other structurally characterized derivatives of **1**[4,12] and are believed to be nucleophilic charge transfer interactions.[13]

The novel[3] dicoordinate cationic environment for arsenic is stabilized by a number of factors,[4,14] including the delocalized, 10π-electron, naphthalenic framework, which necessitates the employment of As–S $4p\pi$–$3p\pi$ and As–N $4p\pi$–$2p\pi$ bonding. As such, compound **1e** represents the first structural evidence of As–S $p\pi$-bonding and indicates energetic competition with As–N $p\pi$-bonding.[15] Template **1** is now available for the generalization and diversification of $p\pi$–$p\pi$ bonding between the heavier elements of the p-block and emphasizes the importance of isolobal[16] relationships in rationalizing nonmetal chemistry.

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Registry No. **1e**($AlCl_4$), 119998-84-4; **2**, 119998-85-5; $AlCl_3$, 7446-70-0; $AsCl_3$, 7784-34-1; *o*-aminothiophenol, 137-07-5.

Supplementary Material Available: Crystal structure experimental details, unit cell packing diagrams, and tables of atomic positional parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and planes (10 pages); table of observed and calculated structure factors for $C_6H_5NSAs^+AlCl_4^-$ (17 pages). Ordering information is given on any current masthead page.

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Preparation and X-ray Crystal Structure of the First Pentacoordinate Silylsilicates[1]

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Received December 16, 1988

We wish to report herein the first synthesis and characterization of pentacoordinate silylsilicates in which a hitherto unknown type of a silicon–silicon σ bond is involved. Cleavage of the silicon–silicon bond of disilanes by nucleophiles like alkoxide and fluoride ions[2] has been well documented and often used as a method of preparing synthetically useful silyl anions. Pentacoordinate silylsilicates are implicitly postulated as key intermediates in these reactions. Very recently, Damrauer et al.[3] have reported detection of a silylsilicate by a gas-phase mass spectroscopic method, while Gordon et al.[4] have derived the pessimistic conclusion about the actual existence of such species from the ab initio MO calculation.

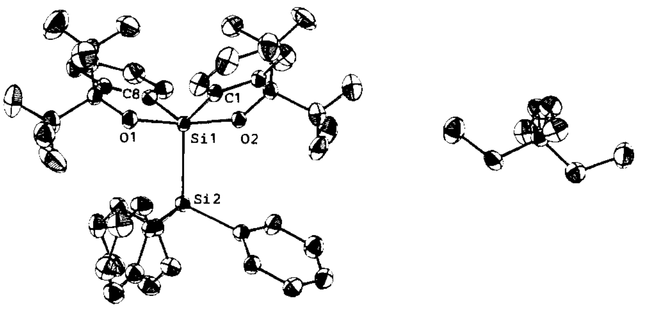
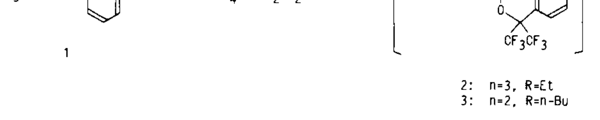


Figure 1. ORTEP drawing of pentacoordinate silylsilicate **2**. Selected bond distances (Å) and angles (deg) are as follows: Si1–Si2 = 2.403 (3), Si1–O1 = 1.831 (5), Si1–O2 = 1.838 (5), Si1–C1 = 1.903 (7), Si1–C8 = 1.899 (7); Si2–Si1–O1 = 94.3 (1), Si2–Si1–O2 = 93.6 (1), Si2–Si1–C1 = 114.1 (2), Si2–Si1–C8 = 118.8 (2), O1–Si1–O2 = 171.8 (2), O1–Si1–C1 = 93.2 (2), O1–Si1–C8 = 84.7 (2), O2–Si1–C1 = 84.6 (2), O2–Si1–C8 = 90.1 (2), C1–Si1–C8 = 126.9 (3).

Tetraethylammonium bis(α,α-bis(trifluoromethyl)benzenemethanolato(2–)C^2,O)(triphenylsilyl)silicate (**2**) and tetrabutylammonium bis(α,α-bis(trifluoromethyl)benzenemethanolato-(2–)C^2,O)(diphenylmethylsilyl)silicate (**3**) were prepared by the reaction of bis(α,α-bis(trifluoromethyl)benzenemethanolato-(2–)C^2,O)silane (**1**)[8] with 2 equiv of triphenylsilyl- or diphenylmethylsilyllithium in THF at room temperature, in 82% and 84% yields, respectively.[9]

On the other hand, (dimethylphenylsilyl)silicate could not be obtained by the reaction of **1** and (dimethylphenylsilyl)lithium under similar conditions. Substituents on the tetrahedral silicon atom could have a significant role on the stabilization of silylsilicates.



