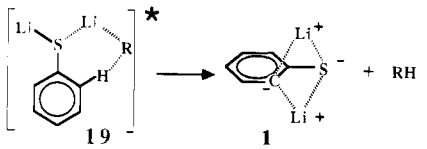
acid. Only after a strong acid (e.g., triflic acid, formed by reaction of TFAT with trifluoroacetic acid) is added to the trifluoroacetic acid solution of **8** do we see its complete ionization to form cation **9**. The lower basicity of **8** relative to **16** is, of course, partly attributed to the difference in the π-electron-donating ability of sulfur and oxygen (σ^+ for *p*-SMe is -0.164, while σ^+ for *p*-OMe is -0.648), making **16** the stronger base.

Conclusions on Ortho-Lithiation of Thiophenols. Although dimetalated thiophenols are clearly highly desirable synthetic intermediates, there has been little earlier success in their preparation. Very limited success was experienced by Gilman in preparing dilithiated thiophenol starting with 2-bromothiophenol.[4b]

The success of direct ortho-lithiation of lithium benzenethiolate is partly attributable to the choice of cyclohexane as a solvent. In a variety of other solvents we found lithiation by *n*-butyllithium-TMEDA to be much less effective. The nonpolar, unreactive cyclohexane solvent may favor coordination of the lithium cations, already coordinated to TMEDA, to the benzenethiolate anionic sulfur. The dilithiated species **1** could be formed via a transition state similar to **19**.[2e-g,16] The pictured ion cluster



structure of **1** was suggested by Streitwieser[17] after our personal communication to him concerning the preparation of **1**. The Coulomb interactions of two cations and a dicarbanion are favorable in such a geometry. (The lithium cations are also coordinated to the bidentate TMEDA ligands.)

The weak C-S bond of **1** provides an antibonding σ^* orbital low enough in energy to provide a stabilizing interaction with the adjacent carbanion lone pair of electrons in the plane of the benzene ring.[18,19] This may significantly contribute to the efficiency of this reaction.

Acknowledgment. The experimental aspects of this research were carried out at the University of Illinois with funding support from the U.S. Department of Health and Human Services (Grants CA-13963, GM-36844). We thank Dr. A. J. Arduengo, III for helpful suggestions, Dr. Eric Block for his cooperative interactions with us in his closely related studies, and Dr. Keith Smith for informing us of his related results.

Registry No. 1, 117526-82-6; **2**, 147-93-3; **3**, 62172-72-9; **4**, 58074-47-8; **5**, 14092-00-3; **8**, 117526-90-6; **9**, 117526-92-8; thiophenol, 108-98-5; diphenyl disulfide, 882-33-7; thioxanthone, 492-22-8; benzene-1,3-dithiol, 626-04-0.

(16) For further examples of species involving suggested chelation of lithium to a sulfide sulfur, see: Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807-1816. Abatjoglou, A. G.; Eliel, E. L.; Kuyper, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 8262-8269.

(17) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922. Compatible calculations on dilithio derivatives were also published by: Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 448.

(18) (a) For a discussion of stabilization of carbanions stabilized by adjacent vacant σ^* S-C bond molecular orbitals, see: Barbarella, G.; Dembech, P.; Garbesi, A.; Bernardi, F.; Bottoni, A.; Fava, A. *J. Am. Chem. Soc.* **1978**, *100*, 200-202. (b) For a discussion that rules out d-orbital effects in the above carbanion stabilization, see: Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M. H.; Wolfe, S. *Ibid.* **1975**, *97*, 2209-2218. (c) For a discussion of stabilization of carbanions next to sulfur through a σ^* interaction, see: Streitwieser, A., Jr.; Ewing, S. P. *Ibid.* **1975**, *97*, 190-191. Streitwieser, A., Jr.; Williams, J. E., Jr. *Ibid.* **1975**, *97*, 191-192. Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *Ibid.* **1976**, *98*, 5435-5439. Bernardi, F.; Schlegel, H. B.; Whangbo, M. H.; Wolfe, S. *Ibid.* **1977**, *99*, 5633-5636. (d) For other related discussions, see: Eliel, E. L.; Willer, R. L. *Ibid.* **1977**, *99*, 1936-1942. Graham, S. L.; Heathcock, C. H. *Ibid.* **1980**, *102*, 3713-3718, and references therein.

(19) The analogous ortho-lithiation of lithium benzeneselenolate (Loop, C.; Martin, J. C., in preparation) is facile, providing data compatible with suggested explanations for the formation of **1**.

o-Lithiothiophenol Equivalents: Generation, Reactions, and Applications in Synthesis of Hindered Thiolate Ligands[1]

Eric Block,* Venkatachalam Eswarakrishnan, Michael Gernon, Gabriel Ofori-Okai, Chantu Saha, Kaluo Tang, and Jon Zubieta

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222. *Received March 14, 1988*

Abstract: Treatment of 2-(phenylthio)tetrahydropyran (**11**) with *tert*-butyllithium in THF-HMPA at -90 °C followed by chlorotrimethylsilane or chlorotriethylsilane and then mercuric chloride-hydrogen sulfide affords 2-(trimethylsilyl)benzenethiol (**13**) or 2-(triethylsilyl)benzenethiol (**14**), respectively. Compounds **13** and **14** can also be obtained directly from thiophenol by conversion of the latter to lithium 2-lithiobenzenethiolate (**16**) followed by quenching of a THF solution of **16** at -78 °C with an equivalent of the appropriate chlorosilane; by this same procedure, 4-*tert*-butylbenzenethiol can be converted into 4-*tert*-butyl-2-(trimethylsilyl)benzenethiol (**18**) via lithium 4-*tert*-butyl-2-lithiobenzenethiolate (**17**) and 2-naphthalenethiol can be transformed into 3-(trimethylsilyl)-2-naphthalenethiol (**31**) via lithium 3-lithio-2-naphthalenethiolate (**30**). Reaction of **13** with *n*-butyllithium in hexane followed by chlorotrimethylsilane gives 2,6-bis(trimethylsilyl)benzenethiol (**15**) together with products derived from lithiation of the silyl methyl groups. Treatment of a solution of **16** in THF with dichlorodimethylsilane, dichlorodiethylsilane, 1,2-dichlorotetramethyldisilane, or 1,2-bis(chlorodimethylsilyl)ethane affords bis(2-mercaptophenyl)-dimethylsilane (**23**), bis(2-mercaptophenyl)diethylsilane (**24**), 1,2-bis(2-mercaptophenyl)tetramethyldisilane (**25a**), or 1,2-bis[(2'-mercaptophenyl)dimethylsilyl]ethane (**25b**), respectively. Oxidation of **23** yields 11,11-dimethyl-11*H*-dibenzo[*c*,*f*]-[1,2,5]dithiasilepin (**26**). Treatment of **17** with diethyldichlorosilane and dichlorodiphenylsilane affords bis(5-*tert*-butyl-2-mercaptophenyl)diethylsilane (**27**) and bis(5-*tert*-butyl-2-mercaptophenyl)diphenylsilane (**28**), respectively. The latter compound upon exposure to air gives **29**, the diphenyl analogue of **26**. Thiophenol can be transformed into 1,2-benzenedithiol (**32a**) by way of **12**; similarly 4-*tert*-butylbenzenethiol can be converted into 4-*tert*-butyl-1,2-benzenedithiol (**32b**). Compound **32a** can be further transformed into 1,2,3-benzenetrithiol (**34**) via a trilithio species **33**. The ^1H and ^{13}C NMR spectra of dilithio salts **16** and **17** were determined.

The intense contemporary interest in metal thiolate chemistry[2] reflects both the biological significance and the structural diversity associated with this fundamental metal-ligand type. In connection with our research on nitrogenase models, we have initiated a

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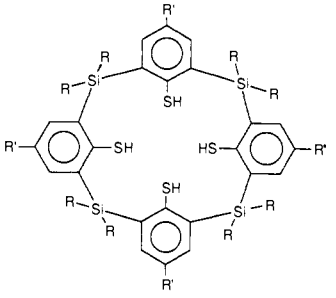
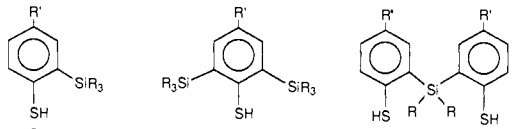
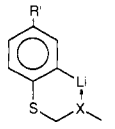
program to synthesize calixarene[3]-like cyclic tetramers of thiophenol, e.g., **1**, which should be capable of binding metals[4] such



1



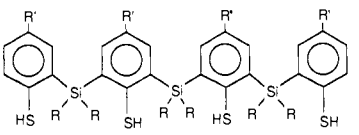
2 **3** **4**



5

as molybdenum and providing a cavity accessible to small linear molecules such as nitrogen. The use of silicon to bridge the rings in **1** should provide a larger cavity size than possible with carbon and could offer opportunities for bridge functionalization, e.g., by having Si–H or Si–Si bonds for construction of an end-capping group. It was our hope that synthesis of a system such as **1** could be achieved by repetitive ortho-lithiation of a thiophenol equivalent and coupling with a dichlorosilane under dilute conditions. Since satisfactory syntheses of 2-(triorganosilyl)thiophenols **2**, 2,6-bis(triorganosilyl)thiophenols **3**, and bis(2-mercaptoaryl)dialkylsilanes **4** were not available,[5a] our immediate goals were to prepare **2**–**4** by way of a suitable *o*-lithiothiophenol equivalent such as **5**.[5b] In the longer term we hope to extend the procedure to prepare acyclic and cyclic polythiophenols such as **6** and **1**. Related types of polythiophenol ligands can be envisioned with the rings linked by other atoms or groups in place of, or in addition to, silicon, e.g., sulfide sulfur (see **7** and **8**). Synthesis of **7** and **8** would require reaction of *o*-lithiothiophenol equivalents with appropriate sulfur electrophiles. We describe here our realization of the initial goals of this project as well as extension to related systems.

