

Steric Hindrance in Pentacoordinated Fluorosilicates. Synthesis and Molecular Structure of the Diphenyl-1-naphthyldifluorosilicate Anion and the Phenylmethyltrifluorosilicate Anion^{1,2}

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New pentacoordinated anionic silicate derivatives, as salts of phenylmethyltrifluorosilicate, [PhMeSiF₃][N(*n*-Bu)₄] (1) and [PhMeSiF₃][NEt₄], and the tris(dimethylamino)sulfonium salt of diphenyl-1-naphthyldifluorosilicate, [Ph₂(1-Np)SiF₂][S(NMe₂)₃] (2), were synthesized. The X-ray crystal structures of 1 and 2 were obtained. The molecular structures are trigonal bipyramidal with fluorine atoms occupying axial positions. The structural data on these and other acyclic five-coordinated anionic silicates are shown to form a series increasing in steric properties in the order SiF₅⁻, PhSiF₄⁻, PhMeSiF₃⁻, Ph₂SiF₂⁻, (1-Np)Ph₂SiF₂⁻, *t*-BuPhSiF₃⁻, and Xyl₂SiF₃⁻ (Xyl = xylyl). The steric effects are reasoned to partly produce the observed increases in axial bond lengths, which are comparable to increases found for equatorial bond lengths. The steric effects are superimposed on changes in electronic effects, i.e., VSEPR terms increasing in the same direction. Bond angle changes over the series show an increase similar to that of the bond length data. As a measure proportional to the steric effect, it is found that the sum of the axial and equatorial angular displacements from the ideal values of 180 and 120°, respectively, increases from 3.1° for SiF₅⁻ to a maximum of 11.8° for the dixylyl anion, Xyl₂SiF₃⁻. The trifluorosilicate 1 crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 9.633 (5) Å, *b* = 16.172 (4) Å, *c* = 17.377 (5) Å, β = 105.85 (3)°, and *Z* = 4. The difluorosilicate 2 crystallizes in the monoclinic space group *C**c* with *a* = 17.449 (4) Å, *b* = 9.005 (1) Å, *c* = 18.822 (3) Å, β = 110.00 (2)°, and *Z* = 4. The final conventional unweighted residuals are 0.064 (1) and 0.057 (2).

Introduction

Only recently have molecular structures of five-coordinated silicon species isoelectronic with phosphoranes been obtained. Schomburg carried out the first precise crystallographic analysis of anionic silicates containing acyclic ligands, i.e., [SiF₅][PhCH₂NMe₃],⁴ [PhSiF₄][Pr₄N],⁵ and [Ph₂SiF₃][Me₄N].⁴ The structures of the anions are, as expected, trigonal bipyramidal with fluorine atoms occupying axial sites. Damrauer and co-workers⁶ showed that the ¹⁹F NMR spectra of the 18-crown-6 potassium salts of Ph₂SiF₃⁻ and PhMeSiF₃⁻ exhibit a temperature dependence indicative of intramolecular ligand exchange with structures in the slow-exchange region consistent with that deduced from the above X-ray work. Earlier Klanberg and Muetterties⁷ observed dynamic NMR behavior of salts of the anions SiF₅⁻ and RSiF₄⁻ (R = alkyl, aryl), suggesting rapid intramolecular exchange and, in the case of Ph₂SiF₃⁻, the appearance of two fluorine environments at reduced temperatures, but they did not establish an exchange mechanism in this case. Also consistent with a trigonal-bipyramidal structure are the matrix isolation studies by Ault, who identified the existence of cesium salts of SiF₅⁻⁸ and MeSiF₄⁻⁹ from infrared spectral data.

We have explored the structural variations encountered when cyclic ligands are utilized.¹⁰⁻¹⁵ By altering the number and type

of cyclic substituents attached to silicon, we found a continuous range of structures from near trigonal bipyramidal (TBP) to square or rectangular pyramidal (RP) by X-ray analysis. The criterion here as with other pentacoordinated main-group elements¹⁵⁻¹⁷ is that the idealized RP geometry is approached when two unsaturated five-membered rings are present with like atoms in any one ring directly bonded to the central atom. The distortion coordinate followed is along the Berry pseudorotational pathway.¹⁷ Presumably, this is the process occurring in solution for derivatives exhibiting ligand-exchange phenomena.

The present work concentrates effort on additional five-coordinated derivatives of silicon containing acyclic ligands. We report the synthesis and crystal structures of [PhMeSiF₃][N(*n*-Bu)₄] (1) and [Ph₂(1-Np)SiF₂][S(NMe₂)₃] (2). The Δ*G*[‡] of activation for fluorine exchange in the anion of the former substance has been reported as 9.9 kcal/mol.⁶ The X-ray structural analysis of the latter compound represents the first study of an anionic five-coordinated silicon derivative having three Si-C bonds. As a result of this work, trends in bond parameters in the series SiF₅⁻, RSiF₄⁻, R₂SiF₃⁻, and R₃SiF₂⁻, useful for theoretical investigations, are revealed.

Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer R12 spectrometer and are referenced to tetramethylsilane. The samples were dissolved in either CD₃CN or CCl₄. The chemical shifts are reported in ppm. Compounds listed under preparations a and b were prepared by following a procedure of Sommer et al.¹⁸ on related compounds. Preparation c follows a synthesis reported by Gilman et al.,¹⁹ while preparation d is modified from a U.S. Patent report.²⁰ All of the compounds reported in this paper are new derivatives.

