Å),[23] the difference is hardly significant.

Preliminary studies show that solid-state thermolysis of **1** from 200 to 375 °C under vacuum results in the formation of a mixture of volatile products containing **9**, $Me_3SiTeSi(SiMe_3)_3$,[17] and other uncharacterized $SiMe_3$-containing products (by ^1H NMR spectroscopy), along with a black powder containing zirconium telluride.[28] Further details regarding these reactions, and those in other related complexes, will be presented in a full account.

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Registry No. 1, 141784-70-5; **2**, 141784-71-6; **3**, 141784-64-7; **4**, 141784-65-8; **5**, 141784-66-9; **6**, 141784-67-0; **7**, 141784-68-1; **8**, 141784-69-2; **9**, 141784-63-6; $HTeSi(SiMe_3)_3$, 133100-98-8; $Zr(CH_2Ph)_4$, 24356-01-2; $Hf(\textit{neo}\text{-}C_5H_{11})_4$, 50654-35-8; 2,6-dimethylisocyanobenzene, 2769-71-3.

Supplementary Material Available: Details of structure determinations including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes for **1** and **7** (31 pages); listing of observed and calculated structure factors for **1** and **7** (124 pages). Ordering information is given on any current masthead page.

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[28] Elemental analysis showed the powder to contain low levels of carbon and hydrogen (1.4% and 0.4%, respectively). X-ray powder diffraction indicated the presence of $ZrTe_3$. Further studies are in progress.

Preparation of Stable Magnesium, Calcium, Strontium, and Barium Tellurolates and the X-ray Crystal Structures of $Mg[TeSi(SiMe_3)_3]_2(THF)_2$ and $Ca[TeSi(SiMe_3)_3]_2(THF)_4$

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It is well known that tellurium inserts into reactive magnesium–carbon bonds of aryl Grignards to form solutions containing tellurolate ($^-$TeR) species.[1-5] Although reactivity studies have shown these compounds to be useful reagents in organotellurium chemistry, their apparent instability has prohibited their isolation and characterization; as a result, little is known regarding their structures and properties. Tellurolate derivatives of calcium, strontium, or barium are, to the best of our knowledge, unknown. Recently we reported some remarkably stable alkali metal tellurolate derivatives based on the sterically hindered $^-TeSi(SiMe_3)_3$ ("sitel") ligand, together with preliminary studies of their synthetic potential.[6,7] Here we describe an extension of this chemistry leading to the first isolable, well-characterized examples of group 2 tellurolates.

Methods relying on direct insertion of tellurium into metal–$Si(SiMe_3)_3$ bonds could not be tested as the necessary starting materials are unknown, and metathesis reactions between the lithium tellurolate $(THF)_2LiTeSi(SiMe_3)_3$ and group 2 dihalides led only to intractable mixtures. In contrast, tellurolysis reactions[6] involving metal–nitrogen or metal–carbon bonds afforded an extremely clean and simple route to the metal tellurolates. For example, eq 1 shows the tellurolysis of dibutylmagnesium in hexane, which gave the base-free, homoleptic sitel compound as pale yellow plates in high yield.

$$Mg(C_4H_9)_2 + 2HTeSi(SiMe_3)_3 \rightarrow Mg[TeSi(SiMe_3)_3]_2 + 2C_4H_{10} \quad (1)$$

The structure of this derivative is presently unknown; however, a bis-THF adduct, prepared by recrystallization in the presence of THF, has been characterized by X-ray crystallography (see below). Reactions between the well-defined, hydrocarbon-soluble group 2 silylamides[8] and 2 equiv of $HTeSi(SiMe_3)_3$[6] in hexane gave high yields of the corresponding sitel complexes of calcium, strontium, and barium, which were isolated and crystallized as THF adducts.[9]

$$M[N(SiMe_3)_2]_2(THF)_2 + 2HTeSi(SiMe_3)_3 \rightarrow M[TeSi(SiMe_3)_3]_2(THF)_n + 2HN(SiMe_3)_2 \quad (2)$$

$$(M = Ca, Sr, n = 4; M = Ba, n = 5)$$

At room temperature, the THF complexes slowly lose coordinated solvent, but they are otherwise stable to heat and normal room light and can be kept under nitrogen for prolonged periods of time. The analogous pyridine adducts were readily prepared by recrystallization of the THF complexes from pyridine.

