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Alkyl-, Silyl-, and Germyl-Substituted Thiolate, Selenolate, and Tellurolate Derivatives and Interconversion of Silyl Species by Chalcogen Metathesis

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Abstract: The preparation of a series of chalcogenolate species $(sol)_nLiEY(SiMe_3)_3$ (sol = THF, $n = 1, 2$; sol = DME, $n = 1$; E = S, Se, Te; Y = C, Si, Ge) by direct insertion of elemental E into Li–Y bonds of $(THF)_3LiC(SiMe_3)_3$, $(THF)_3LiSi(SiMe_3)_3$, or $(THF)_3LiGe(SiMe_3)_3$ is reported. Two derivatives, $(THF)_2LiSeSi(SiMe_3)_3$ and $(THF)LiSSi(SiMe_3)_3$, are more conveniently prepared by novel chalcogen metathesis reactions whereby tellurium is displaced from $(THF)_2LiTeSi(SiMe_3)_3$ by either Se or S in THF at −55 °C. Protonation of the chalcogenolate anions leads to the stable chalcogenols, $HEY(SiMe_3)_3$, which have been fully characterized. In methyl isobutyl ketone (MIBK), the pK_a values of $HTeC(SiMe_3)_3$, $HTeSi(SiMe_3)_3$, $HTeGe(SiMe_3)_3$, $HSeC(SiMe_3)_3$, $HSeSi(SiMe_3)_3$, and $HSSi(SiMe_3)_3$ are determined to be 9.3, 7.3, 7.4, 10.8, 8.3, and 10.7, respectively. The X-ray structure of the mono-THF adduct $(THF)LiTeSi(SiMe_3)_3$, prepared from $(THF)Li[N(SiMe_3)_2]$ and $HTeSi(SiMe_3)_3$, is also described; it crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.083(4)$ Å, $b = 11.181(4)$ Å, $c = 12.053(8)$ Å, $\alpha = 93.16(4)°$, $\beta = 104.68(5)°$, $\gamma = 96.63°$, $R = 0.0300$, and $R_w = 0.0372$.

Introduction

Our interest in studying compounds with discrete metal–chalcogen bonds[1–3] has led us to develop improved routes to sources of chalcogenolate anions, RE^- (E = S, Se, Te).[4,5] We have already described the synthesis of silyl tellurolate derivatives based on the sterically demanding $-TeSi(SiMe_3)_3$ substituent[6–8] and now present details of our extension of this reaction to the corresponding sulfur and selenium derivatives along with chemistry of related alkyl- and germyl-substituted species.

Most tellurolates reported to-date incorporate alkyl or aryl substituents and are prepared by direct insertion of elemental chalcogens into reactive Li–C bonds (eq 1).[9–11] In practice,

$$\mathrm{Li{-}CR_3 + E \rightarrow Li{-}E{-}CR_3} \tag{1}$$

however, many of these reactions are not so straightforward with product isolation being hampered by ill-defined side reactions. Several alkyl chalcogenolate derivatives utilizing the $-C(SiMe_3)_3$ ligand have been reported by Sladky and co-workers.[12,13] These authors have also reported further reactions of some alkyl and aryl chalcogenolates with elemental chalcogens to produce chalcogenyl chalcogenolate anions as determined by solution NMR studies (eq 2).[14] Attempts to isolate these compounds resulted in decomposition.

$$\mathrm{LiER + E' \rightarrow LiE'ER} \tag{2}$$

$$\mathrm{R = alkyl,\ aryl}$$

In an attempt to probe substituent effects in chalcogenolate chemistry, we sought to prepare a range of compounds in which we could examine the steric and electronic consequences of varying substituents bound to the chalcogen. Here we describe the synthesis and reactivity of a range of synthetically useful chalcogenolate derivatives incorporating bulky alkyl, silyl, and germyl substituents, along with the first pK_a determinations for tellurols. We also present evidence for a new reaction type in chalcogenolate chemistry that we term "chalcogen metathesis". For the silyl tellurolate this results in the clean, quantitative displacement of tellurium to form new chalcogenolates as shown in eq 3. Reactions of this kind are shown to be of practical importance for the production of synthetically useful quantities of silyl thiolate and selenolate anions.

