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Arylene- and Alkylene-Bridged Siliconates

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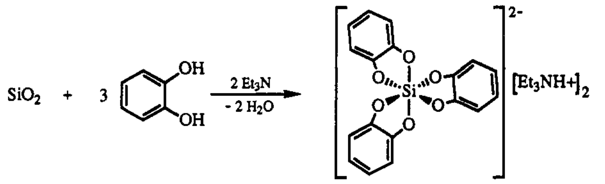
*Summary: Arylene-bridged pentacoordinate siliconates **3–6** (arylene = 1,4-phenylene, 1,3-phenylene, 4,4′-biphenylene, and 9,10-anthracylene) were prepared from bis(triethoxysilyl)arylene precursors, catechol, and triethylamine in tetrahydrofuran. 1,2-Ethylene and 1,6-hexylene-bridged pentacoordinate siliconates **7** and **8** were prepared from 1,2-bis(trimethoxysilyl)ethane and 1,6-bis(trimethoxysilyl)hexane, respectively. The molecular structure of the 1,4-phenylene-bridged siliconate **3** was determined by X-ray diffraction.*

Introduction

While the majority of silicon compounds are tetrasubstituted, penta- and hexacoordinate silicon compounds have been known for quite some time. These penta- and hexacoordinate siliconates are interesting not only from a synthetic and structural viewpoint, but also for their unique reactivity.[2] In addition, hypervalent silicon compounds have been shown to be probable intermediates in nucleophilic substitution reactions at silicon, and mechanistic investigations in support of this proposal have been conducted.[3]

Aside from complexes with fluorine, most stable penta- and hexacoordinate silicon compounds have multidentate oxo and aza ligands.[4] These complexes enjoy greater stability over analogous complexes with monodentate ligands through the "chelate effect". Catechol and other aryl 1,2-diols are bidentate ligands that form stable penta- and hexacoordinate complexes with silicon. Rosenheim discovered that finely divided silica gel could be *depolymerized* in a solution of catechol in aqueous ammonium hydroxide to afford a water-stable hexacoordinate siliconate.[5] This complex was shown by X-ray diffraction studies to have octahedral geometry with three catechol groups coordinated to the silicon atom; the complex prepared under aqueous conditions was hydrated between the silicon and the axial oxygen of one of the catechol ligands.[6] Under anhydrous conditions (triethylamine or sodium alkoxide in anhydrous alcohol or tetrahydrofuran), the symmetric hexacoordinate siliconate was obtained (Scheme I).[5,7]

Scheme I. Depolymerization of Silica with Catechol



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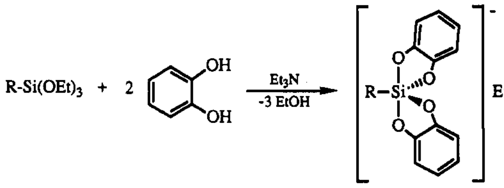
Scheme II. Condensation of Aryltriethoxysilanes with Catechol (R = Aryl)



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Under similar conditions, Frye[7] prepared the pentacoordinate siliconate **2** from phenyltriethoxysilane (PTES) (Scheme II). Representative pentacoordinate siliconate compounds have been prepared with a variety of substituents on silicon and aryl 1,2-diol ligands.[4b,8] The geometry at the silicon atom lies between trigonal-bipyramidal and square-pyramidal depending on the nature of both the R group and the chelating ligands.[8]

We previously reported the synthesis of bis(triethoxysilyl)arylene, ethynylene, and alkylene derivatives. These compounds were converted to polysilsesquioxanes, a novel family of hybrid organic–inorganic materials, by sol-gel processing.[9] The facile conversion of triethoxysilyl aromatic compounds into *pentacoordinate* derivatives prompted us to examine the synthesis of alkylene- and arylene-bridged siliconates. These compounds serve as models for the "building blocks" of a new family of hypervalent siliconate materials prepared by condensation of bis(triethoxysilyl)arylene- or alkylene-bridged monomers (or any tri- or tetraalkoxysilane) with 1,2,4,5-tetrahydroxybenzene.[10] 1,4-Phenylene- (**3**), 1,3-phenylene- (**4**), 4,4′-biphenylene- (**5**), 9,10-anthracylene- (**6**), 1,2-ethylene- (**7**), and 1,6-hexylene- (**8**) bridged siliconates