The group 2 tellurolate adducts are highly crystalline, pale yellow, air-sensitive materials with high melting points. Dissolution in hydrocarbon and ethereal solvents affords concentrated solutions that are stable indefinitely in the absence of O_2 and water. As with the group 1 derivatives, the group 2 compounds react cleanly with water and dry oxygen to give the tellurol and ditelluride $Te_2[Si(SiMe_3)_3]_2$, respectively.[6] For the series of pyridine adducts, ^{125}Te NMR spectra show singlets in the range −1405 to −1578 ppm (relative to Me_2Te at 0 ppm). Although these values occur at significantly higher field than alkyl- and aryltellurolate derivatives,[10] they are typical of salts incorporating the sitel ligand (cf. the lithium derivative $[(THF)_2LiTeSi(SiMe_3)_3]_2$ δ −1622).[7a]

In contrast to the metal amide starting materials, which are all four coordinate, the sitel complexes crystallize with varying numbers of donor ligands as determined by ^1H NMR spectroscopy and elemental analyses. In the case of pyridine, for example, Mg^{2+} (effective ionic radius 0.71 Å)[11] forms a four-coordinate species, whereas the larger Ba^{2+} ion (1.52 Å) accommodates a structure with five donor ligands.

Treatment of the magnesium derivative with 12-crown-4 results in displacement of both the THF and the sitel ligands to form the ionic complex shown in eq 3:

$$Mg[TeSi(SiMe_3)_3]_2(THF)_2 + 2(12\text{-}C\text{-}4) \rightarrow [Mg(12\text{-}C\text{-}4)_2][TeSi(SiMe_3)_3]_2 + 2THF \quad (3)$$

Crystals of the 2:1 salt ($\Lambda_M = 200\ cm^2\ \Omega^{-1}\ mol^{-1}$, 0.1 M MeCN)[12] were isolated as pale yellow plates from THF. At 20 °C, the

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[9] Selected characterization data: $Mg(sitel)_2$ ^1H NMR (400 MHz, C_6D_6) δ 0.44 (s); $Mg(sitel)_2(THF)_2$ ^1H NMR (400 MHz, C_6D_6) δ 3.79 (m, 8 H), 1.23 (m, 8 H), 0.50 (s, 54 H); $Mg(sitel)_2(pyr)_2$ ^1H NMR (300 MHz, C_6D_6) δ 8.86 (d, 4 H), 6.79 (t, 2 H), 6.52 (t, 4 H), 0.45 (s, 54 H), $^{125}Te\{^1H\}$ NMR (157.7 MHz, C_6D_6) δ −1578; $Mg[12\text{-}crown\text{-}4]_2[TeSi(SiMe_3)_3]_2$ ^1H NMR (400 MHz, CD_3CN) δ 3.92 (m, 32 H), 0.13 (s, 54 H); $Ca(sitel)_2(THF)_4$ ^1H NMR (400 MHz, C_6D_6) δ 3.79 (m, 16 H), 1.47 (m, 16 H), 0.48 (s, 54 H); $C(sitel)_2(pyr)_4$ ^1H NMR (400 MHz, C_6D_6) δ 9.51 (d, 8 H), 6.82 (t, 4 H), 6.67 (t, 8 H), 0.42 (s, 54 H), $^{125}Te\{^1H\}$ NMR (157.7 MHz, C_6D_6) δ −1458; $Sr(sitel)_2(THF)_4$ ^1H NMR (400 MHz, C_6D_6) δ 3.83 (m, 16 H), 1.54 (m, 8 H), 0.48 (s, 54 H); $Sr(sitel)_2(pyr)_4$ ^1H NMR (300 MHz, C_6D_6) δ 9.35 (d, 8 H), 6.80 (t, 4 H), 6.64 (t, 8 H), 0.48 (s, 54 H), $^{125}Te\{^1H\}$ NMR (157.7 MHz, C_6D_6) δ −1482 (s); $Ba(sitel)_2(THF)_4$ ^1H NMR (400 MHz, C_6D_6) δ 3.73 (m, 16 H), 1.48 (m, 16 H), 0.52 (s, 54 H); $Ba(sitel)_2(pyr)_5$ ^1H NMR (400 MHz, C_6D_6) δ 9.14 (d, 10 H), 6.82 (t, 5 H), 6.66 (t, 10 H), 0.52 (s, 54 H), $^{125}Te\{^1H\}$ NMR (157.7 MHz, C_6D_6) δ −1405 (s). Satisfactory elemental analyses were determined for all compounds except the THF adducts of Mg, Sr, and Ba, which lose coordinated solvent on drying.