Preparations. (a) **Diphenylmethoxy-1-naphthylsilane, Ph₂(1-Np)-SiOMe.**¹⁸ A Grignard reagent was prepared from 1-bromonaphthalene (83 g, 400 mmol) (Aldrich) and magnesium (9.7 g, 400 mmol) in a solvent mixture of ether/THF/benzene (27:13:40 mL). After this mixture was refluxed for 2 h, dimethoxydiphenylsilane (98 g, 400 mmol) (Petrarch) was added dropwise. The resulting mixture was refluxed overnight and then treated with cold aqueous ammonium chloride, washed with water, and dried over sodium sulfate. The solvent was removed by distillation and the remaining solid recrystallized from heptane: mp 97-99 °C; yield 110.2 g, 81%. ¹H NMR in CCl₄ solution (δ):

- (1) Pentacoordinated Molecules. 69. Part 68: Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1987**, *26*, 163.
- (2) Presented in part at the XXth Organosilicon Symposium, Union Carbide Corp., Tarrytown, NY, April 18-19, 1986, and in part at the Xth International Conference on Phosphorus Chemistry, Bonn, FRG, Aug 31-Sept 6, 1986.
- (3) This work represents portions of the Ph.D. theses of J.J.H. and J.S.P., University of Massachusetts, Amherst, MA.
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- (8) Ault, B. S. *Inorg. Chem.* **1979**, *18*, 3339.
- (9) Ault, B. S.; Tandoc, U. *Inorg. Chem.* **1981**, *20*, 1937.
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- (11) Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984**, *3*, 341.
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3.56 (s, OCH₃, 3 H), 7.2 (m, 10 H), 7.75 (m, 7 H). Anal. Calcd for C₂₃H₂₀OSi: C, 81.1; H, 5.9. Found: C, 80.3; H, 5.9.

(b) **Diphenyl-1-naphthylsilane, 1-NpPh₂SiH**.¹⁸ To a suspension of lithium aluminum hydride (5.65 g, 3.7 equiv) (Aldrich) in diethyl ether (65 mL) was added diphenylmethoxy-1-naphthylsilane (45.5 g, 121 mmol) in dibutyl ether. The diethyl ether was distilled away and the reaction mixture heated to 80–90 °C overnight. The mixture was then treated with ice and concentrated hydrochloric acid. The organic layer was separated and dried over sodium sulfate, and the solvent was removed by distillation. The remaining solid was recrystallized from heptane: mp 88.5–90 °C; yield 31.2 g, 83.3%. ¹H NMR in CCl₄ solution (δ): 5.93 (s, SiH, 1 H), 7.49 (m, 17 H). Anal. Calcd for C₂₂H₁₈Si: C, 85.1; H, 5.8. Found: C, 84.9; H, 5.9.

(c) **(Dimethylamino)diphenyl-1-naphthylsilane, Ph₂(1-Np)SiNMe₂**.¹⁹ *n*-Butyllithium (2.5 M in hexane, 6.2 g, 97 mmol) (Aldrich) was added dropwise to dimethylamine (4.5 g, 100 mmol) (Matheson) with stirring at 0 °C. To this was added dropwise a solution of diphenyl-1-naphthylsilane (30.23 g, 97 mmol) in diethyl ether (150 mL). The mixture was stirred for 1/2 h and filtered. The solvent was removed by distillation and the solid recrystallized from pentane: mp 69–70 °C; yield 29.6 g, 86%. ¹H NMR in CCl₄ solution (δ): 2.51 (s, NCH₃, 6 H), 7.25 (m, 17 H). Anal. Calcd for C₂₃H₂₃NSi: C, 81.53; H, 6.56; N, 3.96. Found: C, 81.31; H, 6.83; N, 3.94.

(d) **Tris(dimethylamino)sulfonium Salt of Diphenyl-1-naphthyl-difluorosilicate, [Ph₂(1-Np)SiF₂][S(NMe₂)₃]** (2).²⁰ Ph₂(1-Np)SiNMe₂ (29.2 g, 82 mmol) in diethyl ether (100 mL) was added slowly to a stirred mixture of sulfur tetrafluoride (2.97 g, 27 mmol) (Matheson) in ether (30 mL) at –78 °C. The mixture was allowed to warm to room temperature and stirred for 3 days. The white solid was filtered from solution under a nitrogen blanket and dried in vacuo.

The crude product was extracted with acetonitrile to separate the desired pentacoordinated product from the side product. After evaporation of the solvent, the resulting solid was recrystallized from acetonitrile/ether (1:2): mp 91–92 °C; yield 9.71 g, 69%. ¹H NMR in CD₃CN (δ): 2.78 (s, NCH₃, 18 H), 7.25 (m, 10 H), 7.65 (m, 3 H), 8.25 (m, 4 H). Anal. Calcd for C₂₈H₃₅F₂N₃SSi: C, 65.71; H, 6.89; N, 8.21. Found: C, 65.54; H, 6.90; N, 8.17.

(e) **Methylphenyldifluorosilane, MePhSiF₂**. Methylphenyldimethoxysilane (40.2 g, 221 mmol) (Petrarch) was added to a solution of boron trifluoride etherate (20.9 g, 147 mmol) (Aldrich) in 30 mL of diethyl ether. The solution was stirred under a positive pressure of nitrogen at room temperature for 48 h. Distillation of the mixture yielded the desired compound: bp 141–144 °C (757 mm) (lit.²¹ bp 141 °C (730 mm)); yield 32.7 g, 94%. ¹H NMR in CD₃CN/Me₄Si (δ): 7.55 (m, 2 H, ortho protons of Ph), 7.15 (m, 3 H, meta and para protons of Ph), 0.40 (t, 3 H).

(f) **Tetraethylammonium Methylphenyltrifluorosilicate, [PhMeSiF₃][Et₄N]**. To a solution of tetraethylammonium fluoride hydrate (4.8 g, 26 mmol) (Aldrich) and 20 mL of acetonitrile was added 4.1 g (26 mmol) of methylphenyldifluorosilane. The solution was stirred under nitrogen for 4 h. Filtration and subsequent volume reduction of the filtrate by vacuum left a viscous liquid. Crystals were obtained by cooling the liquid to –15 °C. Recrystallization was accomplished from methylene chloride: mp 82–84 °C; yield 6.7 g, 84%. ¹H NMR in CD₃CN/Me₄Si (300 MHz) (δ): 7.75 (m, 2 H, ortho protons of Ph), 7.18 (m, 3 H, meta and para protons of Ph), 3.00 (q, 8 H, CH₂), 1.06 (m, 12 H), 0.012 (s, 3 H). Anal. Calcd for C₁₅H₂₅F₃NSi: C, 58.92; H, 9.18; N, 4.56. Found: C, 57.49; H, 9.06; N, 4.53.