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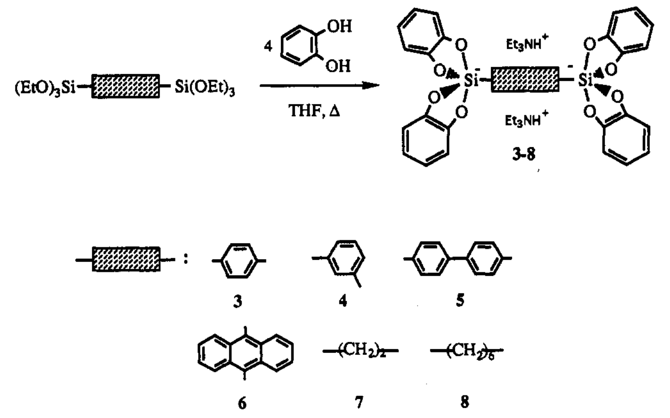
Scheme III. Condensation of Ethoxysilanes and Catechol To Afford Arylene- and Alkylene-Bridged Siliconates



reported in this paper represent additional examples of arylene- and alkylene-bridged pentacoordinate siliconates.[11]

Results and Discussion

Arylene-bridged siliconates **3**–**6** were prepared from 1,4-bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, 4,4′-bis(triethoxysilyl)biphenyl, and 9,10-bis(triethoxysilyl)anthracene, respectively.[9] The alkylene-bridged siliconates (**7**, **8**) were prepared from 1,2-bis(trimethoxysilyl)ethane and 1,6-bis(trimethoxysilyl)hexane. The trialkoxysilane precursors were each condensed with 4 equiv of catechol and 2 equiv of triethylamine in refluxing THF to afford upon cooling the arylene- and alkylene-bridged siliconates (**3**–**8**) as white powders. After recrystallization, fine needle-like crystals were isolated. Alternatively, compound **3** could be prepared in good yield (88%) by heating a "solvent-free" mixture of 1,4-bis(triethoxysilyl)benzene, catechol, and triethylamine. X-ray quality crystals of **3**–**8** were difficult to grow. However, by allowing a solution of **3** in acetonitrile to cool slowly, large, well-defined monoclinic crystals were obtained. The X-ray diffraction crystal structure (Figure 1) shows the bridging phenylene and the two pentavalent silicon atoms each coordinated by two catecholate groups. The siliconate complexes have a slightly distorted trigonal-bipyramidal geometry with O(2), O(3), and C(13) in equatorial positions. Si–O(2) and Si–O(3) bond lengths are 1.731 and 1.704 Å, respectively, while Si–O(1) and Si–O(4) bond lengths are 1.769 and 1.789 Å, respectively; equatorial bonds in trigonal-bipyramidal siliconate complexes have been shown to be shorter than the axial bonds.[4] The O(1)–Si–O(4) is 169.0°, indicating that the trigonal-bipyramid is distorted. The axial axis (O(1)–Si–O(4)) is orthogonal to the π system of the aromatic ring. The triethylammonium ions are above and below the plane of the bridging phenyl with hydrogen bonding interactions with O(2) and O(2)′ in the catechol ligands. In contrast, the triethylammonium ion was shown to lie between the catecholate ligands on the far side of the silicon from the phenyl group in the bis(catechol)phenylene siliconate (**2**).[12]