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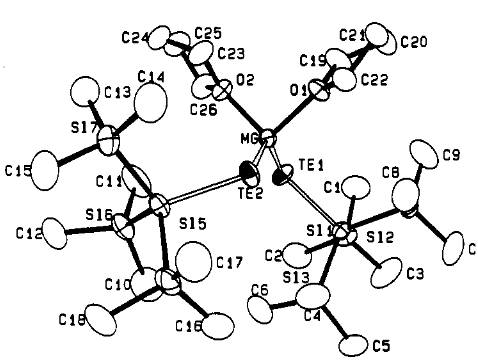
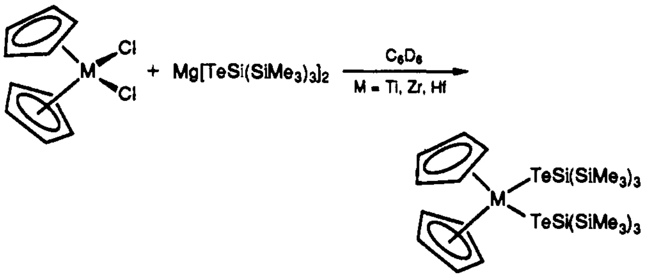


Figure 1. ORTEP view of $Mg[TeSi(SiMe_3)_3]_2(THF)_2$ with thermal ellipsoids at 50% probability.

400-MHz ^1H NMR spectrum shows a singlet for the sitels and a complex AA′BB′ pattern at 3.92 ppm for the ethylene groups of the 12-crown-4 ligands.

All of the group 2 tellurolate derivatives act as clean sources of the sitel ligand in metathesis reactions with metal halides. An illustrative example that leads to the formation of early transition metal-tellurolate compounds[6] cleanly and in high yield is shown below; further details will be described in a full account.



The X-ray structure of $Mg[TeSi(SiMe_3)_3]_2(THF)_2$ shows the magnesium atom surrounded in a distorted tetrahedral fashion by two THF oxygens and two telluriums from the sitel ligands (Figure 1).[13] The Mg-Te bond lengths are virtually equal (2.720, 2.714 (1) Å) and are as predicted on the basis of ionic radii (Mg^{2+}, 0.71 Å; Te^{2-}, 2.07 Å[11]). The bulk of the sitel ligands is no doubt responsible for the large Te-Mg-Te angle of 135.48 (4)° and the rather acute O-Mg-O angle of 94.8 (1)°. The Te-Mg-O angles are not equal, so that for each of the two tellurium atoms there is one large (111.77, 114.37 (7)°) and one small angle (96.37, 94.79 (7)°). This difference may be attributed to steric repulsion from the tellurium sp^3 lone pairs, since the smaller angle appears when the THF oxygen is trans to the Te-Si vector in the sitel ligand, but packing effects cannot be excluded.

$Ca[TeSi(SiMe_3)_3]_2(THF)_4$ crystallizes with four THFs and features a highly distorted octahedral coordination sphere about calcium.[13] Figure 2 shows an ORTEP view of the molecule illustrating the disordered THF. The molecule has strict inversion symmetry with the calcium atom located at the origin of the cell, resulting in angles of 180° for all three trans interactions. Inspection of the angles between cis coordination sites highlights the extent to which the molecule is distorted. These angles, which range from 77.33 (5)° to 92.73 (9)°, appear to result from interligand repulsions. The predicted Ca-Te bond length of 3.21 Å[11] is close to the experimentally determined value of 3.197 (1) Å.