(g) **Tetrabutylammonium Methylphenyltrifluorosilicate, [PhMeSiF₃][N(*n*-Bu)₄]** (1). To a solution of 1.55 g (4.91 mmol) of *n*-Bu₄NF·3H₂O (Aldrich) in 10 mL of methylene chloride was added MePhSiF₂ (0.95 g, 6.0 mmol). The solution was stirred for 12 h under a positive pressure of nitrogen. Filtration of the solution and reduction of the filtrate volume yielded a viscous material, which upon cooling at –15 °C yielded large white crystals: mp 62–64 °C; yield 1.8 g, 91%. Anal. Calcd for C₂₃H₄₄F₃NSi: C, 65.82; H, 10.57; N, 3.34. Found: C, 64.46; H, 9.96; N, 3.29.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.²² Crystals were mounted inside thin-walled glass capillary tubes that were then sealed as a precaution against moisture sensitivity.

X-ray Crystallographic Study for 1. The irregular colorless crystal used for the X-ray study was cut from a polycrystalline mass and had

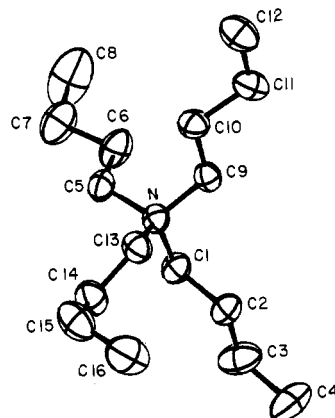
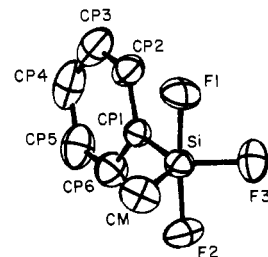


Figure 1. ORTEP plot of [PhMeSiF₃][N(*n*-Bu)₄] (1) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for purposes of clarity.

approximate dimensions of 0.30 × 0.38 × 0.50 mm.

Crystal Data: [PhMeSiF₃][N(*n*-Bu)₄] (1), monoclinic space group *P*₂₁/*c* (*C*_{2h}-No. 14),²³ *a* = 9.633 (5) Å, *b* = 16.172 (4) Å, *c* = 17.377 (5) Å, $\beta = 105.85$ (3)°, *Z* = 4, $\mu_{\text{MoK}\alpha} = 0.124$ mm⁻¹. A total of 2977 independent reflections (+*h*, +*k*, ±*l*) were measured by using the θ - 2θ scan mode for $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 43^\circ$. No corrections were made for absorption.

The structure was solved by using a combination of direct methods (MULTAN) and Fourier difference techniques and was refined by using full-matrix least-squares analyses.²⁴ The 28 independent non-hydrogen atoms were refined anisotropically. The 29 independent aromatic and methylene hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Only six of the independent methyl group hydrogen atoms could be located on a difference Fourier (those on CM and C12), and these were also included in the refinement as fixed isotropic scatterers. The final agreement factors²⁵ were *R* = 0.064 and *R*_w = 0.080 for the 1694 reflections having *I* ≥ 2 σ _{*I*}.

X-ray Crystallographic Study for 2. The colorless crystal used for the X-ray study was cut from a crystalline chunk that was extracted from a gooey residue and had approximate dimensions of 0.25 × 0.33 × 0.45 mm. Conditions for data collection, solution, and refinement were the same as described for 1 unless otherwise noted.

Crystal Data: [Ph₂(1-Np)SiF₂][S(NMe₂)₃] (2), monoclinic space group *Cc* (*C*_s-No. 9),²⁶ *a* = 17.449 (4) Å, *b* = 9.005 (1) Å, *c* = 18.822 (3) Å, $\beta = 110.00$ (2)°, *Z* = 4, $\mu_{\text{MoK}\alpha} = 0.196$ mm⁻¹. A total of 2541 independent reflections were measured for $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 50^\circ$. No corrections were made for absorption.

The 35 independent non-hydrogen atoms were refined anisotropically. The 17 independent aromatic hydrogen atoms were treated as described for 1. The methyl hydrogen atoms of the cation were omitted from the refinement. The final agreement factors²⁵ were *R* = 0.057 and *R*_w =

(23) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(24) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_f$. Mean atomic scattering factors and the real and imaginary dispersion corrections for Si, S, and F were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98, 149, 150.

(25) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. For 2, these values are for the configuration having the lowest *R*_w.

(26) Reference 23, p 89.

(21) Marans, N. S.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1951**, *73*, 5127.

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Table I. Atom Coordinates in Crystalline $[\text{PhMeSiF}_3][\text{N}(n\text{-Bu})_4]$ (1)^a

atom ^b	coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
Si	3707 (2)	8947 (1)	1795 (1)
F1	4315 (4)	9486 (2)	1111 (2)
F2	3024 (4)	8370 (2)	2416 (2)
F3	2654 (4)	8453 (3)	1050 (2)
CM	5534 (8)	8533 (5)	2244 (4)
CP1	3031 (6)	9927 (4)	2153 (4)
CP2	2991 (7)	10676 (5)	1757 (4)
CP3	2557 (9)	11403 (6)	2030 (7)
CP4	2137 (10)	11418 (7)	2713 (8)
CP5	2115 (10)	10696 (7)	3124 (5)
CP6	2572 (8)	9958 (5)	2838 (5)
N	2555 (5)	8451 (3)	8727 (3)
C1	1418 (6)	8037 (4)	9059 (4)
C2	1120 (7)	7141 (4)	8836 (4)
C3	13 (8)	6801 (5)	9241 (5)
C4	-360 (10)	5894 (5)	9048 (6)
C5	2800 (7)	9324 (4)	9065 (4)
C6	1555 (8)	9904 (4)	8774 (5)
C7	1852 (9)	10721 (5)	9209 (5)
C8	733 (10)	11374 (6)	8869 (8)
C9	2054 (6)	8455 (4)	7824 (3)
C10	3042 (7)	8877 (4)	7410 (4)
C11	2401 (8)	8833 (4)	6507 (4)
C12	3392 (9)	9216 (5)	6073 (4)
C13	3990 (7)	7955 (4)	8968 (4)
C14	4579 (8)	7762 (4)	9840 (4)
C15	6009 (8)	7282 (6)	9988 (4)
C16	5883 (11)	6404 (5)	9671 (5)