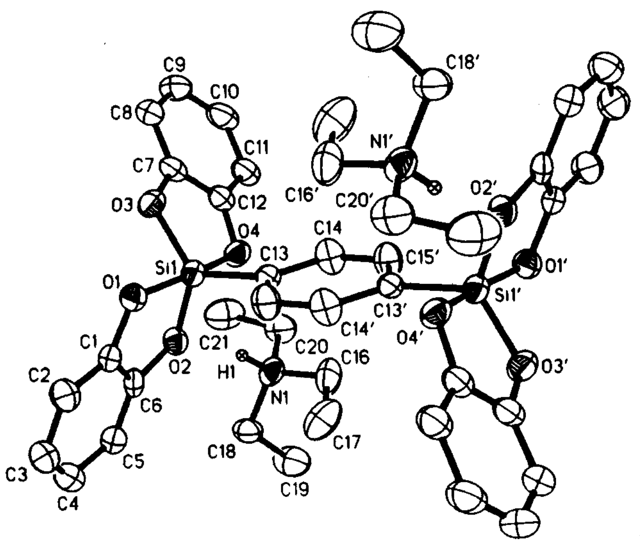


Figure 1. ORTEP plot of siliconate **3**. Hydrogen atoms omitted for clarity.

The infrared spectra of both penta- and hexacoordinate siliconates **1**–**8** display a band between 3410 and 40 cm^{-1} arising from the triethylammonium counterion. Aromatic C–H stretching bands are found between 3070 and 3035 cm^{-1}. There are also four strong, sharp bands at 1487–1491, 1244–1250, 813.8–829.2, and 736.7–744.5 cm^{-1} common to all of the above siliconates (**1**–**8**), but not to catechol or the ethoxysilane precursors.

The ^{1}H NMR spectrum of **1** displays the catecholate hydrogens as a multiplet at 6.17 ppm; **2**–**6** display the catecholate hydrogens as two multiplets at 6.39–6.44 and 6.51–6.57 ppm. The triethylammonium counterions in **1**–**8** have a quartet for the methylene hydrogens between 2.88 and 3.21 ppm and a triplet for the methyl hydrogens between 1.03 and 1.17 ppm. The NH was observed as a broad singlet between 8.75 and 8.81 ppm in **2**, **3**, **6**, **7**, and **8**. In **1**, **4**, and **5** the NH resonance was not discernible in the ^{1}H NMR spectrum. The phenylene hydrogens in **2** appear as two signals at 7.50 and 7.13 ppm. The 1,4-phenylene-bridge hydrogens in **3** have a single absorption at 7.21. The 1,3-phenylene-bridge hydrogens in **4** exhibit the same singlet, doublet, and triplet pattern seen slightly downfield (0.11 ppm) as in its precursor 1,3-bis(triethoxysilyl)benzene.[9c,e] The biphenylene-bridge hydrogen signals in **5** are two doublets at 7.40 ppm. The anthracylene-bridge hydrogens in **6** are found as two doublet of doublets at 9.05 and 7.22 ppm. The arylene-bridge hydrogens in **3**–**6** lie farther upfield than in the corresponding arylene-bridged ethoxysilyl precursors reflecting the greater electropositive character of the siliconate over the tetrahedral (triethoxysilyl)arylene moieties. The methylene ^{1}H resonances from the bridging alkylene groups (**7** and **8**) ranged from 0.33 ppm for the hydrogens α to the silicon to 1.05 ppm for the γ methylenes in the hexylene-bridged siliconate **8**.

In the ^{13}C NMR data (Table I), the catecholate ligands of **1**–**8** have three carbon signals between 150.3–152.2, 115.1–117.6, and 108.8–110.1 ppm. Siliconate **3** has two carbon peaks arising from the phenylene bridge at 141.13

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Table I. ^{13}C and ^{29}Si NMR Data for 1–8

			^{13}C (ppm)		
siliconates	^{13}C catechol (ppm)	^{13}C bridge (ppm)	$\mathrm{N}C\mathrm{H_2CH_3}$	$\mathrm{NCH_2}C\mathrm{H_3}$	^{29}Si (ppm)
1	152.2, 115.1, 108.8		45.8	8.9	−140.0
2	150.5, 117.6, 109.8	141.9, 134.8, 127.9, 126.8	45.8	8.8	−87.5
3	150.5, 117.4, 109.7	141.1, 133.2	45.8	8.7	−87.0
4	150.6, 117.3, 109.8	142.7, 139.4, 134.8, 125.0	45.8	8.9	−86.7
5	150.5, 117.6, 109.9	145.3, 135.4, 125.2, 119.4	45.8	9.0	−87.4
6	150.3, 117.5, 110.1	142.2, 133.3, 131.3, 122.6	45.8	8.6	−81.7
7	150.9, 116.7, 109.5	33.5, 24.6, 18.7	45.8	8.8	−73.7
8	150.7, 117.0, 109.2	11.65	45.7	8.7	−71.9