$$\mathrm{LiTeSi(SiMe_3)_3 + E \rightarrow LiESi(SiMe_3)_3 + Te} \tag{3}$$

Results and Discussion

Synthesis of Chalcogenolate Anions. A range of bulky alkyl, silyl, and germyl chalcogenolates is readily available by direct insertion of S, Se, and Te into Li–R bonds of the known lithium salts[15–17] as shown in eq 4. A comparison of relevant physical

$$\mathrm{Li{-}R + E \rightarrow Li{-}E{-}R} \tag{4}$$

$$\mathrm{R = C(SiMe_3)_3,\ Si(SiMe_3)_3,\ Ge(SiMe_3)_3;\ E = S,\ Se,\ Te}$$

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Table I. Selected Physical and Spectroscopic Data

compd	physical properties	^{1}H NMR, δ	^{125}Te, ^{77}Se NMR, δ	ν_{EH}, cm^{-1}	pK_a
$(THF)_2LiTeSi(SiMe_3)_3$[a]	pale yellow prisms, mp 169–171 °C, air sensitive	3.75 (m, 8 H, THF), 1.43 (m, 8 H, THF), 0.45 (s, 27 H, $SiMe_3$)	C_6D_6, 20 °C, 0.3 M, –1622 (s)		
$(THF)LiTeSi(SiMe_3)_3$	colorless prisms, mp 223–225 °C, air sensitive	3.85 (m, 4 H, THF), 1.41 (m, 4 H, THF), 0.44 (s, 27 H, $SiMe_3$)	C_7D_8, 100 °C, 0.2 M, –1578 (s)		
$HTeSi(SiMe_3)_3$	colorless wax, mp 128–130 °C, air sensitive	0.23 (s, 27 H, $SiMe_3$), –8.82 (s, 1 H, Te*H*), $\lvert J_{HTe}\rvert = 74$ Hz	C_6D_6, 20 °C, 0.5 M, –955 ($\lvert J_{TeH}\rvert = 74$ Hz)	2017	7.3
$(THF)_2LiSeSi(SiMe_3)_3$	colorless prisms, mp 222–229 °C, air sensitive	3.76 (m, 8 H, THF), 1.44 (m, 8 H, THF), 0.43 (s, 27 H, $SiMe_3$)	C_7D_8, –50 °C, 0.42 M, –825 (s)		
$(THF)_2LiSSi(SiMe_3)_3$	colorless prisms, mp > 273 °C, air sensitive	3.77 (m, 4 H, THF), 1.38 (m, 4 H, THF), 0.40 (s, 27 H, $SiMe_3$)			
$(THF)_2LiTeC(SiMe_3)_3$[b]	dark orange-yellow cryst, mp 141–145 °C, air sensitive	3.81 (m, 8 H, THF), 1.45 (m, 8 H, THF), 0.54 (s, 27 H, $SiMe_3$)	THF-d_8, 20 °C, 0.3 M, –287 (s)		
$(THF)_2LiTeGe(SiMe_3)_3$	orange prisms, mp >292 °C (dec), air sensitive	3.79 (m, 8 H, THF), 1.45 (m, 8 H, THF), 0.49 (s, 27 H, $SiMe_3$)	C_6D_6, 20 °C, 0.35 M, –1515 (s)		
$(DME)LiSeC(SiMe_3)_3$	light orange prisms, mp 187–188 °C, air sensitive	3.27 (s, 6 H, DME), 2.99 (s, 4 H, DME), 0.49 (s, 27 H, $SiMe_3$)	C_7D_8, –40 °C, 0.4 M, –15 (s)		
$HSeSi(SiMe_3)_3$	colorless plates, mp 108–111 °C, air sensitive	0.21 (s, 27 H, $SiMe_3$), –3.12 (s, 1 H, Se*H*), $\lvert J_{HSe}\rvert = 36$ Hz	C_6D_6, 20 °C, 0.3 M, –4.7 (d, $\lvert J_{SeH}\rvert = 36$ Hz)	2294	8.3
$HSSi(SiMe_3)_3$[c]	colorless wax, mp 80–84 °C, air stable	0.20 (s, 27 H, $SiMe_3$), –0.78 (s, 1 H, S*H*)		2557	10.7
$HTeC(SiMe_3)_3$	yellow-red wax, mp 153–154 °C, air sensitive	0.24 (s, 27 H, $SiMe_3$), –5.1 (s, 1 H, Te*H*), $\lvert J_{HTe}\rvert = 101$ Hz	C_6D_6, 20 °C, 0.5 M, –63 (d, $\lvert J_{TeH}\rvert = 101$ Hz)	2015	9.3
$HTeGe(SiMe_3)_3$	pale yellow wax, mp 145–147 °C, air sensitive	0.27 (s, 27 H, $SiMe_3$), –9.02 (s, 1 H, Te*H*), $\lvert J_{HTe}\rvert = 95$ Hz	C_6D_6, 20 °C, 0.43 M, –940 (d, $\lvert J_{TeH}\rvert = 95$ Hz)	2021	7.4
$HSeC(SiMe_3)_3$[d]	pale yellow wax, mp 178–185 °C, air sensitive	0.19 (s, 27 H, $SiMe_3$), –1.09 (s, 1 H, Se*H*), $\lvert J_{HSe}\rvert = 25$ Hz	$CDCl_3$, 20 °C, 0.5 M, –1 (d, $\lvert J_{SeH}\rvert = 25$ Hz)	2287	10.8

[a] See refs 6 and 7. [b] See ref 12. [c] See ref 19. [d] See ref 13.

and spectroscopic data is given in Table I. Optimum yields were obtained by performing the insertions at ca. –80 °C in THF, although at ambient temperature the diminution in yields were relatively minor. In most cases, the only contaminant in the crude product from these reactions was the corresponding dichalcogenide (REER) resulting presumably from trace oxidation. On recrystallization from non-polar solvents such as hexane or diethyl ether, pure products were obtained in moderate to high yields. In general, the tellurolates are more intensely colored (yellow or orange) than the pale yellow or colorless selenolates and thiolates.