^aNumbers in parentheses are estimated standard deviations.^bAtoms are labeled to agree with Figure 1.**Table II.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[\text{PhMeSiF}_3][\text{N}(n\text{-Bu})_4]$ (1)^a

Bond Lengths			
Si-F1 ^b	1.701 (4)	Si-CP1	1.882 (7)
Si-F2	1.689 (4)	Si-CM	1.845 (7)
Si-F3	1.621 (4)		
Bond Angles			
F1-Si-F2	175.6 (2)	F2-Si-F3	88.3 (2)
CP1-Si-CM	122.8 (3)	F1-Si-CP1	90.9 (3)
F3-Si-CP1	118.8 (2)	F2-Si-CP1	91.4 (3)
F3-Si-CM	118.4 (3)	F1-Si-CM	90.6 (3)
F1-Si-F3	87.4 (2)	F2-Si-CM	91.3 (3)

^aNumbers in parentheses are estimated standard deviations.^bAtoms are labeled to agree with Figure 1.0.074 for the 1861 reflections having $I \geq 2\sigma_I$.

Results

The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 1, while atomic coordinates and selected bond lengths and angles are given in Tables I and II. The corresponding information for **2** is given in Figure 2 and in Tables III and IV. Thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from selected least-squares mean planes for both **1** and **2** are provided as supplementary material.

Discussion

Basic Structures. Compound **1** represents the first dicarbon-substituted trifluorosilicate having an aliphatic substituent for which a crystal structure has been reported, and compound **2** represents the first X-ray analysis of a tricarbon-substituted pentacoordinated silicate. The molecular geometry about the silicon atom for both **1** and **2** is essentially trigonal bipyramidal with the more electronegative fluorine atoms occupying axial positions, as would be expected. Angular deviations from the idealized trigonal-bipyramidal geometry for **1** are slight and are probably dictated primarily by intramolecular repulsions. Angular distortions for **2** are more pronounced. As discussed below, they are attributable partly to increased steric crowding around silicon.

Table III. Atomic Coordinates in Crystalline $[\text{Ph}_2(1\text{-Np})\text{SiF}_2][\text{S}(\text{NMe}_2)_3]$ (2)^a

atom ^b	coordinates		
	10 ⁴ x	10 ⁴ y	10 ⁴ z
Si	6335 (1)	6844 (2)	1192 (2)
S	9110 ^c	6197 (2)	2640 ^c
F1	7201 (2)	6053 (4)	1117 (2)
F2	5466 (2)	7546 (5)	1305 (3)
CA1	6603 (4)	8736 (8)	878 (4)
CA2	7280 (5)	8945 (8)	657 (5)
CA3	7469 (5)	10359 (10)	438 (5)
CA4	6985 (6)	11551 (9)	434 (5)
CA5	6307 (6)	11372 (9)	628 (5)
CA6	6124 (5)	9983 (8)	846 (5)
CB1	5663 (4)	5533 (7)	432 (4)
CB2	4910 (4)	5079 (8)	405 (4)
CB3	4431 (6)	4157 (10)	-146 (6)
CB4	4679 (6)	3724 (10)	-736 (5)
CB5	5410 (5)	4185 (9)	-756 (5)
CB6	5902 (4)	5083 (8)	-175 (5)
CN1	6732 (4)	6472 (8)	2264 (4)
CN2	6780 (5)	7640 (9)	2728 (4)
CN3	7100 (5)	7530 (10)	3527 (6)
CN4	7341 (5)	6169 (10)	3841 (6)
CN5	7533 (5)	3510 (10)	3757 (5)
CN6	7496 (5)	2286 (10)	3341 (5)
CN7	7221 (5)	2365 (8)	2527 (5)
CN8	6985 (4)	3749 (8)	2180 (4)
CN9	7007 (4)	5030 (8)	2613 (4)
CN10	7296 (4)	4911 (9)	3421 (5)
N1	9433 (4)	5042 (9)	2108 (4)
N2	9314 (5)	7758 (9)	2322 (5)
N3	9747 (4)	5776 (10)	3478 (4)
C1	9035 (6)	5299 (16)	1293 (6)
C2	9365 (8)	3411 (11)	2342 (9)
C3	8815 (7)	9053 (11)	2429 (7)
C4	10113 (7)	8116 (17)	2297 (8)
C5	9483 (6)	6165 (14)	4114 (6)
C6	10621 (6)	5596 (17)	3671 (7)

^aNumbers in parentheses are estimated standard deviations.^bAtoms are labeled to agree with Figure 2. ^cFixed.**Table IV.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[\text{Ph}_2(1\text{-Np})\text{SiF}_2][\text{S}(\text{NMe}_2)_3]$ (2)^a

Bond Lengths			
Si-F1 ^b	1.720 (4)	Si-CA1	1.915 (7)
Si-F2	1.720 (4)	Si-CB1	1.915 (7)
Si-CN1	1.925 (7)		
Bond Angles			
F1-Si-F2	176.4 (2)	F2-Si-CN1	87.2 (2)
CB1-Si-CN1	125.8 (3)	F1-Si-CB1	90.8 (2)
CB1-Si-CA1	118.0 (3)	F2-Si-CB1	88.8 (2)
CN1-Si-CA1	116.1 (3)	F1-Si-CA1	91.6 (2)
F1-Si-CN1	90.1 (2)	F2-Si-CA1	91.7 (3)

^aNumbers in parentheses are estimated standard deviations.^bAtoms are labeled to agree with Figure 2.

