spacing between imidazole nitrogens, freezing of the rotations of these bonds may be responsible for reducing the selectivities.

Acknowledgment. This research is supported by the Whitaker Foundation, the Office of Naval Research (N00014-92-J-1178), and the National Science Foundation (BCS-9108502). F.H.A. gratefully acknowledges a National Science Foundation PYI award and a fellowship from the David and Lucile Packard Foundation.

Preparation of Lanthanide Tellurolates and Evidence for the Formation of Cluster Intermediates in Their Thermal Decomposition to Bulk Metal Tellurides

Douglas R. Cary and John Arnold*

Department of Chemistry
University of California
Berkeley, California 94720

Received November 11, 1992

The transformation of molecular compounds into solid-state materials is an increasingly important process.[1] Surprisingly little is known of the mechanisms involved, as these are generally gas- or solid-phase reactions that take place at elevated temperatures. We recently described a homogeneous solution model for the decomposition of metal chalcogenolates to chalcogenides represented by eq 1. Thus, treatment of the zirconium or hafnium

$$[\mathrm{M(ER)_2}]_n \rightarrow [\mathrm{ME}]_n + n\mathrm{ER_2} \qquad (\mathrm{E = S, Se, Te}) \quad (1)$$

tellurolates $\mathrm{M(TeR)_4}$ [$\mathrm{R = Si(SiMe_3)_3}$] with excess of the donor ligand dmpe [dmpe = 1,2-bis(dimethylphosphino)ethane] produced the unusual terminal telluride species $\mathrm{M({=}Te)(TeR)_2(dmpe)_2}$ and $\mathrm{TeR_2}$.[2]

Working under the assumption that the combination of a hard, electropositive metal and a soft, polarizable tellurolate ligand will make for reactive M–Te bonds, we have been studying the synthesis and reactivity of lanthanide tellurolates. Although compounds of this type are extremely rare,[3,4] interest in them heightened recently with the realization that they may be of use as precursors to solid-state lanthanide(II) chalcogenides.[4,5]

Here we describe the synthesis of reactive homoleptic lanthanide(III) tellurolates which, in the absence of stabilizing donor ligands, decompose to form novel molecular telluride–tellurolate clusters.[6] In addition, we show that these isolable intermediates are converted to bulk lanthanide tellurides on pyrolysis.

Tellurolysis[2,7] of the trivalent metal amide derivatives $\mathrm{M[N(SiMe_3)_2]_3}$ (M = La, Ce)[8] with 3 equiv of $\mathrm{HTeSi(SiMe_3)_3}$ in hexane resulted in a slow color change from orange to brown (Scheme I).[9] Monitoring the lanthanum reaction by ^{1}H NMR spectroscopy in benzene-d_6 at 20 °C revealed that after ca. 2 h both starting materials had disappeared and that a single new product **1** (^{1}H NMR, δ 0.55 ppm; ^{125}Te NMR, δ 1018 ppm) had formed together with 3 equiv of $\mathrm{NH(SiMe_3)_2}$.[10] The homoleptic complex is thermally unstable (see below); however, ^{1}H NMR spectroscopy showed that addition of excess dmpe resulted in immediate quantitative conversion to the stable adduct **3**; this material was subsequently isolated as yellow crystals from preparative scale reactions in hexane,[11] and the paramagnetic cerium derivative (**4**) ($\mu_{\mathrm{eff}} = 2.28\ \mu_{\mathrm{B}}$) was obtained similarly.[10] Isolated yields of analytically pure **3** and **4** were >75%, and no byproducts were detected.