Synthesis and Reactions of *o*-Lithiothiophenol Equivalents. Our success in converting 2-(methylthio)tetrahydropyran (**9**) into lithiomethyl compound **10** and this to (trimethylsilyl)methanethiol



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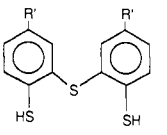

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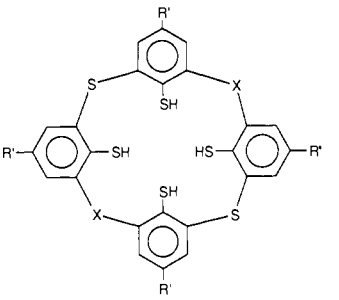
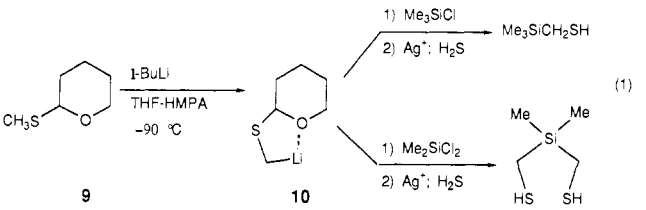


8 (X = S or R_2Si)

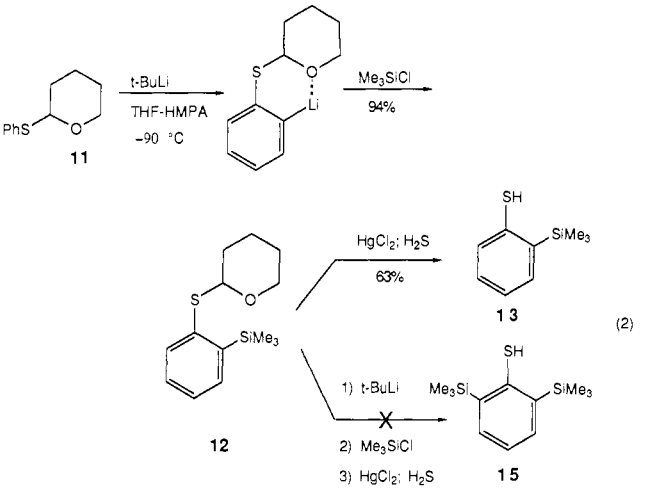
or bis(mercaptomethyl)dimethylsilane (eq 1)[1b,6a] encouraged us to attempt ortho deprotonation of 2-(phenylthio)tetrahydropyran



(1)

9 **10**

(**11**)[6b] under the conditions used with **9**, despite reports by Seebach that this reaction cannot be achieved.[6c] We find that under carefully controlled conditions (1.2 equiv of *tert*-butyllithium, 9:1 THF–HMPA, −90 °C) **11** could be deprotonated in the ortho position and the resultant lithio compound trapped with chlorotrimethylsilane, giving adduct **12**. The THP group of **12** could be removed with mercuric chloride followed by hydrogen sulfide to give 2-(trimethylsilyl)benzenethiol[5a] (**13**) in 63% overall yield (eq 2). In a similar manner 2-(triethylsilyl)benzenethiol (**14**)



(2)

11 **12** **13** **15**

could be prepared in 42% overall isolated yield. The latter compound shows the curious ^1H NMR feature of having a *singlet* for the ethyl group even at 300 MHz due to accidental degeneracy of the methyl and methylene protons. The spectrum could be interpreted by HETCOR experiments (see Experimental Section). We were unable to convert **12** into 2,6-bis(trimethylsilyl)-

(1) (a) Presented in part at the Ninth International Symposium on Sulfur Chemistry, Nijmegen, The Netherlands, June, 1986, the First International Conference on Heteroatom Chemistry, Kobe, Japan, July 1987, and the Eleventh International Symposium on Heterocyclic Chemistry, Heidelberg, West Germany, August 1987. (b) For brief mention of this work and a general review of the chemistry of mixed organosilicon–sulfur compounds, see: Block, E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281. Block, E. *Rev. Heteroatom Chem.* **1988**, *1*, 163.

(2) (a) Dance, I. G. *Polyhedron* **1986**, *5*, 1037. (b) Blower, P. G.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.

(3) Gutsche, C. D. *Acc. Chem. Res.* **1983**, *16*, 161. Gutsche, C. D. *Top. Curr. Chem.* **1986**, *51*, 742, and references therein.

(4) For example, see: Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 8087.

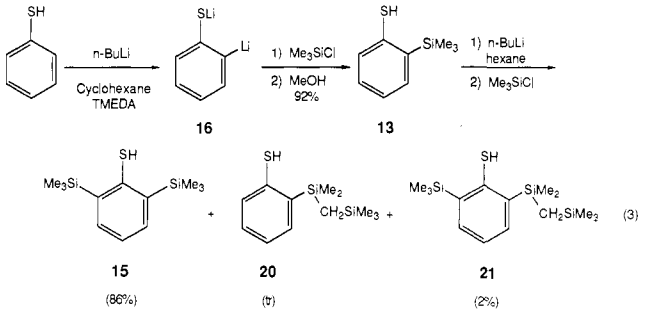
(5) (a) Bailey, F. P.; Taylor, R. *J. Chem. Soc. B* **1971**, 1446. (b) Ortholithiation of aryl sulfones and arenesulfonates and dilithiation of aryl alkyl sulfides is known: Figuly, G. D.; Martin, J. C. *J. Org. Chem.* **1980**, *45*, 3728. Stoyanovich, F. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1980**, *1*, 145. Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155. Bonfiglio, J. N. *J. Org. Chem.* **1986**, *51*, 2833. Cabiddu, S.; Florida, C.; Malis, S. *Tetrahedron Lett.* **1986**, *27*, 4625.

(6) (a) Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1985**, *107*, 6729. (b) Parham, W. E.; DeLaitsch, D. M. *J. Am. Chem. Soc.* **1954**, *76*, 4962. (c) Seebach, D.; Meyer, N.; Beck, A. K. *Justus Liebigs Ann. Chem.* **1977**, 846. (d) Kruse, C. G.; Broekhof, N. L. J. M.; Van der Gen, A. *Tetrahedron Lett.* **1976**, 1725. (e) Grillot, G. F.; Felton, H. R.; Garrett, B. R.; Greenberg, H.; Green, R.; Clementi, R.; Moskowitz, M. *J. Am. Chem. Soc.* **1954**, *76*, 3869.

benzenethiol (**15**) by repetition of the above procedure (see eq 2). We surmise that the presence of the bulky *o*-trimethylsilyl group in **12** prevents the 2-tetrahydropyranylthio group from adopting a conformation suitable for chelating the *o*-lithio group. Attempts to employ 2-(phenylthio)tetrahydrofuran[6d] instead of **11** were not promising. An alternative approach to an *o*-lithiophenol synthon **5** in which X is nitrogen failed. Sequential treatment of phenyl (diethylamino)methyl sulfide[6e] with *tert*-butyllithium in THF–HMPA at −78 °C and chlorotrimethylsilane did not yield any silylated products.

Encouraged by the report of Posner[7] on the ortho-lithiation of phenol, we examined the reaction of thiophenol **13** with *tert*-butyllithium in tetrahydropyran. It was hoped that steric effects might be less pronounced with **13** than with **12**. In the event **13** could be dilithiated with *tert*-butyllithium; silylation gave **15** together with a mixture of other bis- and tris-silylated thiophenols (see below). Following our discovery of the lithiation of **13** we learned that Martin and Figuly had independently discovered that thiophenol itself can readily be converted into an *o*-dilithio compound **16** which could be condensed with various electrophiles.[8] Information was exchanged with Professor Martin, and it was agreed that our two groups would work on different applications of *o*-lithiothiophenol equivalents.

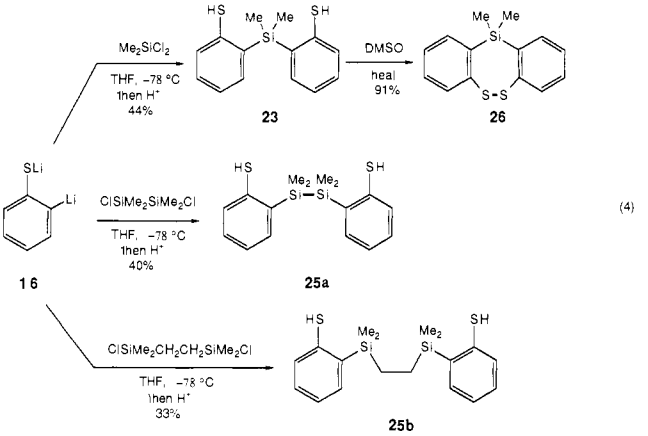
2-(Trialkylsilyl)- or 2-(triarylsilyl)thiophenols can be prepared by adding excess chlorosilane to the cyclohexane suspension of dilithio salt; workup requires refluxing in methanol to remove the silyl group from sulfur (eq 3). Yields decreased as the bulk of



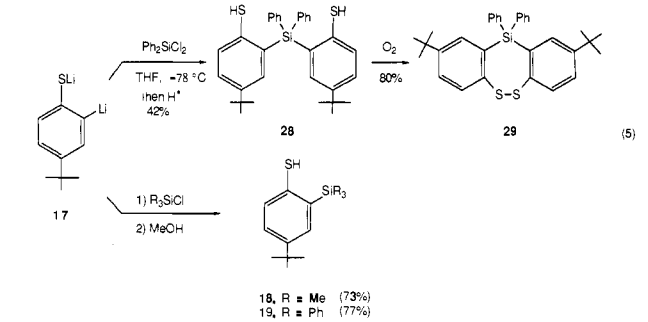
the silylating agent increased. Thus, the isolated yields of 2-(trimethylsilyl)-, 2-(triethylsilyl)-, 2-(triphenylsilyl)-, and 2-(*tert*-butyldimethylsilyl)benzenethiols from reaction of dilithio salt **16** using the Martin and Figuly procedure decreased in the order 92%, 79%, 43%, and 28%, respectively. The Martin and Figuly procedure can also be applied to substituted thiophenols. We have been able to prepare 4-*tert*-butyl-2-(trimethylsilyl)-benzenethiol (**18**) and 4-*tert*-butyl-2-(triphenylsilyl)benzenethiol (**19**) from 4-*tert*-butylbenzenethiol via lithium 4-*tert*-butyl-2-lithiobenzenethiolate (**17**).

