J. Am. Chem. Soc. **1992**, *114*, 5209-5214

New Reagents for the Synthesis of Compounds Containing Metal–Tellurium Bonds: Sterically Hindered Silyltellurolate Derivatives and the X-ray Crystal Structures of $[(\mathrm{THF})_2\mathrm{LiTeSi(SiMe_3)_3}]_2$ and $[(12\text{-crown-}4)_2\mathrm{Li}][\mathrm{TeSi(SiMe_3)_3}]$

Philip J. Bonasia, David E. Gindelberger, Bashir O. Dabbousi, and John Arnold*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received December 13, 1991

Abstract: The synthesis and characterization of several salts of the bulky silyltellurolate ligand $^-$TeSi(SiMe$_3$)$_3$ are reported. Insertion of tellurium into the Li–Si bond of (THF)$_3$LiSi(SiMe$_3$)$_3$ in THF affords colorless crystals of (THF)$_2$LiTeSi(SiMe$_3$)$_3$ (**1**) in high yield. X-ray diffraction shows **1** to be dimeric in the solid state; it crystallizes in the space group $P2_1/n$ with a = 9.775 (3) Å, b = 17.297 (4) Å, c = 17.729 (3) Å, β = 87.58 (2)°, V = 2995 (2) Å^3, d_{calc} = 1.17 g cm^{-3}, and Z = 4. 1,2-Dimethoxyethane (DME) displaces the THF in **1** to form (DME)LiTeSi(SiMe$_3$)$_3$ (**2**). Salts containing the free tellurolate anion are prepared by crowning the Li$^+$ cation in **1**, to form [(12-crown-4)$_2$Li][TeSi(SiMe$_3$)$_3$] (**3**), or by metathesis with Et$_4$NCl, to form [Et$_4$N][TeSi(SiMe$_3$)$_3$] (**4**). The structure of **3** consists of well-separated ions; it crystallizes in the acentric space group $P2_1$ with a = 8.653 (2) Å, b = 19.776 (5) Å, c = 11.423 (2) Å, β = 102.272 (2)°, V = 1910 (1) Å^3, d_{calc} = 1.28 g cm^{-3}, and Z = 2. Reaction of **1** with Me$_3$SiCl produces Me$_3$SiTeSi(SiMe$_3$)$_3$ (**5**) which was isolated as a viscous oil. Acidification of **1** with trifluoromethanesulfonic acid affords colorless crystals of an unusually stable tellurol HTeSi(SiMe$_3$)$_3$ (**6**) in high yield. Treatment of **1** or **6** with dry O$_2$ or CuCl gives dark green ditelluride (SiMe$_3$)$_3$SiTeTe(SiMe$_3$)$_3$ (**7**) in high yield. Reduction of **7** with Na/Hg in THF yields colorless crystals of the sodium derivative (THF)$_{0.5}$NaTeSi(SiMe$_3$)$_3$ (**8**). Tellurolysis of MN(SiMe$_3$)$_2$ (M = Li, Na) or KO-*t*-Bu with **6** in hexane gave the toluene-soluble, base free tellurolate derivatives **9**, **10**, and **11**, respectively. A tetramethylethylenediamine (TMEDA) salt of the potassium complex (TMEDA)KTeSi(SiMe$_3$)$_3$ (**12**) has also been isolated.

Introduction

Much of the recent progress in the chemistry of metal alkoxides and thiolates involves the use of ligands with large, sterically demanding alkyl and aryl groups.[1-8] These developments have afforded a variety of new low-coordinate metal complexes, the study of whose chemistry has traversed such diverse areas as hydrocarbon activation, the sol-gel process,[9-11] and thin-film deposition.[12,13] In contrast, developments in the chemistry of the heavier group 16 elements selenium and tellurium have lagged behind, an effect we believe is due to the limited number of suitable starting materials. As Gysling has pointed out, this situation is further aggravated by the general assumption that organoselenium and tellurium ligands are difficult to prepare and handle, due to their malodorous nature and relative ease of oxidation.[14,15] Nevertheless, a variety of alkyl- and phenyl-substituted selenolate and tellurolate complexes are known[14-17] and, more recently, reports of sterically hindered aryl selenolates have begun to appear.[13,18-20]

By analogy with alkoxides and thiolates, incorporation of bulky substituents is expected to result in a decrease in the tendency of tellurolate ligands to bridge to adjacent metal centers.[1,5,21,22] Ideally, this approach would allow for the study of tellurolate complexes featuring (i) low molecularity, (ii) low coordination numbers, (iii) increased volatility, and (iv) high solubility in nonreactive, hydrocarbon solvents. However, apart from a few substituted aryl tellurolates reported recently,[23-27] isolable examples of sterically demanding tellurolate ligands are remarkably scarce and, prior to our work, no metal complexes had been reported.

We have developed a new class of silyl tellurolate complexes based on the bulky $^-$TeSi(SiMe$_3$)$_3$ anion.[28] This ligand imparts

---

(1) For reviews, see: Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: New York, 1978. Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269. Rothwell, I. P.; Chisholm, M. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 2, p 335.

(2) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153.

(3) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1438.

(4) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977.

(5) Bartlett, R. A.; Ellison, J. J.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2888.

(6) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.

(7) Van Der Sluys, W. G.; Sattelberger, A. P. *Chem. Rev.* **1990**, *90*, 1027.

(8) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969.

(9) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.

(10) Ulrich, D. R. In *NATO ASI Series, No. 141: Transformation of Organometallics into Common and Exotic Materials*; Laine, R. M., Ed.; Martinus Nijhoff: Dordrecht, 1986; p 207.

(11) Livage, J. In *NATO ASI Series, No. 141: Transformation of Organometallics into Common and Exotic Materials*; Laine, R. M., Ed.; Martinus Nijhoff: Dordrecht, 1986; p 250.

(12) Brinker, C. J. In *NATO ASI Series, No. 141: Transformation of Organometallics into Common and Exotic Materials*; Laine, R. M., Ed.; Martinus Nijhoff: Dordrecht, 1986; p 261.

(13) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638.

(14) Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Ed.; Wiley: New York, 1986; Vol. 1; p 679.

(15) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133.

(16) Liesk, J.; Schulz, P.; Klar, G. *Z. Anorg. Allg. Chem.* **1977**, *435*, 98.

(17) Kasemann, R.; Naumann, D. *J. Fluorine Chem.* **1990**, *48*, 207.

(18) Du Mont, W. W.; Kubiniok, S.; Lange, L.; Pohl, S.; Saak, W.; Wagner, I. *Chem. Ber.* **1991**, *124*, 1315.

(19) Du Mont, W. W.; Wagner, I. *Chem. Ber.* **1988**, *121*, 2109.

(20) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683.

(21) Horvath, B.; Möseler, R.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1979**, *449*, 41.

(22) Santos, R. A.; Gruff, E. S.; Koch, S. A.; Harbison, G. S. *J. Am. Chem. Soc.* **1991**, *113*, 469.