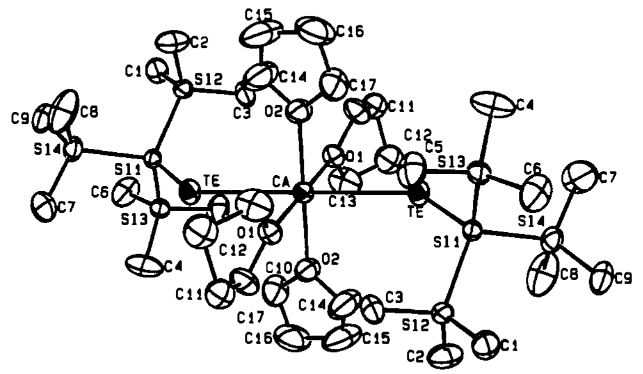


Figure 2. ORTEP view of $Ca[TeSi(SiMe_3)_3]_2(THF)_4$ with thermal ellipsoids at 50% probability.

In summary, we have prepared and fully characterized the first examples of isolable tellurolate derivatives of group 2. Preliminary results indicate that they function as useful tellurolating synthons; further structural and reactivity studies are in progress.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9019675) for support.

Supplementary Material Available: Details of the structure determination including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, and intramolecular distances and angles (17 pages); listings of observed and calculated structure factors (75 pages). Ordering information is given on any current masthead page.

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[13] Crystal data for $Te_2Si_8MgO_2C_{26}H_{70}$: space group $P\bar{1}$ with $a = 12.033$ (2), $b = 12.650$ (2), $c = 16.757$ (3) Å, $\alpha = 98.88$ (2), $\beta = 104.853$ (13), $\gamma = 95.166$ (15)°, $V = 2413$ Å^3, $d_{calcd} = 1.26$ g cm^{-3}, and $Z = 2$. Data were collected at −85 °C with Mo Kα ($\lambda = 0.7107$ Å) radiation. A total of 6281 unique data were collected. The structure was solved by Patterson methods and refined by least-squares and Fourier techniques using 353 variables against 5519 data, for which $F^2 > 3\sigma(F^2)$, to give $R = 2.54\%$, $R_w = 3.29\%$, and GOF = 1.60. Crystal data for $Te_2CaSi_8O_4C_{34}H_{86}$: space group $P\bar{1}$ with $a = 9.965$ (2), $b = 13.822$ (3), $c = 10.434$ (2) Å, $\alpha = 87.157$ (15), $\beta = 86.013$ (14), $\gamma = 89.968$ (18)°, $V = 1432$ Å^3, $d_{calcd} = 1.25$ g cm^{-3}, and $Z = 1$. Data were collected at −88 °C with Mo Kα ($\lambda = 0.7107$ Å) radiation. A total of 6549 unique data were collected. The structure was solved by Patterson methods and refined by least-squares and Fourier techniques using 222 variables against 5377 data, for which $F^2 > 3\sigma(F^2)$, to give $R = 3.32\%$, $R_w = 4.39\%$, and GOF = 1.92. The crystal structures were determined by Dr. F. J. Hollander at the University of California—Berkeley X-ray facility (CHEXRAY).

Microscopic Basis of Wetting: An in Situ Study of the Interaction between Liquids and an Organic Monolayer[†]

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Many macroscopic properties of materials, such as wettability and adhesive strength, are governed by microscopic interfacial interactions between two condensed phases. Direct investigation of such interfaces is difficult, as they are not readily accessible to conventional surface probes. Here we report the use of an in situ technique, sum-frequency vibrational spectroscopy, to study how three liquids—hexane, acetonitrile, and water—interact with a model organic surface: a self-assembled monolayer of 16-methoxyhexadecanethiol ($CH_3O(CH_2)_{16}SH$, MeOHT)[1] adsorbed on gold.[2]

Sum-frequency spectroscopy (SFS)[3] is a nonlinear optical technique in which a fixed-frequency visible laser and a tunable infrared laser are pulsed simultaneously onto an interface and light emitted at the sum frequency is detected.[4] Analysis of SF spectra

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[1] MeOHT was synthesized according to published procedures (ref 2) and was pure by ^1H NMR analysis, mp 30-31 °C (lit. mp 29.5-30.5 °C).

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