At 23 °C, the ^{1}H NMR spectrum of the diamagnetic lanthanum derivative **3** shows a broad singlet for the three equivalent tellurolate ligands and broad peaks due to the dmpe methyl and methylene groups.[10] On lowering of the temperature to −84 °C, the tellurolate ligands gave rise to two peaks integrating to 54 and 27 protons and the dmpe ligands showed two broad peaks that integrated to 12 protons each. (The methylene resonances were, presumably, too broad to be detected.) Over the same temperature range, ^{13}C NMR data showed three peaks at 23 °C (due to dmpe methylenes, methyls, and the tellurolate ligands) whereas at −84 °C a total of six resonances, resulting from the inequivalent ends of the dmpe ligands and two types of tellurolate ligand, were evident. The ^{31}P NMR spectra were also temperature dependent, showing a broad singlet at 23 °C that split into two narrower peaks of equal intensity at −84 °C.[10] Finally, ^{125}Te NMR spectra at −70 °C showed two broad singlets of relative intensity 2:1; no ^{125}Te NMR signal was observed at room temperature. These NMR data are indicative of stereochemical nonrigidity on the NMR time scale, even down to rather low temperatures. NMR data (^{1}H, ^{13}C, and ^{31}P) for the cerium derivative **4** show similar temperature dependent behavior but with resonances that are paramagnetically shifted.

---

[1] For examples, see the following and references therein: Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M.; Kwon, Y.-U. *J. Am. Chem. Soc.* **1992**, *114*, 3155. Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 4940. Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403. O'Brien, P. *Chemtronics* **1991**, *5*, 61. Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643. Gysling, H. J.; Wernberg, A. A.; Blanton, T. N. *Chem. Mater.* **1992**, *4*, 900. Douglas, T.; Theopold, K. H. *Inorg. Chem.* **1991**, *30*, 594. Matchett, M. A.; Viano, A. M.; Adolphi, N.; Stoddard, R. D.; Buhro, W. E.; Conradi, M. S.; Gibbons, P. C. *Chem. Mater.* **1992**, *4*, 508. Huang, S.-P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 5477.

[2] Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240.

[3] Berg, D. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1858.

[4] Strzelecki, A. R.; Timinski, P. A.; Helsel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159.

[5] These materials are of wide interest as a result of their unusual magnetic and electronic properties. See: *Handbook of the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L. R., Eds.; North-Holland: Amsterdam, 1979 and references therein.

[6] We could find only one other example of a crystallographically characterized telluride–tellurolate cluster: $[\mathrm{Fe_4Te_4(TePh)_4}]^{3-}$. See: Simon, W.; Wilk, A.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1009.

[7] Bonasia, P. J.; Gindelberger, D. E.; Dabbousi, B. O.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 5209. Gindelberger, D. E.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6242. Bonasia, P. J.; Arnold, J. *Inorg. Chem.* **1992**, *31*, 2508.

[8] Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

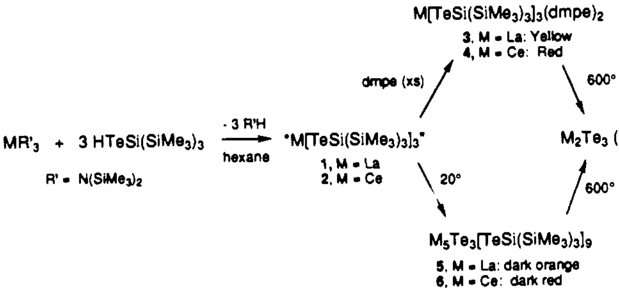
[9] All reactions were conducted under an atmosphere of purified argon using dry, oxygen-free solvents.