(23) Lange, L.; Du Mont, W. W. *J. Organomet. Chem.* **1985**, *286*, C1.

(24) Du Mont, W. W.; Lange, L.; Karsch, H. H.; Peters, K.; Peters, E. M.; Von, S. H. G. *Chem. Ber.* **1988**, *121*, 11.

(25) Giselbrecht, K.; Bildstein, B.; Sladky, F. *Chem. Ber.* **1989**, *122*, 1255.

(26) Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hubner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800.

(27) Bonasia, P. J.; Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1299.

(28) Dabbousi, B. O.; Bonasia, P. J.; Arnold, J. *J. Am. Chem. Soc.* **1991**, *113*, 3186.

a number of desirable characteristics on its metal complexes, including high thermal stability, solubility in nonreactive hydrocarbon solvents, and sufficient volatility to render the compounds suitable for use as precursors to metal telluride thin films via chemical vapor deposition (CVD). Here we present the first in a series of full accounts of this work describing the synthesis, structure, and reactivity of a versatile new class of silyltellurolate synthons.

Experimental Section

General. All manipulations were carried out under nitrogen or argon unless stated otherwise. Tetrahydrofuran (THF), diethyl ether, toluene, benzene, hexane, and 1,2-dimethoxyethane (DME) were pre-dried over 4 Å molecular sieves and then distilled from sodium/benzophenone under N$_2$. Dichloromethane was distilled from calcium hydride under N$_2$. All NMR solvents were treated similarly but distilled under vacuum. Tetramethylethylenediamine (TMEDA) was distilled from sodium under argon. Chlorotrimethylsilane (PCR) was distilled under argon; trifluoromethanesulfonic acid (HOTf, Aldrich) was degassed using a stream of nitrogen or argon. Tellurium powder, anhydrous copper(I) chloride, potassium *tert*-butoxide (all Strem), methyl lithium (Aldrich), and *n*-butyl lithium in hexane (Aldrich) were used as received. 12-Crown-4 (Lancaster) was distilled at reduced pressure and stored under argon. (THF)$_3$LiSi(SiMe$_3$)$_3$[29] was prepared using published procedures. Melting points were determined in sealed capillaries under nitrogen and are uncorrected. Samples for FT IR spectroscopy were prepared as Nujol mulls between KBr plates. Solution conductivity was measured using a Fisher Scientific digital conductivity meter. NMR spectra were recorded in benzene-d_6 at 20 °C unless stated otherwise. Chemical shifts (δ) for ^{1}H NMR spectra are relative to residual protium in the deuterated solvents listed (C$_6$D$_6$, δ 7.15 ppm; CDCl$_3$, δ 7.24 ppm). Tellurium NMR spectra were recorded in 5-mm tubes at ambient temperature at 157.905 MHz in benzene-d_6, unless stated otherwise; spectra are referenced to Me$_2$Te as external standard at δ 0 ppm. Elemental analyses and mass spectra (EI, 70 eV) were performed at the microanalytical laboratory in the College of Chemistry, U.C. Berkeley.

[THF$_2$LiTeSi(SiMe$_3$)$_3$]$_2$ (1). To 16 g (34 mmol) of (THF)$_3$LiSi(SiMe$_3$)$_3$ and 4.3 g (34 mmol) of tellurium powder in a 500-mL round-bottomed flask was added 200 mL of THF. The tellurium rapidly dissolved to give a gray-green mixture which was stirred overnight. The solvent was removed under reduced pressure and, after drying overnight in vacuo, the residue was extracted with two portions of hexane (300 then 100 mL). Concentration and cooling of the saturated extracts to −40 °C afforded pale yellow crystals (mp 169–171 °C) of **1** (14.7 g, 82%). ^{1}H NMR (300 MHz): δ 3.75 (m, 8 H), 1.43 (m, 8 H), 0.45 (s, 27 H). ^{125}Te{^{1}H} NMR (0.3 M): δ −1622 ($\Delta\nu_{1/2} = 80$ Hz). IR: 1236 m, 1048 m, 917 w, 893 w, 834 s, 737 w, 686 m, 623 m cm^{-1}. Anal. Calcd for C$_{17}$H$_{43}$Si$_4$TeLiO$_2$: C, 38.8; H, 8.36. Found: C, 38.5; H, 8.36.

(DME)LiTeSi(SiMe$_3$)$_3$ (2). Compound **1** (0.50 g, 0.95 mmol) was dissolved in 15 mL of DME and the resulting dark orange solution was stirred for 30 min. The solvent was removed under reduced pressure and the gray residue was extracted with diethyl ether (50 mL). The ether solution was concentrated and cooled to −40 °C, yielding 0.37 g (82%) of colorless crystals in two crops. ^{1}H NMR (300 MHz): δ 3.30 (s, 6 H), 3.01 (s, 4 H), 0.48 (s, 27 H). IR: 1388 m, 1367 m, 1305 w, 1277 w, 1250 sh, 1239 s, 1292 w, 1120 m, 1105 m, 1079 s, 1028 w, 1020 w, 869 s, 835 vs, 742 w, 686 s, 622 s cm^{-1}. Anal. Calcd for C$_{13}$H$_{37}$LiO$_2$Si$_4$Te: C, 33.1; H, 7.90. Found: C, 33.1; H, 8.04.

[(12-crown-4)$_2$Li][TeSi(SiMe$_3$)$_3$] (3). To a stirred solution of **1** (0.30 g, 0.57 mmol) in 50 mL of diethyl ether was added 0.20 g (1.1 mmol) of 12-crown-4 in 10 mL of diethyl ether. The solution lightened to pale yellow and a fine white precipitate formed. This mixture was stirred for 2 h and the volatiles were removed under reduced pressure. Extraction of the residue with two 50-mL portions of diethyl ether, followed by concentration and cooling to −40 °C, yielded 0.33 g (79%) of pale brown needles, (mp 202–206 °C). ^{1}H NMR (300 MHz): δ 3.30 (s, 32 H), 0.64 (s, 27 H). IR: 3720 m, 3175 w, 1302 m, 1285 w, 1237 m, 1133 m, 1087 s, 1052 w, 1020 m, 928 m, 861 m, 835 s, 686 m, 622 m, 562 w cm^{-1}. Anal. Calcd for C$_{25}$H$_{59}$O$_8$Si$_4$TeLi: C, 40.9; H, 8.10. Found: C, 40.7; H, 8.04.