2: n=3, R=Et
3: n=2, R=n-Bu

(1)

The structures of **2** and **3** were confirmed by means of NMR and negative-ion FAB MS.[9] The structure of **2** was further elucidated by X-ray analysis of the single crystals.[10] The ORTEP

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(1) Chemistry of Organosilicon Compounds. 255.

(2) (a) Sakurai, H.; Okada, A.; Kira, M; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511. (b) Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, *92*, C46. (c) Watanabe, H; Higuchi, K.; Kobayashi, M.; Hara, M.; Koike, Y.; Kitahara, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 534. (d) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912.

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(9) Triphenylsilyllithium (3 mmol) in 5 mL of THF was added dropwise to **1** (1.5 mmol) in 3.2 mL of diethyl ether at 0 °C under argon. After 30 min kept at 0 °C, the mixture was stirred for 20 h at room temperature. The mixture was quenched with 2.5 mL of 6 M HCl at –60 °C and stirred for 30 min at room temperature. The solvent was removed, and tetraethylammonium bromide (1.875 mmol) in CH_2Cl_2 (25 mL) was added. After stirring for 30 min at room temperature, the mixture was extracted with water and dried over $MgSO_4$. Solvent removal gave yellow oil, which was crystallized from pentane–diethyl ether. The resulting solid was purified by recrystallization from THF–diethyl ether to give pure **2** in 82% yield. **2**: white crystals, mp 184–186 °C dec; ^1H NMR (acetone-d_6) δ 8.3–8.2 (m, 2), 7.7–6.9 (m, 21), 3.44 (q, J = 7.3 Hz, 8), 1.35 (tt, J = 7.3, 1.7 Hz, 12); ^{19}F NMR (acetone-d_6) δ –68.1 (q, J = 10.3 Hz), –69.2 (q, J = 10.3 Hz); negative-ion FAB MS m/e –771 (anion). Similar cation exchange of the crude lithium (diphenylmethylsilyl)silicate (1.5 mmol) with tetrabutylammonium bromide, followed by recrystallization from CH_2Cl_2–diethyl ether, gave white crystals of **3** in 84% yield. **3**: white crystals, mp 168–172 °C dec; ^1H NMR ($CDCl_3$) δ 8.4–8.0 (m, 2), 7.7–6.9 (m, 16), 2.8 (br t, J = 8 Hz, 8), 2.0–0.8 (m, 28), 0.37 (s, 3); ^{19}F NMR ($CDCl_3$) δ –73.4 (q, J = 9 Hz), –75.2 (q, J = 9 Hz); ^{29}Si NMR ($CDCl_3$) δ –21.8, –71.3; negative-ion FAB MS m/e –709 (anion).

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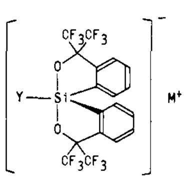
drawing of the molecular geometry of **2** is shown in Figure 1, together with the selected bond distances and angles.

In contrast to the prediction from the ab initio results, **2** had a rather normal trigonal-bipyramidal (TBP) structure around the pentacoordinate silicon atom, where the triphenylsilyl group occupied the equatorial position: the distance of the silicon-silicon bond was 240.3 ppm, which was unexpectedly normal in comparison to the usual Si(sp^3)–Si(sp^3) bonds.[11] Martin et al. have already reported the X-ray analyses of the fluoro- (**4**)[12] and phenyl- (**5**)[13] substituted silicates having the same residual ligand as **2**.



4: Y=F, $M^+=(Me_2N)_3S^+$
5: Y=Ph, $M^+=Me_4N^+$
6: Y=n-Bu, $M^+=Et_4N^+$

Electronegative equatorial ligands should effectively render the silicon atom more electronegative in nature and therefore decrease the atomic radius to result in shortening of the Si–O bonds.[13] In accord with this argument, **2** with an electropositive silyl ligand showed the longest distance of Si–O bonds among **2**, **4**, and **5**. Unexpectedly, the Si–C bond lengths of **2** were even shorter than those of **4** and **5**.

