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Mercury(II) and Methylmercury(II) Complexes of Novel Sterically Hindered Thiolates: ^{13}C and ^{199}Hg NMR Studies and the Crystal and Molecular Structures of [MeHg(SC$_6$H$_2$-2,4,6-Pr$^i_3$)], [Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$], [Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$], and [Hg{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$

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Several series of complexes of the types [MeHg(SR)] and [Hg(SR)$_2$] have been synthesized, where the ligands are members of new classes of sterically hindered thiolates, including (triorganosilyl)methanethiols, 2-(triorganosilyl)benzenethiols, 3-(triorganosilyl)pyridine-2-thiols, and bis(2-mercaptophenyl) derivatives. Detailed ^{1}H, ^{13}C, and ^{199}Hg NMR studies revealed several general trends. The ^{199}Hg chemical shifts moved upfield in the order [MeHg(SR)] < [Hg(SCR'R''R''')$_2$] < [Hg(S–aryl)$_2$] < [Hg(S–pyridyl)$_2$]. For the [MeHg(SR)] series of complexes, ^1J(Hg–C) correlates with $\delta(^{13}$C(methyl)) and with the type of thiolate ligand. Anomalous behavior is observed for oligomeric species. There is only a limited correlation of $\delta(^{199}$Hg) with steric cone angles for a subset of the complexes. Crystal data are as follows. [CH$_3$Hg(SC$_6$H$_2$-2,4,6-Pr$^i_3$)]: triclinic $P\bar{1}$, a = 5.962 (1) Å, b = 9.649 (1) Å, c = 15.951 (2) Å, α = 79.60 (1)°, β = 79.58 (1)°, γ = 84.68 (1)°, V = 886.1 (10) Å^3, Z = 2, D_{calc} = 1.69 g cm^{-3}. Structure solution and refinement based on 2115 reflections (Mo Kα; λ = 0.710 73 Å) converged at R = 0.0497. [Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$]: monoclinic $A2/a$, a = 6.900 (1) Å, b = 12.856 (2) Å, c = 25.974 (5) Å, β = 104.20 (1)°, V = 2234.1 (11) Å^3, Z = 4, D_{calc} = 1.67 g cm^{-3}, 1277 reflections, R = 0.0313. [Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$]: triclinic $P\bar{1}$, a = 9.058 (2) Å, b = 9.982 (2) Å, c = 12.639 (3) Å, α = 82.15 (1)°, β = 71.65 (2)°, γ = 79.98 (2)°, V = 1064.3 (10) Å^3, Z = 2, D_{calc} = 1.77 g cm^{-3}, 3233 reflections, R = 0.0850. [Hg{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$: triclinic $P\bar{1}$, a = 8.680 (2) Å, b = 12.705 (3) Å, c = 15.053 (4) Å, α = 73.94 (2)°, β = 77.56 (2)°, γ = 70.85 (2)°, Z = 2, D_{calc} = 2.12 g cm^{-3}, 1350 reflections, R = 0.0854.

The biological chemistry of mercury is dominated by coordination to cysteine thiolate groups. The high toxicity of mercury to living systems[1] reflects the strong interaction of this metal with cysteine residues,[2] while detoxification of mercury by metallothioneins[3–5] occurs via cysteine complexation and sequestration. Furthermore, mercuric ion induces a bacterial metalloregulatory DNA-binding protein, which exhibits a number of potential cysteinyl sulfur ligating sites[9–11] and has been implicated in mercuric ion reductase and related proteins.[12,13] There is also considerable general interest in the bonding and unusual structural types adopted by metal thiolate complexes.[10–12]

As part of our development of the coordination chemistry of a series of novel sterically hindered thiolates,[14–23] we have in-

Chart I
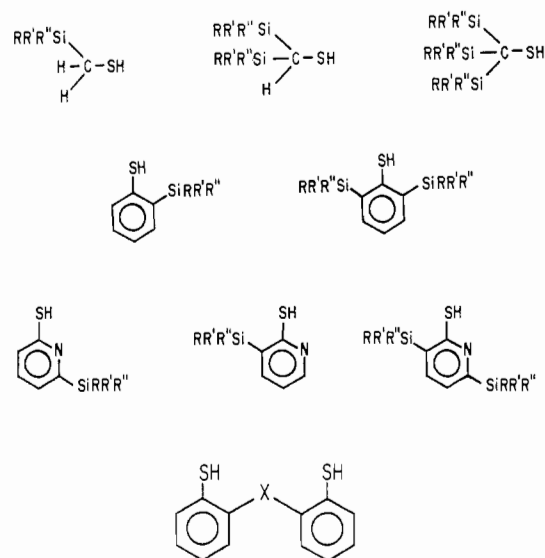
vestigated their complexes with mercury(II) and methylmercury(II), [Hg(SR)$_2$] and [CH$_3$Hg(SR)], respectively. The ligands we have chosen for study include (triorganosilyl)-methanethiols (I), 2-(triorganosilyl)benzenethiols (II), 3-(triorganosilyl)pyridine-2-thiols (III), 6-(triorganosilyl)pyridine-2-thiols (III), 3,6-bis(triorganosilyl)pyridine-2-thiols (III), and bis(2-mercaptophenyl) derivatives (IV), illustrated in Chart I. The silylated thiols represent a new class of hindered ligands with "tunable" steric demands. Variation in the "R" substituent, as well as the number of silyl groups, has been achieved, allowing variation in the steric cone angle of the ligand.[24] In addition, the β-effect of the silicon[25,26] should increase the electron density

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at the sulfur of the (triorganosilyl)methanethiols compared to that in simple alkanethiols. A likely spectroscopic probe for detecting increased steric congestion in [Hg(SR)$_2$] complexes is ^{199}Hg NMR spectroscopy, since the chemical shift should be sensitive to distortions to the limiting digonal coordination geometry induced by steric crowding. Similarly, the carbon–mercury coupling constant, ^1J(C–Hg), in the [CH$_3$Hg(SR)] series of complexes may be correlated with the charge on Hg and thus with the β-effect of silicon in the (triorganosilyl)methanethiolate species.[27]

In this paper we report the synthesis of methylmercury thiolate complexes, [CH$_3$Hg(SR)], and mercury(II) bisthiolate complexes, [Hg(SR)$_2$], with ligand types I–IV. The results of ^{1}H, ^{13}C, and ^{199}Hg NMR studies are reported, and several limited correlations are discussed. The structures of [MeHg(SC$_6$H$_2$-2,4,6-Pr^i$_3$)], [Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$], [Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$], and [Hg-{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$ are also described.

Experimental Section

The ^{1}H NMR spectra were recorded on a Varian EM-360 A and/or Varian XL-300 NMR spectrometer at 60 and 300 MHz, respectively. The ^{13}C and ^{199}Hg NMR spectra were recorded on a Varian XL-300 NMR spectrometer using both 5-mm and 10-mm probes. The standard for proton and carbon NMR spectroscopy was either internal tetramethylsilane or chloroform. The standard for mercury NMR spectroscopy was external 0.1 M dimethylmercury in CDCl$_3$. All ^{199}Hg NMR spectra were run on 0.1 M solutions in CDCl$_3$ at 35 °C. Broad-band Waltz ^{1}H decoupling was employed with all ^{13}C and ^{199}Hg spectra. Relaxation times were measured with a standard inversion–recovery sequence.

The IR spectra were recorded on either a Perkin-Elmer 710B or Perkin-Elmer 1600 series FT spectrometer and were referenced with polystyrene. Mass spectra were recorded on a Hewlett Packard 5070 mass-selective detector interfaced to a Hewlett Packard 5890 gas chromatograph equipped with a 12-m cross-linked phenyl–methyl silicone capillary column. Analytical gas chromatography was done on a 50-m OV-101 fused silica column on a Perkin-Elmer 2B instrument interfaced to a Perkin-Elmer 10B data station. Preparative radial chromatography was carried out on a 7924T Chromatotron (Harrison Research, Palo Alto, CA) using silica gel PF 254 purchased from Merck. X-ray crystallographic studies were performed on a Nicolet R3mV diffractometer. Elemental analyses were performed by either Desert Analytics (Phoenix, AZ) or M-H-W Laboratories (Phoenix, AZ).

Reactions were carried out under an atmosphere of argon. All solvents were dried and purified by standard techniques. Anhydrous tetrahydropyran was purchased from Aldrich and used as is. *n*-Butyllithium was purchased from Aldrich as a solution in hexane, as were most reagents unless otherwise indicated. All silicon reagents were purchased from Petrarch Systems. The (triorganosilyl)methanethiols (I) and 2-(triorganosilyl)benzenethiols (II) were prepared as previously described.[15,19] The (triorganosilyl)pyridine-2-thiols were prepared as described in ref 28. Methylmercury nitrate was prepared by the literature method.[29]

(Benzenethiolato)methylmercury(II) (1). A solution containing methylmercury nitrate (0.138 g, 0.5 mmol), thiophenol (0.055 g, 0.5 mmol), and triethylamine (0.051 g, 0.5 mmol) in methanol (10 mL) was stirred for 2 h at room temperature. The solution was filtered and the filtrate concentrated to about 90% of its original volume. After several days at −20 °C, colorless needles were collected and washed with distilled water to yield 0.270 g (83% yield) of a colorless crystalline product. A modified synthesis of this complex has been reported previously:[30] ^{1}H NMR δ 7.40 (d, 2 H, J = 7.8 Hz), 7.21–7.07 (m, 3 H), 0.91 (s, 3 H); ^{13}C NMR δ 135.22, 133.21, 128.74, 125.33, 12.84; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1127.5 Hz; ^{199}Hg NMR δ −552.6 ($W_{1/2}$ = 16 Hz); ^{199}Hg T_1 = 0.15 s; IR (KBr) 3035, 2920, 1585, 1480, 1090, 1025, 775, 730, 690, 540, 470, 385 cm^{-1}. Anal. Calcd for C$_7$H$_8$SHg: C, 25.9; H, 2.48. Found: C, 26.1; H, 2.47.

[2-(Trimethylsilyl)benzenethiolato]methylmercury(II) (2). A solution containing methylmercury nitrate (0.833 g, 3.0 mmol), 2-(trimethylsilyl)benzenethiol (0.546 g, 3.1 mmol), and triethylamine (0.314 g, 3.1 mmol) in methanol (30 mL) was stirred for 1 h at room temperature.

The resultant solution was filtered and the filtrate kept at −20 °C for several days. A white precipitate was collected and washed with distilled water. After solvent removal at 0.1 mm, 1.035 g (88% yield) of a white powder was obtained: ^{1}H NMR δ 7.44 (dd, 1 H, J = 7.4, 2.1 Hz), 7.43 (dd, 1 H, J = 7.5, 2.1 Hz), 7.16 (ddd, 1 H, J = 7.6, 7.4, 2.1 Hz), 7.10 (ddd, 1 H, J = 7.6, 7.5, 2.1 Hz), 0.89 (s, 3 H), 0.41 (s, 9 H); ^{13}C NMR δ 143.82, 141.87, 135.41, 134.56, 128.98, 124.90, 12.80, 0.25; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1104.5 Hz; ^{199}Hg NMR δ −565.5 ($W_{1/2}$ = 17 Hz); ^{199}Hg T_1 = 0.10 s; IR (KBr) 3040, 2940, 2900, 1570, 1555, 1450, 1415, 1250, 1160, 1110, 1035, 840, 750, 720, 670, 615, 530, 440, 335 cm^{-1}. Anal. Calcd for C$_{10}$H$_{16}$SiSHg: C, 30.3; H, 4.06. Found: C, 30.4; H, 4.17.