In the case of **1**, the steric requirements of the phenyl and methyl groups are larger than those of the fluorine atoms, and distortions away from the idealized geometry reflect this. For the equatorial angles, the angle between the phenyl and methyl group is enlarged (CP1-Si-CM = 122.8 (3)°), while the C-Si-F_{eq} angles are both decreased from the ideal value (118.4 (3) and 118.8 (2)°). For the equatorial-axial angles, the C-Si-F_{ax} angles range from 90.6 (3) to 91.4 (3)°, while the F_{ax}-Si-F_{eq} angles are both smaller than 90° (87.4 (2) and 88.3 (2)°). Even in the presence of these distortions, there are some short F_{ax}-H distances that, in part, reflect the large dihedral angle between the plane of the phenyl group and the equatorial plane (78.2°): HP2-F1 = 2.23 Å; HP6-F2 = 2.26 Å; HM3-F2 = 2.37 Å. The corresponding dihedral angle in $[\text{Ph}_2\text{SiF}_3][\text{NMe}_4]$ is 75°.⁴

In contrast, the molecular geometry about the silicon atom in **2** lies on the coordinate connecting a trigonal bipyramid with axial fluorine atoms to a rectangular pyramid having CA1 in the apical

Table V. Axial and Equatorial Bond Lengths (Å) and Angles (deg) for Trigonal-Bipyramidal Fluorosilicates

	SiF ₅ ⁻	PhSiF ₄ ⁻	PhMeSiF ₃ ⁻	Ph ₂ SiF ₃ ⁻	1-NpPh ₂ SiF ₂ ⁻	<i>t</i> -BuPhSiF ₃ ⁻	Xyl ₂ SiF ₃ ⁻
ref	4	5	this work	4	this work	28b	28a
Si-F _{ax}	1.646	1.668	1.689	1.688	1.720	1.682	1.703
Si-F _{eq}	1.579	1.597	1.621	1.648		1.718	1.725
Si-Ph	1.602	1.604	1.621	1.648		1.639	1.652
Si-Ph		1.871	1.882	1.893	1.915	1.902	1.919
			1.845 ^f		1.925 ^d	1.897 ^e	1.925
F _{ax} -Si-F _{ax} ^b	179.4		184.4	187.6			184.3
F _{ax} -Si-F _{ax} ^c		174.6			176.4	171.9	
F _{eq} -Si-F _{eq}	117.5	121.4				124.3 ^h	
C _{eq} -Si-C _{eq}			122.8	118.9	125.8 ^d		127.5
Δ ^e	3.1	6.8	7.2	8.7	9.4		11.8

^aSi-C bond length to the naphthyl group. ^bThese axial F-Si-F angles are for angles that are on the side of the axial atoms opposite the pivotal equatorial fluorine atoms (labeled 1 in Figure 5). ^cThese axial F-Si-F angles are for angles that are on the side of the axial atoms opposite the pivotal equatorial phenyl group. ^dThis is the 1-Np-Si-Ph bond angle opening up in a Berry type ligand displacement. See Figure 5 caption relative to the diagram contained therein. ^eΔ represents the sum of axial and equatorial bond angle displacements from the values of 180 and 120°, respectively, for the ideal TBP structure. The angles used are shown in the diagrams in Figure 5. ^fSi-CH₃ bond length. ^gSi-*t*-Bu bond length. ^hF_{eq}-Si-C_{eq} bond angle.

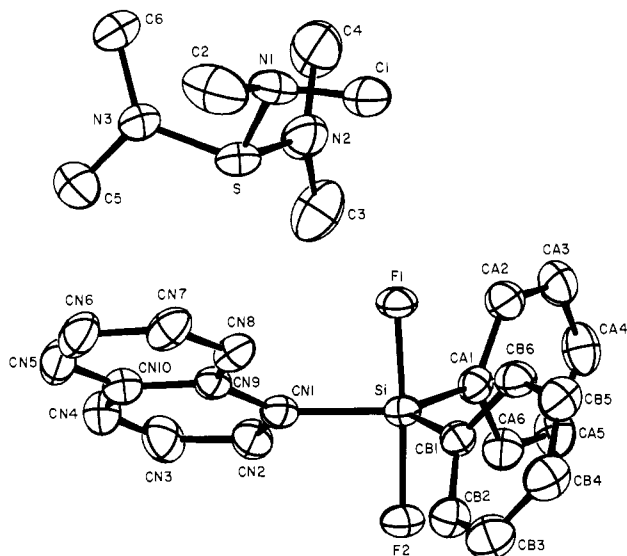


Figure 2. ORTEP plot of [Ph₂(1-Np)SiF₂][S(NMe₂)₃] (**2**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for purposes of clarity.

position. Using the dihedral angle method²⁷ (with unit vectors) to access displacement, we find **2** is displaced 14.1% from the TBP toward the RP structure. The steric requirements of the three equatorial substituents could easily cause such a distortion.

The naphthyl ligand is rotated 34.8° from the equatorial plane, while the adjacent phenyl ring containing CB1 is rotated 58.4° from this plane. Steric crowding between these two groups reasonably accounts for the opening of the angle between them to 125.8 (3)°. The remaining "pivotal" phenyl group is nearly vertical, having a dihedral angle relative to the equatorial plane of 87.2°. This positioning of the aromatic substituents no doubt is dictated by a minimization of steric interactions. There are several short intramolecular H-F distances involving ortho hydrogen atoms of the phenyl substituents or the peri hydrogen atom of the naphthyl substituent: HA2-F1 = 2.27 Å; HA6-F2 = 2.23 Å; HB2-F2 = 2.34 Å; HB6-F1 = 2.44 Å; HN8-F1 = 2.43 Å.