In an earlier report we described the X-ray structure of the dimeric bis-THF solvate $[(THF)_2LiTeSi(SiMe_3)_3]_2$.[1] During the course of further studies involving reactions of this salt with anhydrous metal halides such as YCl_3 and $FeCl_2$ in hydrocarbon solvents, we isolated low and variable yields of a what appeared (by NMR spectroscopy and C&H analyses) to be a mono-THF solvate. Evidently, YCl_3 and $FeCl_2$ act as THF sponges under these conditions. A more efficient route to this material involved reaction of $(THF)Li[N(SiMe_3)_2]$ with $HTeSi(SiMe_3)_3$, which gave the mono-THF adduct in near quantitative yields. X-ray diffraction confirmed the structure as shown in Figure 1 (see also Tables II and III). As with $[(THF)_2LiTeSi(SiMe_3)_3]_2$, the mono-THF solvate exists as a dimer. The moieties are related by crystallographic inversion symmetry, forming a planar Li_2Te_2 core. Not surprisingly, bond lengths to the 3-coordinate planar Li in this molecule are significantly shorter than the analogous distances in $[(THF)_2LiTeSi(SiMe_3)_3]_2$ (see Table III). The $-Si(SiMe_3)_3$ fragment is bent out of the plane of the central core with methyl carbon atoms of one $-SiMe_3$ fragment positioned above and below the Li atoms thereby stabilizing the molecule by van der Waals interactions.

The difference in chemical environment about the Li atoms between the two lithium salts is also reflected in their $^7Li\{^1H\}$ NMR spectra. The bis-THF solvate (δ 1.01) shows an upfield shift of 0.4 ppm relative to the mono-THF solvate. As expected, however, there is little difference in the environments about the tellurium atoms and $^{125}Te\{^1H\}$ NMR shifts of the two salts are similar (Table I).

Protonation Reactions. Reaction of the chalcogenolate salts with protic acids resulted in clean conversions to the corresponding chalcogenols $HSeSi(SiMe_3)_3$, $HSSi(SiMe_3)_3$, $HTeC(SiMe_3)_3$, $HTeGe(SiMe_3)_3$, and $HSeC(SiMe_3)_3$.[18] Selected physical and spectroscopic data are again collected in Table I. All of these derivatives are volatile, low-melting solids that are best isolated and purified by sublimation directly from the reaction pot. An alternative synthesis route to $HSSi(SiMe_3)_3$, involving a four-step procedure from the silane, has also been reported.[19]

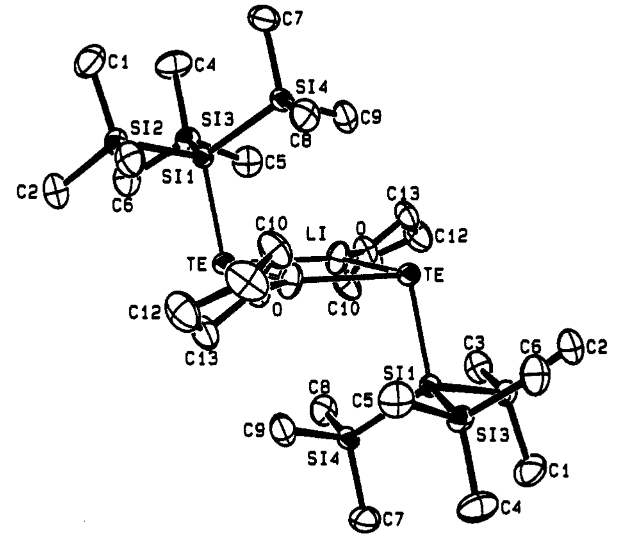

Figure 1. ORTEP view of the structure of $[(THF)LiTeSi(SiMe_3)_3]_2$.

While the pK_a's of numerous alcohols and thiols are well-known, only a handful of organic selenols and organometallic anions containing –TeH functionalities have been investigated.[20-22]

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[18] The isolation of $HSeC(SiMe_3)_3$ was previously described. See: Bildstein, B.; Giselbrecht, K.; Sladky, F. *Chem. Ber.* **1989**, *122*, 2279.