[4-(*tert*-Butyl)-2-(trimethylsilyl)benzenethiolato]methylmercury(II) (3). A solution containing methylmercury chloride (1.4 g, 5.57 mmol) and 4-(*tert*-butyl)-2-(trimethylsilyl)benzenethiol (1.33 g, 5.57 mol) in 1/1 methanol/acetonitrile (v/v, 20 mL) was stirred for 10 min at room temperature. Upon addition of triethylamine (0.566 g, 5.60 mmol) a white precipitate formed immediately. After 10 h of stirring at room temperature, the solid was collected by filtration and washed with distilled water and methanol. Solvent removal at 0.1 mm yielded 2.49 g (98% yield) of a white powder: ^{1}H NMR δ 7.48 (d, 1 H, J = 2.4 Hz), 7.36 (d, 1 H, J = 8.0 Hz), 7.18 (dd, 1 H, J = 8.0, 2.4 Hz), 1.28 (s, 9 H), 0.87 (s, 3 H), 0.42 (s, 9 H); ^{13}C NMR δ 147.55, 143.04, 138.04, 134.43, 132.33, 126.22, 34.34, 31.56, 12.83, 0.34; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1092.1 Hz; ^{199}Hg NMR δ −565.8 ($W_{1/2}$ = 20 Hz); IR (KBr) 3060, 2940, 1440, 1375, 1360, 1240, 1160, 1155, 1130, 1105, 1060, 870, 840, 760, 680, 620, 595, 540, 445, 330 cm^{-1}. Anal. Calcd for C$_{14}$H$_{24}$SSiHg: C, 37.1; H, 5.34. Found: C, 37.5; H, 5.65.

[2-(Triethylsilyl)benzenethiolato]methylmercury(II) (4). A solution containing methylmercury nitrate (0.083 g, 0.3 mmol), 2-(triethylsilyl)benzenethiol (0.067 g, 0.3 mmol), and triethylamine (0.030 g, 0.3 mmol) in methanol (5 mL) was stirred at room temperature for 3 h. The resultant solution was concentrated to 3 mL and stored at −20 °C for 3 days. Colorless block crystals were collected by filtration and washed with distilled water. Solvent removal at 0.1 mm yielded 0.061 g (49% yield) of a colorless crystalline product: ^{1}H NMR δ 7.73–7.20 (m, 4 H), 1.07 (s, 15 H), 0.90 (s, 3 H); ^{13}C NMR δ 142.10, 141.06, 136.62, 134.66, 128.73, 124.70, 12.76, 7.81, 4.05; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1096.4 Hz; IR (KBr) 3040, 2940, 2870, 1575, 1560, 1450, 1410, 1235, 1185, 1100, 1040, 1000, 735, 590, 540 cm^{-1}. Anal. Calcd for C$_{13}$H$_{22}$SiSHg: C, 35.6; H, 5.05. Found: C, 35.3; H, 5.12.

[2-(Triphenylsilyl)benzenethiolato]methylmercury(II) (5). A solution containing methylmercury chloride (0.61 g, 2.43 mmol), 2-(triphenylsilyl)benzenethiol (0.895 g, 2.43 mmol), and triethylamine (0.26 g, 2.65 mmol) in 1/1 methanol/acetonitrile (v/v, 20 mL) was stirred at room temperature for 20 h. The white precipitate was collected and washed with distilled water and methanol. Solvent removal at 0.1 mm yielded 0.972 g (69% yield) of a white powder: ^{1}H NMR δ 7.68–7.16 (m, 19 H), 0.87 (s, 3 H); ^{13}C NMR δ 142.49, 139.43, 138.84, 136.35, 135.60, 130.02, 129.20, 127.88, 127.76, 125.55, 12.44; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1088.4 Hz; ^{199}Hg NMR δ −620.6 ($W_{1/2}$ = 33 Hz); IR (KBr) 3070, 3050, 2960, 2920, 1590, 1565, 1480, 1430, 1260, 1250, 1190, 1100, 1040, 1030, 1000, 765, 750, 730, 695, 520, 510, 490, 410, 335 cm^{-1}.

[2,6-Bis(trimethylsilyl)benzenethiolato]methylmercury(II) (6). A solution containing methylmercury chloride (0.969 g, 3.86 mmol), triethylamine (0.389 g, 3.86 mmol), and 2,6-bis(trimethylsilyl)benzenethiol[18] (0.981 g, 3.86 mmol) in methanol (10 mL) was stirred at room temperature for 1 h. The methanol was removed in vacuo and the solid product washed with distilled water and a small amount of methanol. Solvent removal at 0.1 mm yielded 1.52 g (84% yield) of a white powder: ^{1}H NMR δ 7.48 (d, 2 H, J = 7.3 Hz), 7.15 (t, 1 H, J = 7.3 Hz), 0.81 (s, 3 H), 0.44 (s, 18 H); ^{13}C NMR δ 146.94, 146.18, 136.03, 125.14, 12.09, 1.44; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1080.4 Hz; ^{199}Hg NMR δ −592.9 ($W_{1/2}$ = 56 Hz); ^{199}HgT_1 = 0.06 s; IR (KBr) 2950, 1340, 1240, 1185, 1040, 830, 785, 755, 725, 680, 615, 540, 445 cm^{-1}.

[3-(Phenyldimethylsilyl)-2-mercaptopyridinato]methylmercury(II) (7). This compound was prepared as was 6. From methylmercury chloride (0.25 g, 1.0 mmol), triethylamine (0.101 g, 1.0 mmol), and 3-(phenyldimethylsilyl)-2-mercaptopyridine (0.245 g, 1.0 mmol), 0.48 g (87% yield) of a white powder was obtained: ^{1}H NMR δ 8.10 (dd, 1 H, J = 4.8, 2.0 Hz), 7.55 (dd, 2 H, J = 7.6, 2.6 Hz), 7.43 (dd, 1 H, J = 7.3, 2.0 Hz), 7.39–7.33 (m, 3 H), 6.88 (dd, 1 H, J = 7.3, 4.8 Hz), 0.85 (s, 3 H) 0.68 (s, 6 H); ^{13}C NMR δ 171.55, 147.84, 144.05, 137.51, 134.33, 134.07, 129.12, 127.75, 118.73, 10.52, −2.37; J(1 bond, ^{199}Hg–^{13}C) = 1249.6 Hz; ^{199}Hg NMR δ −583.4 ($W_{1/2}$ = 20 Hz); IR (KBr) 3060, 2950, 1550, 1430, 1360, 1250, 1210, 1180, 1135, 1110, 1065, 1040, 820, 775, 740, 700, 660, 640, 540, 480, 440, 385, 350, 315 cm^{-1}. Anal. Calcd for C$_{14}$H$_{17}$NSiSHg: C, 36.6; H, 3.72; N, 3.04. Found: C, 36.7; H, 4.01; N, 3.30.

[6-(*tert*-Butyldimethylsilyl)-2-mercaptopyridinato]methylmercury(II) (8). The procedure is identical with that used to prepare 6. From

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6-(*tert*-butyldimethylsilyl)-2-mercaptopyridine (0.224 g, 1.0 mmol), 0.35 g (80% yield) of a white powder was obtained: ^{1}H NMR δ 7.30 (dd, 1 H, J = 7.9, 7.7 Hz), 7.13 (d, 1 H, J = 7.7 Hz), 7.09 (d, 1 H, J = 7.9 Hz), 0.89 (s, 3 H), 0.86 (s, 9 H), 0.22 (s, 6 H); ^{13}C NMR δ 165.17, 164.87, 134.50, 125.72, 124.52, 26.55, 16.77, 11.30, −6.37; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1251.2 Hz; ^{199}Hg NMR δ −569.9 ($W_{1/2}$ = 27 Hz); ^{199}Hg T_1 = 0.1 s; IR (KBr) 3040, 2940, 1540, 1460, 1415, 1360, 1350, 1245, 1120, 1010, 980, 940, 830, 770, 740, 680, 650, 540, 530, 510, 415, 400, 380, 340 cm^{-1}. Anal. Calcd for C$_{12}$H$_{21}$NSiSHg: C, 32.8; H, 4.81; N, 3.18. Found: C, 33.4; H, 5.15; N, 3.53.

[3,6-Bis(*tert*-butyldimethylsilyl)-2-mercaptopyridinato]methylmercury(II) (9). The procedure is identical with that used to prepare **6**. From 3,6-bis(*tert*-butyldimethylsilyl)-2-mercaptopyridine (1.156 g, 3.41 mmol), 1.250 g (66% yield) of a white powder was obtained: ^{1}H NMR δ 7.47 (d, 1 H, J = 7.4 Hz), 7.10 (d, 1 H, J = 7.4 Hz), 0.94 (s, 9 H), 0.87 (s, 9 H), 0.84 (s, 3 H), 0.39 (s, 6 H), 0.22 (s, 6 H); ^{13}C NMR δ 171.69, 164.47, 142.52, 132.57, 125.14, 27.40, 26.61, 18.39, 16.81, 11.11, −3.62; J(1 bond, ^{199}Hg–^{13}CH$_3$) = 1242.8 Hz; ^{199}Hg NMR δ −563.8 ($W_{1/2}$ = 50 Hz); IR (KBr) 2950, 2860, 1540, 1515, 1470, 1390, 1360, 1290, 1250, 1185, 1165, 1145, 1115, 940, 840, 815, 770, 675, 580, 530, 510, 425, 340 cm^{-1}. Anal. Calcd for C$_{18}$H$_{35}$NSi$_2$SHg: C, 39.0; H, 6.36; N, 2.53. Found: C, 38.8; H, 6.50; N, 2.82.

(2,4,6-Triisopropylbenzenethiolato)methylmercury(II) (10). A solution containing 0.0989 g (0.35 mmol) of methylmercury nitrate and 0.035 g (0.35 mmol) of triethylamine in methanol was slowly added to a solution of 0.083 g (0.35 mmol) of 2,4,6-triisopropylthiophenol in 10 mL of methanol at room temperature. After 2 h of stirring, the resultant solution was filtered, the filtrate was concentrated to ∼5 mL, and 5 mL of acetonitrile was added slowly. The solution was kept at −20 °C for several days. The colorless block-shaped crystals were collected and recrystallized from CH$_3$OH/CH$_3$CN at −20 °C. Yield: 0.066 g (42%). IR (KBr): 3040, 2960, 2870, 1600, 1565, 1460, 1380, 1250, 1180, 1175, 1165, 1105, 1060, 1030, 875, 775, 760, 530, 325 cm^{-1}.