[Et$_4$N][TeSi(SiMe$_3$)$_3$] (4). To 0.48 g (2.9 mmol) of Et$_4$NCl and 0.50 g (0.95 mmol) of **1** was added 30 mL of diethyl ether. The light yellow mixture was stirred vigorously for 20 h and the solvent was removed under reduced pressure. The residue was extracted with THF (50 mL), filtered, concentrated, and cooled to −40 °C. The light yellow crystalline product was isolated by filtration to yield 0.36 g (76%) in three crops (mp 187–188 °C). ^{1}H NMR (400 MHz): δ 2.79 (q, $J = 7$ Hz, 8 H), 0.80 (t, $J = 7$ Hz, 12 H), 0.63 (s, 27 H). IR: 1395 sh, 1300 m, 1249 sh, 1231 s, 1180 s, 1117 w, 1076 w, 1030 s, 1004 m, 856 sh, 841 s, 797 s, 739 s, 732 s, 682 s, 619 s cm^{-1}. Anal. Calcd for C$_{17}$H$_{47}$NSi$_4$Te: C, 40.4; H, 9.37; N, 2.77. Found: C, 40.4; H, 9.38; N, 2.63. Λ_M (MeCN, 1.4 mM): 151 ohm^{-1} cm^2 mol^{-1}.

Me$_3$SiTeSi(SiMe$_3$)$_3$ (5). Chlorotrimethylsilane (0.21 mL, 1.6 mmol) was added dropwise to a stirred solution of **1** (0.50 g, 0.95 mmol) in hexane (50 mL). A fine white precipitate formed over the course of 30 min. Volatile components were removed under reduced pressure and the residue was extracted with two 20-mL portions of hexane and filtered. Removal of the solvent under reduced pressure yielded 0.35 g (82%) of **5** as a pale green oil. ^{1}H NMR (300 MHz): δ 0.55 (s, 9 H), 0.33 (s, 27 H). ^{125}Te{^{1}H} NMR (0.2 M): δ −1081 ($J_{\mathrm{TeSi}} = 316$ Hz; $\Delta\nu_{1/2} = 40$ Hz). MS (EI, 70 eV): m/z 450 (M$^+$), 377, 289. IR: 2955 s, 2884 s, 2814 m, 2778 m, 2085 w, 1990 w, 1437 s, 1396 s, 1308 m, 1243 s, 1085 sh, 1044 m, 1020 sh, 832 s, 744 s, 685 s, 620 s cm^{-1}.

HTeSi(SiMe$_3$)$_3$ (6). Method A: To 1.00 g (1.90 mmol) of **1** in 40 mL of hexane was added 0.17 mL (1.9 mmol) of trifluoromethanesulfonic acid. This mixture was stirred for 30 min and the solvent was removed under reduced pressure. The light green residue was sublimed at 40–80 °C (10^{-3} Torr) onto a cold finger at −78 °C, to yield 0.648 g (91%) of white, waxy product; mp 128–130 °C. This reaction has been successfully scaled up by a factor of 20 without diminution in yield.

Method B: THF (30 mL) was added to a mixture of 5.0 g (11 mmol) of (THF)$_3$LiSi(SiMe$_3$)$_3$ and 1.3 g (11 mmol) of tellurium powder in a 100-mL round-bottomed flask cooled to 0 °C. The grey-green mixture was allowed to warm to room temperature and was stirred for 1 h. Trifluoromethanesulfonic acid (0.94 mL, 11 mmol) was added dropwise and the resulting black mixture was stirred for 30 min. After drying under vacuum, the product was purified as above. Yield: 2.2 g (56%). ^{1}H NMR (300 MHz): δ 0.23 (s, 27 H), −8.82 (s, 1 H, $J_{\mathrm{HTe}} = 74$ Hz). ^{125}Te NMR (0.5 M): δ −955 (d, $J_{\mathrm{TeH}} = 74$ Hz, $\Delta\nu_{1/2} = 27$ Hz). IR: 2017 m, 1397 m, 1311 w, 1256 m, 1245 s, 837 s, 745 m, 691 s, 623 s cm^{-1}. MS (EI, 70 eV): m/z 378 (M$^+$), 304, 289, 73 (base peak). Anal. Calcd for C$_9$H$_{28}$Si$_4$Te: C, 28.7; H, 7.50. Found: C, 29.0; H, 7.52.

Te$_2$[Si(SiMe$_3$)$_3$]$_2$ (7). Method A: To 2.00 g (3.80 mmol) of **1** and 0.38 g (3.8 mmol) of anhydrous CuCl in a 100-mL Schlenk round-bottomed flask was added 50 mL of pentane. The resulting dark green solution was stirred for 22 h and then filtered into a 100-mL Schlenk tube. The solution was concentrated under reduced pressure and cooled to −40 °C overnight, yielding 1.08 g (76%) of dark green crystals (mp 177–183 °C).

Method B: A stream of dry O$_2$ was gently blown over 2.00 g (3.80 mmol) of **1** dissolved in 50 mL of hexane in a 100-mL Schlenk round-bottomed flask. The solution warmed slightly and gradually turned dark green. The mixture was stirred for 15 min and the solvent was removed under reduced pressure. The resulting green solid was extracted with hexane (50 mL) and filtered. The solution was concentrated under reduced pressure until it was saturated and slowly cooled to −40 °C, yielding, in two crops, 1.35 g (95%) of the ditelluride as dark green crystals. ^{1}H NMR (300 MHz): δ 0.37 (s). ^{125}Te{^{1}H} NMR (0.6 M): δ −678 ($J_{\mathrm{TeSi}} = 289$ Hz). IR: 1245 s, 839 s, 691 m, 623 m cm^{-1}. MS (EI, 70 eV): m/z 750 (M$^+$), 551, 289, 73 (base peak). Anal. Calcd for C$_9$H$_{27}$Si$_4$Te: C, 28.8; H, 7.25. Found: C, 29.0; H, 7.31.

THF$_{0.5}$NaTeSi(SiMe$_3$)$_3$ (8). To a 100-mL Schlenk round-bottomed flask containing 77 mg (3.3 mmol) of sodium dissolved in mercury (10 g) and 1.0 g (1.3 mmol) of **7** was added 50 mL of THF. After being stirred for 1 h the mixture was filtered, concentrated under reduced pressure, and then cooled to −40 °C overnight to yield 0.81 g (70%) of product (mp 320–330 °C). ^{1}H NMR (250 MHz): δ 3.75 (m, 2 H), 1.50 (m, 2 H), 0.43 (s, 27 H). IR: 1236 m, 1046 m, 864 m, 835 s, 688 m, 625 m cm^{-1}. Anal. Calcd for C$_{11}$H$_{31}$O$_{0.5}$Si$_4$TeNa: C, 30.42; H, 7.31. Found: C, 30.42; H, 7.19.

LiTeSi(SiMe$_3$)$_3$ (9). A solution of 0.50 g (1.3 mmol) of **6** in 15 mL of hexane was layered on to a solution of 0.23 g (1.3 mmol) of LiN(SiMe$_3$)$_2$ in 15 mL of toluene in a narrow 100-mL Schlenk tube. The tellurol solution was allowed to diffuse into the toluene layer for 24 h before cooling the mixture to −40 °C over 48 h. The product was isolated by filtration to yield 0.27 g (54%) of light yellow crystals (mp 179–189 °C). ^{1}H NMR, (300 MHz): δ 0.46 (s). IR: 1257 w, 1236 m, 955 w, 864 m, 835 s, 786 w, 686 w, 625 w cm^{-1}. Anal. Calcd for C$_9$H$_{27}$Si$_4$TeLi: C, 28.28; H, 7.12. Found: C, 28.28; H, 7.09.