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Table II. Crystallographic Data for $[(THF)LiTeSi(SiMe_3)_3]_2$

formula	$C_{13}H_{35}LiOSi_4Te$
mol weight	454.3
cryst size, mm	0.25 × 0.44 × 0.55
space group	$P\bar{1}$
a, Å	9.083(4)
b, Å	11.181(4)
c, Å	12.053(8)
α, deg	93.16(4)
β, deg	104.68(5)
γ, deg	96.63(3)
V, Å^3	1171.7
Z	2
d_{calcd}, g cm^{-3}	1.29
radiation, (λ, Å)	Mo Kα (0.710 73)
scan mode	θ–2θ
2θ range, deg	3–45
colln range	$+h,\pm k,\pm l$
abs coeff (μ), cm^{-1}	14.7
no. of unique reflcns	3037
reflcns with $F^2 > 3\sigma(F^2)$	2771
final R, R_w	0.0300, 0.0372
T, °C	−108

Table III. Comparison of Metrical Data for Mono-THF and Bis-THF Solvates of $LiTeSi(SiMe_3)_3$

	$[(THF)LiTeSi(SiMe_3)_3]_2$	$[(THF)_2LiTeSi(SiMe_3)_3]_2$[a]
	Intramolecular Distances, Å	
Li–Te	2738(7)	2.82(2)
Li′-Te	2.747(7)	2.88(2)
Li–O	1.882(8)	1.99(2), 1.90(2)
Te–Si	2.504(1)	2.480(3)
$(Si–Si)_{av}$	2.343(2)	2.322(6)
$(Si–C)_{av}$	1.868(5)	1.90(2)
	Intramolecular Angles, deg	
Li–Te–Li	70.17(25)	90.4(6)
Te–Li–Te	109.83(25)	86.6(6)
Li–Te–Si	98.26(17), 103.47(17)	123.2(5), 130.2(5)
Te–Li–O	123.0(3)	107.4(10), 110.1(10)
Te–Li′–O′	127.0(3)	118.6(10), 132.6(11)

[a] See ref 7.

In contrast to all alkyl and aryl tellurols previously reported,[23] the tellurols we describe here are easily handled at ambient temperatures, making pK_a measurements relatively straightforward. These determinations were carried out potentiometrically by titrating the chalcogenol dissolved in MIBK with 1.0 M tetrabutylammonium hydroxide in methanol. A nonaqueous method was employed as it avoids problems associated with the insolubility of the hydrophobic chalcogenols in water, and the technique is well-documented.[24–27]

The silyl tellurol, $HTeSi(SiMe_3)_3$, and its germyl analogue were found to have pK_a values of 7.3 and 7.4, respectively, while a pK_a value of 9.3 was determined for the alkyl derivative, $HTeC(SiMe_3)_3$. Similarly, the silyl selenol was found to be more acidic than the alkyl derivative with respective pK_a values of 8.3 and 10.8. A pK_a value of 10.7 was determined for the silyl thiol, $HSSi(SiMe_3)_3$. Under similar conditions, phenol, thiophenol, and benzeneselenol gave pK_a values of 11.9, 10.5, and 8.8 respectively. (We estimate an error of ±0.5 pK_a units for all these values.) It is interesting to note that the silyl and germyl derivatives are 100–1000 times more acidic than their alkyl counterparts. This is consistent with the electronegativity differences in the elements bound to tellurium in these compounds (Pauling values for C, Si, and Ge are 2.5, 1.9, and 2.0, respectively). We note that the same trend is echoed in the ^{125}Te NMR data for $HTeSi(SiMe_3)_3$, $HTeGe(SiMe_3)_3$, and $HTeC(SiMe_3)_3$, which show chemical shifts of −955, −940, and −63 ppm, respectively (Table I).

We have already described the synthetic utility of the silyl compounds $(THF)_2LiTeSi(SiMe_3)_3$ and $HTeSi(SiMe_3)_3$.[7] The addition of alkyl and germyl derivatives is significant as it allows us to probe substituent effects in reactions of related metal chalcogenolates.[28]

Chalcogen Metathesis Reactions. Treatment of $(THF)_2LiTeSi(SiMe_3)_3$ with 1 equiv of elemental selenium in THF at −55 °C produced a purple solution that quickly lightened in color to orange with precipitation of a black solid. Warming to room temperature followed by evaporation of the volatile materials afforded the silyl selenolate $(THF)_2LiSeSi(SiMe_3)_3$ and elemental tellurium as the sole reaction products (eq 5). Chalcogen

$$(THF)_2LiTeSi(SiMe_3)_3 + Se \rightarrow (THF)_2LiSeSi(SiMe_3)_3 + Te \quad (5)$$

metathesis also occurred when $(THF)_2LiTeSi(SiMe_3)_3$ was treated with elemental sulfur in THF at −55 °C. Again, the metathesis products $(THF)_2LiSSi(SiMe_3)_3$ and elemental tellurium were isolated quantitatively. In neither case was the putative tellurenyl chalcogenolate, $(THF)_2LiETeSi(SiMe_3)_3$ (E = S, Se), observed. The initial temperature at which these reactions were carried out was important. For example, reaction of $(THF)_2LiTeSi(SiMe_3)_3$ with selenium at room temperature gave $HSeSi(SiMe_3)_3$ and ditelluride as the major products, while the corresponding reaction with sulfur gave only an intractable mixture of starting material, ditelluride, and thiol as evidenced by ^{1}H and ^{13}C NMR measurements.