Efforts to silylate the 6-position of 2-(trimethylsilyl)benzenethiol (**13**) are complicated by the fact that **13** undergoes deprotonation and silylation at *both* the 6-position and the methyl groups attached to silicon[9] giving rise to difficultly separable mixtures of 2,6-bis(trimethylsilyl)benzenethiol (**15**), 2-[dimethyl[(trimethylsilyl)methyl]silyl]benzenethiol (**20**), and 2-(trimethylsilyl)-6-[dimethyl[(trimethylsilyl)methyl]silyl]benzenethiol (**21**) (eq 3). Fortunately, we find that if the lithiation of **13** is conducted in hexane pure **15** can be isolated by fractional distillation in 60% yield. Silylation α to silicon could also be prevented through use of 2-(triethylsilyl)benzenethiol (**14**), although conversion of **14** to 2,6-bis(triethylsilyl)benzenethiol (**22**) is poor even after several days. From our results it is clear that the Martin and Figuly procedure is simpler and gives superior yields compared to procedures involving a THP group, primarily because of difficulties in removing the THP group from sulfur. In particular, strongly acidic conditions cannot be used to deprotect silylated THP–thiophenol derivatives because of possible protiodesilylation.

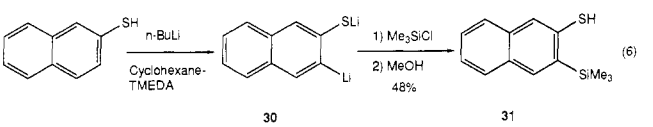
The Martin and Figuly procedure employing the cyclohexane suspension of dilithio salts **16** and **17** cannot be used to prepare bis(thiophenol) **4** since both the thiolate and carbanionic centers compete for silicon, leading to polymer. However, if solid **16** and **17** are allowed to settle, the solvent is removed via syringe, and the solid is washed several times with pentane and then dissolved in the minimal amount of cold tetrahydrofuran, reactions involving **16** and **17** can now be conducted at −78 °C with a resultant increase in selectively ("modified Martin and Figuly" procedure). We were delighted to discover that using this modified procedure **16** reacted with dichlorodimethylsilane, dichlorodiethylsilane, 1,2-dichloro-1,1,2,2-tetramethyldisilane, and 1,2-bis(chlorodimethylsilyl)ethane exclusively at the carbanionic center affording good yields of the corresponding bis(2-mercaptophenyl) derivatives (**23–25**) as products which could be directly crystallized from pentane giving colorless solids (eq 4). Bisthiophenol **23** could



be oxidized in high yield to 11,11-dimethyl-11*H*-dibenzo[*c*,*f*][1,2,5]dithiasilepin (**26**) (eq 4). In a similar manner, reaction of the dilithio salt **17** of 4-*tert*-butylbenzenethiol with dichlorodiethylsilane gave diethyl bis(2-mercapto-5-*tert*-butylphenyl)silane (**27**) while dichlorodiphenylsilane directly gave 2,9-di-*tert*-butyl-11,11-diphenyl-11*H*-dibenzo[*c*,*f*][1,2,5]dithiasilepin (**29**) (eq 5). In this latter case, dithiol **28** undergoes rapid oxidation by



oxygen to **29**; **28** can be isolated if care is taken to exclude oxygen during workup. The cyclic disulfides contain a new type of heterocyclic ring system and offer possibilities for preparation of metal complexes by insertion of metals into the S–S bonds. Using the modified Martin and Figuly procedure, we could also directly prepare *o*-(trialkylsilyl)thiophenols in high yields without the methanol reflux step. We have also been able to dilithiate 2-naphthalenethiol and silylate the resultant dilithio salt **30** affording 3-(trimethylsilyl)-2-naphthalenethiol (**31**) in 96% yield based on unrecovered starting material (eq 6).



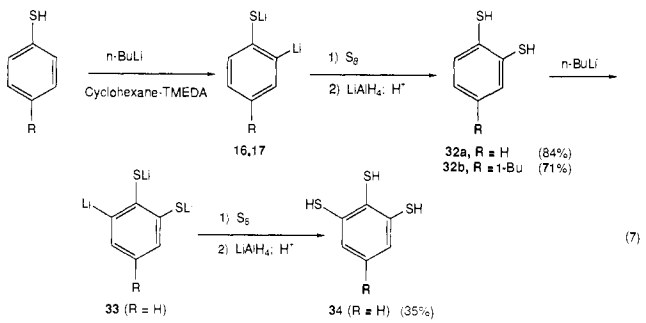
(7) Posner, G. H.; Canella, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 2571.
(8) (a) Figuly, G. D. Ph.D. Thesis, University of Illinois—Urbana, 1981. (b) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.*, preceding paper in this issue. (c) For earlier efforts to prepare lithium 4-lithiobenzenethiolate from 4-bromothiophenol, see: Gilman, H.; Gainer, G. C. *J. Am. Chem. Soc.* **1947**, *69*, 1946. Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 339.
(9) For a recent related example, see: Macdonald, J. E.; Poindexter, G. S. *Tetrahedron Lett.* **1987**, *28*, 1851.

Table I. ^1H and ^{13}C NMR Chemical Shifts of Lithium 2-Lithiobenzenethiolate (**16**) and Lithium 4-*tert*-Butyl-2-lithiobenzenethiolate (**17**)

compd	^1H or ^{13}C	chemical shift, δ
16[c]	^1H[a]	7.61 (dd, 1 H, J = 6.6, 2.0 Hz, C_3), 7.39 (d, 1 H, J = 7.4 Hz, C_6), 6.73 (ddd, 1 H, J = 7.8, 7.0, 2.0 Hz, C_5), 6.65 (dd, 1 H, J = 7.0, 6.6 Hz, C_4), 2.30 (s, 4 H, TMEDA CH_2), 2.14 (2, 12 H, TMEDA CH_3)
	^{13}C[a]	143.73 (CH), 134.39 (C), 132.02 (CH), 127.18[e] (C), 126.16 (CH), 120.31 (CH), 58.29 (TMEDA CH_2), 46.19 (TMEDA CH_3)
17[d]	^1H[b]	7.61 (s, 1 H, C_3), 7.15 (d, 1 H, J = 8.3 Hz, C_6), 6.67 (d, 1 H, J = 89.3 Hz, C_5), 2.25 (s, 4 H, TMEDA CH_2), 2.10 (s, 12 H, TMEDA CH_3), 1.18 (s, 9 H, $(CH_3)_3C$)
	^{13}C[b]	140.30 (C), 134.11 (C), 131.43 (CH), 124.08 (CH), 123.26 (CH), 140.27 (C), 58.79 (TMEDA CH_2), 46.30 (TMEDA CH_3), 34.50 (C), 32.56 ($(CH_3)_3C$)

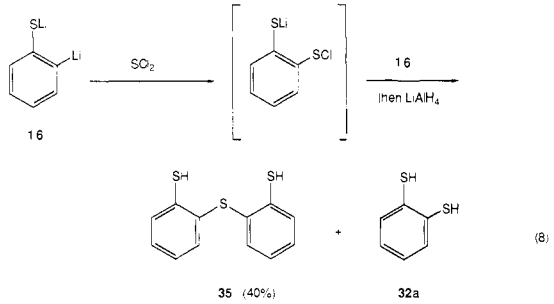
[a] THF–C_6D_6. [b] THF–THF-d_8. [c] Lithium benzenethiolate: ^1H NMR[a] δ 7.39 (d, 2 H, J = 8.0 Hz, $C_{2,6}$), 6.81 (t, 2 H, J = 7.8 Hz, $C_{3,5}$), 6.64 (t, 1 H, J = 7.4 Hz, C_4); ^{13}C NMR[a] δ 152.06 (C), 134.35 (CH), 127.25 (CH), 119.78 (CH). [d] Lithium 4-*tert*-butylbenzenethiolate: ^1H NMR[b] δ 7.19 (d, 2 H, J = 8.3 Hz, $C_{2,6}$), 6.78 (d, 2 H, J = 8.3 Hz, $C_{3,5}$), 1.16 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR[b] δ 148.77 (C), 141.78 (C), 133.95 (CH), 123.93 (CH), 34.24 (C), 31.93 (CH_3). [e] Assignment uncertain.

Illustrative of the considerable utility of the Martin and Figuly procedure is our observation that benzene-1,2-dithiol (**32a**; eq 7)



(7)

can be prepared in 84% distilled yield in a one-pot process from thiophenol! In a similar manner 4-*tert*-butylbenzenethiol could be converted to 4-*tert*-butylbenzene-1,2-dithiol (**32b**) in 71% isolated yield. Our preparation of **32** compares favorably with earlier procedures[10] in terms of ease of reaction as well as yield and may offer advantages due to the mild conditions. Furthermore, treatment of dithiol **32a** with excess *n*-butyllithium followed by sulfur directly gave benzene-1,2,3-trithiol (**34**) in 35% isolated yield. This reaction presumably involves trilithio species **33**. In an effort to develop syntheses of **7** and **8**, the reaction of dilithio salt **16** with sulfur dichloride was examined. Following lithium aluminum hydride reduction a mixture of products was obtained containing dithiol **32a** and the desired product bis(2-mercaptophenyl) sulfide (**35**), both in ca. 40% yield (eq 8). We suggest that **32a** and **35** are formed by S–Li and C–Li attack, respectively, on the S–Cl bond of lithium 2-(chlorosulfenyl)benzenethiolate (eq 8).



(8)

If residual cyclohexane is removed from the dilithio salts **16** and **17** under vacuum, the free-flowing off-white powders can be kept in an inert atmosphere and retain their activity indefinitely. Data on the ^1H and ^{13}C NMR spectra of the dilithio salts **16** and **17** dissolved in THF are given in Table I. NMR analysis indicates that both solids contain 1 mol of TMEDA/mol of dilithio salt. The NMR data is in accord with the proposed structures and with data on related compounds. Efforts to obtain an X-ray crystal structure of **16** or **17** are currently underway.