NaTeSi(SiMe$_3$)$_3$ (10). Using a similar procedure to that for **9**, 0.24 g (1.3 mmol) of NaN(SiMe$_3$)$_2$ was allowed to react with 0.50 g (1.3 mmol) of **6** in 10 mL of hexane. This yielded 0.32 g (61%) of pale green crystalline product in two crops (mp > 300 °C). ^{1}H NMR (200 MHz): δ 0.42 (s). IR: 1257 w, 1243 m, 1229 m, 864 m, 835 s, 688 m, 625 m cm^{-1}. Anal. Calcd for C$_9$H$_{27}$Si$_4$TeNa: C, 27.1; H, 6.83. Found: C, 27.2; H, 6.58.

KTeSi(SiMe$_3$)$_3$ (11). To 0.15 g (1.3 mmol) of potassium *tert*-butoxide and 0.50 g (1.3 mmol) of **6** in a 100-mL Schlenk round-bottomed flask

---

(29) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

Table I. Crystallographic Data for **1** and **3**

	1	**3**
formula	$C_{17}H_{43}Si_4O_2LiTe$	$C_{25}H_{59}Si_4O_8LiTe$
mol weight	526.4	734.6
space group	$P2_1/n$	$P2_1$
a, Å	9.775 (3)	8.653 (2)
b, Å	17.297 (4)	19.776 (5)
c, Å	17.729 (3)	11.423 (2)
β, deg	87.58 (2)	102.27 (2)
vol, Å^3	2994 (2)	1910 (1)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.17	1.28
crystal size, mm	0.25 × 0.33 × 0.40	0.21 × 0.32 × 0.38
scan mode	ω	θ–2θ
2θ range, deg	3–45	2–50
collection range	$+h, +k, \pm l$	$+h, \pm k, \pm l$
absorption coeff	$\mu = 11.6$	$\mu = 9.4$
no. of unique reflns	3915	3462
reflns with $F^2 > 2\sigma$(or 3σ)	$1708 > 2\sigma(F^2)$	$2554 > 3\sigma(F^2)$
final R, R_w	0.092, 0.088	0.0648, 0.0753
T, °C	25	−90

was added 50 mL of hexane and the mixture was stirred overnight. After drying under reduced pressure, the light purple solid was extracted with toluene (50 mL) and filtered. Concentration under reduced pressure, followed by cooling to −40 °C overnight, yielded 0.41 g (74%) of pale purple microcrystalline product (mp 171–172 °C). ^{1}H NMR (300 MHz): δ 0.42 (s). IR: 1250 m, 1229 m, 828 s, 688 m, 625 m cm^{-1}. Anal. Calcd for $C_9H_{27}Si_4TeK$: C, 26.1; H, 6.57. Found: C, 26.1; H, 6.54.

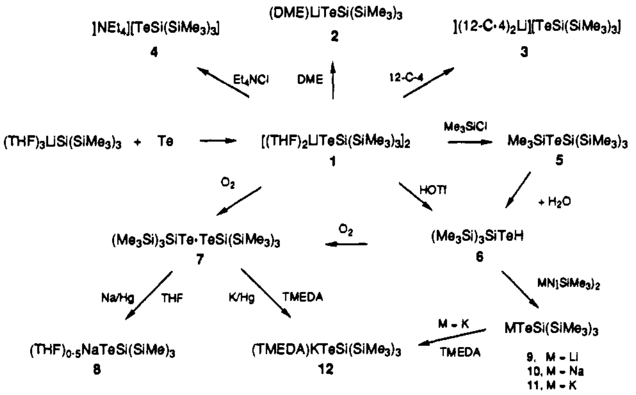
(TMEDA)KTeSi(SiMe$_3$)$_3$ (12). To 0.10 g (0.024 mmol) of **11** dissolved in 10 mL of toluene was added 0.036 mL (0.024 mmol) of TMEDA dropwise with stirring. The red-brown solution was stirred for 10 min and then the solvent was removed under reduced pressure. The orange residue was extracted with hexane (40 mL) and the resulting solution was concentrated and cooled to −40 °C to afford 0.062 g (49%) of dark orange crystals. ^{1}H NMR (300 MHz): δ 2.24 (s, 4 H), 2.13 (s, 12 H), 0.43 (s, 27 H). IR: 2798 s, 1293 s, 1237 s, 1193 m, 1152 m, 1124 m, 1082 m, 1040 m, 1026 m, 941 m, 864 s, 840 vs, 780 s, 738 m, 681 m, 625 m cm^{-1}.

X-ray Crystallography. The crystal structures for **1** and **3** were solved by Patterson methods and refined via standard least-squares and Fourier techniques. Table I contains details of crystal and data collection parameters. These determinations were carried out by Dr. F. J. Hollander at the U.C. Berkeley College of Chemistry X-ray facility (CHEXRAY).

[(THF)$_2$LiTeSi(SiMe$_3$)$_3$]$_2$ (1). Transparent, light-green prisms were obtained by slow crystallization from a saturated hexane solution at −40 °C. An appropriate crystal (0.25 × 0.33 × 0.40 mm) 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 allowed to remain at ambient temperatures, as cooling of the crystals led to fracturing. The unit cell was determined to be primitive monoclinic, space group $P2_1/n$. Hydrogen atoms were assigned idealized locations and were included in structure factor calculations, but were not refined. The final residuals for 155 variables refined against the 1708 data for which $F^2 > 2\sigma(F^2)$ were $R = 0.092$, $R_w = 0.088$, and GOF = 2.71. The R value for all 4081 data was 0.201. The [(THF)$_2$LiTe]$_2$ core of each molecule is disordered. Disorder in the THF ligands appears to involve only the carbon atoms, with the oxygen atoms remaining relatively fixed. Refinement was carried out using isotropic thermal parameters and assumed 0.50 occupancy at various sites. The tellurium atoms are disordered over two positions and were refined at unequal occupancies of 0.88 and 0.12. The minority position, Te′, was refined with an isotropic thermal parameter. The Li atoms are apparently not disordered. Though the –Si(SiMe$_3$)$_3$ groups appear to be ordered, they are almost certainly disordered as well, at least to the extent that the Te positions are disordered. This disordering is not resolvable, in part due to the large amount of thermal motion associated with the room temperature structure.