and 133.17 ppm. The remaining three arylene-bridged siliconates **4–6** exhibit the expected four arylene-bridged carbon signals. The methylene carbons in the ethylene-bridged siliconate **7** resonances are found at 11.65 ppm. Methylene resonances in the hexylene-bridged siliconate ranged from 18.73 ppm for the α carbon to 33.47 ppm for the γ carbon. The triethylammonium resonances at 45.78–45.84 and 8.60–8.86 ppm can easily be distinguished from residual ethoxysilane resonances at 59 and 18 ppm that might arise from unreacted starting material.

The ^{29}Si NMR signal of hexacoordinate siliconate **1** lies at −135 ppm.[13] Pentacoordinate siliconates display ^{29}Si NMR resonances between −85 and −88 ppm.[13] Siliconate **2** and arylene-bridged siliconates **3–5** have signals between −86.95 and −87.50 ppm (Table I). Anthracylene-bridged siliconate **6** has a resonance at −81.71 ppm. The ethylene- and hexylene-bridged siliconates displayed ^{29}Si resonances at −73.65 and −71.90 ppm, respectively. Additional ^{29}Si resonances corresponding to the tetracoordinate silicon were not observed.

Conclusions

A new class of pentacoordinate silicon complexes, the arylene- and alkylene-bridged siliconates **3–8**, are readily synthesized by condensing bis(trialkoxysilyl)arylene and alkylene precursors with catechol in the presence of triethylamine. The bridged siliconates can be prepared in tetrahydrofuran, acetonitrile, or ethanol or in the absence of solvent. The siliconates were characterized by standard spectroscopic methods and, in the case of **3**, by an X-ray crystal structure. All of the bridged materials displayed ^{29}Si NMR chemical shifts in the range characteristic of pentacoordinate silicon. Solution of the single-crystal X-ray diffraction data from the phenylene-bridged siliconate **3** established a slightly distorted trigonal-bipyramidal pentacoordinate silicon atom on both ends of the phenylene bridge. These novel additions to the family of pentacoordinate siliconates provide models for the synthesis and characterization of polymeric siliconates derived from bis(trialkoxysilyl)arylene- and alkylene-bridged monomers condensed with 1,2,4,5-tetrahydroxybenzene.[10]

Experimental Section

General Procedures. Catechol and phenyltriethoxysilane were purchased from Aldrich Chemical Co. and were used as received. Tetraethoxysilane was purchased from Aldrich and distilled from CaH_2 before using. 1,4-Bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, and 4,4′-bis(triethoxysilyl)biphenyl were prepared from TEOS and the appropriate aryl dibromides by a Barbier–Grignard reaction.[9] 9,10-Bis(triethoxysilyl)anthracene was prepared by lithium bromide exchange from 9,10-dibromoanthracene and *tert*-butyllithium followed by condensation with chlorotriethoxysilane.[9c,e] 1,2-Bis(trimethoxysilyl)ethane and 1,6-bis(trimethoxysilyl)hexane were obtained from Huls America and were used as received. The reactions were run in flame-dried glassware under nitrogen atmosphere. All solvents were purified using normal purification methods.

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM-250 (250 MHz), General Electric QE-300 (300 MHz), GN-500 (500 MHz), or Omega-500 (500 MHz) spectrometers. The chemical shifts are reported in ppm with either tetramethylsilane (0.00 ppm) or DMSO-d_6 (2.49 ppm) as internal standards. ^{13}C NMR were recorded with QE-300 (75.4 MHz), GN-500, and Omega-500 (125.5 MHz) spectrometers with DMSO-d_6 (39.6 ppm) as internal standard. ^{29}Si NMR were obtained with the GN-500 and Omega-500 instruments (99.34 MHz) with tetramethylsilane (0.00 ppm) as internal standard. Infrared spectra were obtained with an Analect RFX-40 FTIR spectrometer.