It is of interest to compare the bond parameters for **1** and **2** to those of known structures. For the series of anions [SiF₅]⁻, [PhSiF₄]⁻, and [Ph₂SiF₃]⁻, it was observed⁴ that the replacement of one fluorine atom by a phenyl group resulted in a significant lengthening of only the axial Si-F bond, while the replacement of two fluorine atoms by phenyl groups caused both the axial and equatorial Si-F bond lengths to increase by about the same amount. With the availability of the present data on **1** and **2** and

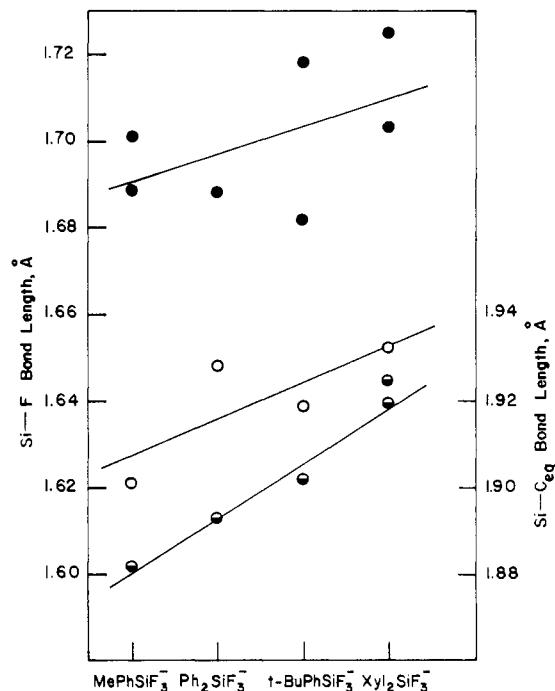


Figure 3. Variations in silicon-ligand bond lengths for the series of pentacoordinated anionic fluorosilicates R₂SiF₃⁻. The filled circles refer to axial Si-F bond lengths (left scale), the unfilled circles refer to equatorial Si-F bonds (left scale), and the half-filled circles refer to equatorial Si-C bond lengths (right scale).

preliminary X-ray studies of the 18-crown-6 potassium salts of dioxyltrifluorosilicate [Xyl₂SiF₃][C₁₂H₂₄O₆K]^{28a} and [*t*-BuPhSiF₃][C₁₂H₂₄O₆K]^{28b} a better perspective is achieved.

Table V summarizes the bond parameter data on the series of acyclic five-coordinated silicates. Trends in bond lengths in the series R₂SiF₃⁻ and R_nSiF_{5-n}⁻ are shown separately in Figures 3 and 4, respectively. Least-squares lines are drawn through the points for each graph. It is seen that there is a general increase in both the axial and equatorial bond lengths, Si-F_{ax}, Si-F_{eq}, and Si-C_{eq}(aryl), and the rate of increase over this series is nearly the same for all of these bond types within each series. This contrasts with that observed for the isoelectronic methylfluorophosphoranes Me_nPF_{5-n} (n = 0 → 3) studied by electron diffraction.²⁹ In this

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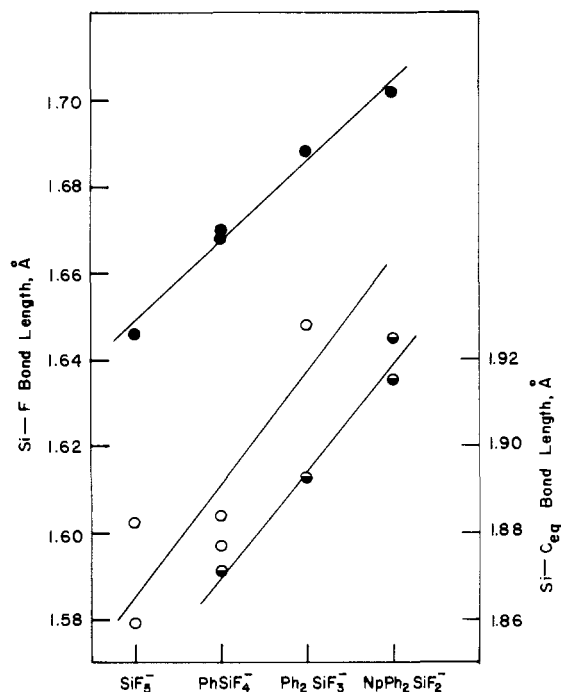


Figure 4. Variations in silicon-ligand bond lengths for a series of pentacoordinated anionic fluorosilicates undergoing increasing fluorine atom substitution. The filled circles refer to axial Si-F bond lengths (left scale), the unfilled circles refer to equatorial Si-F bonds (left scale), and the half-filled circles refer to equatorial Si-C bond lengths (right scale).

series, a much more modest increase in the P-F equatorial bond took place (0.019 Å from PF_5 to Me_2PF_3) compared to the increase for the P-F axial bond (0.066 Å from PF_5 to Me_2PF_3). The equatorial P-C bond length increases 0.033 Å from MePF_4 to Me_3PF_2 whereas the axial P-F bond length undergoes an increase of 0.073 Å over this same series change.

The relative rate of bond length change found by Oberhammer³⁰ in the recent gas-phase electron diffraction study of the phosphorus chlorofluorides³¹ $\text{Cl}_n\text{PF}_{5-n}$ is even less than the rate of change that exists in the $\text{Me}_n\text{PF}_{5-n}$ series. The axial P-F bond length increases 0.016 Å from PF_5 to Cl_2PF_3 , while the equatorial P-F bond length only suffers a 0.004 Å increase, within the statistical error of the experiment. From ClPF_4 to Cl_3PF_2 , the axial P-F bond length increases 0.015 Å, while again the equatorial P-Cl length increases hardly a significant amount, 0.005 Å. In this series, the more modest bond length changes are consistent with that expected from fluorine substitution by chlorine atoms, which are much closer in electronegativity to fluorine than to methyl groups. However, the sizes of the methyl and chlorine ligands are close to one another, so the comparative study of these two series illustrates directly bond length variations due to electronegativity changes.