[(12-crown-4)$_2$Li][TeSi(SiMe$_3$)$_3$] (3). Clear, colorless blade-like crystals of the compound were obtained by slow crystallization from diethyl ether. A suitable fragment (0.21 × 0.32 × 0.38 mm) was cleaved and was mounted in a similar fashion to that used for **1**. After the crystal was transferred to the diffractometer and centered in the beam, it was cooled to −90 °C. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the systematic absences indicated possible space groups $P2_1$ and $P2_1/m$. The choice of the acentric group was confirmed by the successful solution and refinement of the structure. Removal of the systematic absences and averaging of redundant data left 3462 unique data in the final data set. A crown–lithium–crown sandwich is clearly observed, but the ether ligands are seriously disordered and were modeled as partially occupied carbon atoms refined with one common isotropic thermal parameter for each of the two crown ligands. Electron density calculations showed that 84% of the electron density expected from two 12-crown-4 ligands could be accounted for in the region about the Li atom. Refinement of the two enantiomorphs on unaveraged (Friedel unique) data led to equal residuals and no change in the refinement, so the final refinement was performed on averaged data and with the imaginary component of the scattering factor removed from all atoms. In the structure solution process no clear molecular connectivity could be ascertained. The tellurium atom and the atoms of the –Si(SiMe$_3$)$_3$ ligand (except for C8) were refined anisotropically. The final residuals for 263 variables refined against the 2554 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0684$, $R_w = 0.0753$, and GOF = 2.13. The R value for all 3462 data was 0.0984.

Scheme I



Results and Discussion

The lithium tellurolate derivative **1** is formed cleanly and rapidly in THF by the insertion reaction shown in Scheme I. Crystallization from hexane affords air-sensitive prisms of the salt in high yield; the reaction has been scaled up to produce over 20 g of product without diminution in yield. The compound is thermally stable at room temperature and can be stored indefinitely under nitrogen. Although insertion of tellurium into reactive alkali metal–carbon bonds is a well-established synthetic route for the in situ preparation of alkyl and aryl tellurolate anions,[30] these reactions are never clean and the resulting solutions appear to contain a mixture of products. We[27] and others[31,32] have shown that, in some cases, pure products can be obtained in two further steps, consisting of complete oxidation of the reaction mixture to form the ditelluride (which is air-stable and readily purified), followed by re-reduction with reagents such as LiBEt$_3$H or sodium amalgam. In contrast, the simple one-step synthesis of **1** and its straightforward isolation and purification present clear practical advantages.

Compound **1** contains 2 equiv of THF as determined by ^{1}H NMR spectroscopy and elemental analysis. The solid-state structure, determined by X-ray crystallography, is shown as an ORTEP view in Figure 1. Crystallographic data and pertinent bond distances and angles are given in Table II. These data clearly reveal the dimeric nature of the molecule and its four-membered Li$_2$Te$_2$ core. There are no apparent interactions between adjacent dimeric units. Overall, the structure is similar to that for the thiolate derivative [(THF)$_2$LiSC(SiMe$_3$)$_3$]$_2$ determined by Power.[33] The Te–Li bond lengths (2.82 (2) and 2.88 (2) Å) are within experimental error of that determined for the monomeric aryl tellurolate (THF)$_3$LiTe(2,4,6-^{t}Bu$_3$C$_6$H$_2$) ($d_{(Li-Te)} = 2.82$ (1) Å)[34]

---

(30) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1974.

(31) Du Mont, W. W.; Hensel, R.; Kubiniok, S. *Phosphorus and Sulfur* **1988**, *38*, 85.

(32) Jones, C. H.; Sharma, R. D. *J. Organomet. Chem.* **1983**, *255*, 61.

(33) Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Sigel, G. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1674.

(34) Bonasia, P. J.; Arnold, J. Manuscript in preparation.

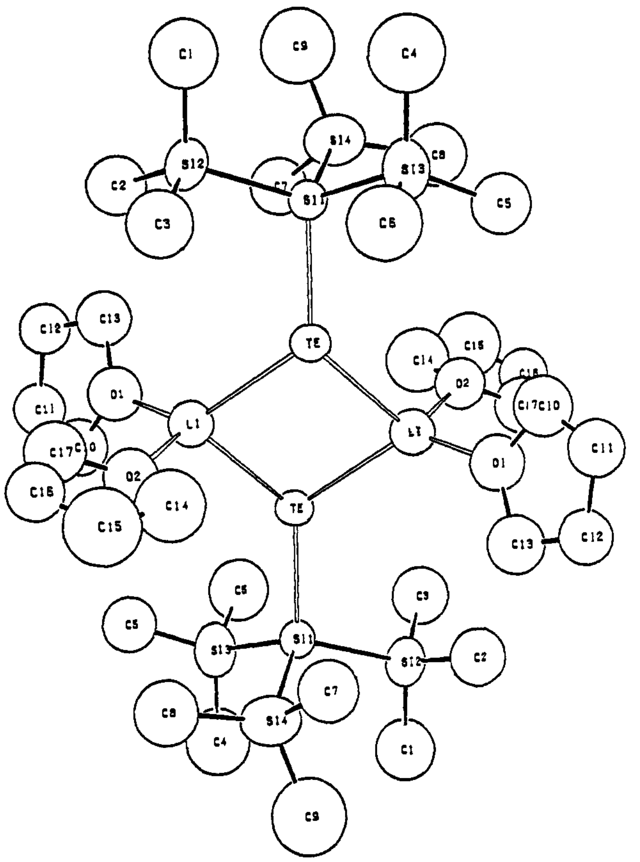


Figure 1. ORTEP view of the molecular structure of $[(THF)_2LiTeSi(SiMe_3)_3]_2$ (**1**).

Table II. Selected Bond Distances (Å) and Angles (deg) for **1** and **3**

$[(THF)_2LiTeSi(SiMe_3)_3]_2$ (**1**)					
Te–Si(1)	2.480 (3)	Li–O(1)	1.90 (2)	Si–Si(ave)	2.322 (6)
Te–Li	2.82 (2)	Si–C(ave)	1.90 (2)	O(1)–C(10)	1.52 (4)
Te–Li(−1)	2.88 (2)			Li–O(2)	1.99 (2)
Si(1)–Te–Li	123.2 (5)	Te(−1)–Li–O(1)	110.1 (10)		
Si(1)–Te–Li(−1)	130.2 (5)	Te(−1)–Li–O(2)	118.6 (10)		
Li–Te–Li(−1)	90.4 (6)	O(1)–Li–O(2)	100.1 (11)		
Te–Li–Te(−1)	89.6 (6)	Te–Si(1)–Si(2)	108.2 (2)		
Te–Li–O(1)	132.6 (11)	Te–Si(1)–Si(3)	105.6 (2)		
Te–Li–O(2)	107.4 (10)	Te–Si(1)–Si(4)	112.6 (2)		
$[(12\text{-crown-}4)_2Li][TeSi(SiMe_3)_3]$ (**3**)					
Te–Si(1)	2.468 (3)	Li–C(crown, ave)	2.33 (5)		
Si–Si(ave)	2.338 (11)	Si–C(ave)	1.90 (3)		
Te–Si(1)–Si(2)	112.4 (2)	C(1)–Si(2)–C(2)	120 (2)		
Te–Si(1)–Si(3)	114.8 (3)	C(1)–Si(2)–C(3)	103 (2)		
Te–Si(1)–Si(4)	104.9 (3)	C(2)–Si(2)–C(3)	104 (2)		
Si(2)–Si(1)–Si(3)	114.1 (4)	Si(1)–Si(2)–C(1)	111.2 (8)		
Si(2)–Si(1)–Si(4)	102.9 (5)	Si(1)–Si(2)–C(2)	111.2 (9)		
Si(3)–Si(1)–Si(4)	106.3 (3)	Si(1)–Si(2)–C(3)	106.2 (9)		

and are close to the value of 2.80 Å predicted on the basis of ionic radii (Li^+ 0.73 Å; Te^{2-} 2.07 Å[35,36]). Similarly, the calculated (Si^{4+} 0.40 Å) tellurium-silicon bond length of 2.47 Å is only slightly shorter than the observed distance of 2.480 (3) Å. Substantial thermal motion in the $-Si(SiMe_3)_3$ ligands and some disordering of the tellurium positions limit the usefulness of further discussion.