[10] Selected charactization data. **1**: ^{1}H NMR ($\mathrm{C_7D_8}$, 300 MHz, 21 °C) δ 0.55 (s); ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, 75.5 MHz, 21 °C) δ 2.77; ^{125}Te{^{1}H} NMR ($\mathrm{C_7D_8}$, 94.6 MHz, 21 °C) δ 1018 (s, $\Delta\nu_{1/2}$ = 57 Hz). **3**: ^{1}H NMR ($\mathrm{C_7D_8}$, 400 MHz, 23 °C) δ 1.46 (s, 8 H), 1.44 (s, 24 H), 0.45 (s, 81 H); ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, 75.5 MHz, 23 °C) δ 32.0, 16.1, 1.80; ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$, 162 MHz, 23 °C) δ −29.4 (s, $\Delta\nu_{1/2}$ = 312 Hz); ^{1}H NMR ($\mathrm{C_7D_8}$, 400 MHz, −84 °C) δ 1.64 (s, 12 H, $\Delta\nu_{1/2}$ = 10 Hz), 1.13 (s, 12 H, $\Delta\nu_{1/2}$ = 10 Hz), 0.68 (s, 27 H, $\Delta\nu_{1/2}$ = 5.7 Hz), 0.52 (s, 54 H, $\Delta\nu_{1/2}$ = 5.2 Hz); ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, 75.5 MHz, −84 °C) δ 32.4, 23.4, 16.3 ($\Delta\nu_{1/2}$ = 14 Hz), 14.8, 1.81, 1.44; ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$, 162 MHz, −84 °C) δ −21.9 (s, 1 P, $\Delta\nu_{1/2}$ = 57 Hz), −34.0 (s, 1 P, $\Delta\nu_{1/2}$ = 49 Hz); ^{125}Te{^{1}H} NMR ($\mathrm{C_7D_8}$, 94.6 MHz, −70°C) δ −894 (s, 1 Te, $\Delta\nu_{1/2}$ = 290 Hz), −1074 (s, 1 Te, $\Delta\nu_{1/2}$ = 155 Hz). Anal. Calcd for $\mathrm{C_{39}H_{113}P_4Si_{12}Te_3La}$: C, 29.9; H, 7.28. Found: C, 29.9; H, 7.35. **4**: ^{1}H NMR ($\mathrm{C_7D_8}$, 400 MHz, 23 °C) δ 5.87 (s, 8 H, $\Delta\nu_{1/2}$ = 30 Hz), 4.07 (s, 24 H, $\Delta\nu_{1/2}$ = 14 Hz), −0.28 (s, 81 H, $\Delta\nu_{1/2}$ = 32 Hz); ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, 75.5 MHz, 23 °C) δ 33.4 ($\Delta\nu_{1/2}$ = 8.5 Hz), 21.4 ($\Delta\nu_{1/2}$ = 12 Hz), 1.44 ($\Delta\nu_{1/2}$ = 3.9 Hz); ^{1}H NMR ($\mathrm{C_7D_8}$, 400 MHz, −78 °C) δ 11.45 (s, 4 H, $\Delta\nu_{1/2}$ = 55 Hz), 8.51 (s, 4 H, $\Delta\nu_{1/2}$ = 59 Hz), 7.65 (s, 12 H, $\Delta\nu_{1/2}$ = 44 Hz), 5.38 (s, 12 H, $\Delta\nu_{1/2}$ = 35 Hz), 1.16 (s, 27 H, $\Delta\nu_{1/2}$ = 9.8 Hz), −2.12 (s, 54 H, $\Delta\nu_{1/2}$ = 8.1 Hz); ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, 75.5 MHz, −78 °C) δ 28.2 ($\Delta\nu_{1/2}$ = 31 Hz), 22.0, 3.08 ($\Delta\nu_{1/2}$ = 8.5), −1.17 ($\Delta\nu_{1/2}$ = 4.8 Hz); ^{31}P{^{1}H} NMR ($\mathrm{C_7D_8}$, 122 MHz, −78 °C) δ 765.5 ($\Delta\nu_{1/2}$ = 262 Hz), 652.2 ($\Delta\nu_{1/2}$ = 186 Hz). Anal. Calcd for $\mathrm{C_{39}H_{113}P_4Si_{12}Te_3Ce}$: C, 29.9; H, 7.27. Found: C, 29.9; H, 7.15. IR data for **5**: 1244 (s), 858 (s), 832 (s), 742 (w), 688 (m), 623 (m) cm^{-1}. IR data for **6**: 1306 (w), 1256 (w), 858 (m), 836 (s), 746 (w), 735 (w), 722 (w), 689 (m), 623 (m) cm^{-1}.

[11] See supplementary material for further details.