Bis[2-(trimethylsilyl)benzenethiolato]mercury(II) (11). To a solution containing mercuric chloride (0.543 g, 2.0 mmol) and triethylamine (0.202 g, 2.0 mmol) in methanol (5 mL) was added 2-(trimethylsilyl)benzenethiol[8] (0.729 g, 4.0 mmol) in methanol (10 mL). White solid was produced immediately, and the solution was stirred at room temperature for 1 h. The solid was collected by filtration and washed with methanol and distilled water to yield, after solvent removal at 0.1 mm, 0.425 g (38% yield) of a white powder. Recrystallization from warm CH$_2$Cl$_2$/CH$_3$CN afforded colorless crystals of needle habit, which were collected by filtration and dried in air: ^{1}H NMR δ 7.46–7.41 (m, 4 H), 7.17–7.12 (m, 4 H), 0.39 (s, 18 H); ^{13}C NMR δ 143.78, 138.93, 135.54, 135.50, 129.40, 126.08, 0.21; ^{199}Hg NMR δ −1074.6 ($W_{1/2}$ = 16 Hz); IR (KBr) 3040, 2940, 2890, 1575, 1555, 1450, 1415, 1260, 1240, 1160, 1100, 1030, 840, 750, 710, 680, 610, 445, 435, 400, 340 cm^{-1}. Anal. Calcd for C$_{18}$H$_{26}$Si$_2$S$_2$Hg: C, 38.4; H, 4.65. Found: C, 37.9; H, 4.63.

Bis[4-(*tert*-butyl)-2-(trimethylsilyl)benzenethiolato]mercury(II) (12). 12 was prepared as was **11**. Thus, from 4-(*tert*-butyl)-2-(trimethylsilyl)benzenethiol (0.476 g, 2.0 mmol), 0.50 g (75% yield) of a white powder was obtained: ^{1}H NMR δ 7.46 (d, 2 H, J = 2.5 Hz), 7.36 (d, 2 H, J = 8.0 Hz), 7.18 (dd, 2 H, J = 8.0, 2.5 Hz), 1.29 (s, 18 H), 0.39 (s, 18 H); ^{13}C NMR δ 148.81, 143.10, 135.41, 135.31, 132.42, 126.65, 34.47, 31.31, 0.30; ^{199}Hg NMR δ −1072.1 ($W_{1/2}$ = 19 Hz); IR (KBr) 2960, 1480, 1450, 1380, 1245, 1160, 1125, 1030, 875, 840, 760, 680, 620, 595, 440, 340 cm^{-1}. Anal. Calcd for C$_{26}$H$_{42}$Si$_2$S$_2$Hg: C, 46.2; H, 6.27. Found: C, 46.5; H, 6.38.

Bis[2-(triethylsilyl)benzenethiolato]mercury(II) (13). 13 was prepared as was **11**. Thus, from 2-(triethylsilyl)benzenethiol (2.24 g, 10.0 mmol), 3.0 g (92% yield) of white powder was obtained: ^{1}H NMR δ 7.44–7.37 (m, 4 H), 7.17–7.10 (m, 4 H), 0.95–0.92 (m, 30 H); ^{13}C NMR δ 141.07, 139.03, 136.68, 135.61, 129.16, 125.91, 7.74, 4.06; ^{199}Hg NMR δ −1067.83 ($W_{1/2}$ = 21 Hz); IR (KBr) 3040, 2870, 1550, 1445, 1410, 1230, 1100, 1030, 1000, 955, 730, 670, 590, 445, 360, 330 cm^{-1}.

Bis(2,4,6-triisopropylbenzenethiolato)mercury(II) (14). 14 was prepared as was **11**. Thus, from 2,4,6-triisopropylbenzenethiol (2.35 g, 10.0 mmol), 3.1 g (92% yield) of a white powder was obtained: ^{1}H NMR δ 6.95 (s, 4 H), 4.00 (sept, 4 H, J = 6.8 Hz), 2.86 (sept, 2 H, J = 6.8 Hz), 1.23 (d, 12 H, J = 7.7 Hz), 1.14 (d, 24 H, J = 6.8 Hz); ^{13}C NMR δ 151.97, 148.49, 125.61, 121.42, 34.17, 31.95, 24.05, 23.64; ^{199}Hg NMR δ −1079.55 ($W_{1/2}$ = 20 Hz); IR (KBr) 3035, 2860, 1595, 1560, 1450, 1425, 1380, 1360, 1305, 1240, 1155, 1095, 1060, 1025, 935, 920, 880, 760, 635, 525, 350 cm^{-1}.

Bis[3-(trimethylsilyl)-2-mercaptopyridinato]mercury(II) (15). 15 was prepared as was **11**. Thus, from 3-(trimethylsilyl)-2-mercaptopyridine (0.366 g, 2.0 mmol), 0.46 g (82% yield) of a white powder was obtained. Recrystallization from CH$_3$CN/CH$_3$OH afforded colorless crystals of block habit, which were collected by filtration and dried in air: ^{1}H NMR δ 8.06 (dd, 2 H, J = 4.7, 2.0 Hz), 7.55 (dd, 2 H, J = 7.4, 2.0 Hz), 6.94

(dd, 2 H, J = 7.4, 4.7 Hz), 0.40 (s, 18 H); ^{13}C NMR δ 169.45, 147.97, 143.00, 133.73, 119.18, −1.27; ^{199}Hg NMR δ −1133.4 ($W_{1/2}$ = 27 Hz); ^{199}Hg T_1 = 0.05 s; IR (KBr) 3035, 2950, 2900, 1545, 1360, 1250, 1205, 1130, 1070, 1040, 840, 795, 755, 690, 655, 620, 480, 435, 355, 340 cm^{-1}. Anal. Calcd for C$_{16}$H$_{24}$N$_2$Si$_2$S$_2$Hg: C, 34.0; H, 4.28; N, 4.96. Found: C, 34.1; H, 4.41; N, 4.94.

Bis[3-(triethylsilyl)-2-mercaptopyridinato]mercury(II) (16). 16 was prepared as was **11**. Thus, from 3-(triethylsilyl)-2-mercaptopyridine (0.45 g, 2.0 mmol), 0.65 g (89% yield) of a white powder was obtained: ^{1}H NMR δ 8.06 (dd, 2 H, J = 4.8, 2.0 Hz), 7.52 (dd, 2 H, J = 7.3, 2.0 Hz), 6.92 (dd, 2 H, J = 7.3, 4.8 Hz), 1.00–0.95 (m, 30 H); ^{13}C NMR δ 169.84, 147.80, 144.17, 131.15, 118.93, 7.52, 2.83; ^{199}Hg NMR δ −1130.7 ($W_{1/2}$ = 29 Hz); IR (KBr) 3040, 2950, 2875, 1545, 1460, 1420, 1360, 1235, 1200, 1130, 1070, 1000, 725, 600, 390, 350, 320 cm^{-1}. Anal. Calcd for C$_{22}$H$_{36}$N$_2$Si$_2$S$_2$Hg: C, 40.7; H, 5.59; N, 4.31. Found: C, 40.6; H, 5.65; N, 4.16.

Bis[3-(phenyldimethylsilyl)-2-mercaptopyridinato]mercury(II) (17). 17 was prepared as was **11**. Thus, from 3-(phenyldimethylsilyl)-2-mercaptopyridine (0.49 g, 2.0 mmol), 0.61 g (73% yield) of a white powder was obtained: ^{1}H NMR δ 8.05 (dd, 2 H, J = 4.8, 2.0 Hz), 7.58 (dd, 4 H, J = 6.5, 2.6 Hz), 7.45 (dd, 2 H, J = 7.4, 2.0 Hz), 7.42–7.36 (m, 6 H), 6.90 (dd, 2 H, J = 7.4, 4.8 Hz), 0.70 (s, 12 H); ^{13}C NMR δ 169.76, 148.24, 144.20, 137.08, 134.34, 132.11, 129.28, 127.84, 119.08, −2.53; ^{199}Hg NMR δ −1142.0 ($W_{1/2}$ = 65 Hz); IR (KBr) 3050, 2930, 2860, 1550, 1470, 1425, 1365, 1250, 1180, 1140, 1010, 990, 940, 840, 785, 770, 740, 675, 655, 580, 460, 410, 340 cm^{-1}. Anal. Calcd for C$_{26}$H$_{28}$N$_2$Si$_2$S$_2$Hg: C, 45.30; H, 4.09; N, 4.06. Found: C, 45.17; H, 4.16; N, 4.29.

Bis[6-(*tert*-butyldimethylsilyl)-2-mercaptopyridinato]mercury(II) (18). 18 was prepared as was **11**. Thus, from 6-(*tert*-butyldimethylsilyl)-2-mercaptopyridine (0.45 g, 2.0 mmol), 0.55 g (85% yield) of a white powder was obtained: ^{1}H NMR δ 7.32 (dd, 2 H, J = 8.4, 7.0 Hz), 7.19 (dd, 2 H, J = 8.4, 1.9 Hz), 7.14 (dd, 2 H, J = 7.0, 1.9 Hz), 0.81 (s, 18 H), 0.19 (s, 12 H); ^{13}C NMR δ 165.84, 163.74, 134.63, 126.09, 122.18, 26.57, 16.81, −6.38; ^{199}Hg NMR δ −1112.8 ($W_{1/2}$ = 28 Hz); ^{199}Hg T_1 = 0.06 s; IR (KBr) 3040, 2950, 1545, 1430, 1360, 1250, 1200, 1130, 1065, 840, 815, 780, 730, 695, 665, 470, 450, 430, 400, 360 cm^{-1}. Anal. Calcd for C$_{22}$H$_{36}$N$_2$Si$_2$S$_2$Hg: C, 40.7; H, 5.59; N, 4.31. Found: C, 40.9; H, 5.72; N, 4.33.

Bis[3,6-bis(*tert*-butyldimethylsilyl)-2-mercaptopyridinato]mercury(II) (19). 19 was prepared as was **11**. Thus, from 3,6-bis(*tert*-butyldimethylsilyl)-2-mercaptopyridine (0.678 g, 2.0 mmol), 0.85 g (97% yield) of a white powder was obtained: ^{1}H NMR δ 7.45 (d, 2 H, J = 7.3 Hz), 7.10 (d, 2 H, J = 7.3 Hz), 0.96 (s, 18 H), 0.80 (s, 18 H), 0.412 (s, 12 H), 0.175 (s, 12 H); ^{13}C NMR δ 170.63, 165.47, 142.48, 130.57, 125.38, 27.45, 26.65, 18.41, 16.88, −3.80, −6.28; ^{199}Hg NMR δ −1098 ($W_{1/2}$ = 27 Hz).