The variations in the bond parameters for the methylfluorophosphoranes have been interpreted in terms of expectations from valence shell electron pair repulsions by Gillespie.³² While electron pair repulsions may partly rationalize the present trends, the substitutions along the silicon series contain more complex groups than methyl and moreover these are solid-state, not gas-phase, studies. Lattice effects are apparent in the SiF_5^- anion, for example, which exhibits two equatorial Si-F bond lengths (1.579 (2) and 1.602 (2) Å). However, we feel an overriding steric effect in the silicon series $\text{R}_n\text{SiF}_{5-n}^-$ in Figure 3, increasing as bond lengths increase, is an important factor in accounting for the differences in bond length variations between this and the phosphorane series. Steric crowding between equatorial aryl and alkyl groups as these groups replace fluorine atoms should result in increased bond

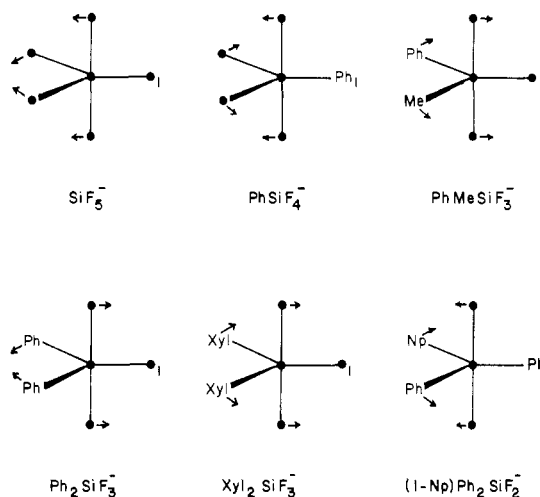


Figure 5. Angle-bending displacements from ideal trigonal-bipyramidal values for the series $\text{R}_n\text{SiF}_{5-n}^-$. The ligand atom displacements represent Berry angle type for PhSiF_4^- , *t*-Bu PhSiF_3^- , and $(1\text{-Np})\text{Ph}_2\text{SiF}_2^-$, anti-Berry angle displacements for $\text{Ph}_2\text{SiF}_3^-$, and non-Berry angle displacements for the others. Groups labeled 1 are pivotal ligands. For *t*-Bu PhSiF_3^- (not shown), the *tert*-butyl group is the pivotal ligand.

lengths. This effect added to the increase in bond electron pair repulsions due to replacement of equatorial fluorine atoms by substituents of reduced electronegativity in the series $\text{R}_n\text{SiF}_{5-n}^-$ in Figure 4 provides an additional factor accelerating increases in bond lengths not found in the $\text{Me}_n\text{PF}_{5-n}$ series. On this basis, one can rationalize the greater rate of bond length increases along the series in Figure 4 compared to that for the series in Figure 3.

The electronegativity effects and hence the bond electron pair repulsion terms should be relatively constant in the disubstituted series that consists of the four members, PhMeSiF_3^- , $\text{Ph}_2\text{SiF}_3^-$, *t*-Bu PhSiF_3^- , and $\text{Xyl}_2\text{SiF}_3^-$, in Figure 3. Hence, more confidence may be assumed in ascribing the increase in axial and equatorial bond lengths over this series to reflect increases in steric terms.

The changes in bond angles along the silicon series (Table V) bear out the steric argument. For each of the compounds, the axial fluorine atoms tilt away from the equatorial ligand or ligands providing the most steric effect (Figure 5). For the first five derivatives shown in Figure 5, the tilt from linearity is toward the remaining equatorial fluorine atoms. For the more highly substituted difluoro compound, the axial fluorine atoms tilt away from the pivotal phenyl group. The latter is oriented almost in the axial plane. Preferential steric relief is achieved in this derivative, as was noted earlier, by an opening of the remaining phenyl-Si-naphthyl equatorial angle to 125.8 (3)°. Both the naphthyl derivative and PhSiF_4^- follow the Berry exchange coordinate,³³ an angle-bending process that helps to relieve incipient steric crowding.²⁷ Steric effects are in evidence also in the dixylyl-substituted fluorosilicate. The equatorial angle between the xyl groups, 127.5°, is the largest in the series. The extent of lattice effects can be gauged by the angular deviation of the equatorial angles from 120° in the SiF_5^- anion. This amounts to 2.5° as measured by the $\text{F}_{\text{eq}}\text{-Si-F}_{\text{eq}}$ angle opposite the fluorine atom labeled as the pivotal one in Figure 5. As noted in Table V, changes in the axial and equatorial angles complement each other to some degree. This most likely is associated with the relief of steric and VSEPR effects. In terms of bond angle variations, a measure of the increase in these terms along the series toward the xyl derivative is obtained by summing in each case the equatorial and axial angle deviations from the 120 and 180° angles, respectively, that are present in the ideal TBP structure. Starting with SiF_5^- and proceeding along the series in Table V, these are 3.1, 6.8, 7.2, 8.7, 9.4, 12.4, and 11.8°, again showing increasing distortion, with the *tert*-butyl and dixylyl compounds exhibiting the greatest effects.

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The bond parameters made available in this study should prove useful in ascertaining the magnitude of steric and electronic effects for new members as well as an aid in calibrating theoretical investigations. Future papers³⁴ take advantage of this feature.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE85-04737) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

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Registry No. 1, 106568-07-4; 2, 106568-09-6; [PhMeSiF₃][Et₄N], 106568-10-9; Ph₂(1-Np)SiOMe, 106543-90-2; 1-NpPh₂SiH, 100447-84-5; Ph₂(1-Np)SiNMe₂, 106543-91-3; MePhSiF₂, 328-57-4; 1-bromonaphthalene, 90-11-9; dimethoxydiphenylsilane, 6843-66-9; methylphenyldimethoxysilane, 3027-21-2.