These results are intriguing in light of Sladky's studies which involved reactions of chalcogenolates with lighter alkyl and aryl substituents.[14] In these cases, lighter chalcogens (E′) insert into the Li–ER bond to form chalcogenyl chalcogenolates of the type LiE′ER that are stable in solution. In order to determine if chalcogen metathesis might be a general phenomenon in bulky chalcogenolates, we investigated similar reactions with the alkyl species $(THF)_2LiTeC(SiMe_3)_3$ and the germyl derivative $(THF)_2LiTeGe(SiMe_3)_3$. For the alkyl tellurolate, our results mirrored those observed by Sladky, showing that $(THF)_2LiTeC(SiMe_3)_3$ reacts with selenium in THF at −55 °C to form a homogeneous dark-red solution containing the tellurenyl selenolate $(THF)_2LiSeTeC(SiMe_3)_3$. In THF-d_8 the compound showed a singlet in the ^{125}Te{^{1}H} NMR spectrum at δ 409 ppm flanked by ^{77}Se satellites ($|^1J_{TeSe}|$ = 649 Hz); a singlet with a coupling constant of equal magnitude was also observed at δ −213 ppm in the ^{77}Se{^{1}H} spectrum. This material is quite stable in solution for several days at 20 °C; however, attempts to isolate the compound as a solid resulted in decomposition to a mixture of uncharacterized products.

Reactions of the germyl tellurolate $(THF)_2LiTeGe(SiMe_3)_3$ with selenium in THF at −55 °C are more complex. In this case, an intractable mixture was produced; neither the tellurenyl selenolate nor the chalcogen metathesis product, $(THF)_2LiSeGe(SiMe_3)_3$, were detected. Interestingly, direct reaction of the germyl lithium salt with selenium in THF at −55 °C similarly failed to yield a tractable product.

Although these results show that the nature of the –R group plays a key role in determining the outcome of reactions of chalcogenolates with elemental chalcogens, the extent to which these complex reactivities depend on simple electronic or steric

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(23) For examples see: Hamada, K.; Morishita, H. *Jpn. J. Appl. Phys.* **1976**, *15*, 748. Hamada, K.; Morishita, H. *Synth. React. Inorg. Met. Org. Chem.* **1977**, *7*, 355. Drake, J. E.; Hemmings, R. T. *Inorg. Chem.* **1980**, *19*, 1879. Sink, C. W.; Harvey, A. B. *J. Chem. Phys.* **1972**, *57*, 4434. Bochmann, M.; Coleman, A. P.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 973. Herberhold, M. *J. Organomet. Chem.* **1993**, *443*, 1.

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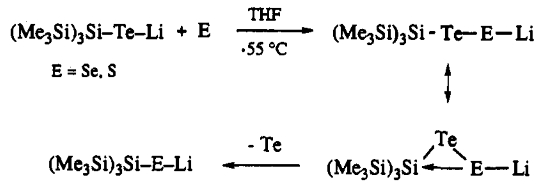
Scheme I



effects is unclear. In the $-Si(SiMe_3)_3$ systems, participation of an intermediate tellurenyl chalcogenolate (analogous to the stable alkyl species noted above) appears reasonable (Scheme I). The transient purple color we observed when the reactants were mixed at low temperature may be due to such a species; however, we found no evidence for its existence by low-temperature NMR spectroscopy. The ability of silicon to form higher coordinate structures than carbon may provide a low-energy pathway to metathesis, but why the $-Si(SiMe_3)_3$ substituted tellurolate undergoes clean chalcogen metathesis reactions when the germanium analogue apparently does not is not easily rationalized, as both may form hypervalent species.[29] It is worth noting, however, that there are well-known similarities between many aspects of carbon and germanium chemistry and between silicon and tin;[30] as we have not investigated the analogous tin compounds, we are presently unable to make the latter comparison. To investigate the possibility of radical processes, we repeated the chalcogen metathesis reactions in the presence of the potential silyl radical trap, 9,10-dihydroanthracene. In no case, however, was the course of the reaction diverted.[31]