Efforts to prepare solvent-free analytically pure samples (vacuum drying, elevated temperatures) resulted in partial decomposition. The resulting elemental composition from combustion analysis was not within acceptable limits. We were, however, able to obtain accurate mass data using high-resolution mass spectrometry utilizing liquid secondary ion mass spectrometry (LSIMS) conditions. Complete results will be published elsewhere. The high-resolution mass spectrometry was performed on a VG-Autospec instrument utilizing LSIMS techniques in the positive ion mode. Samples were run using *m*-nitrobenzyl alcohol as the matrix, Cs^+ as the ion source, and 1% PEG-600 as an internal standard.

$(Et_3NH)_2[Si(Cat)_3]$ (1; Cat = catecholate).[5] Triethylamine (2.10 mL, 15.0 mmol) was added to a solution of TEOS (1.56 g, 7.49 mmol) and catechol (2.47 g, 22.5 mmol) in THF (75 mL). The resulting solution was heated to reflux for 2 h and then allowed to cool overnight. Large clear colorless crystals were collected and recrystallized from acetonitrile (1.91 g, 54.3%): ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.21 (m, 6 H, catecholate), 3.13 (q, J = 7.17 Hz, 12 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 1.15 (t, J = 7.23 Hz, 18 H, $\mathrm{NCH_2C}H_3$); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 152.17, 115.12, 108.81, 45.80, 8.73; ^{29}Si NMR (99.34 MHz, DMSO-d_6) δ −139.99; IR (KBr) ν 3440, 3022, 2945, 1595, 1491, 1250, 1223, 1095, 1016, 885.2, 871.7, 813.8, 736.7, 690.4, 522.6 cm^{-1}; HRMS (Pos LSIMS, Cs^+, $C_7H_7NO_3$) m/z calcd for $C_{30}H_{44}N_2O_6Si$ (M + 1) 557.3043, found (M + 1) 557.3069.

$(Et_3NH)[PhSi(Cat)_2]$ (2).[7] Triethylamine (2.9 mL, 20.8 mmol) was added to a solution of PTES (5.00 g, 20.8 mmol) and catechol (4.58 g, 41.6 mmol) in THF (100 mL). The resulting solution was heated to reflux for 1 h. The solvent was removed in vacuo to afford an oil. Trituration with diethyl ether resulted in a white precipitate which was collected, washed with diethyl ether (250 mL), and recrystallized from acetonitrile (4.80 g, 54%): ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.8 (s, 1 H, NH), 7.50 (s, 2 H, PhH), 7.13 (s, 3 H, PhH), 6.59 (s, 4 H, catecholate), 6.48 (s, 4 H, catecholate), 3.04 (q, 6 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 1.13 (t, 9 H, $\mathrm{NCH_2C}H_3$); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 150.49, 141.94, 134.82, 127.86, 126.83, 117.55, 109.85, 45.84, 8.75; ^{13}C DEPT 90 NMR (75.5 MHz, DMSO-d_6) δ 134.82, 127.89, 126.85, 117.56,

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109.87; ^{29}Si NMR (99.34 MHz, DMSO-d_6) δ −87.50; IR (KBr) ν 3066, 3045, 1489, 1358, 1246, 829.2, 738.6 cm^{-1}.