Bis[bis(2-mercaptophenyl) etherato]mercury(II) (20). A solution containing mercuric chloride (0.27 g, 1.0 mmol), triethylamine (0.202 g, 2.0 mmol), and bis(2-mercaptophenyl) ether (0.234 g, 1.0 mmol) in methanol (15 mL) was stirred at room temperature for 1 h. The solid product, which formed immediately upon mixing of the reagents, was collected by filtration and washed with methanol and distilled water. After solvent removal in vacuo, 0.42 g (87% yield) of a white powder was obtained. The solid contained approximately 1 triethylamine molecule per 2 ligand molecules: ^{1}H NMR δ 7.41 (dd, 2 H, J = 8.1, 2.1 Hz), 6.91–6.78 (m, 8 H), 6.62 (dd, 2 H, J = 7.8, 2.3 Hz), 2.75 (q, approximately 3 H, J = 7.3 Hz), 0.97 (t, approximately 4.5 H, J = 7.3 Hz); ^{13}C NMR δ 155.36, 135.05, 129.61, 125.89, 123.59, 118.71, 46.30, 8.01; ^{199}Hg NMR δ −827.43 ($W_{1/2}$ = 710 Hz). The compound was recrystallized from acetonitrile/methanol to yield a crystalline material that unlike the original powder was insoluble in CDCl$_3$: IR (KBr) 3060, 1715, 1565, 1465, 1440, 1255, 1225, 1160, 1125, 1060, 1040, 880, 800, 750, 670, 460 cm^{-1}. Anal. Calcd for C$_{12}$H$_8$OS$_2$Hg: C, 33.3; H, 1.86. Found: C, 33.2; H, 2.42.

Bis(2,2-dimethylpropanethiolato)mercury(II) (21). To a solution containing mercuric chloride (0.543 g, 2.0 mmol) and triethylamine (0.202 g, 2.0 mmol) in methanol (5 mL) was added 2,2-dimethylpropanethiol (0.416 g, 4.0 mmol) in methanol (10 mL). White solid was produced immediately, and the solution was stirred at room temperature for 1 h. The solid was collected by filtration and washed with methanol and distilled water to yield, after solvent removal at 0.1 mm, 0.41 g (50% yield) of a white powder: ^{1}H NMR δ 3.03 (s, 4 H), 1.01 (s, 18 H); ^{13}C NMR δ 44.27, 32.79; 28.45; ^{199}Hg NMR δ −783.24 ($W_{1/2}$ = 321 Hz); IR (KBr) 2940, 2895, 2860, 1460, 1395, 1365, 1165, 1030, 820, 580, 380, 340 cm^{-1}.

Bis[(trimethylsilyl)methanethiolato]mercury(II) (22). 22 was prepared as was **21**. Thus, from (trimethylsilyl)methanethiol (1.2 g, 10 mmol), 1.8 g (82% yield) of a white solid was obtained: ^{1}H NMR δ 2.17 (s, 4 H), 0.11 (s, 18 H); ^{13}C NMR δ 13.42, −2.08; ^{199}Hg NMR δ −851.25

Table I. Summary of the Crystallographic Data for the Structure Determinations of $[CH_3Hg(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)]$ (10), $[Hg(SC_6H_4\text{-}2\text{-}SiMe_3)_2]$ (11), $[Hg(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ (15), and $[Hg\{(2\text{-}SC_6H_4)_2SiMe_2\}]_2$ (25)

	10	11	15	25
formula	$C_{16}H_{26}SHg$	$C_{18}H_{26}Si_2S_2Hg$	$C_{16}H_{24}N_2Si_2S_2Hg$	$C_{14}H_{14}S_4Si_2Hg_2$
fw	451.02	562.90	565.07	950.12
space group	$P\bar{1}$	$A2/a$	$P\bar{1}$	$P\bar{1}$
a, Å	5.962 (1)	6.900 (1)	9.058 (2)	8.680 (2)
b, Å	9.649 (1)	12.856 (2)	9.982 (2)	12.705 (3)
c, Å	15.951 (2)	25.974 (5)	12.639 (3)	15.053 (4)
α, deg	79.60 (1)	90.00	82.15 (1)	73.94 (2)
β, deg	79.58 (1)	104.20 (1)	71.65 (2)	77.56 (2)
γ, deg	84.68 (1)	90.00	79.98 (2)	70.85 (2)
V, Å^3	886.1 (10)	2234.1 (11)	1064.3 (10)	1492.6 (12)
Z	2	4	2	2
T, K	296	296	263	236
D(calcd), g cm^{-3}	1.69	1.67	1.77	2.12
μ, cm^{-1}	87.8	71.7	86.5	106.2
transm coeff	0.67–0.80	0.73–0.89	0.71–0.94	0.81–0.88
R	0.050	0.031	0.085	0.085
R_w	0.0512	0.032	0.081	0.085

Table II. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors (Å$^2 \times 10^3$) for $[CH_3Hg(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)]$ (10)

atom	x	y	z	U(eq)^a
Hg(1)	1074 (1)	2144 (1)	4543 (1)	68 (1)*
S(1)	1147 (7)	726 (4)	4013 (2)	66 (1)*
C(1)	2883 (45)	3524 (23)	4976 (14)	131 (12)*
C(11)	−208 (19)	1134 (11)	2861 (7)	42 (3)
C(12)	−1239 (20)	2286 (12)	2366 (7)	47 (3)
C(13)	−441 (21)	2564 (13)	1489 (8)	50 (3)
C(14)	1213 (22)	1720 (13)	1066 (8)	55 (3)
C(15)	2140 (24)	574 (15)	1587 (9)	62 (3)
C(16)	1504 (21)	232 (13)	2448 (8)	51 (3)
C(121)	−3065 (21)	3288 (13)	2785 (9)	55 (3)
C(122)	−5088 (26)	3582 (17)	2320 (10)	75 (4)
C(123)	−2021 (27)	4684 (16)	2849 (11)	78 (4)
C(141)	2176 (27)	2002 (17)	73 (11)	77 (4)
C(142)	3788 (37)	3179 (23)	−85 (16)	93 (6)
C(143)	339 (44)	2176 (26)	−429 (16)	106 (8)
C(161)	2613 (26)	−1002 (16)	2962 (11)	74 (4)
C(162)	1945 (38)	−2396 (23)	2826 (15)	92 (6)
C(163)	5235 (55)	−983 (36)	2713 (19)	146 (11)

^{a} Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{eq}$ tensor.

($W_{1/2}$ = 16 Hz); IR (KBr) 2950, 2900, 1405, 1380, 1245, 1130, 840, 750, 690, 640, 370, 298 cm^{-1}.

Bis(di-*tert*-butylmethanethiolato)mercury(II) (23). 23 was prepared as was 21. Thus, from di-*tert*-butylmethanethiol (0.38 g, 2.0 mmol), 0.26 g (49% yield) of a white solid was obtained: ^{1}H NMR δ 3.16 (s, 2 H), 1.17 (s, 36 H); ^{13}C NMR δ 66.20, 38.63, 31.45; ^{199}Hg NMR δ −824.39 ($W_{1/2}$ = 16 Hz); IR (KBr) 2940, 1920, 1465, 1390, 1360, 1255, 1210, 1150, 1070, 1020, 855, 795, 750, 720, 380 cm^{-1}.

Bis[bis(trimethylsilyl)methanethiolato]mercury(II) (24). 24 was prepared as was 21. Thus, from bis(trimethylsilyl)methanethiol (0.573 g, 3.0 mmol), 0.18 g (30% yield) of a white solid was obtained: ^{1}H NMR δ 1.55 (s, 2 H), 0.14 (s, 36 H); ^{13}C NMR δ 13.28, −0.26; ^{199}Hg NMR δ −831.23 ($W_{1/2}$ = 17 Hz); IR (KBr) 2940, 2880, 1400, 1375, 1240, 1125, 1015, 840, 760, 690, 635, 290 cm^{-1}.

[Bis(2-mercaptophenyl)dimethylsilanato]mercury(II) (25). A solution containing mercuric chloride (0.543 g, 2.0 mmol) and bis(2-mercaptophenyl)dimethylsilane (1.104 g, 4.0 mmol, 2-fold excess) in 1/1 acetonitrile/methanol (50 mL, v/v) was stirred at room temperature for 5 min, and then triethylamine (0.83 g, 8.2 mmol) was added. The solution was stirred for 24 h and then concentrated in vacuo to a yellow oil. The oil was dissolved in 10 mL of acetonitrile to which 30 mL of methanol was carefully added. After several days, colorless crystals were collected by filtration and dried in air: IR (KBr) 3050, 2950, 1570, 1550, 1440, 1405, 1250, 1160, 1100, 1030, 830, 810, 745, 670, 630, 510, 450, 435, 350, 340 cm^{-1}. Anal. Calcd for $C_{14}H_{14}SiS_2Hg$: C, 35.4; H, 2.94. Found: C, 35.7; H, 2.84.

X-ray Structure Determinations. Crystals of $[CH_3Hg(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)]$ (10), $[Hg(SC_6H_4\text{-}2\text{-}SiMe_3)_2]$ (11), $[Hg(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ (15) and $[Hg\{(2\text{-}SC_6H_4)_2SiMe_2\}]_2$ (25) were obtained from dichloromethane/acetonitrile or acetonitrile/methanol solution. Intensities were measured on a Nicolet R3mV four-circle diffractometer equipped with

Table III. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors (Å$^2 \times 10^3$) for $[Hg(SC_6H_4\text{-}2\text{-}SiMe_3)_2]$ (11)

	x	y	z	U(eq)^a
Hg	2500	937 (1)	0	50 (1)
S	52 (3)	1102 (2)	483 (1)	54 (1)
Si	−676 (4)	3201 (2)	1167 (1)	58 (1)
C(1)	1452 (10)	1249 (6)	1150 (3)	47 (3)
C(2)	1108 (10)	2114 (6)	1447 (3)	45 (2)
C(3)	2172 (13)	2131 (7)	1992 (3)	64 (3)
C(4)	3526 (13)	1376 (9)	2212 (4)	70 (4)
C(5)	3854 (14)	539 (9)	1914 (4)	74 (4)
C(6)	2765 (13)	452 (8)	1370 (3)	63 (3)
C(7)	91 (20)	3863 (7)	596 (4)	82 (4)
C(8)	−516 (21)	4207 (8)	1707 (5)	90 (5)
C(9)	−3357 (13)	2686 (8)	948 (4)	82 (4)

^{a} Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors (Å$^2 \times 10^3$) for $[Hg(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ (15)

	x	y	z	U(eq)^a
Hg	5910 (1)	−876 (1)	7104 (1)	44 (1)
S(1)	7580 (4)	402 (4)	5677 (3)	51 (1)
S(2)	4231 (5)	−2196 (4)	8481 (3)	51 (1)
Si(1)	8471 (4)	2762 (4)	3483 (3)	44 (1)
Si(2)	2350 (4)	−3223 (4)	11156 (3)	43 (1)
N(1)	4604 (12)	1380 (13)	5972 (9)	48 (4)
N(2)	6291 (11)	−1391 (11)	9242 (9)	41 (4)
C(11)	6084 (14)	1557 (13)	5325 (10)	39 (4)
C(12)	6420 (14)	2598 (12)	4451 (9)	36 (4)
C(13)	5111 (17)	3477 (15)	4269 (13)	51 (6)
C(14)	3602 (16)	3297 (16)	4919 (13)	54 (6)
C(15)	3403 (16)	2250 (15)	5771 (13)	53 (6)
C(16)	9274 (19)	1180 (18)	2727 (13)	67 (7)
C(17)	9785 (17)	3075 (17)	4269 (12)	55 (6)
C(18)	8304 (20)	4279 (17)	2441 (12)	66 (7)
C(21)	4973 (14)	−1969 (12)	9573 (11)	38 (4)
C(22)	4236 (14)	−2421 (12)	10667 (10)	36 (4)
C(23)	4974 (15)	−2254 (13)	11460 (11)	42 (5)
C(24)	6343 (17)	−1680 (16)	11104 (13)	56 (6)
C(25)	6933 (15)	−1247 (14)	10015 (11)	45 (5)
C(26)	717 (20)	−2059 (19)	10818 (19)	85 (9)
C(27)	1859 (26)	−3611 (25)	12732 (15)	97 (10)
C(28)	2640 (18)	−4830 (15)	10490 (13)	53 (6)

^{a} Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

a graphite monochromator, using Mo Kα radiation (λ = 0.71073 Å). The crystallographic data for the structure determinations are given in Table I. Full details of the experimental procedures may be found in ref 31 and in the supplementary material.