Conclusion. The facile preparation of lithium 2-lithiobenzenethiolate offers many interesting possibilities for coupling with diverse electrophiles affording novel benzenethiol derivatives not readily available by other methods. Extension of the lithiation procedure to other aromatic thiols (e.g., 2-pyridinethiol[11a]) and polythiols offers additional opportunities for arenethiol synthesis. We describe elsewhere use of the new arenethiols made available by this work for preparation of unusual metal complexes.[11]

Experimental Section

Phenyl 2-Tetrahydropyranyl Sulfide (11). A solution of dihydropyran (70.7 g, 0.84 mol), thiophenol (92.4 g, 0.84 mol), and pyridinium *p*-toluenesulfonate[12] (21.1 g, 0.084 mol) in methylene chloride (500 mL) was stirred at 25 °C for 4 h and then washed with 10% NaOH (4 × 300 mL) and saturated brine (2 × 300 mL). The organic layer was dried ($MgSO_4$), filtered, concentrated in vacuo, and distilled giving 150 g (92% yield) of the title compound: bp 90 °C (0.15 mmHg) [lit.[6b] bp 130–131 °C (4 mmHg)], 98% pure by GC; ^1H NMR δ 7.45 (d, 2 H, J = 7.4 Hz), 7.3–7.1 (m, 3 H), 5.18 (t, 1 H, J = 4.6 Hz), 4.13 (ddd, 1 H, $J \cong$ 5.4 Hz), 3.53 (ddd, 1 H, $J \cong$ 5.4 Hz), 2.10–1.90 (m, 2 H), 1.9–1.7 (m, 2 H), 1.7–1.5 (m, 2 H); ^{13}C NMR δ 135.52, 130.73, 128.70, 126.58, 85.15, 64.28, 31.54, 25.50, 21.58; GC–MS, m/e 194 (M^+, 4), 110 (20), 85 (100), 67 (24), 57 (28).

2-(Trimethylsilyl)benzenethiol (13). Procedure 1. A mixture of dry THF (160 mL), dry HMPA (18 mL), and phenyl 2-tetrahydropyranyl sulfide (**11**; 7.8 g, 0.04 mol) was cooled under argon to −95 °C (CH_2Cl_2–liquid nitrogen) and then treated dropwise with 1.7 M *tert*-butyllithium (30 mL, 0.051 mol), keeping the temperature below −90 °C. The dark red solution was stirred at −95 °C for 2 h, quenched with chlorotrimethylsilane (7.0 g, 0.065 mol), warmed to 25 °C, and concentrated in vacuo and the concentrate was diluted to 600 mL with ether. The solution was extracted with 5% HCl (2 × 300 mL). The ether layer was separated, dried ($MgSO_4$), concentrated, and kept at 0.1 mm for 8 h. The intermediate, 2-(trimethylsilyl)phenyl 2-tetrahydropyranyl sulfide (**12**; 10.1 g, 94% yield), was 90% pure by GC analysis: ^1H NMR δ 7.61 (d, 1 H, J = 7.1 Hz), 7.42 (d, 1 H, J = 7.2 Hz), 7.25 (dd, 1 H, J = 7.1 Hz), 7.15 (dd, 1 H, J = 7.1 Hz), 5.15–5.05 (m, 1 H, 4.21 (m, 1 H), 3.50 (m, 1 H), 2.1–1.9 (m, 2 H), 1.9–1.7 (m, 2 H), 1.7–1.5 (m, 2 H), 0.38 (s, 9 H); ^{13}C NMR δ 142.49, 141.73, 134.53, 131.73, 129.60, 126.05, 86.20, 64.28, 31.85, 25.62, 21.66, 0.20; MS, m/e 266 (M^+, 1), 182 (5), 167 (7), 166 (10), 151 (15), 85 (100). The intermediate was taken up in absolute MeOH (150 mL) to which was added solid K_2CO_3 (2.8 g, 0.02 mol). An aqueous solution of silver nitrate (6.4 g, 0.038 mol; 40 mL water) was added slowly with stirring, and the resulting suspension was stirred for 3 h. The solid silver salt was collected by vacuum filtration and washed (pentane, water). The off-white solid was dried under vacuum (9.1 g, 83% yield) and had mp 80 °C (dec). The solid was suspended in CH_2Cl_2 (200 mL), through which hydrogen sulfide was bubbled for 1.5 h. The resultant silver sulfide was removed by filtration through Celite. The filtrate was concentrated in vacuo and distilled to give the title compound (4.6 g, 63% yield) as a colorless oil: bp 55 °C (0.1 mm), 98% pure by GC (GC retention time 5.4 min, 150 °C); ^1H NMR (C_6D_6) δ 7.34 (dd, 1 H, J = 6.1, 3.5 Hz), 7.05–6.90 (m, 3 H), 3.22 (s, 1 H) 0.35 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 139.21, 137.39, 135.10,

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131.57, 129.61, 125.16, −0.44; IR (neat) 3055, 2960, 2900, 2560 (w), 1580, 1560, 1460, 1420, 1410 cm^{-1}; GC–MS, *m/e* 182 (M^+, 17), 167 (66), 166 (72), 151 (100). Anal. Calcd for $C_9H_{14}SSi$: C, 59.28, H, 7.74. Found: C, 59.87; H, 8.15.

2-(Trimethylsilyl)benzenethiol (13). Procedure 2. Lithium 2-lithiobenzenethiolate (**16**) was prepared by the procedure of Martin and Figuly.[8a] A 1-L three-necked flask equipped with magnetic spin bar, an addition funnel, a three-way adapter, and a septum was flame-dried under vacuum, cooled under argon, and charged with dry cyclohexane (350 mL), TMEDA (37.2 g, 0.32 mol), and 2.5 M *n*-butyllithium (130 mL, 0.325 mol; added by syringe). Thiophenol (16.5 g, 0.15 mol) in cyclohexane (20 mL) was added to the resultant suspension at 0 °C. The solution, which became homogeneous, was stirred at 25 °C for 24 h, during which time an off-white solid formed. To this well-stirred suspension was added chlorotrimethylsilane (40.8 g, 0.37 mol), and the now bright white suspension was stirred for an additional 12 h. Water (50 mL) was added, the mixture concentrated in vacuo, the residue taken up in ether (1 L), and the ether extracted with 5% HCl (3 × 400 mL) and concentrated brine (2 × 200 mL). The ether solution was dried ($MgSO_4$) and concentrated in vacuo and the residue dissolved in absolute MeOH (250 mL) and refluxed for 12 h. Concentration in vacuo followed by distillation yielded the title compound (24.4 g, 89% yield) as a colorless oil, 98% pure by GC.

2-(Trimethylsilyl)benzenethiol (13). Procedure 3. Lithium 2-lithiobenzenethiolate (**16**) was prepared as described above in procedure 2 from thiophenol (8.25 g, 0.075 mol) by using dry cyclohexane (225 mL), TMEDA (21.75 g, 0.188 mol), and 2.5 M *n*-butyllithium (75 mL, 0.188 mol). After 24 h, the solid was allowed to settle and the solvent was removed by syringe. The residue was washed twice with dry cyclohexane or pentane. Each time the suspension was vigorously stirred before being allowed to settle. After removal of solvent by syringe the reaction flask was cooled to −78 °C and dry THF (175 mL) was added with stirring. The cooling bath was removed, and the mixture was stirred, allowed to warm until it became homogeneous (20 min), and was then cooled back to −78 °C. Chlorotrimethylsilane (8.13 g, 0.075 mol) dissolved in dry THF (15 mL) was slowly added to the vigorously stirred reaction mixture at −78 °C, and stirring was continued for 1 h at −78 °C. The reaction mixture was warmed to 25 °C during 3 h, water (25 mL) was added, and solvent was removed in vacuo. The residue was dissolved in water (500 mL) which was acidified at 0 °C with 3% HCl to ca. pH 2–3. The reaction mixture was extracted with CH_2Cl_2 (3 × 250 mL); the organic phase was washed with water (2 × 250 mL), dried ($MgSO_4$), and concentrated in vacuo, ultimately at 0.3 mm for 2 h. The title compound was obtained as a yellow liquid (10.25 g, 75% yield); distillation gave a colorless oil (8.5 g, 62% yield 99% pure by GC).

2-(Triethylsilyl)benzenethiol (14). Dilithio salt **16** (0.10 mol), prepared as described in the synthesis of **13** by procedure 2, was quenched with chlorotriethylsilane (0.22 mol). Workup as above, followed by careful distillation (discarding low-boiling fractions) and chromatography, gave the title compound as a colorless oil (17.8 g, 79% yield): bp 65–75 °C (0.05 mm), 96% pure by GC. An analytical sample prepared by further purification of the distilled material using a Chromatotron (2-mm silica gel plate; hexane) gave the following: ^1H NMR δ 7.37 (d, 1 H, *J* = 6.6 Hz), 7.23 (d, 1 H, *J* = 7.4 Hz), 7.18–7.05 (m, 2 H), 3.44 (s, 1 H), 0.96 (s, 15 H); ^{13}C NMR δ 137.69, 136.59, 136.25, 131.52, 129.49, 125.00, 7.57 (CH_3), 3.73 (CH_2); IR (neat) 3050, 2950, 2870, 2560 (very weak), 1580, 1560, 1460, 1420, 1380 cm^{-1}; GC–MS, *m/e* 224 (M^+, 2), 196, (18), 194, (22), 195 (100), 167 (59), 165 (34), 139 (93), 137 (54), 79 (41), 78 (22), 77 (87). HETCOR experiments removed the degeneracy of the 0.96 ppm singlet in the ^1H NMR spectrum, indicating that it consists of both methyl and methylene protons. Anal. Calcd for $C_{12}H_{20}SSi$: C, 64.22; H, 8.98. Found: C, 64.43; H, 9.24.

2-(*tert*-Butyldimethylsilyl)benzenethiol. As in the preparation of **13** by procedure 2, dilithio salt **16** was prepared from thiophenol (2.5 g, 0.023 mol) and quenched with chloro-*tert*-butyldimethylsilane (10.7 g, 0.070 mol). Workup as above (MeOH reflux, Kugelrohr distillation) gave the title compound as a colorless oil (1.41 g, 28% yield): bp 52–54 °C (0.01 mmHg), 98% pure by GC; ^1H NMR δ 7.43–7.08 (m, 4 H), 3.52 (s, 1 H), 0.93 (s, 9 H), 0.41 (s, 6 H); ^{13}C NMR δ 138.25, 136.89, 136.73, 131.33, 129.43, 124.47, 27.16, 18.28, −3.01; IR (neat) 2960, 2950, 2850, 2520 (very weak), 1480, 1260, cm^{-1}; GC–MS, *m/e* 224 (M^+, 12), 167 (100), 166 (23), 151 (49), 91 (22). Anal. Calcd for $C_{12}H_{20}SSi$: C, 64.22; H, 8.98. Found: C, 64.15; H, 9.09.

