corresponding model compounds [Me₂(PhCO₂)Si]₂ (**3**) and [Me(PhCO₂)₂Si]₂ (**4**), respectively, at the B3LYP/6-31G* level (ZPE corrections are included).¹⁴ For disilane **3**, bearing two carboxylate ligands, the TBP structure, in which the two PhCO₂ ligands bridge the two silicon atoms, is thermodynamically less stable than a tetra-

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(11) The structure of **2a** similar to that of **2b** was confirmed by X-ray analysis, though disorder of the oxygen atoms prevented a detailed discussion.

(12) The pentacoordination character is used as the indicator of the structure around silicon in terms of the percentage TBP geometry along the tetrahedron → TBP reaction coordinate based on the bond angles; see: (a) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099. (b) Kano, N.; Kikuchi, A.; Kawashima, T. *Chem. Commun.* **2001**, 2096.

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(14) See Supporting Information for details and references.

hedral structure like **1** by 2.2 kcal mol⁻¹. This is in accordance with the experimental results. In contrast, for disilane **4**, bearing four carboxylate ligands, a TBP structure (*C*_{2h} symmetry) is thermodynamically more stable than the tetrahedral structure (*C*_i symmetry) by only 1.6 kcal mol⁻¹. The activation energy for changing **4** from the TBP structure to the tetrahedral structure is calculated to be only 1.7 kcal mol⁻¹.¹⁴ Taking into consideration the very small differences in the thermodynamic and kinetic stabilities of **4** obtained by the theoretical calculation, the interconversion of disilane **2a** between the TBP and tetrahedral structures was expected to occur in solution and, indeed, was observed in THF-*d*₈ by NMR spectroscopy.

In summary, high coordination states of the silicon atoms with the intramolecular Si···O interactions were achieved in disilanes by the use of μ²-bridging benzoyloxy ligands. Disilane **2b** showed TBP geometry around its two silicon atoms with parallel apical bonds in the crystalline state, providing the first example of such a structure which was often observed in binuclear transition metal carboxylate complexes. It is significant as the first example of silicon compounds showing a bridging structure reminiscent of the binuclear transition metal complexes despite the absence of the contribution of the

d orbitals for construction of such a structure. The dynamic behavior of **2a** in solution indicated a bridging structure so weak that it was in equilibrium with the tetrahedral, noncoordinated structure in solution. The use of such a μ²-bridging ligand with interactions stronger than those described here would be valuable for designing polysilanes and oligosilanes with high-coordinate silicon atoms with a fixed chain conformation.

Acknowledgment. This work was supported by Grants-in-Aid from the Saijiro Endo Foundation (Y.N.) and from the Ministry of Education, Culture, Sports, Science and Technology, Japan, for The 21st Century COE Program for Frontiers in Fundamental Chemistry (T.K.) and for Scientific Research No. 15105001 (T.K.). We thank Shin-etsu Chemical Co., Ltd and Tosoh Finechemical Corp. for the gifts of silicon compounds and alkyllithiums, respectively.

Supporting Information Available: Details of synthetic procedures of **1** and **2a** and theoretical calculation of **3** and **4** (PDF). X-ray crystallographic files in CIF format for **1** and **2b**·C₆H₆. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050321P