(31) Nicholson, T.; Zubieta, J. *Polyhedron* **1988**, *7*, 171.

Table V. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{Å}^2 \times 10^3$) for $[Hg\{(2\text{-}SC_6H_4)_2SiMe_2\}]_2$ (**25**)

	x	y	z	$U(eq)^a$
Hg(1)	5506 (2)	1288 (2)	10757 (2)	42 (2)
Hg(2)	6793 (2)	−48 (2)	13425 (2)	49 (2)
S(1)	5286 (15)	3170 (11)	9915 (16)	49 (11)
S(2)	6006 (13)	−646 (10)	11513 (15)	53 (11)
S(3)	6738 (14)	1730 (10)	12424 (14)	39 (10)
S(4)	7192 (22)	−1733 (12)	14582 (19)	80 (14)
Si(1)	3203 (15)	3454 (11)	8201 (16)	43 (11)
Si(2)	3123 (13)	3449 (10)	13326 (16)	46 (11)
C(1)	3054 (53)	4233 (39)	12150 (55)	42 (13)
C(2)	1631 (55)	4412 (42)	13994 (58)	62 (16)
C(3)	2550 (60)	3380 (46)	7128 (61)	61 (16)
C(4)	2567 (60)	4911 (40)	8389 (59)	66 (16)
C(11)	6367 (31)	2776 (23)	8826 (21)	36 (12)
C(12)	5526	2932	8086	24 (10)
C(13)	6403	2758	7221	52 (14)
C(14)	8120	2428	7095	59 (17)
C(15)	8961	2272	7835	60 (16)
C(16)	8084	2447	8700	28 (11)
C(21)	7494 (32)	−1331 (22)	10695 (25)	34 (12)
C(22)	7815	−2501	10776	29 (11)
C(23)	8959	−3036	10114	56 (16)
C(24)	9781	−2401	9372	47 (14)
C(25)	9460	−1231	9291	63 (16)
C(26)	8316	−696	9952	33 (11)
C(31)	6687 (33)	2461 (25)	13303 (27)	32 (12)
C(32)	5263	3201	13669	34 (12)
C(33)	5347	3776	14315	36 (12)
C(34)	6856	3612	14595	33 (12)
C(35)	8280	2873	14229	65 (17)
C(36)	8195	2297	13583	44 (14)
C(41)	7276 (36)	−1177 (29)	15525 (24)	35 (12)
C(42)	7268	−1967	16379	28 (11)
C(43)	7452	−1692	17178	46 (13)
C(44)	7645	−627	17123	39 (12)
C(45)	7653	163	16270	54 (15)
C(46)	7469	−112	15471	45 (22)

^{a} Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[CH_3Hg(SC_6H_2\text{-}2,4,6\text{-}Pr^i_3)]$ (**10**)

Hg(1)–S(1)	2.344 (4)	Hg(1)–C(1)	2.070 (27)
C(11)–C(16)	1.426 (16)	S(1)–C(11)	1.804 (11)
C(12)–C(121)	1.531 (17)	C(11)–C(12)	1.403 (15)
C(14)–C(15)	1.394 (18)	C(12)–C(13)	1.381 (16)
C(15)–C(16)	1.345 (18)	C(13)–C(14)	1.378 (17)
C(121)–C(122)	1.506 (22)	C(14)–C(141)	1.568 (21)
C(141)–C(142)	1.513 (29)	C(16)–C(161)	1.491 (19)
C(161)–C(162)	1.501 (29)	C(121)–C(123)	1.561 (22)
Hg···S(1a)	3.269 (3)	C(141)–C(143)	1.451 (33)
C(161)–C(163)	1.543 (35)		
S(1)–Hg(1)–C(1)	175.7 (7)	Hg(1)–S(1)–C(11)	102.3 (4)
S(1)–Hg(1)–S(1a)	79.4 (1)	C(1)–Hg(1)–S(1a)	104.2 (6)

Table VII. Selected Bond Lengths (Å) and Angles (deg) for $[Hg(SC_6H_4\text{-}2\text{-}SiMe_3)_2]$ (**11**)

Hg–S	2.349 (2)	Si–C(8)	1.893 (12)
S–C(1)	1.775 (7)	Si–C(9)	1.915 (9)
Si–C(2)	1.887 (7)	Hg···S	3.243 (2)
Si–C(7)	1.893 (12)		
S–Hg–S	169.7 (1)	C(2)–Si–C(8)	107.8 (4)
Hg–S–C(1)	103.9 (3)	C(2)–Si–C(9)	110.5 (4)
S–C(1)–C(2)	119.6 (5)	C(7)–Si–C(8)	107.3 (5)
S–C(1)–C(6)	117.7 (6)	C(7)–Si–C(9)	111.0 (5)
C(2)–C(1)–C(6)	122.5 (7)	C(8)–Si–C(9)	109.4 (6)
C(2)–Si–C(7)	110.7 (5)		

Empirical absorption corrections were applied to the data in each case. Hydrogen atom positions were calculated geometrically, fixed at a C–H distance of 1.08 Å, and not refined. Final positional parameters for the structures of **10**, **11**, **15**, and **25** are given in Tables II–V, respectively. Tables VI–IX provide selected bond length and angle information for the structures.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $[Hg(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2]$ (**15**)

|			
Hg–S(1)	2.345 (2)	Hg···N(1)	2.789 (5)
Hg–S(2)	2.341 (4)	Hg···N(2)	2.799 (5)
S(1)–C(11)	1.749 (13)	S(2)–C(21)	1.769 (16)
Si(1)–C(12)	1.896 (11)	Si(2)–C(22)	1.902 (13)
Si(1)–C(16)	1.874 (18)	Si(2)–C(26)	1.840 (19)
Si(1)–C(17)	1.859 (19)	Si(2)–C(27)	1.899 (18)
Si(1)–C(18)	1.885 (16)	Si(2)–C(28)	1.853 (17)
S(1)–Hg–S(1)	178.0 (2)	Hg–S(1)–C(11)	95.9 (4)
Hg–S(2)–C(2)	95.3 (4)		

Table IX. Selected Bond Lengths (Å) and Angles (deg) for $[Hg\{(2\text{-}SC_6H_4)_2SiMe_2\}]_2$ (**25**)

Hg(1)–S(1)	2.343 (16)	Hg(1)–S(2)	2.343 (14)
Hg(2)–S(4)	2.333 (22)	Hg(2)–S(3)	2.336 (15)
S(2)–C(21)	1.764 (27)	S(1)–C(11)	1.817 (34)
S(4)–C(41)	1.776 (36)	S(3)–C(31)	1.800 (33)
Si(1)–C(4)	1.834 (45)	Si(1)–C(3)	1.858 (81)
Si(2)–C(1)	1.778 (76)	Si(1)–C(12)	1.890 (28)
Si(2)–C(32)	1.938 (31)	Si(2)–C(2)	1.808 (53)
Hg(1)···S(3)	3.176 (18)		

|			
S(2)–Hg(1)–S(1)	174.0 (5)	S(4)–Hg(2)–S(3)	168.3 (6)
C(11)–S(1)–Hg(1)	95.0 (10)	C(21)–S(2)–Hg(1)	102.5 (13)
C(31)–S(3)–Hg(2)	96.8 (15)	C(41)–S(4)–Hg(2)	99.0 (13)
C(4)–Si(1)–C(3)	112.9 (33)	C(12)–Si(1)–C(3)	108.6 (21)
C(12)–Si(1)–C(4)	107.5 (18)	C(2)–Si(2)–C(1)	103.9 (29)
C(32)–Si(2)–C(1)	109.4 (20)	C(32)–Si(2)–C(2)	107.4 (22)
C(12)–C(11)–S(1)	121.4 (11)	C(16)–C(11)–S(1)	118.1 (10)
C(11)–C(12)–Si(1)	121.6 (12)	C(13)–C(12)–Si(1)	118.3 (12)
C(22)–C(21)–S(2)	120.0 (10)	C(26)–C(21)–S(2)	119.9 (10)
C(32)–C(31)–S(3)	123.7 (9)	C(36)–C(31)–S(3)	116.2 (9)
C(31)–C(32)–Si(2)	122.1 (9)	C(33)–C(32)–Si(2)	117.9 (9)
C(42)–C(41)–S(4)	112.9 (14)	C(46)–C(41)–S(4)	126.9 (14)

Results and Discussion

Preparations. The syntheses of the (triorganosilyl)methanethiols and 2-(triorganosilyl)benzenethiols have been described previously.[15,19] The synthesis of the 3-(triorganosilyl)pyridine-2-thiol series exploits the utility of the mercapto group in directing *ortho*-lithiation in carbocyclic and heterocyclic aromatic substrates. In this fashion, the reaction of 2-pyridinethiol with trimethylsilyl chloride in thf with lithium diisopropylamide (LDA) yielded 3-(trimethylsilyl)-2-pyridinethiol (eq 1). Under similar reaction

$$\text{(1)}$$
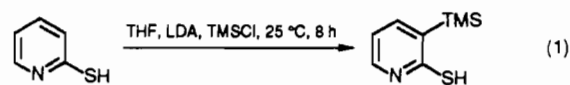
conditions, more hindered chlorosilanes such as *tert*-butyl-chlorodimethylsilane and *tert*-butylchlorodiphenylsilane unexpectedly yielded the previously unknown 3,6-disubstituted 2-pyridinethiols (eq 2). Full details of the synthetic procedures will be described elsewhere.[28]

$$\text{(2)}$$
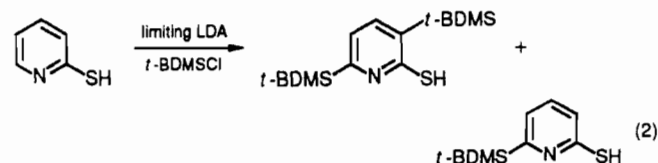
The preparation of methylmercury(II) thiolates and mercury(II) bisthiolate complexes is readily accomplished by mixing a solution of the appropriate mercury salt with the desired thiol in the presence of base (eqs 3 and 4). Since the base serves to buffer

$$\text{(3)}$$

$$\text{(4)}$$
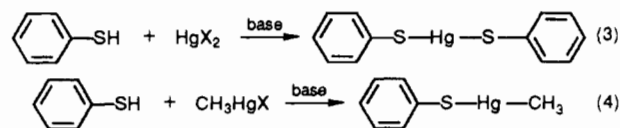
the reaction, as well as to act as a deprotonating reagent, the choice
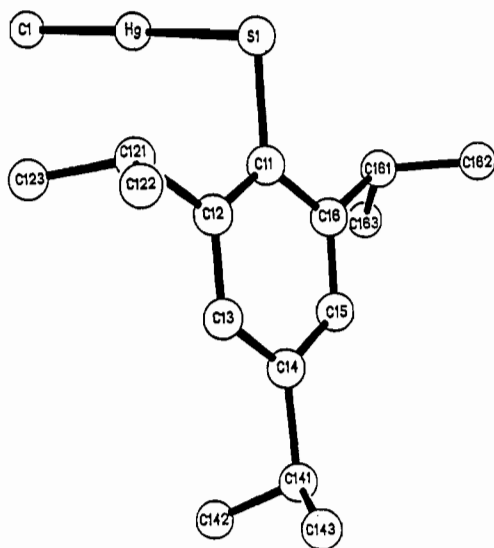
Figure 1. ORTEP view of [MeHg(SC$_6$H$_4$-2,4,6-Pr$^i_3$)], showing the atom-labeling scheme.

of base is critical in preventing the formation of intractable, presumably polymeric materials.