A minor (ca. 3%) side product isolated by preparative TLC from the distillation residue was identified as 2-[[*tert*-butyl[(*tert*-butyldimethylsilyl)methyl]methyl]silyl]benzenethiol: ^1H NMR δ 7.48–7.06 (m, 4 H), 3.53 (s, 1 H), 0.93 (s, 9 H), 0.91 (s, 9 H), 0.48 (s, 3 H), −0.07 (s, 6 H), −0.29 (s, 2 H); ^{13}C NMR δ 136.98, 131.342, 129.28, 124.24, 27.31, 26.40, 19.10, 17.30, −1.96, −3.30, −4.20, −6.81; IR (neat) 2950, 2850, 2510 (very weak), 1480, 1260, 1050 cm^{-1}; GC–MS, *m/e* 282 (15), 265 (33), 223 (100), 151 (7), 91 (81), 73 (41).

2-(Triphenylsilyl)benzenethiol. As in procedure 3 for **13**, dilithio salt **16** was prepared from thiophenol (5 g, 0.045 mol), dissolved in THF (100 mL), and quenched with chlorotriphenylsilane (10.7 g, 0.036 mol) in THF (60 mL). Workup, including washing the residual solid with hexane (20 mL), filtering, and drying under vacuum, gave the title compound as a colorless solid (6.4 g, 48% yield). Further purification using a Chromatotron (9:1 hexane–CH_2Cl_2) followed by recrystallization (CH_2Cl_2–hexane) gave colorless plates: mp 163–165 °C (43% purified yield); ^1H NMR δ 7.7–7.0 (m, 19 H, aromatic), 3.4 (s, 1 H, SH); ^{13}C NMR δ 139.36 (C), 139.09 (CH), 136.40 (CH), 134.06 (C), 133.82 (C), 131.53 (CH), 130.57 (CH), 129.68 (CH), 128.02 (CH), 125.24 (CH).

2,6-Bis(trimethylsilyl)benzenethiol (15), 2-[Dimethyl[(trimethylsilyl)methyl]silyl]benzenethiol (20), and 2-(Trimethylsilyl)-6-[dimethyl[(trimethylsilyl)methyl]silyl]benzenethiol (21). A mixture of TMEDA (9 mL, 0.06 mol) and **13** (10.9 g, 0.06 mol) was cooled to 0 °C and treated under argon with 2.5 M *n*-butyllithium (48 mL, 0.12 mol). The initial colorless precipitate dissolved after being stirred for ca. 5 h at 25 °C. After 18 h a voluminous precipitate appeared. Hexane (100 mL) was added, and stirring was continued for a further 6 h. At this time the suspension was cooled to −78 °C, chlorotrimethylsilane (13 g, 0.12 mol) was slowly added by syringe, the mixture was slowly warmed to 25 °C, and stirring was continued for 24 h. The product was then concentrated in vacuo, acidified with dilute H_2SO_4 to pH 3, and extracted into ether; the organic phase was washed with water, dried ($MgSO_4$), and concentrated, and the residue refluxed in MeOH for 15 h. The MeOH was removed under vacuum and the residue fractionally distilled through a 15-cm Vigreux column affording an impure first fraction [3.7 g; bp 45–80 °C (0.025 mmHg)] containing 33% **13** and 68% **15** and a purer second fraction [9.5 g; bp 82–84 °C (0.025 mmHg)] containing 96.5% **15** (63% isolated yield), 3.5% **21**, and a trace of **20**. Overall yield of **15** based on unrecovered **13** is 86%.

Different results were obtained if procedure 2 for **13** was used [cyclohexane (240 mL), TMEDA (30 mL, 0.20 mol), and 2.5 M *n*-butyllithium (100 mL, 0.25 mol) cooled to 0 °C and treated with **13** (18.2 g, 0.10 mol); suspension stirred at 25 °C for 16 h, quenched with chlorotrimethylsilane (26.0 g, 0.24 mol), and stirred at 25 °C for 12 h]. Workup as above gave a residue consisting of 45% **15**, 30% **20**, and 25% **21** by GC. Column chromatography (silica gel–hexane) followed by Kugelrohr distillation afforded **15** (9.4 g, 37% yield).

The percentage of **20** in the mixture could be increased if tetrahydropyran was used instead of cyclohexane–TMEDA and *tert*-butyllithium was used instead of *n*-butyllithium. Thus, 1.7 M *tert*-butyllithium (80 mL, 0.14 mol) was added dropwise by syringe to a solution of **13** (9.1 g, 0.05 mol) in anhydrous tetrahydropyran (50 mL) under argon at 25 °C in an apparatus fitted with a reflux condenser. The reddish-orange solution, which boiled briefly during *tert*-butyllithium addition, was stirred for 2 h, quenched with chlorotrimethylsilane (14.0 g, 0.13 mol), and stirred for an additional 0.5 h. Workup as above gave a crude product consisting of 5% **15**, 60% **20**, and 35% **21**. Chromatography of the mixture followed by Kugelrohr distillation gave **20** (2.0 g, 16% yield). The yield was not optimized.

The percentage of **21** in the mixture could be increased by using a larger excess of *n*-butyllithium than in the procedure giving predominantly **15** and by replacing the cyclohexane after 24 h with THF. Thus, at 0 °C, **13** (18.2 g, 0.10 mol) was added to cyclohexane (240 mL), TMEDA (30 mL, 0.20 mol), and 2.5 M *n*-butyllithium (150 mL, 0.38 mol) prepared as above. The suspension was stirred at room temperature for 24 h. The stirring was then stopped, and the solid was washed with dry cyclohexane as in the preparation of **13** by procedure 3. The flask was chilled in an ice bath, anhydrous THF (240 mL) was added, and the mixture was stirred until the solution became homogeneous. The pale yellow solution was quenched with chlorotrimethylsilane (38 g, 0.35 mol) and stirring continued at 25 °C for 12 h. Then water (50 mL) was added, and the mixture was concentrated in vacuo. Workup as above gave a crude product consisting of 10% **15**, 10% **20**, and 80% **21** by GC. Purification by vacuum distillation [bp 110–120 °C (0.05 mm)] followed by column chromatography (silica gel, hexane) gave **21** as a colorless oil (7.8 g, 14% yield).

15 (95% pure by GC): GC retention time 15.1 min (150 °C); ^1H NMR ($CDCl_3$) δ 7.46 (d, 2 H, *J* = 7.2 Hz), 7.19 (t, 1 H, *J* = 7.2 Hz), 3.50 (s, 1 H), 0.39 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 169.79, 143.46, 136.16, 125.62, 0.31; IR (neat) 3050, 2950, 2900, 2500 (very weak), 1560 (weak), 1350, 1240 cm^{-1}; GC–MS, *m/e* 254 (M^+, 5) 238 (28), 223 (81), 133 (22), 104 (25), 91 (12), 73 (100). Anal. Calcd for $C_{12}H_{22}SSi_2$: C, 56.63; H, 8.71. Found: C, 56.01; H, 9.11.

20 (99% pure by GC): GC retention time 16.0 min (150 °C); ^1H NMR δ 7.38–7.34 (m, 1 H), 7.00–6.88 (m, 3 H), 3.17 (s, 1 H), 0.40 (s, 6 H), 0.18 (s, 2 H), −0.02 (s, 9 H); ^{13}C NMR δ 140.11, 137.48, 135.13, 131.79, 129.57, 125.23, 3.09, 1.31, 0.82; GC–MS, *m/e* 254 (M^+, 1), 223

(84), 166 (100), 151 (30), 105 (10), 91 (28), 77 (18), 75 (14), 73 (77), 45 (37), 44 (10), 43 (26).

21 (98% pure by GC): GC retention time 8.45 min (190 °C); ^{1}H NMR ($CDCl_3$, external TMS) δ 7.63–7.58 (m, 2 H), 7.32 (dd, 1 H, $J \cong 7.3$ Hz), 3.64 (s, 1 H), 0.58 (s, 6 H), 0.55 (s, 9 H), 0.25 (s, 2 H), 0.09 (s, 9 H); ^{13}C NMR ($CDCl_3$; external TMS) δ 144.09, 143.54, 142.03, 136.13, 136.08, 125.73, 3.73, 1.65, 1.31, 0.47; IR (neat) 3050, 2975, 2900, 1560, 1410, 1360 cm^{-1}, GC–MS, m/e 326 (M^+, 0.4), 295 (41), 238 (87), 223 (85), 73 (100), 45 (32). Anal. Calcd for $C_{15}H_{30}SSi_3$: C, 55.14; H, 9.26. Found: C, 55.09; H, 9.54.

Characterization of Lithium 2-Lithiobenzenethiolate (16). The title compound was prepared as described above in the synthesis of **13**. Following the final removal of cyclohexane or pentane by syringe, either (1) anhydrous THF was added slowly to the stirred solid cooled at 0 °C until it became homogeneous or (2) the sample was placed under high vacuum to remove remaining cyclohexane and afford an off-white solid. The THF solution when fresh was pale yellow but upon standing became deep red-brown. A 0.7-mL aliquot of this freshly prepared THF solution was transferred by syringe to an NMR tube containing a small quantity of benzene-d_6 in an argon atmosphere: ^{1}H NMR δ 7.61 (dd, 1 H, J = 6.6, 2.0 Hz), 7.35 (d, 1 H, J = 7.8 Hz), 6.73 (ddd, 1 H, J = 7.8, 7.0, 2.0 Hz), 6.65 (dd, 1 H, J = 7.0, 6.6 Hz); ^{13}C NMR (C_6D_6–THF) δ 143.70, 134.39, 132.01, 127.18, 126.19, 120.31.

^{1}H NMR analysis of a THF-d_8 solution of **16** indicated the presence of 1 mol of TMEDA/mol of **16**.

The original THF solution prepared above was found to be ca. 0.5 M (by titration with excess chlorotrimethylsilane) and was stable at dry ice temperature for ca. 1 month and at 0 °C for ca. 4 h. Decomposition most probably involves deprotonation of the THF solvent since ^{1}H NMR signals characteristic of acetaldehyde enolate (a known decomposition product of the THF anion) appear with time. The solvent-free solid **16** is stable at 25 °C under anhydrous conditions for ca. 1 month.