(Et$_3$NH)$_2$[(Cat)$_2$SiPhSi(Cat)$_2$] (3). Triethylamine (2.79 mL, 20.00 mmol) was added to a solution of 1,4-bis(triethoxysilyl)benzene (4.026 g, 10.0 mmol) and catechol (4.40 g, 40.0 mmol) in dry THF (100 mL). The resulting solution was heated to reflux for 1 h and then cooled to afford a white powder. The THF was removed in vacuo, and the white solids were washed with diethyl ether and dried under dynamic vacuum (<1 mmHg) for 4 h (4.6 g, 55%): ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.8 (s, 2 H, NH), 7.21 (s, 4 H, PhH), 6.52 (m, 8 H, catecholate), 6.42 (m, 8 H, catecholate), 3.03 (q, J = 7.14 Hz, 12 H, NCH_2CH$_3$), 1.12 (t, J = 7.23 Hz, 18 H, NCH$_2$CH_3); ^{13}C NMR (25 MHz, DMSO-d_6) δ 150.52, 141.13, 133.17, 117.35, 109.68, 45.83, 8.74; ^{29}Si NMR (99.34 MHz, DMSO-d_6) δ −86.95; IR (KBr) ν 3064, 3006, 2981, 1487, 1356, 1236, 1126, 1101, 1012, 835, 825.2, 815.7, 756.0, 750.2, 684.6, 530.3 cm^{-1}; HRMS (Pos LSIMS, Cs$^+$, C$_7$H$_7$NO$_3$) m/z calcd for $C_{42}H_{52}N_2O_8Si_2$ (M + 1) 769.3337, found (M + 1) 769.3347.

Melt Condensation Preparation of 3. A mixture of catechol (2.20 g, 20.0 mmol) and BESP (2.01 g, 5.0 mmol) was carefully purged of air with N$_2$ and heated to 100 °C over 15 min. Triethylamine (2.5 mL) was syringed into the hot, clear, and colorless solution with an immediate and exothermic formation of white solid. The solid was cooled, broken up, and washed with diethyl ether (3 × 100 mL). After filtration and drying, a white powder was collected (3.40 g, 88.0%): ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.23 (s, 4 H, PhH), 6.53 (m, 8 H, catecholate), 6.43 (m, 8 H, catecholate), 3.03 (q, J = 7.19 Hz, 12 H, NCH_2CH$_3$), 1.14 (t, J = 7.10 Hz, 18 H, NCH$_2$CH_3).

(Et$_3$NH)$_2$[(Cat)$_2$Si-1,3-C$_6$H$_4$Si(Cat)$_2$] (4). Triethylamine (2.0 mL, 14.3 mmol) was added to a refluxing solution of 1,3-bis(triethoxysilyl)benzene (2.01 g, 5.0 mmol) and catechol (2.20 g, 20.0 mmol) in THF (20 mL). After 2 h at reflux, the solution was cooled and the solvent removed in vacuo. Recrystallization from acetonitrile afforded white needle-like crystals (1.89 g, 49%): ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.88 (s, 1 H, PhH), 7.31 (dd, J = 8.71, 0.97 Hz, 2 H, PhH), 6.83 (t, J = 8 Hz, 1 H, PhH), 6.51 (m, 8 H, catecholate), 6.43 (m, 8 H, catecholate), 3.03 (q, J = 7.28 Hz, 12 H, NCH_2CH$_3$), 1.14 (t, J = 7.27 Hz, 18 H, NCH$_2$CH_3); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 150.6, 142.7, 139.4, 134.8, 125.0, 117.3, 109.8, 45.84, 8.86; ^{29}Si NMR (99.34 MHz, DMSO-d_6) δ −86.68; IR (KBr) ν 3436, 3043, 2985, 2273, 1601, 1487, 1358, 1244, 1227, 1099, 1014, 827.3, 736.7, 513 cm^{-1}; HRMS (Pos LSIMS, Cs$^+$, C$_7$H$_7$NO$_3$) m/z calcd for $C_{42}H_{52}N_2O_8Si_2$ (M + 1) 769.3337, found (M + 1) 769.3320.

(Et$_3$NH)$_2$[(Cat)$_2$SiBiPhSi(Cat)$_2$] (5; BiPh = 4,4′-Biphenyldiyl). In a similar manner, triethylamine (0.16 mL, 2.32 mmol) was added to a solution of 4,4′-bis(triethoxysilyl)biphenyl (0.55 g, 1.16 mmol) and catechol (0.51 g, 4.63 mmol) in THF (10 mL) and heated at reflux for 2 h. Trituration into diethyl ether (2 × 75 mL) produced a white precipitate (0.29 g, 30%): ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.40 (dd, 8 H, ArH), 6.57 (m, 8 H, catecholate), 6.44 (m, 8 H, catecholate), 3.05 (q, 12 H, NCH_2CH$_3$), 1.14 (t, 18 H, NCH$_2$CH_3); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 150.46, 145.34, 135.36, 125.17, 119.35, 109.89, 45.84, 9.01; ^{29}Si NMR (99.34 MHz, DMSO-d_6) δ −87.38; IR (KBr) ν 3401, 3032, 1487, 1242, 811.9, 742.5, 711.6 cm^{-1}; HRMS (Pos LSIMS, Cs$^+$, C$_7$H$_7$NO$_3$) m/z calcd for $C_{48}H_{50}N_2O_8Si_2$ (M + 1) 845.3648, found (M + 1) 845.3642.