Mercuric acetate, mercuric oxide, and the corresponding methylmercury salts have all been used successfully in the synthesis of mercury thiolate compounds.[32,33] Although tertiary amines, alkali-metal hydroxides, alkali-metal carbonates, and metal oxides have been employed as bases in these syntheses, only triethylamine proved consistently useful in our work. Analytically pure, crystalline materials were isolated for five distinct series of complexes: methylmercury (triorganosilyl)benzenethiolates (compounds **2–6**), methylmercury 3-(triorganosilyl)pyridine-2-thiolates (compounds **7–9**), mercury bis(triorganosilyl)benzenethiolates (compounds **11–14**), mercury bis(triorganosilyl)pyridine-2-thiolates (compounds **15–19**), and mercury bis(triorganosilyl)methanethiolates (compounds **22–24**).

A significant feature of the chemistry of the entire class of complexes **1–24** is their solubility in chloroform at 35 °C, a property conferred by the triorganosilyl substituents, which allowed all NMR studies to be conducted under identical conditions. Since good solubility is generally not a feature of mercury thiolate chemistry, much of the ^{199}Hg NMR data presented to date relies on comparisons between studies in different solvents, a difficult task indeed, in view of marked solvent dependence of ^{199}Hg chemical shifts.[34–37] Furthermore, two examples of mercury complexes of bisthiolate ligands, bis(2-mercaptophenyl) ether and bis(2-mercaptophenyl)dimethylsilane (compounds **20** and **25**, respectively) were synthesized.

We were unable to prepare the methylmercury (triorganosilyl)methanethiolate series of complexes, [CH$_3$Hg(SCRR'R'')], in analytically pure form. Repeated syntheses and crystallizations under a variety of conditions yielded at best white powders contaminated with the amine base and other methylmercury by-products. The NMR parameters for these preparations were clearly unreliable.

The infrared spectra of the methylmercury (2-triorganosilyl)benzenethiolate and methylmercury 3-(triorganosilyl)-pyridine-2-thiolate series of complexes (**2–9**) exhibit bands
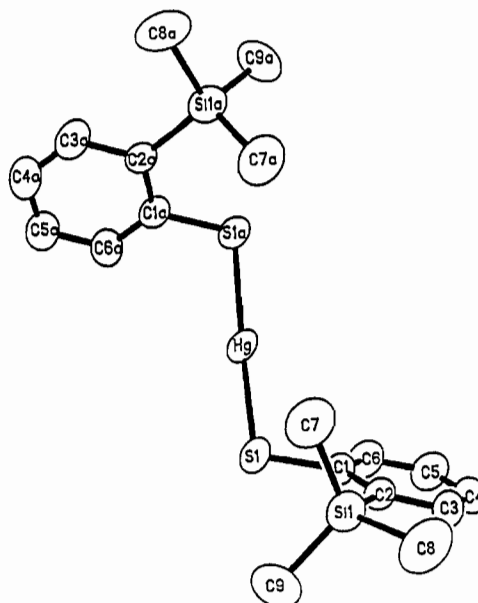
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Figure 2. ORTEP view of [Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$], showing the atom-labeling scheme.
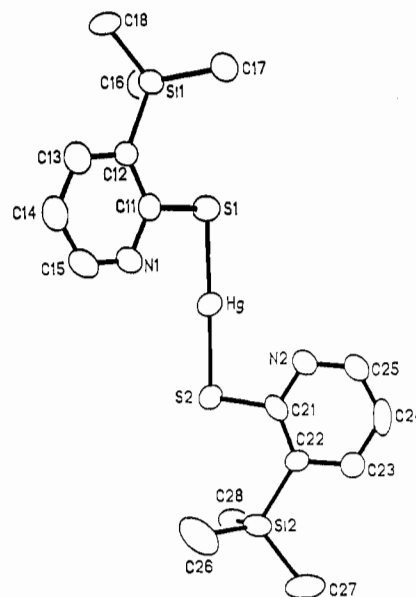
Figure 3. ORTEP view of [Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$], showing the atom-labeling scheme.
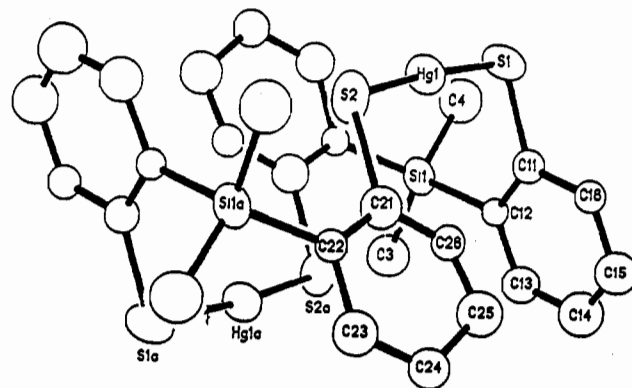
Figure 4. ORTEP view of the binuclear species [Hg{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$.

characteristic of MeHgL species. A medium-intensity feature in the 1170–95-cm^{-1} region is associated with δ_{sym}(CH$_3$), while the 520–550-cm^{-1} region displays a band assigned to ν(Hg–C).[38]

Table X. ^{13}C NMR Spectra (ppm from SiMe$_4$ in CDCl$_3$ as Solvent)

compd	aromatic resonances						other resonances
A. Pyridine-2-thiol Series							
2-MeSC$_5$H$_4$N	159.9	149.3	135.7	121.4	119.0		13.2
2-HSC$_5$H$_3$N-3-SiMe$_3$	181.00	144.55	144.10	137.13	113.57		−1.31
2-HSC$_5$H$_3$N-3-SiEt$_3$	181.35	145.80	141.71	137.02	113.31		7.54, 2.67
2-HSC$_5$H$_3$N-6-SiBu^{t}Me$_2$	180.10	152.49	135.42	134.04	120.73		26.21, 16.87, −7.03
2-HSC$_5$H$_2$N-3,6-(SiBu^{t}Me$_2$)$_2$	184.58	152.52	143.94	142.69	119.84		27.90, 26.24, 18.32
							16.87, −3.80, −7.16
[MeHg(2-SC$_5$H$_4$N)]	165.16	146.60	136.51	125.70	118.97		11.1
[MeHg(2-SC$_5$H$_3$N-6-SiBu^{t}Me$_2$)] (8)	165.17	164.87	134.50	125.72	124.52		26.55, 16.77, 11.30, −6.3
[MeHg(2-SC$_5$H$_2$N-3,6-SiBu^{t}Me$_2$)] (9)	171.69	164.47	142.52	132.57	125.14		27.40, 26.61, 18.39, 16.8, 11.11, −3.62, −6.32
[Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$] (15)	169.45	147.97	143.00	133.73	119.18		−1.27
[Hg(2-SC$_5$H$_3$N-3-SiEt$_3$)$_2$] (16)	169.84	147.84	144.17	131.15	118.93		7.52, 2.83
[Hg(2-S-C$_5$H$_3$N-6-SiBu^{t}Me$_2$)$_2$] (18)	165.84	163.74	134.63	126.90	122.18		26.57, 16.81, −6.38
[Hg(2-SC$_5$H$_2$N-3,6-SiBu^{t}Me$_2$)$_2$] (19)	170.63	165.47	142.41	130.57	125.38		27.45, 26.65, 18.41, 16.8, −3.80, −6.28
B. Benzenethiol Series							
HSC$_6$H$_4$-2-SiMe$_3$	139.21	137.39	135.10	131.52	139.61	125.16	−0.44
HSC$_6$H$_4$-2-SiEt$_3$	137.69	136.59	136.25	131.52	129.49	125.00	7.57, 3.73
HSC$_6$H$_3$-2,6-(SiMe$_3$)$_2$	169.79	143.46	136.16	125.62			0.31
HSC$_6$H$_3$-2,6-(SiEt$_3$)$_2$	142.93	140.29	137.17	125.23			7.73, 4.38
HSC$_6$H$_3$-4-Bu^t-2-SiMe$_3$	147.77	139.38	133.69	132.22	131.89	126.92	34.36, 31.35, −0.20
[MeHg(SC$_6$H$_5$)] (1)	135.22	133.21	128.74	125.33			12.84
[MeHg(SC$_6$H$_4$-2-SiMe$_3$)] (2)	143.82	141.82	135.41	134.46	128.98	124.90	12.80, 0.25
[MeHg(SC$_6$H$_3$-4-Bu^t-2-SiMe$_3$)] (3)	147.55	143.04	138.04	134.43	152.33	126.22	34.34, 31.56, 12.83, 0.34
[MeHg(SC$_6$H$_4$-2-SiEt$_3$)] (4)	142.10	141.06	136.62	134.66	128.73	124.70	12.76, 7.81, 4.05
[MeHg(SC$_6$H$_3$-2,6-SiMe$_3$)] (6)	146.94	146.18	136.07	125.14			12.09, 1.44
[Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$] (11)	143.78	138.93	135.54	135.50	129.40	126.08	0.21
[Hg(SC$_6$H$_3$-4-Bu^t-2-SiMe$_3$)$_2$] (12)	148.87	143.10	135.41	126.65			34.47, 31.31, 0.30
[Hg(SC$_6$H$_4$-2-SiEt$_3$)$_2$] (13)	141.07	139.03	136.68	135.61	129.16	125.91	7.74, 4.06
[Hg{(2-SC$_6$H$_4$)$_2$O}]$_2$ (20)	155.36	135.05	129.61	125.89	123.59	118.71	46.30, 8.01

A medium-intensity band at 320–340 cm^{-1} has been assigned to ν(Hg–S), though it may not be a pure band.[39] In addition, medium-strong bands in the 750–850-cm^{-1} range are typical of ν(Si–C) and are observed for the entire class of organosilyl derivatives, **2–19** and **21–25**.

The bisthiolate series of complexes [Hg(SR)$_2$] display medium-intensity features in the 320–340-cm^{-1} region associated with ν(Hg–S). Other features in the infrared spectra are unexceptional.

Description of the Structures. The structures of [CH$_3$Hg-(SC$_6$H$_2$-2,4,6-Pr$^i_3$)] (**10**), [Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$] (**11**), [Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$] (**15**), and [Hg{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$ (**25**) are illustrated in Figures 1–4, respectively. Bonding parameters are collected in Tables VI–IX.