Experimental Section

General operating procedures were as described previously.[7] Tellurium (−200 mesh) and selenium (−325 mesh) powders were from Strem; sulfur (sublimed) was from Mallinckrodt. Trifluoromethanesulfonic acid (triflic acid) (Strem) was stored under argon. $(THF)_2LiTeSi(SiMe_3)_3$[7] and $(THF)_2LiGe(SiMe_3)_3$[16] were prepared by literature methods. MIBK (Eastman) was dried over 4-Å molecular sieves and degassed with N_2 before use. Tetrabutylammonium hydroxide (TBAH, Aldrich, 1.0 M in methanol) was standardized using 0.1 M HCl. IR samples were prepared as Nujol mulls between KBr plates. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperatures. Chemical shifts (δ) are relative to residual protium in the deuterated solvent. Selenium-77 spectra were recorded at 76.4 or 57.2 MHz and were indirectly referenced to $SeMe_2$ at 0 ppm by direct reference to KSeCN at −322 ppm.[32] Tellurium-125 spectra were recorded at 94.7 MHz and were indirectly referenced to $TeMe_2$ at 0 ppm by direct reference to $Te(OH)_6$ at 712 ppm.[32–35] Lithium-7 spectra were recorded at 155.5 MHz relative to 1 M LiCl in D_2O at 0 ppm. Elemental analyses and mass spectra were determined by laboratories within the College of Chemistry, University of California, Berkeley, CA.

$(THF)_2LiSeSi(SiMe_3)_3$. Selenium (1.50 g, 0.019 mol) and $(THF)_2LiTeSi(SiMe_3)_3$ (10.0 g, 0.019 mol) were combined in a 250-mL round-bottomed flask. The flask was cooled to −50 °C in a dry ice/acetone bath, and THF (100 mL) was added with stirring. The solution turned purple and then quickly became orange as more of the selenium dissolved and a black solid began to precipitate. The mixture was allowed to warm slowly to −5 °C, the bath was removed, and stirring was continued for 30 min at room temperature. The yellow mixture was filtered to remove precipitated tellurium (2.3 g, 93%), and the solvent was removed under reduced pressure. The resulting colorless powder (8.56 g, 94%) was pure by ^1H NMR analysis and was used in subsequent reactions without further purification. Samples for elemental analysis and X-ray crystallography were obtained by crystallization from diethyl ether at −40 °C. IR: 1234 s, 1048 m, 1034 m, 918 sh, w, 886 sh, m, 862 sh, m, 833 s, 739 w, 682 m, 619 m cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 68.5, 25.5, 0.83. Anal. Calcd for $C_{17}H_{43}LiO_2SeSi_4$: C, 40.8; H, 9.1. Found: C, 40.8; H, 8.9.

$(THF)LiTeSi(SiMe_3)_3$. A mixture of $(THF)Li[N(SiMe_3)_2]$ (0.87 g, 3.63 mmol) and $HTeSi(SiMe_3)_3$ (1.45 g, 3.85 mmol) was dissolved in hexanes (50 mL), and the solution was stirred at room temperature. Immediately upon addition of the hexanes, the solution became pale yellow, and within 5 min colorless crystals had begun to precipitate. Stirring was continued for 2 h, and then the volatiles were removed under reduced pressure to give a yellow-green residue. This residue was redissolved in hexanes, concentrated, and cooled to −40 °C giving the product as very pale green crystals. Repeated recrystallizations from hexanes eventually gave the product as colorless tabular crystals (1.03 g, 2.27 mmol, 63%). IR: 1240 m, 1035 m, 836 vs, br, 686 m, 623 m cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 69.39, 25.29, 1.41. $^7Li\{^1H\}$ NMR (156 MHz, C_6D_6): δ 1.402. Anal. Calcd for $C_{13}H_{35}LiOSi_4Te$: C, 34.4; H, 7.76. Found: C, 34.0; H, 7.66.

$(THF)LiSSi(SiMe_3)_3$. Sulfur (0.18 g, 5.7 mmol) and $(THF)_2LiTeSi(SiMe_3)_3$ (3.0 g, 5.7 mmol) were combined in a 100-mL round-bottomed flask. The flask was cooled to −55 °C in a dry ice/acetone bath, and THF (60 mL) was added with stirring. The solution became purple-red as the sulfur dissolved and a black solid precipitated. The mixture was allowed to warm to room temperature and was stirred for an additional 30 min. The pale orange mixture was then filtered to remove tellurium (0.70 g, 96%), and the THF was removed under reduced pressure affording 1.83 g (90%) of colorless product that was pure by ^1H NMR analysis. Recrystallization from hexane gave colorless prismatic crystals. All characterization data are for the mono-THF adduct, except elemental analysis where the sample was recrystallized three times from hexane and dried under vacuum for several hours, affording the hemi-THF adduct $(THF)_{0.5}LiSSi(SiMe_3)_3$. IR: 1236 s, 1048 s, 915 sh, m, 895 sh, m, 836 vs, 741 m, 683 s, 621 m, 529 s, 512 sh, m, 460 w cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 68.9, 25.3, 0.8. Anal. Calcd for $C_{11}H_{31}LiO_{0.5}SSi_4$: C, 40.9; H, 9.68. Found: C, 40.4; H, 9.93.