Supplementary Material Available: For 1 and 2, respectively, anisotropic thermal parameters (Tables S1 and S4), fixed hydrogen atom parameters (Tables S2 and S5), additional bond lengths and angles (Tables S3 and S6), and deviations from selected least-squares mean planes (Tables S7 and S8) (13 pages); tables of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555

Synthesis and Characterization of *tert*-Butyl(*tert*-butyltellurio)mercury(II)

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The compound (*t*-Bu)₂HgTe(*t*-Bu) was prepared by the reaction of (*t*-Bu)₂HgCl with (*t*-Bu)TeLi in tetrahydrofuran solution at -5 °C. The yellow crystalline light-sensitive solid is stable in an inert atmosphere but decomposes in solution at 20 °C. It gives a strong (M + 1)⁺ peak in the methane chemical ionization mass spectrum. ¹H, ¹³C, ¹²⁵Te, and ¹⁹⁹Hg NMR spectra (toluene, -15 °C) show two distinct *tert*-butyl groups, one type on mercury (δ_{Hg} = -883 vs. dimethylmercury) and one type on tellurium (δ_{Te} = 339 vs. dimethyl telluride), with couplings ¹J_{Te-C} = 390, ¹J_{Hg-C} = 1285, ²J_{Hg-C} = 17, ³J_{Te-C-C-H} = 20, and ³J_{Hg-C-C-H} = 196 Hz. The far-infrared spectrum is interpreted in terms of Hg-Te stretching at 151 cm⁻¹, C-Hg-Te and C-Te-Hg bending at 239 and 224 cm⁻¹, and Te-C and Hg-C stretching at 491 and 511 (shoulder) cm⁻¹. The ultraviolet spectrum (pentane solution) exhibits bands at 365 (shoulder, log ε = 2.6), 295 (shoulder, log ε = 3.6), and 227 nm (log ε = 4.7). Nuclear magnetic resonance, far-infrared, and ultraviolet spectra are also reported for (*t*-Bu)₂Hg and (*n*-Bu)₂Te.

Introduction

Mercury cadmium telluride is an important semiconductor with applications in infrared detection.¹⁻³ Photolysis of a mixture of the organometallic compounds RHgTeR and RCdTeR could produce mercury cadmium telluride. As an initial test of this idea, we prepared (*t*-Bu)₂HgTe(*t*-Bu), the first compound of the type RHgTeR, and demonstrated⁴ that it produces a film of mercury telluride upon photolysis in the gas phase. We report here the synthesis and characterization of the title compound, *tert*-butyl(*tert*-butyltellurio)mercury(II).

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under Ar atmosphere in a fume hood by using Schlenk techniques.⁵ Sample preparation for spectroscopy was done in a Vacuum Atmospheres drybox. Tetrahydrofuran and toluene were distilled from sodium and benzophenone. Pentane was distilled from sodium. Melting points were measured with sealed capillaries and are uncorrected. Infrared spectra were recorded with a Nicolet 60SX Fourier transform infrared spectrophotometer. Solids were examined by diffuse reflectance. Liquid samples for mid-infrared spectra were thin films on CsBr plates. For far-infrared spectra, neat liquids in polyethylene cells with 0.2-mm path length were used. Ultraviolet-visible spectra were measured with a Cary 17D spectrophotometer using Teflon-stoppered cuvettes. To measure the spectrum of (*t*-Bu)₂HgTe(*t*-Bu), the sample compartment was purged with Ar and cooled to 0 °C.

NMR Measurements. Spectra of (*t*-Bu)₂HgTe(*t*-Bu) were recorded on a Nicolet NT-200-WB spectrometer. Saturated samples were prepared with toluene/toluene-*d*₈ (2:1) in serum-capped 12-mm tubes and run at -15 °C. ¹⁹⁹Hg spectra were recorded at 35.84 MHz and referenced to an external solution of HgCl₂ (1.0 M in dimethyl sulfoxide), whose

chemical shift was taken to be -1501.6 ppm relative to neat dimethylmercury at 0 ppm.^{6,7} Positive chemical shifts are downfield of the reference. A 45° pulse and 1.5-s recycle time were employed. ¹²⁵Te spectra were recorded at 63.20 MHz by using a 45° pulse and 3.6-s recycle time. The reference was 1.0 M TeCl₄ in tetrahydrofuran, with a chemical shift taken to be 1725 ppm relative to neat dimethyl telluride at 0 ppm.⁷ Chemical shifts in ¹³C spectra were referenced to the center of the deuterated methyl carbon atom of toluene at 20.4 ppm (relative to tetramethylsilane at 0 ppm). ¹H spectra were referenced to the CHD₂ multiplet of deuteriotoluene at 2.09 ppm. Spectra of other compounds in toluene-*d*₈ were run on an IBM NR-80 spectrometer whose probe temperature was ~39 °C.

***tert*-Butylmercuric Chloride.** To 29 g (107 mmol) of mercuric chloride dissolved in 180 mL of tetrahydrofuran at 0 °C was added 55 mL (88 mmol) of *tert*-butyllithium in pentane (1.6 M from Aldrich), dropwise with stirring over 25 min. After 1 h of additional stirring at 0 °C, the mixture of liquid plus gray solid was treated with 5 mL of water, allowed to settle for 1 h, and decanted in the air through a medium-porosity fritted-glass filter with suction. The filtrate, including solid that precipitated during filtration, was concentrated to dryness under vacuum. The solid residue was fractionated between 300 mL of benzene and 200 mL of water in a separatory funnel. The organic phase was extracted five times with 150-mL portions of water, dried over calcium chloride, filtered, and concentrated to dryness under vacuum. The white residue was crystallized (in the air under dim light) by dissolution in 150 mL of refluxing methanol and slow cooling to -40 °C to give 6.2 g (24%) of white needles. The crude product was crystallized a second time to give material used for further synthesis. An analytical sample was crystallized four times; mp 105.5-108 °C (lit.⁸ mp 117-119 °C dec). Anal. Calcd for C₄H₉HgCl: C, 16.39; H, 3.09; Hg, 68.42; Cl, 12.09. Found: C, 16.42; H, 3.00; Hg, 68.49; Cl, 11.28. The ¹³C and ¹⁹⁹Hg NMR spectra were in good agreement with those in the literature,⁹ with the previously unreported coupling, ³J_{199Hg-1H} = 256 Hz.

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