(Et$_3$NH)$_2$[(Cat)$_2$SiAnthSi(Cat)$_2$] (6; Anth = 9,10-Anthracenediyl). Triethylamine (0.21 mL, 1.51 mmol) was added to a solution of 9,10-bis(triethoxysilyl)anthracene (0.375 g, 0.75 mmol) and catechol (0.328 g, 2.98 mmol) in EtOH (20 mL) and the solution heated to reflux for 1 h. After the solution was cooled to room temperature, yellow-white crystals formed. The crude product was collected by filtration, washed with diethyl ether (100 mL), and dried under vacuum (0.62 g, 95%). After recrystallization from acetonitrile, fine needle-like crystals (0.45 g, 69%) were obtained: ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.01 (dd, J = 6.92, 3.25 Hz, 4 H, anthracene), 7.19 (dd, J = 6.89, 3.23 Hz, 8 H, anthracene), 6.51 (m, 8 H, catecholate), 6.34 (m, 4 H, catecholate), 2.88 (q, J = 7.19 Hz, 12 H, NCH_2CH$_3$), 1.03 (t, J = 7.22 Hz, 18 H, NCH$_2$CH_3); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 150.34, 142.25, 133.27, 131.29, 122.61, 117.46, 110.09, 45.78, 8.60; ^{13}C DEPT-90 NMR (75.4 MHz, DMSO-d_6) δ 131.29, 122.63, 117.47, 110.10; ^{29}Si NMR (99.35 MHz, DMSO-d_6) δ −81.71; IR (KBr) ν 3427, 3035, 2983, 1487, 1246, 829.2, 738.6, 518.8 cm^{-1}; HRMS (Pos LSIMS, Cs$^+$, C$_7$H$_7$NO$_3$) m/z calcd for $C_{50}H_{56}N_2O_8Si_2$ (M + 1) 869.3653, found (M + 1) 869.3660.

(Et$_3$NH)$_2$[(Cat)$_2$Si(C$_2$H$_2$)$_2$Si(Cat)$_2$] (7). Triethylamine (1.75 mL, 12.6 mmol) was added to a solution of 1,2-bis(trimethoxysilyl)ethane (4.87 g, 18.0 mmol) and catechol (7.93 g, 72.0 mmol) in THF (60 mL) and the solution heated to reflux overnight. The solvent was removed in vacuo to yield a white solid that was washed with diethyl ether (2 × 50 mL) and dried under dynamic vacuum (10 mTorr, 20 h) to afford a white solid (9.80 g, 75.5%): ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.81 (s, 2 H, NH), 6.38 (m, 16 H, catecholate), 3.07 (q, J = 7.24 Hz, 12 H, NCH_2CH$_3$), 1.14 (t, J = 7.27 Hz, 18 H, NCH$_2$CH_3), 0.34 (s, 4 H, SiCH_2); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 150.88, 116.71, 109.22, 45.73, 11.65, 8.69; ^{29}Si NMR (99.35 MHz, DMSO-d_6) δ −73.65; IR (KBr) ν 3407.6, 3043.1, 2985.3, 2944.8, 2923.6, 2802.1, 2732.6, 1598.7, 1488.8, 1459.8, 1415.5, 1396.2, 1357.6, 1280.5, 1246.0, 1174.4, 1141.6, 1101.2, 1056.8, 1033.7, 1014.4, 891.0, 825.4, 744.4, 676.9, 628.7, 588.2 cm^{-1}; HRMS (Pos LSIMS, Cs$^+$, C$_7$H$_7$NO$_3$) m/z calcd for $C_{38}H_{52}N_2O_8Si_2$ (M + 1) 721.3340, found (M + 1) 721.3387.