$(THF)_2LiTeC(SiMe_3)_3$. THF (250 mL) was added to a mixture of 10.0 g (29 mmol) of $(THF)_{1.5}LiC(SiMe_3)_3$ and tellurium (3.70 g, 29 mmol) at room temperature. The solution turned yellow and then began to darken within minutes to red-brown as more tellurium dissolved. After stirring the mixture overnight, the volatiles were removed under reduced pressure leaving a sticky red paste that slowly dried to a yellow powder under vacuum (ca. 10^{-2} Torr). Extraction with diethyl ether (200 mL) and filtration gave a homogeneous dark orange solution that was concentrated (100 mL) and cooled to −40 °C for 12 h. The tellurolate was isolated by filtration as dark yellow-orange crystals (7.7 g, 56%). Recrystallized samples were invariably contaminated by small amounts (<5%) of the ditelluride and $HC(SiMe_3)_3$.

$(THF)_2LiTeGe(SiMe_3)_3$. THF (130 mL) was added to a mixture of $(THF)_2LiGe(SiMe_3)_3$ (5.0 g, 11 mmol) and tellurium powder (1.4 g, 11 mmol) at 20 °C. The cloudy yellow-green solution was stirred for 12 h after which time it had darkened to orange-brown with some unreacted tellurium still evident. The solution was filtered to afford a homogeneous orange solution, the THF was removed under reduced pressure, and the orange solid was dried under vacuum for 1 h. Extraction with hexane (150 mL) followed by filtration gave an orange solution that was concentrated to 75 mL and cooled to −40 °C for 12 h. Filtration gave the product as large orange rectangular prisms (2.1 g, 48%). This material is extremely soluble in hexane and often forms an oil during attempted recrystallizations. Crystallization from DME afforded the mono-DME adduct that behaved well on further recrystallization. IR: 1237 s, 1045 s, 914 sh, m, 892 sh, s, 834 vs, 739 w, 686 s, 618 s cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 68.8, 25.5, 1.89. Elemental analysis was conducted on the DME adduct. Anal. Calcd for $C_{13}H_{37}GeLiO_2Si_3Te$: C, 30.2; H, 7.22. Found: C, 30.0; H, 7.12.

$(DME)LiSeC(SiMe_3)_3$. DME (75 mL) was added to a mixture of 2.0 g (5 mmol) of $(THF)_2LiC(SiMe_3)_3$ and selenium powder (0.41 g, 5 mmol) in a flask cooled to −78 °C. The stirred mixture was allowed to warm to 20 °C over 6 h. After initially passing through a yellow-green stage, the homogeneous solution turned from dark orange at −40 °C to light orange by 5 °C. The solvent was removed under reduced pressure, and the orange solid was extracted with hexanes (200 mL). Filtration, followed by concentration and cooling to −40 °C, afforded 1.5 g (73%) of light orange prisms that were collected by filtration. IR: 1250 s, 1238 s, 1192 w, 1119 m, 1085 s, 1031 w, 1020 w, 866 s, 839 s, 770 w, 682 m, 651 m,

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613 w, 601 w, 440 w cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 69.9, 59.4, 3.98. Anal. Calcd for $C_{14}H_{37}LiO_2SeSi_3$: C, 41.3; H, 9.15. Found: C, 41.4; H, 9.13.

$HSeSi(SiMe_3)_3$. Using a syringe, triflic acid (0.78 mL, 8.8 mmol) was added to a diethyl ether solution of $(THF)_2LiSeSi(SiMe_3)_3$ (3.73 g, 8.81 mmol in 100 mL) in a 250-mL round-bottomed flask. The solution was stirred for 4 h before removal of solvent under reduced pressure. Sublimation of the residue at 85 °C (10^{-2} Torr) onto a cold finger cooled to −78 °C gave 2.0 g (69%) of colorless plates. IR: 2294 w, 1399 m, 1243 s, 835 s, 742 m, 688 m, 620 m cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.01. MS (EI, 70 eV): m/z 328 (M^+), 73 ($SiMe_3$, base peak). Anal. Calcd for $C_9H_{28}SeSi_4$: C, 33.0; H, 8.61. Found: C, 32.6; H, 8.49.

$HSSi(SiMe_3)_3$. Degassed water (56 μL, 3.1 mmol) was added to a solution of $(THF)_2LiSSi(SiMe_3)_3$ (1.0 g, 3.1 mmol) in diethyl ether (50 mL). The clear colorless solution immediately became clouded by a fine white precipitate. After stirring of the mixture for 1.5 h, the ether was removed from the mixture under dynamic vacuum leaving a sticky colorless paste, which was extracted with hexanes (60 mL), filtered, and then pumped to dryness. Sublimation at 80 °C (10^{-2} Torr) onto the upper walls of the Schlenk vessel (cooled to ca. −100 °C) afforded 0.74 g (85%) of the thiol as a colorless, waxy film. IR: 2557 w, 1394 s, 1246 s, 833 vs, 741 s, 690 s, 622 s, 480 s cm^{-1}.