The S–Hg–C(1) fragment of **10** is essentially linear with a bond angle of 175.7 (7)°. The Hg–S and Hg–C(1) bond lengths are those of covalent single bonds and are within the ranges previously found in other HgMe$^+$ complexes.[33,40–43] In addition, the sulfur atom of one neighboring molecule approaches to 3.269 (3) Å of the Hg, a distance shorter than 3.5 Å, the sum of the van der Waals radii of Hg and S.[44,45] Such secondary interactions are a common feature of the structural chemistry of methylmercury(II) thiolate complexes.

Depending on the nature of the thiolate ligand and the reaction conditions employed in their synthesis, mercury(II) thiolate complexes [Hg(SR)$_n$L$_m$]^x adopt a variety of structures. These include the essentially linear molecular species [Hg(SR)$_2$],[46–48] anionic trigonal-planar complexes [Hg(SR)$_3$]$^-$,[49] tetrahedral homoleptic species [Hg(SC$_6$H$_4$Cl)$_4$]$^{2-}$[50] and mixed-ligand complexes [HgCl$_2$(HSR)$_2$],[48,51] binuclear species [Hg$_2$(SMe)$_6$]$^{2-}$,[52] trinuclear species [Hg$_3$(SCH$_2$CH$_2$S)$_4$]$^{2-}$,[53] adamantane-like cage complexes [Hg$_4$(PPh$_3$)$_4$(SPh)$_6$]$^{2+}$,[54,55] polymeric materials [Hg-(SR)$_2$]$_n$[56] and [XHg(SR)]$_n$,[57] and molecular mixed-ligand types [(BuS)HgCl]$_4$L$_2$.[58,59] The structure of [Hg(SC$_6$H$_4$-2-SiMe$_3$)$_2$] (**11**) is of the first type, consisting of nearly linear S–Hg–S units. The Hg–S distance of 2.349 (2) Å is similar to that observed for other mercury(II) thiolate structures.[46–59] In addition, the Hg enjoys secondary interactions with the S atoms of two neighboring molecules at a distance of 3.234 (2) Å. The angle at the Hg produced by these long-range sulfur interactions is 71.7 (1)°, producing a highly distorted flattened tetrahedral geometry at the Hg center.

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Table XI. NMR Data and Cone Angles for Methylmercury(II) Thiolates

compd	no.	$\delta(^{199}Hg)$, ppm[a]	$\delta(^{13}C(methyl))$, ppm[b]	$^1J(Hg–C(methyl))$, Hz	cone angle, deg[c]
[CH₃Hg(SC₆H₅)]	1	−552.6	12.84	1128	0
[CH₃Hg(SC₆H₄-2-SiMe₃)]	2	−565.5	12.80	1104	47.5
[CH₃Hg(SC₆H₃-2-SiMe₃-4-Buᵗ)]	3	−565.8	12.83	1092	47.5
[CH₃Hg(SC₆H₄-2-SiEt₃)]	4	−578.2	12.76	1096	48.9
[CH₃Hg(SC₆H₄-2-SiPh₃)]	5	−620.6	12.44	1088	58.8
[CH₃Hg(SC₆H₃-2,6-SiMe₃]	6	−592.9	12.09	1080	61.0
[CH₃Hg(2-SC₅H₃N-6-SiPhMe₂)]	7	−583.4	10.52	1250	
[CH₃Hg(2-SC₆H₃N-3-SiBuᵗMe₂)]	8	−569.9	11.30	1251	
[CH₃Hg(2-SC₆H₂N-3,6-SiBuᵗMe₂)]	9	−563.8	11.11	1243	

[a] The chemical shifts are reported in ppm relative to 0.1 M dimethylmercury in CDCl₃. [b] The chemical shifts are reported in ppm relative to tetramethylsilane. All measurements of $\delta(^{199}Hg)$ and $\delta(^{13}C)$ were made in 0.1 M solutions of complex in CDCl₃ at 36 °C. [c] Calculated as described in the text.

The Hg atom of [Hg(2-SC₅H₃N-3-SiMe₃)₂] (**15**) exhibits the anticipated linear coordination to two sulfur atoms with an angle S(1)–Hg–S(2) of 178.0 (2)°. The Hg–S distances are comparable to those observed for [Hg(SC₆H₄-2-SiMe₃)₂] (**11**) and within the range for other [Hg(SR)₂] complexes. The average S–C distance and 1.759 (20) Å is consistent with a single bond in the thiol form of the ligand. A significant feature of the structure of **15** is the close approach of the pyridyl nitrogen donors to the mercury center with Hg–N(1) and Hg–N(2) distances of 2.789 (5) and 2.799 (5) Å, respectively. Assuming a value of 1.73 Å for the van der Waals radius of Hg,[44] the Hg–N distances are well within the sum of the van der Waals radii, 3.2 Å. Secondary interactions between Hg and N have been described previously for a number of methylmercury thiolate complexes.[33,38,60] It is instructive to compare the Hg–S–C angles of **15**, 95.3 (4) and 95.9 (4)°, where the Hg–N interaction forces a contraction of the angle, with that observed for **11**, 103.9 (3)°, where the normal valence angle is maintained.

The ¹³C NMR data indicate that the weak Hg–N interaction persists in solution. When the lone pair of the pyridine nitrogen is involved in bonding, the carbon atom resonances are affected.[61] As illustrated in Table X, the significant signal shifts observed for **15** relative to the values observed for 2-(methylthio)pyridine are similar to those previously noted for [MeHg(2-SC₅H₄N)], where persistence of the Hg–N secondary interaction in solution has been argued.[33] A comparison of the ¹³C NMR spectra of HSC₆H₄-2-SiMe₃ and [Hg(SC₆H₄-2-SiMe₃)₂] (**11**) does not reveal such large shifts in signal positions for corresponding ring carbon atoms, a feature consistent with this interpretation. Similar ¹³C NMR spectra are observed for the entire family of mercury bis(pyridinethiolate) complexes, as illustrated by the data compiled in Table X.

The structure of the binuclear [Hg{(2-SC₆H₄)₂SiMe₂}]₂ (**25**) reveals two diagonally coordinated Hg centers sandwiched between two bisthiolate ligands. The metrical parameters are unexceptional, as is the observation of secondary Hg⋯S interactions between discrete binuclear units. Although the ligand could conceivably coordinate a single Hg²⁺ center to give the mononuclear [Hg{(2-SC₆H₄)₂SiMe₂}]₂, the valence angle at the Hg would be necessarily strained from the linear limit. Furthermore, the requirement of forming an eight-membered chelate ring renders such a species unlikely. In practice, the bisthiolate acts as a binucleating ligand. The most unusual feature of the structure is the 16-membered heteronuclear ring [−Hg–S–C–C–Si–C–C–S–]₂ unique to this structure. Although ring structures are not uncommon in mercury thiolate chemistry, these are generally limited to [HgS]ₙ types with n = 2 or 3.[53,55] Larger heteronuclear rings are, however, encountered in the structures of mercury with oxygen and nitrogen donors, such as 2-pyrrolidonate, where an eight-membered ring structure [−Hg–N–C–O–]₂ has been described.[81]

NMR Studies. The usefulness of natural-abundance ¹⁹⁹Hg NMR spectroscopy in the study of organomercurials is well es-

tablished.[36] The known chemical shift range for mercury compounds is from −3451 ppm for K₂HgI₄ to +1681 ppm for Li₂Hg(SiMe₂Ph)₄,[62] with most common organomercury compounds falling in a smaller range of +400 to −1600 ppm.[36,62] However, the large dependence of ¹⁹⁹Hg chemical shifts on solvent, temperature, and concentrations has been noted,[63–65] necessitating a careful adherence to standard conditions when attempts are made to correlate chemical shifts from a variety of compounds.

Since mercury coupling constants generally exhibit only minor dependence on solvent, temperature, and concentration,[66] these are often more useful than ¹⁹⁹Hg chemical shifts for correlations of NMR parameters with molecular properties. The 3-bond coupling constants of ¹⁹⁹Hg nuclei to ¹H nuclei have been shown to adhere to a Karplus type relationship,[67] suggesting that at least in some cases simple assumptions of orbital overlap can explain the major trends in mercury coupling constants. Typical values of ¹⁹⁹Hg 1-bond coupling constants range from 5010 Hz for $^1J(Hg–^{31}P)$ in [Hg(ClO₄)₂{P(Ph)₃}₂][68] to 1800 Hz for $^1J(Hg–^{13}C)$ in [CH₃HgNO₃].[62] There exists an abundant literature on the tabulation of ¹⁹⁹Hg coupling constants.[62–68]

Mercury-199 NMR spectroscopy has been applied to studies of formation constants of mercury thiolate complexes,[69] of mercury thiol ligand exchange kinetics,[70] and of interactions between biologically important molecules and mercury.[71] Our interest was the potential use of ¹⁹⁹Hg NMR spectroscopy for the study of steric hindrance in mercuric thiolate complexes. Since ligand steric constraints may affect hybridization at the metal center, either the ¹⁹⁹Hg chemical shift, the coupling constant of Hg to the methyl carbons in the [CH₃Hg(SR)] series of complexes, and/or the spin–lattice relaxation time of the mercury atom in mercury thiolate complexes should correlate with the steric bulk of the substituents on the thiolate residue. The direct bonding of the thiolato sulfur to mercury in these complexes should allow the effects of steric hindrance in the ligand to be communicated to the mercury center. The triorganosilyl-derivatized thiolates presented several attractive features: the degree of steric hindrance can be modified by variation both in the organic substituents and in the number of organosilyl groups attached to the ligand and, furthermore, the bulky organic ligands render the mercury complexes highly soluble in organic solvents. The latter feature

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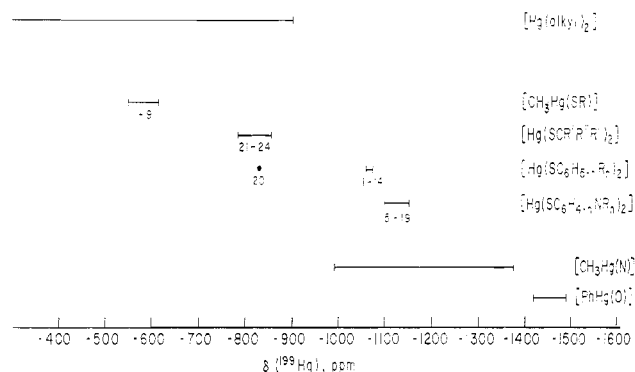
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Figure 5. ^{199}Hg chemical shift ranges observed for the complexes of this study and for various chemical environments previously reported.

Figure 6. Schematic representation of the cone angle definition used in this study.

guaranteed that the entire class of complexes could be studied under identical conditions of solvent, temperature, and concentration.