0002-7863/93/1515-2520$04.00/0

Scheme I



Evidence for the solid-state structures of these adducts was obtained from a crystallographic study of **3** (Figure 1).[12] The lanthanum is coordinated in a pseudopentagonal bipyramidal fashion, with the dmpe ligands and one tellurolate in the equatorial plane (La–Te 3.141(1) Å) and the other two tellurolates axial (La–Te 3.170(1), 3.168(1) Å). Steric interaction of the equatorial tellurolate with dmpe ligands is apparent from consideration of the two different sets of La–P bond lengths, which range from 3.143(2) and 3.127(2) Å for P1 and P4 to 3.208(2) and 3.216(2) Å for P2 and P3. The Te1–La–Te2 angle (145.69(2)°) and the wide variation in La–Te–Si angles (ca. 135–154°) also suggest that steric effects are important in defining the structure.

In the absence of donor ligands, both **1** and **2** decompose in benzene-d_6 to give dark-colored solutions that contain a complex mixture of products as determined by ^{1}H NMR spectroscopy. The formation of substantial amounts of the telluride $Te[Si(SiMe_3)_3]_2$ suggests the participation of elimination reactions similar to those previously observed (cf. eq 1).[2] Preparative scale reactions in hexane were more informative, however, as moderate yields of two new products **5** and **6** were obtained by slow crystallization directly from the reaction solution (Scheme I). In both cases the crude products were contaminated with unknown impurities. Evidently these reactions are not straightforward, and isolation of **5** and **6** is only made possible by their removal from solution by precipitation or crystallization. Further purification was impossible as both derivatives are unstable in the usual range of organic solvents. Fortunately, however, a batch of well-formed needles of the cerium complex **6** was obtained and its X-ray structure was determined.[11,12] An ORTEP view of the molecule with $SiMe_3$ groups omitted is shown in Figure 2. The structure may be viewed as comprising a six-membered $-[TeCe]_3-$ ring capped above and below by two triply-bridging $Ce(TeR)_3$ moieties. As expected, the Ce–Te bonds to the terminal unbridged ligands are the shortest at 3.026(3) Å, compared to values for the bridging tellurolate of 3.183(2) and 3.235(1) Å. The Ce–Te bonds in the Ce_3Te_3 ring alternate from 3.124(3) to 3.278(3) Å and are similar in length to those seen from Ce to the bridging tellurolates. The capping ceriums are also well within bonding distance (3.258 Å) of the tellurides in the ring.

Pyrolysis of **3**–**6** at 600 °C under vacuum resulted in elimination of the telluride $Te[Si(SiMe_3)_3]_2$ and formation of the corresponding metal tellurides as gray powders. Identical results were obtained when the residues resulting from evaporation of solutions of **1** or **2** were pyrolyzed. X-ray powder diffraction confirmed the formation of crystalline M_2Te_3 phases.[13]

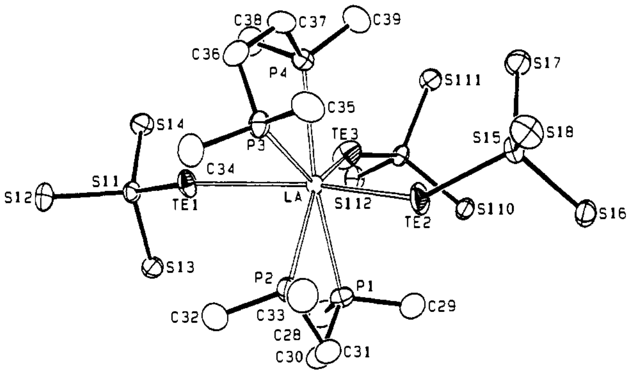


Figure 1. ORTEP drawing of $La[TeSi(SiMe_3)_3]_3(dmpe)_2$ (**3**) with $-SiMe_3$ groups omitted for clarity.