The DME adduct of **1** has also been isolated. Dissolution of **1** in DME followed by drying and crystallization from diethyl ether gave the mono-DME adduct **2** as colorless needles. A 1:1 ratio of DME–tellurolate is indicated by ^1H NMR spectroscopy and elemental analysis. A structure similar to that of **1**, but with a bidentate DME ligand in place of two THF's, appears most likely. As expected, the subsequent reactivity of **1** and **2** is similar.

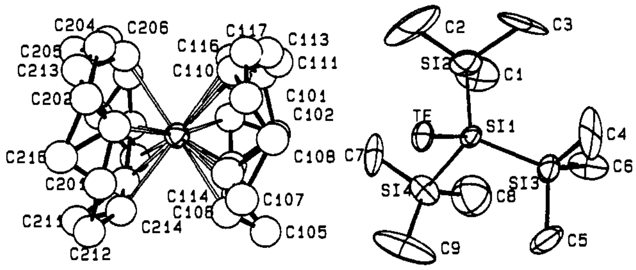


Figure 2. ORTEP view of the molecular structure of $[(12\text{-crown-}4)_2Li][TeSi(SiMe_3)_3]$ (**3**).

Power and co-workers have recently exploited the strong complexing ability of crown ethers with alkali metals to stabilize unusual structures incorporating "naked" anions. Examples include cuprates, carbanions, phosphides, and amides.[37,38] In an effort to examine the possibility that a "free" tellurolate anion might be stable, we reacted **1** with 2 equiv of 12-crown-4 in diethyl ether. Upon cooling, large pale-brown needles of the crown ether salt **3** crystallized from the saturated solution. The compound is thermally stable, melting cleanly from 202 to 206 °C; however, it decomposes rapidly in air. The structure of this compound, as determined by X-ray diffraction, is very different from that of **1**. As shown in Figure 2, it exists as ion pairs with well-separated $Li(12\text{-C-}4)_2^+$ cations and "free" tellurolate anions. The Te–Si bond length of 2.468 (3) Å (Table II) is within experimental error of that determined for **1**, showing that coordination to lithium in the latter compound has little effect on the anion. The closest approach to the one-coordinate tellurium atom comes from two equidistant $Li(12\text{-C-}4)_2^+$ moieties and is in the range 4.0–5.4 Å. The geometry around Si1 is distorted from tetrahedral, with angles ranging from 102.9 (3) to 114.8 (3)°. The Si–Si bonds are also unequal, ranging from 2.246 (8) up to 2.451 (11) Å. The cause of these deviations is impossible to ascribe with any degree of certainty given the substantial level of thermal motion apparent in the $-Si(SiMe_3)_3$ ligand (see Experimental Section for further details).

Reaction of **1** with Et_4NCl in diethyl ether gave air-sensitive crystals of the tetraethylammonium salt, **4**, in high yield. The compound is insoluble in hydrocarbons or diethyl ether, but large yellow crystals were isolated from concentrated THF. The salt-like character of **4** was demonstrated by conductivity measurements, which show that **4** behaves as a 1:1 electrolyte in acetonitrile. Reports of tellurolate salts are limited to aromatic substituted species such as $[Ph_4P][TePh]$ prepared by Klar and co-workers some years ago,[16] and $[Ph_4P][TeC_4H_3S]$ prepared very recently by Zhao and Kolis.[39]

Trimethylsilyl ethers and their thioether analogs are valuable reagents for the preparation of a wide range of metal alkoxides and thiolates via metathesis reactions with metal chlorides to liberate Me_3SiCl, and some tellurolate derivatives have been prepared.[40,41] The trimethylsilyl derivative **5** is readily formed on treatment of **1** with Me_3SiCl in diethyl ether. The telluride **5**, which was isolated in high yield as a colorless viscous oil, was characterized by ^1H NMR spectroscopy and mass spectrometry. In common with known trimethylsilyl tellurides, **5** is rather air sensitive and addition of excess water in benzene results in rapid hydrolysis to the tellurol **6** (see below) as determined by ^1H NMR

---

(35) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925. Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(36) Huheey, J. E. *Inorganic Chemistry*; 3rd ed.; Harper and Row: New York, 1983.

(37) Power, P. P. *Acc. Chem. Res.* **1988**, *21*, 147.

(38) Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. P. *Organometallics* **1991**, *10*, 1282.

(39) Zhao, J.; Adcock, D.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 4358.

(40) Drake, J. E.; Glavincevski, B. M.; Hemmings, R. T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 457.

(41) Stuczynski, S. M.; Brennan, J. G.; Steigerwald, M. L. *Inorg. Chem.* **1989**, *28*, 4431.

Table III. Spectroscopic Data of Reported Tellurols

compd	ν_{Te-H} (cm^{-1})	^{1}H NMR δ Te–H (ppm)	^{125}Te NMR^a δ Te–H (ppm)	$\lvert J_{(TeH)}\rvert$ (Hz)	ref
6^b	2021	−8.82	−955	74	this work
H_3SiTeH^c	nr^g	−7.46	nr	58	45
H_3GeTeH^c	nr	−7.44	nr	52	45
$MeTeH^d$	2053	−5.5	nr	nr	42, 43, 46
$PhTeH^e$	nr	−2.4	nr	50	40
$Me_3C_6H_2TeH^f$	nr	−2.68	−91.41	63	47
$^iPr_3C_6H_2TeH^f$	nr	−2.95	−134.77	48.6	47
$^tBu_3C_6H_2TeH^f$	nr	−1.25	153.77	51.9	47

^{a}Referenced to Me_2Te at 0.0 ppm. ^{b}NMR data recorded in benzene-d_6. ^{c}NMR data recorded in $CHCl_3$. ^{d}NMR data recorded neat. ^{e}NMR data recorded in C_6H_{12}. ^{f}NMR data recorded in chloroform-d. ^{g}nr = not reported.

spectroscopy. Cleavage of the Me_3Si–Te bond in preference to the $(Me_3Si)_3Si$–Te bond highlights the degree of kinetic stabilization imparted by the bulkier silyl substituent.