(Et$_3$NH)$_2$[(Cat)$_2$Si(C$_2$H$_2$)$_6$Si(Cat)$_2$] (8). Triethylamine (1.75 mL, 12.6 mmol) was added to a solution of 1,6-bis(trimethoxysilyl)hexane (2.01 g, 6.16 mmol) and catechol (2.70 g, 24.5 mmol) in THF (30 mL) and the solution heated to reflux overnight. The solution crystallized upon cooling and was washed with diethyl ether (2 × 20 mL) and dried under vacuum (0.25 mmHg, 5 h) to afford a white solid (2.63 g, 55.3%): ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.81 (s, 2 H, NH), 6.43 (m, 16 H, catecholate), 3.09 (q, J = 6.93 Hz, 12 H, NCH_2CH$_3$), 1.17 (t, J = 7.25 Hz, 18 H, NCH$_2$CH_3), 1.05 (m, 4 H, SiCH$_2$CH$_2$CH_2), 0.92 (m, 4 H, SiCH$_2$CH_2CH$_2$), 0.36 (m, 4 H, SiCH_2CH$_2$CH$_2$); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 150.72, 117.01, 109.48, 45.82, 33.47, 24.55, 18.73, 8.75; ^{29}Si NMR (99.35 MHz, DMSO-d_6) δ −71.90; IR (KBr) ν 3407.6, 3048.9, 2979.5, 2921.6, 2883.1, 2852.2, 2732.6, 1598.7, 1486.8, 1461.8, 1427.1, 1398.1, 1357.6, 1349.9, 1280.5, 1243.9, 1228.4, 1205.3, 1157.1, 1101.2, 1035.6, 1014.4, 896.7, 821.5, 742.5, 717.5, 594.0, 526.5, 501.4, 433.9 cm^{-1}; HRMS (Pos LSIMS, Cs$^+$, C$_7$H$_7$NO$_3$) m/z calcd for $C_{42}H_{60}N_2O_8Si_2$ (M + 1) 777.3960, found (M + 1) 777.3930.

Collection of X-ray Diffraction Data. A clear crystal of approximate dimensions 0.23 × 0.23 × 0.30 mm was oil mounted on a glass fiber and transferred to the Syntex P2$_1$ automated four-circle diffractometer which is equipped with a modified LT-1 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[14] Intensity data were collected at 183 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table III (supplementary material). All 2899 unique data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The space group is therefore uniquely defined as the centrosymmetric monoclinic $P2_1/c$ (C^5_{2h}; No. 14).

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[15] or the SHELXTL PLUS program set.[16] The analytical scattering factors for neutral atoms were used throughout the analysis;[17a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[17b] were included. The quantity mini-

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(14) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(15) UCLA Crystallographic Computing Package, University of California Los Angeles, 1981; C. Strouse: personal communication.

(16) Siemens Analytical X-Ray Instruments, Inc.; Madison, WI, 1989.

(17) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; (a) pp 99–101; (b) pp 149–150.

mized during the least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0008(|F_o|)^2$.

The structure was solved by direct methods (SHELTXS PLUS); the positions of all non-hydrogen atoms were determined from a single "E-map". Hydrogen atoms were included using a riding model with fixed isotropic U values. The molecule is an anionic dimer and is located on an inverse center at $0,{}^1/_2,0$. There are two Et_3NH^+ cations per dimer. Refinement of positional and thermal parameters led to convergence with $R_f = 6.9\%$; $R_{wf} = 6.9\%$, and GOF = 1.41 for 245 variables refined against those 2107 data with $|F_o| > 2.0\sigma(|F_o|)$. A final difference Fourier map was "clean".

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Supplementary Material Available: Tables of experimental data for the X-ray diffraction study, atomic coordinates and equivalent isotropic displacement coefficients, interatomic distances and angles, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients (5 pages). Ordering information is given on any current masthead page.

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