The NMR data for the methylmercury thiolate complexes (1–9) are collected in Table XI, while Table X gives NMR data for the bis(thiolato)mercury(II) series of complexes. The ^{199}Hg chemical shift ranges for different chemical environments have been tabulated.[72] Dialkylmercury compounds cover the range $\delta = 0$ for [HgMe$_2$] to $\delta = -1187$ ppm for [HgPh(CBr$_2$Cl)]. Substitution of an alkyl group by a nitrogen donor results in increased shielding such that [CH$_3$HgN] complexes absorb in the $\delta = -940$ to $\delta = -1317$ ppm region. Oxygen donors results in progressively greater shielding, such that [PhHg(O)] complexes are found in the $\delta = -1400$ ppm range, while [Hg(O)$_2$] coordination types occur at $\delta = -2253$ to $\delta = -2389$ ppm.[73] Limited data on mercury thiolate complexes showed that sulfur ligands cause deshielding relative to oxygen ligands, such that the shielding ranges for [Hg(SR)$_2$] and [MeHg(SR)] environments are displaced about 400 ppm downfield from the δ-values of their oxygen counterparts.[74] Figure 5 displays the ^{199}Hg chemical shift ranges for the complexes of this study and compares these to other chemical environments. The chemical shift values observed for the complexes 1–25 fall into four distinct ranges. As anticipated, the [CH$_3$Hg(SR)] series of complexes are shifted downfield in the –550 to –620 ppm range. There is no obvious correlation between ^{199}Hg chemical shift and the nature of thiolate ligand, whether thiophenol derived (1–6) or pyridine-2-thiol derived (7–9) for the [CH$_3$Hg(SR)] series.

In contrast, the [Hg(SR)$_2$] class of complexes falls into three distinct ranges depending on thiolate ligand type. The complexes with methanethiol-derived ligands exhibit $\delta(^{199}$Hg) in the –780 to –831 ppm range, while the two series of complexes with benzenethiol- and pyridine-2-thiol-derived ligands are shifted upfield to ranges of –1060 to –1079 ppm and –1098 to –1142 ppm, respectively. A clear pattern of ^{199}Hg chemical shift ranges emerges with mercury(II) bis(alkanethiolate) complexes occupying a range intermediate to the downfield methylmercury thiolate complexes and to the upfield-shifted mercury(II) bis(arenethiolate) and mercury(II) bis(pyridine-2-thiolate) complexes. Furthermore, the trigonal class of mercuric thiolates, [Hg(SR)$_3$]$^-$,[82–84] exhibit ^{199}Hg chemical shifts in the –150 to –350 ppm range. Such a three-coordinate environment has been proposed for the mercury binding site in MerR.[85,86]

The major anomaly in the chemical shift data is complex **20**, which would be expected to fall in the range for complexes with benzenethiol-derived ligands (–1060 to –1079 ppm) but which is rather found at –827 ppm. However, complex **20** is not a simple mononuclear [Hg(SR)$_2$] species but a binuclear complex analogous to [Hg{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$ (**25**). In the case of Cd–S environments, Holm and coworkers[75] have demonstrated that a sequential
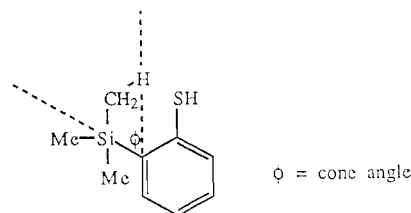
deshielding of cadmium occurs as the number of thiolate sulfurs increases. There may be a similar trend for Hg–SR complexes that follows the degree of aggregation of the complexes [Hg(SR)$_2$]$_n$. Although there are insufficient examples to allow any but the most tentative conclusions, the ^{199}Hg chemical shifts for Hg–S(aryl) complexes do reflect the degree of aggregation for the limited data set: [Hg(S-aryl)$_2$], ca. –1100 ppm; [Hg{(2-SC$_6$H$_4$)$_2$SiMe$_2$}]$_2$ (**20**), –827 ppm; [Hg$_4$L$_4$(S-aryl)$_6$]$^{2+}$, –443 ppm.[55]

The methylmercury thiolate series of complexes 1–9 also provide mercury–carbon(methyl) coupling constants ^1J(Hg–C), tabulated in Table XI. In contrast to the ^{199}Hg chemical shift data, the coupling constants clearly distinguish between the methylmercury arenethiolate complexes 1–6, which exhibit ^1J(Hg–C) values in the range 1080–1131 Hz and the methylmercury pyridine-2-thiolate complexes 7–9, which show ^1J(Hg–C) values in the 1243–1251 Hz range. Attempts to correlate ^1J(Hg–C) parameters for [MeHgX] complexes indicate that ^1J(Hg–C) decreases with reduction of s character of the Hg–C bond.[27] The structures of [MeHg(2-SC$_5$H$_4$N)],[33] [MeHg(2-mercaptobenzothiazole)],[38] and [Hg(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$] (**15**) reveal significant secondary interactions between Hg and the nitrogen of the ring. Such a virtual increase in the Hg coordination number should result in a degree of rehybridization and a consequent change in the ^1J(Hg–C) coupling constants. In fact, increasing the number of N donors in methylmercury complexes of the type [CH$_3$HgN] to [CH$_3$HgN$_2$] results in an upfield shift in the ^{199}Hg chemical shift and a corresponding increase in ^1J(Hg–C).[76,77]

The trend in coupling constants for complexes 1–9 is paralleled by the ^{13}C chemical shifts of the methyl group. Thus, the δ-(^{13}C(methyl)) values for **1–6** are in the 12.09–12.84 ppm range, while **7–9** exhibit shifts in the 10.52–11.30 ppm range. The $\delta(^{13}$C(methyl)) values for methylmercury pyridine-2-thiolate [MeHg(2-SC$_5$H$_4$N)][33] and methylmercury 2-mercaptobenzothiozolate[38] are 11.08 and 11.4 ppm, respectively, suggesting that the secondary coordination of the N donor is an important contributor to the properties of these complexes. The upfield shift in $\delta(^{13}$C(methyl)) for complexes 7–9 relative to 1–6 is consistent with the increase in coupling constants ^1J(Hg–C) noted above.

A feature of particular interest to us was the structural and electronic consequences of varying steric bulk at the ligand and the potential application of NMR spectroscopy to obtain a quantitative measure of the steric constraints imposed by the ligand. The best established method for assigning a quantitative value to steric hindrance is the cone angle.[78] Cone angle measurements determine the solid angle of space that is subtended by a particular group. In this case, the hindering groups are positioned in either one or both of the ortho positions in an arenethiol.

With use of MM2 molecular mechanics calculations, minimum energy geometries were determined for the arenethiols and 2-pyridinethiols of this study. From these minimum energy geometries cone angles were calculated. The cone angle is defined as the angle between the bond vector ortho to the sulfhydryl group

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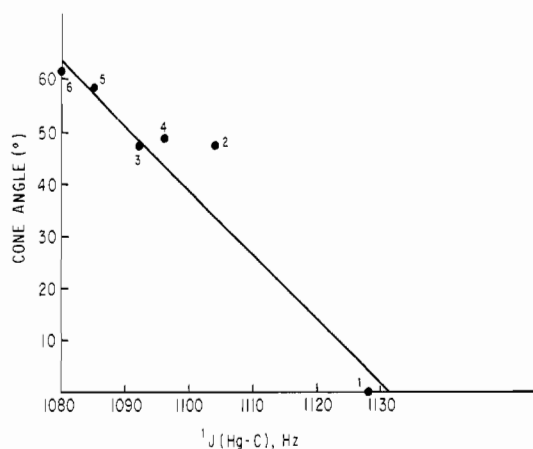
Figure 7. Correlation of cone angle with ^{199}Hg chemical shift for the [MeHg(SCR'R''R''')] series of complexes (1–6).

and the vector between the ortho ring carbon and the hydrogen of the ortho substituent most closely approaching the sulfur atom of the sulfhydryl group (Figure 6). If groups were substituted at both ortho positions, then a separate calculation was carried out for each group and the sum of both values was taken as the overall cone angle. When no groups were substituted at the ortho positions, the cone angle was taken to be zero. For a number of complexes cone angles could not be calculated as bonds within these molecules were not parametrized in the MM2 base set. In several other cases, the MM2 calculations yielded false minima. As a consequence of the inherent limitations of this approach, only the methylmercury arenethiolate series of complexes 1–6 yielded a complete set of cone angles.

Correlations of ^{199}Hg NMR chemical shifts with δ–π hyperconjugation in alkylmercury compounds[79] and of mercury chemical shifts with the electron-donating properties of substituents in mercuric thiolate compounds have been attempted with limited success.[80] However, the correlation of ^{199}Hg NMR parameters with steric cone angles has not previously been attempted. Least-squares correlation of a limited set of the coupling constant

data in Table XI (compounds 1–6) with the calculated cone angles yielded a linear relationship with a value of 0.9506 for the correlation coefficient (Figure 7). Correlations of larger sets of coupling constant data or of any chemical shift data with calculated cone angles yielded much poorer linearity. It is not surprising that such correlations are valid only for limited sets of data, as changes in bond hybridization and charge density will accompany the changes in steric hindrance that result from changing the ortho substituents of an arenethiol. Thus, ^{199}Hg NMR parameters appear to be of only limited value in the quantification of steric hindrance.

Although the correlation of the β-silicon effect in [MeHg-(SCR'R''R''')] complexes was of some interest to us, attempts to prepare this series of complexes resulted in intractable materials. Compounds 22 and 24 of the [Hg(SR)$_2$] series exhibit Si atoms in positions β to the thiolate sulfur. However, no obvious influence on $\delta(^{199}$Hg) is apparent and, in fact, the chemical shifts are in the range for the non-silylated derivatives of the series 21 and 23. Due to the limitations of the data available, no conclusions can be drawn on the possible correlation of β-silicon effects at the thiolate sulfur with Hg NMR parameters.

Conclusions

Thiols variously substituted with triorganosilyl groups represent a novel class of sterically hindered thiolate ligands that allow tuning of steric constraints by variation in organic substituents and number of silyl groups. Furthermore, these ligands imbue their metal complexes with dramatically improved solubility in organic solvents, allowing the study by NMR techniques of a large class of complexes under identical conditions of solvent, temperature, and concentration.

Detailed NMR studies of the [MeHg(SR)] and [Hg(SR)$_2$] series of complexes reveal several general trends: (1) The ^{199}Hg chemical shifts move upfield in the order [MeHg(SR)] < [Hg-(SCR'R''R''')$_2$] < [Hg(S–aryl)$_2$] < [Hg(S–pyridyl)$_2$]; (2) anomalous behavior is observed for oligomeric species; (3) for the [MeHg(SR)] series of complexes ^1J(Hg–C) correlates with δ-(^{13}C(methyl)) and the type of thiolate ligand; (4) there is only a limited correlation of $\delta(^{199}$Hg) with steric cone angles for a subset of the complexes.

Supplementary Material Available: Tables of experimental conditions for the structures of **10, 11, 15,** and **25** (Tables S.1, S.7, S.13, and S.19), bond lengths and bond angles (Tables S.2 and S.3, S.8 and S.9, S.14 and S.15, and S.20 and S.21), and calculated hydrogen atom positions and anisotropic temperature factors (Tables S.4 and S.5, S.10 and S.11, S.16 and S.17, and S.22 and S.23) (21 pages); tables of observed and calculated structure factors (Tables S.6, S.12, S.18, and S.24) (50 pages). Ordering information is given on any current masthead page.

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