In considering new synthetic routes to metal tellurolates we hoped to exploit the tellurolysis reaction shown below, but we were limited by the scarcity of stable tellurols.

$$L_nM\text{—}R' + RTeH \rightarrow L_nM\text{—}TeR + R'H$$

It has been known for some time that protonation of alkyl and aryl tellurolates forms thermally sensitive tellurols,[27,42-46] but they are all unstable at room temperature and have only been isolated in pure form by low-temperature distillation or crystallization.[47] In contrast, when **1** is treated with triflic acid in hexane, tellurol **6** may be isolated in high yield by vacuum sublimation at 40–80 °C. An alternative one-pot procedure using $(THF)_3LiSi(SiMe_3)_3$ as the starting material gives slightly lower overall yields (ca. 50–60%), but it is an easier route to the compound since it avoids a recrystallization step.

Tellurol **6** is a colorless, crystalline solid that appears to be stable for at least several days at room temperature under nitrogen in the dark. Exposure to ambient room light under nitrogen results in slow darkening, but spectroscopic properties of resulting solutions show no measurable decomposition and the compound remains analytically pure. (We generally store the compound in a refrigerator to prevent this discoloring.) This behavior is consistent with photodecomposition at the surface which renders the bulk solid inert from further degradation. In solution, these reactions occur much more readily, so that exposure of benzene-d_6 solutions of the tellurol to bright sunlight quickly results in the formation of a tellurium mirror, along with a number of uncharacterized silicon-containing products. In air, **6** decomposes rapidly to form the ditelluride **7** described below.

Compound **6** has been characterized by MS, IR, and NMR spectroscopy and by its derivative chemistry. Electron-impact MS showed a strong signal for the parent ion at m/z 378. Spectroscopic data for tellurols are limited, as shown in Table III. A medium strength Te–H stretch in **6** (at 2021 cm^{-1}) occurs at a similar frequency to that found in MeTeH vapor (2053 cm^{-1}).[46] Two peaks at 0.23 and −8.82 ppm (ratio 27:1) in the proton NMR spectrum are easily assigned to the $Si(SiMe_3)_3$ methyls and the tellurol proton, respectively. Tellurium satellites were apparent on the latter signal (J_{TeH} = 74 Hz) and a similar value was observed in the proton-coupled ^{125}Te NMR spectrum (Figure 3); the doublet at δ −955 ppm collapsed to a singlet on proton decoupling. This signal is considerably upfield of shifts reported for the substituted aryl derivatives shown in Table III. The most likely cause of this shielding may be attributed to the decreased electronegativity of the silyl substituent in **6**; we also note, however, that a wide range of chemical shifts is frequently observed in ^{125}Te NMR.[48,49]

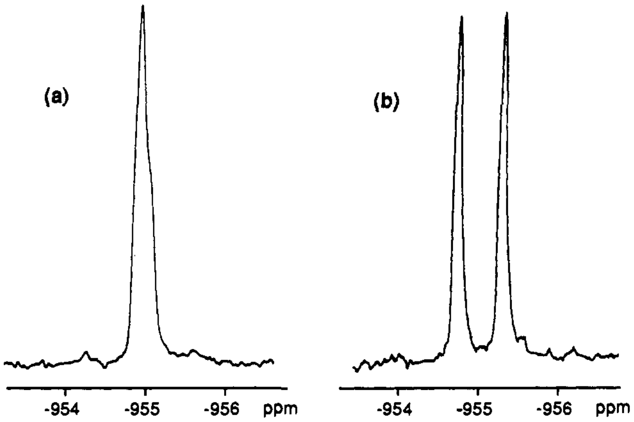


Figure 3. $^{125}Te\{^1H\}$ NMR spectrum (a) and ^{125}Te NMR spectrum (b) of $HTeSi(SiMe_3)_3$ (**6**).

Oxidation of **1** or **6** with dry oxygen or CuCl gives dark green solutions from which high yields of the ditelluride **7** can be isolated as emerald-green crystals (λ_{max} 652 nm). The reaction is remarkably clean as determined by reactions monitored by ^{1}H NMR spectroscopy. In contrast, oxidations of aryltellurolates are often complex, low-yield reactions. The dramatic color change from colorless **1** to dark green **7** provides a useful indication of oxidation in subsequent reactions. The green color is somewhat unusual considering the fact that the majority of alkyl and aryl ditellurides are orange or red,[30] but we note that the carbon analog of this compound, $Te_2[C(SiMe_3)_3]_2$, is also dark green.[26] Compound **7** can be handled in air for quite long periods without noticeable decomposition, but it is slightly hygroscopic, turning black after prolonged (several weeks) exposure to moist air.

Two-electron reduction of **7** with sodium amalgam in THF results in Te–Te bond homolysis and reformation of the tellurolate anion. Pale yellow crystals of the hemi-THF solvate $THF_{0.5}NaTeSi(SiMe_3)_3$ (**8**) were isolated in 70% yield after cooling the concentrated solution to −40 °C. The solid-state structure of **8** is currently unknown, but an oligomeric or polymeric structure appears most likely.[27]

Base-free alkali metal salts are easily synthesized via tellurolysis using **6** in nonpolar media. Base-free lithium (**9**), sodium (**10**), and potassium (**11**) tellurolates are formed by tellurolysis of either the corresponding amide or *tert*-butoxide in hydrocarbons (Scheme I). They precipitate from hexane as they are formed but are readily soluble in toluene. Their solid-state structures are currently unknown, as several attempts to grow crystals suitable for X-ray diffraction have failed, but polymeric structures appear most likely. In accord with their lack of volatility, no peaks were observed for the parent ions by EI MS. Treatment of the lithium salt **9** with THF followed by recrystallization from hexane afforded **1**. Potassium salt **11** was also isolated as the more soluble TMEDA derivative $(TMEDA)KTeSi(SiMe_3)_3$ (**12**), which crystallized from hexane as red-brown needles. Addition of dry oxygen to **9**, **10**, and **11** in benzene-d_6 forms ditelluride **7** in quantitative yield as shown by ^{1}H NMR spectroscopy.

The absence of donor ligands in these compounds may present practical advantages over solvated species such as **1** for the preparation of coordinatively unsaturated derivatives by reaction with, for example, a metal halide. We have frequently encountered difficulties in preparing pure samples of homoleptic transition-metal tellurolates due to solvent incorporation from **1**.[28] The only other base-free alkali metal derivatives of which we are aware are the sodium and potassium phenyltellurolates prepared by Klar

---

(42) Hamada, K.; Morishita, H. *Jpn. J. Appl. Phys.* **1976**, *15*, 748.

(43) Hamada, K.; Morishita, H. *Synth. React. Inorg. Met. Org. Chem.* **1977**, *7*, 355.

(44) Drake, J. E.; Hemmings, R. T. *Inorg. Chem.* **1980**, *19*, 1879.

(45) Glidewell, C.; Rankin, D. W. H.; Sheldrick, G. M. *Trans. Faraday Soc.* **1969**, 1409.

(46) Sink, C. W.; Harvey, A. B. *J. Chem. Phys.* **1972**, *57*, 4434.