Interestingly, among the known spirobicyclic silicates, **2** has the highest TBP character of the geometry around the pentacoordinate silicon atom (78.2% of TBP character measured by using the dihedral angle method employing unit vectors[14]). The TBP character may depend on the electronic nature of ligands. Further investigation is required for elucidating the relationship as well as its origin.

In the UV spectra, absorption maxima of **2** and **3** appeared at 252 nm (ϵ 17 400, dichloromethane) and 254 nm (ϵ 8800, diethyl ether), respectively. It is clear that the existence of the Si–Si σ bond is responsible for the absorption, because the related pentacoordinate butylsilicate **6**[13] did not show the absorption maxima longer than 200 nm. Both **2** and **3** showed the absorption maxima at longer wavelength than tetracoordinate phenyldisilanes (240 nm for 1,1,2,2-tetraphenyldimethyldisilane and 247 nm for hexaphenyldisilane).[15] The results are suggestive of the high-lying Si–Si σ bonding orbital in the pentacoordinate silylsilicates, because the ^1L_a electronic transition of the phenyldisilanes has been regarded essentially to be the transition from the Si–Si σ bonding orbital to the phenyl π^* orbital.[16]

Further works are in progress.

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Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond distances and angles, and anisotropic temperature factors (9 pages); listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Isolation and Characterization of 1,2-Dilithio[tetrakis(trimethylsilyl)]ethane. The First Crystal Structure of Nonconjugated 1,2-Dilithioethane[1]

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Recently we have reported unusual chemical and physical properties of tetrakis(trimethylsilyl)ethylene (**1**) due to σ(Si–C)–π mixing resulting from the distorted nonplanar structure in the ground state.[2] An interesting feature of **1** is that a cation radical was readily generated upon oxidation with aluminum trichloride, and also an anion radical and subsequently a dianion were formed by reduction with alkali metals. The existence of the dianion **2** of **1** has been indicated only in solution, though. We now wish to report herein synthesis and characterization of 1,2-dilithio[tetrakis(trimethylsilyl)]ethane, the first stable alkyl-substituted 1,2-dilithioethane derivative as well as its chemical reactions.

The renewed interest in the reactivity, structure, and bonding of organolithium compounds has remarkably increased in recent years.[3] Dilithioalkanes such as 1,3-dilithiopropane, 1,4-dilithiobutane, and higher α,ω-dilithioalkanes are available by the direct lithiation of dihaloalkanes[4] or transmetallations.[5] The structure of dilithium trimethyl[(phenylsulfonyl)methyl]silane, the first 1,1-dilithiomethane derivative, is also demonstrated very recently.[6] Although 1,2-dilithioethane has been briefly described as a black-gray amorphous substance[7] or as a reaction intermediate,[8] the structural proof is ambiguous.

Reduction of **1** (162 mg, 0.51 mmol) with excess lithium metal (ca. 70 mg) in dry-oxygen free THF (10–15 mL) at room temperature under argon at first gives a dark green solution of the anion radical of **1** (λ_{max} 697 nm). Further reduction of the anion radical leads to a dark red solution of the dianion with long tailing of the absorption into a visible region. Reduction to the dianion completes within a few hours. The resulting mixture was filtered, the solvent was removed in vacuo, and then dry degassed hexane was introduced by vacuum transfer. Crystallization at −10 °C in hexane afforded yellow crystals of the tetrahydrofuran adduct

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(10) Crystal data of **2** [$C_{44}H_{43}F_{12}NO_2Si_2$ (fw 901.7)] are as follows: monoclinic space group *Aa*; $a = 19.142$ (2) Å, $b = 18.263$ (2) Å, $c = 12.514$ (1) Å; $\beta = 105.03$ (1); $V = 4225.0$ (9) Å^3; $D_{calcd} = 1.41$ g/cm^3 ($Z = 4$). A total of 3659 independent reflections were collected on a Rigaku AFC-5R diffractometer using graphite monochromated Mo- Kα radiation. The final *R* factor was 0.047 for 2792 reflections with $F_o > 3\sigma(F_o)$.

(11) The Si–Si bond orbital would formally be described by the overlap between an sp^3 orbital on the tetragonal Si atom and an sp^2 orbital on the pentacoordinate Si atom. The detailed feature of the Si–Si bonding may be obtained by elucidating the molecular orbitals. Studies along this line are in progress.

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