4-*tert*-Butyl-2-(trimethylsilyl)benzenethiol (18). As in the preparation of **13** by procedure 2, 4-*tert*-butylbenzenethiol[13] (4.0 g, 0.024 mol) in cyclohexane (5 mL) was added to a mixture of 2.5 M *n*-butyllithium (24 mL, 0.06 mol), cyclohexane (40 mL), and TMEDA (6.2 g, 0.054 mol) at 0 °C in a 100-mL three-necked flask under argon. The solution was stirred for 24 h at room temperature, during which time no solid appeared. The solution was then quenched with chlorotrimethylsilane (6.9 g, 0.063 mol), and the resulting suspension of a colorless solid was stirred for 12 h. The mixture was concentrated in vacuo, the residue was acidified with 10% HCl and extracted with ether (2 × 100 mL), and the combined ether fractions were washed with 5% HCl (3 × 50 mL) and brine (2 × 50 mL). The ether phase was dried ($MgSO_4$) and concentrated in vacuo and the residue refluxed with MeOH for 12 h. Concentration in vacuo followed by Kugelrohr distillation afforded the title compound as a colorless oil (4.2 g, 73% yield): bp 120 °C (0.1 mm), 97% pure by GC [GC retention time 12.9 min (150 °C)]; ^{1}H NMR (C_6D_6) δ 7.51–7.50 (m, 1 H), 7.06–7.05 (m, 2 H), 3.15 (s, 1 H), 1.22 (s, 9 H), 0.39 (s, 9 H); ^{13}C NMR (C_6D_6) δ 147.77, 139.38, 133.69, 132.22, 131.89, 126.92, 34.36, 31.35, –0.20; IR (neat) 2960, 2900, 2860, 2580 (w), 1490, 1480, 1380, 1240 cm^{-1}; GC–MS, m/e 238 (M^+, 16), 222 (25), 207 (100), 167 (44), 41 (22). Anal. Calcd for $C_{13}H_{22}SSi$: C, 65.48; H, 9.30. Found: C, 65.17; H, 9.44.

4-*tert*-Butyl-2-(triphenylsilyl)benzenethiol (19). In a modification of the preparation of **13** by procedure 3, 4-*tert*-butylbenzenethiol[13] (1.65 g, 9.9 mmol) was added slowly to the complex prepared from TMEDA (3.35 mL) and *n*-butyllithium (10 mL of 2.5 M hexane solution, 25 mmol) at 0 °C and the mixture was stirred for 24 h. An orange-white precipitate was formed which was isolated by filtration under argon in a Schlenck tube on a medium frit, washed with dry hexane (2 × 50 mL), and transferred as a hexane (50-mL) slurry under argon to a three-necked flask containing a magnetic spinbar. The hexane was removed by syringe, the residue was cooled to –78 °C, THF (30 mL) was added, and the mixture was warmed to –30 °C to dissolve the dianion and then cooled once more to –78 °C and treated with vigorous stirring during the course of 1 h with a solution of chlorotriphenylsilane (1.77 g, 6 mmol) in THF (30 mL). The mixture was warmed to room temperature overnight, concentrated in vacuo, and treated with dilute sulfuric acid at 0 °C followed by ether. The ether layer was dried ($MgSO_4$) and concentrated, affording the title compound as an oil (1.97 g, 77% crude yield, ca. 80% pure). An analytical sample was prepared by thick-layer chromatography (silica gel, 1:9 CH_2Cl_2–hexane) followed by purification on a Chromatotron (hexane, 1:9 CH_2Cl_2–hexane, CH_2Cl_2) (18% yield after chromatography) and recrystallization from hexane: mp 192–194 °C; ^{1}H NMR δ 7.1–7.6 (br m, 18 H, phenyl), 3.26 (s, 1 H, SH), 1.04 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR δ 147.93 (C), 136.38 (CH), 135.27 (C), 134.08 (C), 133.72 (C), 131.49 (CH), 129.58 (CH), 127.92 (CH), 127.80 (CH), 127.66 (CH), 34.35 (C), 31.04 (CH_3). Anal. Calcd for $C_{28}H_{28}SSi$: C, 79.19; H, 6.65. Found: C, 79.17; H, 6.75.

2,6-Bis(triethylsilyl)benzenethiol (22). As in the preparation of **13** by procedure 2, 2-(triethylsilyl)benzenethiol (**14**; 2.24 g, 0.01 mol) was added to cyclohexane (40 mL), TMEDA (2.5 g, 0.022 mol), and 2.5 M *n*-butyllithium (14 mL, 0.035 mol) at 0 °C in a 100-mL three-necked flask under argon. The solution was stirred for 24 h at room temperature. The solution was then quenched with chlorotriethylsilane (3.8 g, 0.025 mol), and the resulting suspension was stirred for 12 h. Workup in the usual manner gave a crude product consisting of 80% 2-(triethylsilyl)-benzenethiol and 20% of the title compound. Chromatography (silica gel, hexane) followed by Kugelrohr distillation gave the title compound as a viscous, colorless oil (0.32 g, 9% yield): 95% pure by GC; ^{1}H NMR δ 7.42 (d, 2 H, J = 7.2 Hz), 7.17 (t, 1 H, J = 7.2 Hz), 3.50 (s, 1 H), 0.96 (s, 30 H); ^{13}C NMR ($CDCl_3$) 142.93, 140.29, 137.17, 125.23, 7.73, 4.38; GC–MS, m/e 338 (M^+, 0.3), 309 (100), 308 (36), 279 (82), 253 (44), 251 (84), 223 (66), 167 (53), 126 (33), 112 (52), 98 (52), 87 (42), 59 (49).

Bis(2-mercaptophenyl)dimethylsilane (23). Following the synthesis of **13** by procedure 2, the pentane-washed solid lithium 2-lithiobenzenethiolate (**16**), prepared from thiophenol (16 g, 0.145 mol) employing cyclohexane (300 mL), TMEDA (37.7 g, 0.325 mol), and *n*-butyllithium (2.5 M, 130 mL, 0.325 mol), was dissolved in dry THF (300 mL). Dichlorodimethylsilane (6.8 g, 0.053 mol) dissolved in dry THF (15 mL) was slowly added to the reaction mixture with vigorous stirring at –78 °C over the course of 1 h. Stirring was continued for 1 h at –78 °C. The reaction mixture was allowed to warm to 25 °C during 1 h, water (25 mL) was added, solvent was removed in vacuo, and the residue was dissolved in water (500 mL) which was then acidified at 0 °C with 3% HCl to ca. pH 2–3. The reaction mixture was extracted with CH_2Cl_2 (3 × 250 mL), and the organic phase was washed with water (2 × 250 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. After pumping on the concentrate at 0.05 mmHg and 60 °C for 2 h to remove thiophenol, the title compound was obtained as a light yellow solid (6.4 g, 44% yield), mp 77–78 °C after recrystallization from pentane or preparative TLC. The material purified by TLC was colorless: ^{1}H NMR δ 7.55–7.52 (m, 2 H), 7.31–7.17 (m, 6 H), 3.40 (s, 1 H, SH), 0.74 (s, 6 H, Me_2Si); ^{13}C NMR δ 137.74 (w), 137.59, 136.04 (w), 131.51, 130.07, 125.56, –1.42; IR (KBr) 3042, 2946, 2536 (m, SH), 1574, 1553, 1451, 1412, 1252, and 1102 cm^{-1}; GC–MS, m/e 276 (M^+, 0.6), 274 (3), 259 (9), 167 (17), 166 (100), 152 (15), 151 (78), 110 (12), 109 (5), 91 (23), 77 (12). Anal. Calcd for $C_{14}H_{16}SiS_2$: C, 60.85; H, 5.79. Found: C, 60.59; H, 5.71.

Bis(2-mercaptophenyl)diethylsilane (24). Following the synthesis of **13** by procedure 3, **16** was prepared from thiophenol (8.25 g, 0.075 mol) by using cyclohexane (200 mL), TMEDA (21.75 g, 0.188 mol), and 2.5 M *n*-butyllithium (82.5 mL, 0.206 mol). The washed solid was dissolved in THF (200 mL), and dichlorodiethylsilane (5.9 g, 0.038 mL) in THF (10 mL) was slowly added. Workup as in the case of **13** gave the title compound as a yellow solid (5.66 g, 50%). After recrystallization from pentane or preparative TLC, an analytical sample was obtained as a colorless solid: mp 94–95 °C; ^{1}H NMR δ 7.53–750 (m, 2 H), 7.29–7.15 (m, 6 H), 3.42 (s, 1 H, SH), 1.35 (q, 4 H, J = 7.6 Hz), 0.91 (t, 6 H, J = 7.6 Hz); ^{13}C NMR δ 137.84 (w), 136.58, 136.10 (w), 131.28, 129.89, 125.37, 7.43 (CH_2); IR (KBr) 2535 cm^{-1} (m, SH), all other peaks identical with **17**; MS, m/e 304 (M^+, 0.1), 302 (0.2), 275 (10), 273 (12), 213 (11), 195 (18), 194 (99), 166 (20), 165 (100), 137 (65), 110 (23), 109 (12), 77 (49). Anal. Calcd for $C_{16}H_{20}SiS_2$: C, 63.11; H, 6.61. Found: C, 63.36; H, 6.72.

1,2-Bis(2-mercaptophenyl)tetramethyldisilane (25a). Following the synthesis of **13** by procedure 3, lithium 2-lithiobenzenethiolate (**16**) was prepared from thiophenol (8.25 g, 0.075 mol) by using cyclohexane (250 mL), TMEDA (21.8 g, 0.188 mol), and *n*-butyllithium (2.5 m, 75 mL, 0.188 mol). The washed solid **16** was dissolved in THF (250 mL), and 1,2-dichlorotetramethyldisilane (5.6 g, 0.030 mol) in THF (10 mL) was slowly added as before. Workup as above gave the title compound as a yellow solid (4 g, 40% yield): mp 60–64 °C; ^{1}H NMR δ 7.40–7.12 (m, 8 H), 3.32 (s, 2 H, SH), 0.46 (s, 12 H, Me_2Si); ^{13}C NMR ($CDCl_3$; $CHCl_3$ internal standard at 77.0 ppm) δ 140.96 (w), 136.54, 135.21 (w), 131.80, 129.19, 125.54, –1.68. Anal. Calcd for $C_{16}H_{22}Si_2S_2$: C, 57.43; H, 6.63. Found: C, 57.19; H, 6.57.