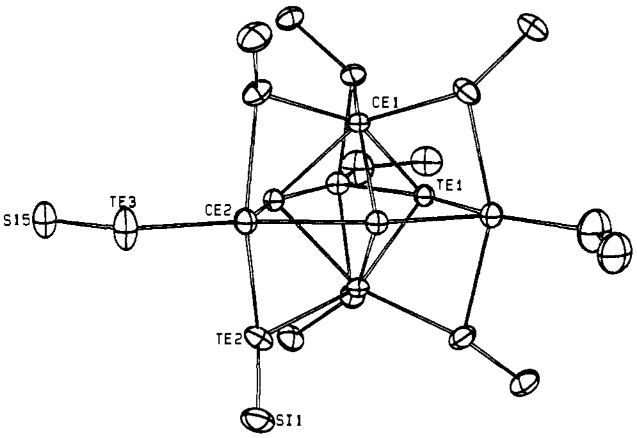


Figure 2. ORTEP drawing of $Ce_5Te_3[TeSi(SiMe_3)_3]_9$ (**6**) with $-SiMe_3$ groups omitted for clarity.

In conclusion, we have isolated and characterized unusual examples of metal telluride cluster species formed as a result of thermal decomposition of metal tellurolates and have shown that further pyrolysis leads to formation of bulk metal tellurides. This is the first time that such a cluster intermediate has been observed in a tellurolate to telluride transformation. Attempts to better understand the reaction mechanism(s) involved, to determine the solution behavior of the cluster species, and to characterize other products formed in these reactions are continuing.[14]

Acknowledgment. We thank the National Science Foundation (CHE-90-19675) for financial support, the Department of Education for a fellowship (to D.R.C.), and Dr. Allen Seligsen for XRD measurements.

Supplementary Material Available: Experimental procedures, characterization, XRD data, and 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 (13 pages); listing of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

---

(12) Crystal data for **3** ($LaTe_3P_4Si_{12}C_{39}H_{113}$): space group $C2/c$ with $a = 51.207(11)$ Å, $b = 15.725(3)$ Å, $c = 18.903(3)$ Å, $\alpha = 90°$, $\beta = 92.698(15)°$, $\gamma = 90°$, $V = 15\,204$ Å^3, $d_{calcd} = 1.37$ g cm^{-3}, and $Z = 8$. Data collected at −110 °C with Mo Kα ($\lambda = 0.7107$ Å) and $2\theta = 12.2°$; 9872 unique data were collected. The structure was solved by direct methods (SHELXS) and refined by least squares and Fourier techniques. Refinement of 6504 data for which $F^2 > 3\sigma(F^2)$ gave $R = 3.74\%$, $R_w = 3.73\%$, and GOF = 1.16. Crystal data for **6** ($Ce_5Te_{12}Si_{36}C_{81}H_{243}$): space group $P6_3/m$ with $a = 20.456(5)$ Å, $b = 20.456(5)$ Å, $c = 28.063(9)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 10\,169$ Å^3, $d_{calcd} = 1.46$ g cm^{-3}, and $Z = 2$. Data collected at −103 °C with Mo Kα ($\lambda = 0.7107$ Å) and $2\theta = 12.2°$; 4539 unique data were collected. The structure was solved by direct methods and refined by least squares and Fourier techniques. Despite some disorder in the $Si(SiMe_3)_3$ groups, the remaining atoms were all well-behaved. Refinement of 2607 data for which $F^2 > 3\sigma(F^2)$ gave $R = 6.1\%$, $R_w = 7.7\%$, and GOF = 2.22. Both structure determinations were carried out by Dr. F. J. Hollander of the CHEXRAY facility, U. C. Berkeley.

(13) We also note that combustion analysis invariably showed that low amounts of carbon, but no hydrogen, were retained in all these samples; see supplementary material for further information and XRD data.

(14) Purification and characterization of **5** has proven difficult; its formulation rests on the following: (i) the method of formation and solubility properties are similar to those for **6**, (ii) the infrared spectra of **5** and **6** are almost superimposable, and (iii) the soluble byproduct composition (primarily disilyl telluride with traces of ditelluride) is similar (by ^{1}H and ^{13}C NMR spectroscopy).