(47) Bochmann, M.; Coleman, A. P.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 973.

(48) Fazakerley, G. V.; Celotti, M. *J. Magn. Reson.* **1979**, *33*, 219.

(49) Zumbulyadis, N.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *192*, 183.

and co-workers.[16] These relatively insoluble materials were isolated via metal reduction of diphenyl ditelluride in liquid ammonia and were characterized by elemental analysis.

Summary and Conclusions

We have presented the first detailed study of the synthesis, structure, and reactivity of a wide variety of sterically hindered tellurolate derivatives based on the bulky $^{-}TeSi(SiMe_3)_3$ ligand. These materials are thermally stable, hydrocarbon soluble, crystalline compounds that are easy to prepare on large scales and in high yields. They show excellent potential as synthetic reagents for the formation of metal–tellurium bonds. Crystal structures of two of these derivatives show the tellurolate anion to be stable either as a partner in a covalent interaction or as the free anion. Further examples of the synthetic potential of these reagents will be reported in due course.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-90-19675), the Department of Education (fellowship to P.J.B.), and U. C. Berkeley for financial support. We thank Dr. Victor Christou for help with ^{125}Te NMR spectroscopy.

Supplementary Material Available: Details of the structure determinations of **1** and **3**, including tables of temperature factor expressions, positional parameters, and intramolecular distances and angles (11 pages); listing of observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

Organotransition-Metal Metallacarboranes. 25.[1] Redox Chemistry and Electronic Studies of Mono- and Dinuclear Iron(II)/Iron(III) Sandwich Complexes

Martin Stephan,[2a,b] James H. Davis, Jr.,[†,2a] Xiangsheng Meng,[2a] Kevin J. Chase,[2a] Jan Hauss,[2b] Ulrich Zenneck,[‡,2b] Hans Pritzkow,[2b] Walter Siebert,[*,2b] and Russell N. Grimes[*,2a]

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, Germany. *Received January 22, 1992*

Abstract: The mononuclear 7-vertex *closo*-ferracarborane clusters $(C_5Me_5)Fe^{II}H(Et_2C_2B_4H_4)$ (**1**) and $(C_5Me_5)Fe^{III}(Et_2C_2B_4H_4)$ (**2**) and the phenylene-linked diiron species $(Et_2C_2B_4H_4)M(C_5Me_4\text{–}C_6H_4\text{–}C_5Me_4)M'(Et_2C_2B_4H_4)$ (**3**, $M = M' = Fe^{II}H$; **4**, $M = Fe^{II}H$, $M' = Fe^{III}$; and **5**, $M = M' = Fe^{III}$) were prepared and isolated via column and/or plate chromatography on silica or Al_2O_3. Their chemical interconversion was examined, and the air-stable products were characterized from their ^{1}H, ^{13}C, and ^{11}B NMR, infrared, UV–visible, mass spectra, and elemental analysis and an X-ray diffraction study of **3**. The crystallographic data established the location of the Fe–H hydrogen atom in each of the two equivalent ferracarborane clusters; this hydrogen is coordinated both to iron and to the neighboring boron atoms in the carborane ligand and can be described as capping an Fe–B–B triangular face. The paramagnetic species **2**, **4**, and **5** were investigated via ESR spectroscopy in toluene and THF between 4.5 and 298 K. Magnetic susceptibility measurements conducted on **4** and **5** showed one and two unpaired electrons, respectively, with strong spin–orbit couplings. The ^{1}H and ^{13}C NMR spectra of paramagnetic **2** were assigned by recording a series of spectra during quantitative stepwise reduction of the complex in THF-d_8, via a potassium mirror in a sealed NMR tube, to form diamagnetic $\mathbf{2}^{-}$. The latter anion was characterized from its multinuclear NMR spectra. Cyclic voltammetry was conducted on compounds **1**–**5**. Although **2** exhibits reversible reduction, oxidation and/or reduction of **1**, **3**, or **4** leads to hydrogen abstraction and the formation of Fe(III) species, detectable from their reversible signals and ESR spectra. Crystal data for **3**: $M = 689.0$; monoclinic, space group $P2_1/c$; $Z = 2$; $a = 8.698$ (2), $b = 14.949$ (4), $c = 14.931$ (4) Å; $\beta = 106.54$ (2)°; $V = 1861$ Å^3; $R = 0.045$ for 4135 reflections having $I > 2\sigma(I)$.

Introduction

The *nido*-$RR'C_2B_4H_4^{2-}$ ligands (R, R′ = alkyl) have a remarkable and well-documented ability to stabilize organometallic complexes of both transition metals and main-group elements.[3] This property is particularly evident in mixed-ligand sandwiches in which the C_2B_3 open face of the carborane is η^5-coordinated to a transition metal that is also bound to a hydrocarbon ligand. For example, although π-arene complexes of Fe(III) and Ru(III) are unstable and almost unknown, neutral, diamagnetic sandwiches of the type $(arene)M^{II}(Et_2C_2B_4H_4)$ (M = Fe, Ru) are readily oxidized electrochemically to generate stable $(arene)M^{III}(Et_2C_2B_4H_4)^{+}$ cations.[1e,4] Clearly, the properties of these small *nido*-carborane ligands open many opportunities for studying organometallic groups that are otherwise inaccessible. We have exploited this stabilizing power extensively in synthesis and have described the isolation and characterization of novel complex types including linked triple- and tetradecker sandwich oligomers,[5,6] air-stable bimetallic fulvalene complexes,[5] indenylferracarboranes

---

[†] Present address: Department of Chemistry, Brandeis University, Waltham, MA 02254.

[‡] Present address: Friedrich-Alexander Universität Erlangen—Nürnberg, Erlangen, Germany.

(1) (a) Part 24: Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. *Organometallics*, in press. (b) Part 23: Piepgrass, K. W.; Grimes, R. N. *Organometallics*, in press. (c) Part 22: Chase, K. J.; Grimes, R. N. *Inorg. Chem.* **1991**, *30*, 3957. (d) Part 21: Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics* **1991**, *10*, 2631. The present paper continues our joint research effort which has been reported in earlier publications; see: (e) Fessenbecker, A.; Stephan, M.; Grimes, R. N.; Pritzkow, H.; Zenneck, U.; Siebert, W. *J. Am. Chem. Soc.* **1991**, *113*, 3061 and references therein.

(2) (a) University of Virginia. (b) University of Heidelberg.

(3) Recent reviews: (a) Grimes, R. N. *Pure Appl. Chem.* **1991**, *63*, 369 (transition-metal complexes). (b) Grimes, R. N. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991 (transition-metal complexes). (c) Hosmane, N. S.; Maguire, J. A. In *Advances in Boron and the Boranes* [*Mol. Struct. Energ. Vol. 5*]; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; Chapter 14. (main-group-element complexes).

(4) (a) Merkert, J. M.; Geiger, W. E., Jr.; Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1989**, *8*, 1580. (b) Merkert, J. M.; Geiger, W. E., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1991**, *10*, 3545.

(5) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4784.