11,11-Dimethyl-11*H*-dibenzo[*c*,*f*][1,2,5]dithiasilepin (26). Bis(2-mercaptophenyl)dimethylsilane (**23**, 0.276 g, 1 mmol) was dissolved in DMSO (250 mL) and heated at 80–85 °C for 20 h. Water (100 mL) was added to the reaction mixture and it was extracted with ether (3 × 100 mL). The ether solution was washed with water (5 × 300 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo to give a yellowish thick oil (250 mg, 91%) which after purification as above gave a colorless solid: mp 73–74 °C; ^{1}H NMR δ 7.71–7.68 (m, 2 H), 7.46–7.43 (m, 2 H), 7.25–7.23 (m, 4 H), 0.68 (s, 6 H); ^{13}C NMR δ 146.06 (w), 141.24 (w),

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136.53, 130.47, 129.21, 127.71, 1.06; IR (neat) 3050, 2950, 1575, 1420, 1260, 1250, 1130, 1050 cm^{-1}; GC–MS, *m/e* 274 (M^+, 33), 260 (21), 259 (100), 196 (14), 195 (73), 184 (15), 165 (10), 91 (11), 75 (9). Anal. Calcd for $C_{14}H_{14}SiS_2$: C, 61.27; H, 5.14. Found: C, 61.00; H, 5.12.

Bis(5-*tert*-butyl-2-mercaptophenyl)diethylsilane (27). The solvents used to isolate the dithiol were degassed by passing argon through them for about 1 h. Lithium 4-*tert*-butyl-2-lithiobenzenethiolate (**17**) was prepared as described in the preparation of **19**. 4-*tert*-Butylbenzenethiol[13] (5 g, 30 mmol) was added to TMEDA (10.2 mL, 68 mmol) and *n*-butyllithium (27 mL of 2.5 M hexane solution, 68 mmol). Solid **17**, isolated by filtration, was washed off the frit with dry, cold THF (80 mL; −78 °C). Dichlorodiethylsilane (1.89 g, 12 mmol) in dry THF (60 mL) was added dropwise to the stirred homogeneous solution of **17** at −78 °C over a period of 1.5 h, and the reaction mixture was warmed to 25 °C overnight. The resulting solution was acidified (1 M H_2SO_4 at 0 °C) and concentrated in vacuo and the residue extracted into ether. The ether was washed with water, dried ($MgSO_4$), and again concentrated. The ^1H NMR spectrum indicated mainly **27** and 4-*tert*-butylbenzenethiol. The product was chromatographed on the Chromatotron under nitrogen with hexane and hexane–CH_2Cl_2 (9:1) to elute 4-*tert*-butylbenzenethiol and a second fraction which upon recrystallization from hexane gave the title compound as a colorless powder (2 g, 40% yield): mp 58–59 °C; ^1H NMR δ 7.2–7.6 (br m, 6 H, aryl group), 3.34 (s, 2 H, SH), 1.31 (s, 18 H, $(CH_3)_3C$), 1.41 (q, 4 H, *J* = 8 Hz, $SiCH_2$), 1.01 (t, 6 H, *J* = 8 Hz, CH_3); ^{13}C NMR δ 147.98 (C), 136.02 (C), 133.89 (C), 133.83 (CH), 131.40 (CH), 126.84 (CH), 34.40 (C), 31.24 ($(CH_3)_3$), 7.64 (CH_3), 3.90 (CH_2).

When the workup was done without degassed solvents, and the products were separated on 1-mm silica TLC plates, a solid compound characterized as 2,9-di-*tert*-butyl-11,11-diethyl-11*H*-dibenzo[*c*,*f*][1,2,5]dithiasilepin was isolated: ^1H NMR δ 7.2–7.8 (br m, 6 H, aryl), 1.34 (s, 18 H, $(CH_3)_3C$), 1.15 (q, 4 H, *J* = 7.5 Hz, $SiCH_2$), 0.93 (t, 6 H, *J* = 7.5 Hz, CH_3); ^{13}C NMR δ 150.26 (C), 143.76 (C), 138.55 (C), 134.14 (CH), 130.57 (CH), 125.94 (CH), 34.64 (C), 31.25 ($(CH_3)_3C$), 7.67 (CH_3), 7.28 (CH_2).

2,9-Di-*tert*-butyl-11,11-diphenyl-11*H*-dibenzo[*c*,*f*][1,2,5]dithiasilepin (29). As in the synthesis of 4-*tert*-butyl-2-(triphenylsilyl)benzenethiol (**19**), a mixture of 4-*tert*-butylbenzenethiol (5.0 g, 30 mmol), TMEDA (11 mL; 67 mmol), and *n*-butyllithium (30 mL of 2.5 M hexane solution, 75 mmol) was stirred for 48 h at 25 °C. The precipitate was isolated by filtration, washed with dry hexane (2 × 50 mL), and transferred as a hexane (50 mL) slurry under argon to a three-necked flask containing a magnetic spinbar. The hexane was removed by syringe, the residue was cooled to −78 °C, THF (30 mL) was added, and the mixture was warmed to −30 °C to dissolve the dianion and then cooled once more to −78 °C and treated with vigorous stirring during the course of 1 h with a solution of dichlorodiphenylsilane (3.05 g, 21 mmol) in THF (30 mL). The mixture was warmed to 25 °C overnight, quenched with solid NH_4Cl (4.5 g, 84 mmol) at 0 °C, concentrated in vacuo, acidified (1 M H_2SO_4 at 0 °C), and extracted (CH_2Cl_2). The separated organic layer was dried ($MgSO_4$) and concentrated at high vacuum to give the title compound as a oil (4.93 g, crude yield 80%). An analytical sample was prepared by preparative TLC of 0.6 g of crude product (silica gel, CH_2Cl_2 followed by hexane) giving 0.23 g of a white solid which upon crystallization from hexane gave the pure title compound (76 mg, 10% yield): mp 152–3 °C, ^1H NMR δ 7.45–7.25 (m, 16 H, phenyl), 1.14 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR δ 150.15 (C), 143.62 (C), 137.46 (CH), 137.11 (C), 136.25 (C), 135.86 (CH), 130.23 (CH), 129.28 (CH), 127.70 (CH), 126.82 (CH), 34.56 (C), 31.02 (CH_3). Anal. Calcd for $C_{32}H_{25}S_2Si$: C, 75.24; H, 6.71. Found: C, 75.17; H, 6.87.

If great care was taken to exclude oxygen during the workup and chromatography of the product, bis(5-*tert*-butyl-2-mercaptophenyl)diphenylsilane (**28**) could be isolated as a colorless solid with spectral properties similar to those of **19**.

3-(Trimethylsilyl)-2-naphthalenethiol (31). As in the preparation of **13** by procedure 2, the dilithio salt **30** of 2-naphthalenethiol was prepared by using cyclohexane (10 mL), TMEDA (10 mL), 2.5 M *n*-butyllithium (20 mL, 50 mmol), and 2-naphthalenethiol (1.6 g, 10 mmol; Aldrich). The latter compound was added as a cyclohexane–TMEDA solution (1:1, 40 mL). The solid suspension was stirred at 25 °C for 24 h, then cooled to 0 °C, and treated with chlorotrimethylsilane (5.4 g, 50 mmol). The solution was stirred for 4 h, then quenched with water (10 mL), and concentrated. The residue was extracted with ether (200 mL) and washed with 10% HCl (3 × 100 mL) and water (100 mL), and the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was refluxed with methanol (100 mL) for 12 h and concentrated and the residue purified with a Chromatotron (silica gel, hexane) affording recovered 2-naphthalenethiol (0.8 g) along with the title compound as a colorless oil (1.12 g, 48% yield, 96% yield based on unrecovered starting material): 99% pure by GC; ^1H NMR ($CDCl_3$) δ 7.89 (s, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.67 (s, 1 H), 7.56 (d, *J* = 7.2 Hz, 1 H), 7.42–7.32 (m, 2 H), 3.62 (s, 1 H), 0.45 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 137.91, 135.74, 133.99, 133.19, 131.01, 129.06, 127.84, 126.94, 126.22, 125.49, −0.11; IR (neat) 3050, 2950, 2900, 2560 (w), 1620, 1570, 1480, 1420, 1250, 900 cm^{-1}; GC–MS, *m/e* 232 (M^+, 22), 216 (71), 201 (100). Anal. Calcd for $C_{13}H_{16}SSi$: C, 67.18; H, 6.94. Found: C, 67.37; H, 6.99.

1,2-Benzenedithiol (32a). As in the preparation of **13** by procedure 2, dilithio salt **16** was prepared by using cyclohexane (200 mL), TMEDA (19 g, 0.0163 mol), 1.6 M *n*-butyllithium (100 mL, 0.16 mol), and thiophenol (8.0 g, 0.073 mol). Sublimed sulfur (5.0 g, 0.16 mol) was added via Gooch tubing to the well-stirred suspension of the dianion, and the now yellow suspension was stirred for an additional 12 h. The cyclohexane was removed in vacuo and replaced with an equal volume of dry THF. The THF solution was treated at 0 °C with $LiAlH_4$ (3.0 g, 0.08 mol). After the initial exothermic reaction subsided, the solution was refluxed for 8 h, then cooled to 25 °C, and poured slowly into 2 M HCl (400 mL) at 0 °C. The acidic solution (check pH!) was extracted with ether (2 × 500 mL), and then the combined organic phase was extracted with 5% HCl (2 × 200 mL) and brine (200 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo, and the residue was distilled to give the title compound (8.7 g, 84% yield) as a clear oil, bp 75 °C (1 mm), which partially solidified during distillation (the condenser was *not* continually water cooled). The product was 97% pure by GC [retention time 4.8 min (150 °C)]; ^1H NMR δ 7.23 (dd, 2 H, *J* = 5.9, 3.4 Hz), 6.95 (dd, 2 H, *J* = 5.9, 3.4 Hz) 3.67 (s, 2 H); ^{13}C NMR δ 130.90 (w), 130.82, 126.48; IR (neat) 3040, 2550, 1580, 1480, 1460, 1430 cm^{-1}; GC–MS, *m/e* 142 (M^+, 100), 109 (31), 78 (91).