$HTeC(SiMe_3)_3$. Using a procedure similar to that described above, triflic acid (1.2 mL, 14 mmol) was added to a solution of 6.9 g (14 mmol) of $(THF)_2LiTeC(SiMe_3)_3$ dissolved in diethyl ether (150 mL). A similar workup procedure as described above, with sublimation at 90 °C, gave a yellow-orange wax (4.1 g, 81%). (Note that heating at higher temperatures resulted in decomposition to the alkane $HC(SiMe_3)_3$.) IR: 2015 m, 1401 m, 1252 s, 1008 s, 850 br, s, 773 m, 678 s, 661 m, 634 m, 614 w, 588 m, 520 w cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.53. MS (EI, 70 eV): m/z 360 (M^+), 345 ($M^+ - CH_3$), 287 ($M^+ - SiMe_3$), 231 ($HC(SiMe_3)$), 73 ($SiMe_3$, base peak). Anal. Calcd for $C_{10}H_{28}Si_3Te$: C, 33.4; H, 7.84. Found: C, 33.0; H, 7.86.

$HTeGe(SiMe_3)_3$. Using a procedure similar to that described above, 0.50 g (0.88 mmol) of $(DME)LiTeGe(SiMe_3)_3$ dissolved in 40 mL of hexanes was acidified with 77 μL (0.88 mmol) of triflic acid. Workup and sublimation (70 °C) yielded 0.27 g (73%) of pale yellow waxy product. IR: 2021 w, 1396 w, 1245 s, 837 s, 743 w, 688 m, 617 m cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.29. MS (EI, 70 eV): m/z 421 (M^+), 73 ($SiMe_3$, base peak). Anal. Calcd for $C_9H_{28}GeSi_3Te$: C, 25.7; H, 6.71. Found: C, 25.8; H, 6.99.

$HSeC(SiMe_3)_3$.[18] Using a procedure similar to that described above, 5.2 g (13 mmol) of $(THF)_2LiSeC(SiMe_3)_3$ dissolved in diethyl ether (50 mL) was acidified using 1.2 mL (13 mmol) of triflic acid. Workup and sublimation (70 °C) onto a water-cooled probe afforded 3.8 g (93%) of a pale yellow wax. IR: 2287 m, 1046 m, 1291 m, 1257 s, 1192 w, 1077 w, 1029 m, 859 s, 775 s, 680 s, 656 s, 617 w, 518 w cm^{-1}.

Determination of pK_a's. An Orion 91-04 combination pH electrode with Ag/AgCl internal reference immersed in a filling solution of 4 M KCl saturated with AgCl was used for each titration; this unit was used in conjunction with an Orion Research Model 601A ionalyzer. An Oxford Sampler System was used to add 40 μL volumes of the titrant. All titrations were carried out under dry dinitrogen in a glovebag.

A sample of chalcogenol (0.5–1.5 mmol) was dissolved in 25 mL of MIBK, and the pH electrode was immersed into the titration beaker. The solution was stirred magnetically and allowed to equilibrate for approximately 5 min. TBAH titrant was added in 40-μL increments, and pH and EMF readings were recorded. Titrations were typically carried 40–80 μL beyond the end points. The values reported in Table I are averages of at least two determinations using samples from different batches of freshly sublimed material.

X-ray Structure Determination. Clear tabular crystals of $(THF)LiTeSi(SiMe_3)_3$ were obtained by slow crystallization from hexane at −40 °C. One of these crystals was mounted on a glass fiber using Paratone-N hydrocarbon oil. The crystal was transferred to an Enraf-Nonius CAD-4 diffractometer, centered in the beam, and cooled to −108 °C by a nitrogen flow low-temperature apparatus. Automatic peak searching and indexing procedures yielded a triclinic reduced primitive cell. Inspection of Niggli values revealed no conventional cell of higher symmetry. The 3037 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. The structure was solved by Patterson methods and refined using standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of all but one of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.2 times the B_{eqv} of the atoms to which they were attached. They were included in the structure factor calculations but not refined. In the final cycles of least-squares refinement, nine data with abnormally large weighted difference values (attributed to multiple diffraction) were given zero weight. The final residuals for 181 variables refined against the 2771 accepted data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0300$, $R_w = 0.0372$, and GOF = 1.956. The R value for all 3037 data was 0.0338. The crystal structure was solved by Dr. F. J. Hollander of the U. C. Berkeley College of Chemistry X-ray Facility (CHEXRAY).

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Supplementary Material Available: Details of the structure determination including tables of temperature factor expressions, positional parameters, and intramolecular distances and angles (4 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.