1,2,3-Benzenetrithiol (34). Trianion **33** of **32a** was prepared in a manner similar to the preparation of **13** by procedure 2. Cyclohexane (100 mL), TMEDA (11.6 g, 0.1 mol), and 2.5 M *n*-butyllithium (40 mL, 0.1 mol) were mixed and cooled. 1,2-Benzenedithiol (**32a**; 2.84 g, 0.02 mol) dissolved in cyclohexane (20 mL) was added slowly, and the suspension was stirred at 25 °C for 24 h. Sublimed sulfur (3.2 g, 0.1 mol) was added via Gooch tubing, and the suspension was stirred for an additional 12 h. The cyclohexane was removed in vacuo and replaced by an equal volume of THF. The THF solution was cooled, $LiAlH_4$ (2.0 g, 0.05 mol) was added slowly, and the suspension was refluxed for 8 h. The solution was cooled and poured into 15% ice-cold HCl. The acidic aqueous phase was extracted with ether (400 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo to yield a dark oil (3.1 g), analyzing by GC–MS for 80% **34**, 10% **32a**, and ca. 10% 1,2,3,4-benzenetetrathiol. The crude product was chromatographed on silica gel (PF-254, Chromatotron, hexane) to give the title compound[14] as a white crystalline material (1.2 g, 35% yield), mp 62–63 °C after crystallization from hexane. The material yellowed upon exposure to air and should be handled under nitrogen: ^1H NMR δ 7.16 (d, 2 H, *J* = 7.9 Hz), 6.88 (t, 1 H, *J* = 7.9 Hz), 3.94 (br s, 3 H); ^{13}C NMR δ 133.91, 129.45 (w), 128.13, 126.45; IR (KBr) 2960, 2940, 2530 (s, SH), 1560, 1440, 1420, 1340, 1190, 1150, 780, 740 cm^{-1}; GC–MS, *m/e* 174 (M^+, 100), 141 (29), 140 (29), 110 (22), 109 (19).

The crude reaction product could be directly methylated by the procedure of Gilman[15] to produce the known 1,2,3-tris(methylthio)benzene. Thus, the crude trithiol (1.74 g) was treated with dimethyl sulfate (2.52 g, 0.02 mol) to yield, after chromatography (hexane, silica gel), the trimethylated derivative as white crystals (0.45 g, 20% yield based on **32a**): mp 110–111 °C (from ethanol) (lit.[10,16] mp 110–111 °C). The physical and spectral properties agreed with those reported in the literature.[10,16]

4-*tert*-Butyl-1,2-benzenedithiol (32b). As in the preparation of **13**, the dianion of 4-*tert*-butylbenzenethiol was prepared by using 2.8 g (0.017 mol) of the thiol[13] along with cyclohexane (40 mL), TMEDA (6.4 g, 0.055 mol), and 2.5 M *n*-butyllithium (22 mL, 0.055 mol). After 24 h sublimed sulfur (2.0 g, 0.062 mol) was added at room temperature via Gooch tubing, and then the suspension was stirred for an additional 12 h. The cyclohexane was removed in vacuo and replaced with an equal volume of dry THF. The solution was cooled to 0 °C, and $LiAlH_4$ (1.0 g, 0.026 mol) was added. After the initial exothermic reaction subsided, the solution was refluxed for 12 h. The solution was cooled to room temperature and poured into cold 2 M HCl (150 mL). The solution was extracted with ether (2 × 150 mL), and the combined ether phase was extracted with 10% NaOH (3 × 100 mL). The combined basic washings were acidified with concentrated HCl and extracted with $CHCl_3$ (3 × 200 mL). The $CHCl_3$ layer was dried ($MgSO_4$) and concentrated in vacuo and the residue distilled to afford the title compound as a colorless

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oil (2.4 g, 71% yield): bp 100 °C (0.25 mmHg), 98% pure by GC (retention time 3.8 min at 200 °C); ^{1}H NMR (C_6D_6) δ 7.27 (d, 1 H, J = 1.7 Hz), 7.06 (d, 1 H, 8.4 Hz), 6.80 (dd, 1 H, J = 8.4, 1.7 Hz) 3.55 (s, 1 H), 3.41 (s, 1 H), 1.10 (s, 9 H); ^{13}C NMR (C_6D_6) δ 149.93, 131.48, 131.24, 128.11, 127.97, 124.02, 34.13, 30.99; IR (neat) 2960, 2910, 2870, 2550, 1480, 1460, 1380, 1260 cm^{-1}; GC-MS, m/e 198 (M^+, 38), 183 (100). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11. Found: C, 60.91; H, 7.29.

Bis(2-mercaptophenyl) Sulfide (35). As in procedure 3 for **13**, dilithio salt **16** was prepared from thiophenol (8.8 g, 0.08 mol), dissolved in THF, and treated at −78 °C during a period of 10 min with a solution of freshly distilled sulfur dichloride (4.08 g, 0.04 mol) in pentane (10 mL). The solution was slowly warmed to room temperature, $LiAlH_4$ (3.0 g, 0.08 mol) was *carefully* added after fitting the flask with a reflux condenser, and the suspension was refluxed for 4 h. The mixture was then cooled to 0 °C and poured into ice-cold HCl (50 mL of concentrated acid diluted with 400 mL of ice water). The aqueous phase was extracted with ether (4 × 200 mL), and the ether extracts were combined and extracted with 10% NaOH solution (3 × 200 mL). The combined NaOH extract was acidified with concentrated HCl and extracted with CH_2Cl_2 (3 × 200 mL), and the CH_2Cl_2 extract was dried ($MgSO_4$), filtered, and concentrated in vacuo, affording a dark brown oil (ca. 10 g) which analyzed by GC-MS for ca. 40% of the title compound, 15% thiophenol, 40% 1,2-benzenedithiol (**32a**), and several minor products. Purification using a Chromatotron (silica gel, hexanes) gave an analytical sample of the title compound (4% yield; 10% yield based on unrecovered starting material) as a colorless solid: mp 90-91 °C; ^{1}H NMR δ 7.42-7.38 (m, 2 H), 7.20-7.05 (m, 6 H), 4.08 (s, 2 H, SH); ^{13}C NMR δ 134.93, 132.37, 132.31, 130.13, 128.23, 126.52; IR (KBr) 3050, 2510 (SH), 1570, 1450, 1430, 1260, 750 cm^{-1}; GC-MS, m/e 250 (M^+, 100), 217 (52), 216 (51), 184 (83), 140 (84). Anal. Calcd for $C_{12}H_{10}S_3$: C, 57.56; H, 4.02. Found: C, 57.59; H, 4.03.

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Registry No. 11, 20965-36-0; **12**, 117526-61-1; **13**, 33356-45-5; **14**, 117526-62-2; **15**, 117526-63-3; **16**, 117526-82-6; **17**, 117526-83-7; **18**, 117526-64-4; **19**, 117526-65-5; **20**, 117526-66-6; **21**, 117526-67-7; **22**, 117526-68-8; **23**, 117526-69-9; **24**, 117526-70-2; **25**, 117526-71-3; **26**, 117526-72-4; **27**, 117526-73-5; **28**, 117526-74-6; **29**, 117526-75-7; **30**, 117526-84-8; **31**, 117526-76-8; **32a**, 117526-15-5; **32b**, 117526-80-4; **33**, 117526-85-9; **34**, 89375-31-5; **35**, 117526-77-9; dihydropyran, 110-87-2; thiophenol, 108-98-5; chlorotrimethylsilane, 75-77-4; 2-trimethylsilylbenzenethiol, silver(I) salt, 117526-81-5; chlorotriethylsilane, 994-30-9; 2-(*tert*-butyldimethylsilyl)benzenethiol, 117526-58-6; 2-[[*tert*-butyl[(*tert*-butyldimethylsilyl)methyl]methyl]silyl]benzenethiol, 117526-59-7; chloro-*tert*-butyldimethylsilane, 18162-48-6; 2-(triphenylsilyl)benzenethiol, 117526-60-0; chlorotriphenylsilane, 76-86-8; 4-(*tert*-butyl)benzenethiol, 2396-68-1; dichlorodimethylsilane, 75-78-5; dichlorodiethylsilane, 1719-53-5; 1,2-dichlorotetramethyldisilane, 4342-61-4; 10,13-di-*tert*-butyl-5,5-diethyldibenzo[*b*,*e*]-5-sila-1,2-dithiepin, 117526-78-0; dichlorodiphenylsilane, 80-10-4; 2-naphthalenethiol, 91-60-1; sulfur, 10544-50-0; 1,2,3,4-benzenetetrathiol, 117526-79-1; 1,2,3-tris(thiomethyl)benzene, 65516-81-6; sulfur dichloride, 10545-99-0.

Supplementary Material Available: General experimental procedures and that for 2-(triethylsilyl)benzenethiol (**14**) (procedure 2), 2-(*tert*-butyldimethylsilyl)benzenethiol (procedure 2), and 1,2-bis[(2′-mercaptophenyl)dimethylsilyl]ethane (**25b**) (1 page). Ordering information is given on any current masthead page.

Directed Lithiation of Arenethiols

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Abstract: Benzenethiol, toluene-4-thiol, and 3,5-dimethylbenzenethiol are doubly lithiated (on sulfur and on carbon) by *n*-butyllithium in tetramethylethylenediamine. C-Lithiation occurs ortho to the thiol group, and subsequent treatment with electrophiles provides a convenient approach to ortho-substituted arenethiol derivatives. The reactions with tetraisopropylthiuram disulfide provide direct access to the corresponding *o*-phenylene trithiocarbonates. Double lithiation of 4-methoxybenzenethiol results in C-lithiation adjacent to the methoxy group rather than the thiolate residue, indicating that methoxy is a more powerfully ortho-directing substituent in this type of metalation reaction. 3-Methoxybenzenethiol is lithiated between the methoxy and thiolate groups.

Lithiation of aromatic compounds can often be directed to occur ortho to substituents that possess oxygen or nitrogen atoms.[1,2] Apparently, complexation occurs between the substituent group and the lithium reagent prior to metalation, and this serves to bring the metalating agent into closer proximity with the ortho proton, which is then selectively removed. Groups that encourage such ortho-metalation include SO_2NR_2, $CONR_2$, $OCONR_2$, CH_2NMe_2, OCH_2OMe, and OMe.[1-3] There are occasions when it would be extremely useful to be able to direct lithiation ortho to a simple thiol group as a means of producing ortho-substituted arenethiols. However, an early attempt at lithiation of benzenethiol resulted in only a 3% yield of the appropriate product after trapping with carbon dioxide.[4] A more recent literature statement implied that lithiation ortho to a simple thiol group was possible, but gave no details.[5] We therefore decided to explore the possibility of effecting such ortho-lithiation in a synthetically useful manner by appropriate choice of solvent, reagent, or reaction conditions[6] and now report success in this endeavor. Since completion of our work we have become aware of parallel studied by

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