Molecular Precursors to Lanthanide(II)-Based Semiconductors: Synthetic Pathways toward the Preparation of Lanthanide Monochalcogenide Precursors

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We describe the preparation of homoleptic complexes of divalent europium, samarium, ytterbium, and lead and tetravalent tin with selenolates and tellurolates incorporating bulky aryl substituents, and the characterization of these complexes by ^{1}H, ^{13}C, ^{77}Se, ^{207}Pb, ^{125}Te, and ^{151}Yb NMR spectroscopy and magnetic measurements. All derivatives $Ln(QR)_2(solv)_x$ (Ln = Eu, Sm, Yb; Q = Se, Te; R = mesityl, supermesityl) can be prepared by transmetalation of $LnX_2(THF)_3$ (X = Br, I) with the potassium salt of the arylselenolate or -tellurolate anions. NMR studies suggest that these complexes exist as monomers in solution down to −60 °C. Ytterbium selenolates can also be prepared by the reaction of the divalent ytterbium amide $Yb[N(TMS)_2]_2DME_2$ with organoselenols, but this route leads to some oxidation of ytterbium to ytterbium(III) and is therefore less satisfactory than the transmetalation route. $Pb(SeMes)_2$ (Mes = 2,4,6-trimethylphenyl) can be prepared by reaction of lead(II) acetylacetonate with mesitylselenol, and $Sn(TeMes)_4$ by transmetalation of SnX_2 (X = Cl, Br) with the potassium salt of mesityltellurolate; in these syntheses, no reduction of tin or lead to the zerovalent metals is seen, unlike other attempted synthetic routes to these complexes.

Introduction

The synthesis of molecular precursors to semiconducting materials has attracted considerable attention since these materials are technologically important and at times difficult to synthesize by conventional methods.[1−4] The preparation of low-temperature precursors to II−VI semiconductors has been particularly explored since this family of materials are important as optical materials. Among these are a class known as the diluted magnetic semiconductors, which are ternary alloys of conventional II−VI or IV−VI materials, such as HgTe and PbSe, substituted with paramagnetic centers such as Mn^{2+} or Fe^{2+}. These materials have a wide range of potential magnetooptic applications.[5] The rare earth monochalcogenides LnQ (Ln = Yb, Eu, Sm; Q = S, Se, Te) are of interest in this area due to the great variety of dilute magnetic semiconductors they could be used to form, as well as for their range of magnetic and luminescent properties.[6] Conventional syntheses of these materials, particularly those containing the heavier chalco-

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(1) (a) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200. (b) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, 2, 403. (c) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228. (d) Brennan, J.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1990**, *112*, 9233. (e) Brennan, J. G.; Siegrist, T.; Stuczynski, S. M., Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240. (f) Sprinkle, C. R.; Steigerwald, M. L. *Organometallics* **1988**, *7*, 245. (g) Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52. (h) Stuczynski, S. M.; Brennan, J. G.; Steigerwald, M. L. *Inorg. Chem.* **1989**, *28*, 4431. (i) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141. (j) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 193. (k) Stuczynski, S. M.; Kwon, Y.-U.; Steigerwald, M. L. *J. Organomet. Chem.* **1993**, *449*, 167. (l) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 4940. (m) Bawendi, M. G.; Kortan, A. R.; Steigerwald, M. L. *J. Chem. Phys.* **1989**, *91*, 7282. (n) Berardini, M.; Emge, T.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, *20*, 1537. (o) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501.

(2) (a) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638. (b) Bochmann, M.; Coleman, A. P.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 973. (c) Bochmann, M.; Bwembya, G.; Grinter, R. *Inorg. Chem.* **1993**, *32*, 532. (d) Bochmann, M.; Webb, K. J. *J. Chem. Soc. Dalton Trans.* **1991**, 2325. (e) Bochmann, M.; Coleman, A. P.; Powell, A. K. *Polyhedron* **1992**, *11*, 507.

(3) (a) Bonasia, P. J., Arnold J. *J. Chem. Soc., Chem. Commun.* **1990**, 1299. (b) Dabbousi, B. O.; Bonasia, P. J.; Arnold, J. *J. Am. Chem. Soc.* **1991**, *113*, 3186. (c) Bonasia, P.; Arnold, J. *Inorg. Chem.* **1992**, *31*, 2508. (d) Cary, D. R.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520. Cary, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791. (e) Bonasia, P. J.; Arnold, J. *J. Organomet. Chem.* **1993**, *449*, 147. (f) Arnold, J.; Walker, J. M.; Yu, K. M.; Bonasia, P. J.; Seligson, A. L.; Bourret, E. D. *J. Cryst. Growth* **1992**, *124*, 647. (g) Cary, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791.

(4) (a) Jeffries, P. M.; Girolami, G. S. *Chem. Mater.* **1989**, *1*, 8. (b) Cowley, A. H.; Harris, P. R.; Jones, R. A.; Nunn, C. M. *Organometallics* **1991**, *10*, 652. (c) Atwood, D.A.; Cowley, A. H.; Jones, R. A. *J. Organomet. Chem.* **1993**, *449*, C1. (d) Williams, J.O. *Angew. Chem., Int. Ed. Eng. Adv. Mater.* **1989**, *28*, 1110. (e) Healy, M. D.; Laibinis, P. E.; Stupik, P. D.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1989**, 359. (f) Okamoto, Y; Takefumi, Y. *J. Organomet. Chem.* **1971**, *29*, 99. (g) Dance, N.S.; Jones, C. H. W. *J. Organomet. Chem.* **1978**, *152*, 175. (h) Kern, R. J. *J. Am. Chem. Soc.* **1953**, *75*, 1865. (i) Peach, M. E. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1046. (j) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133. (k) Atwood, D. A.; Cowley, A. H.; Jones, R. A. *Organometallics* **1993**, *12*, 236. (l) Atwood, D. A.; Contreras, L.; Cowley, A. H. *Organometallics* **1993**, *12*, 17. (m) Jensen, J. A.; Gozum, J. E.; Pollina, D.M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *100*, 1643. (n) Cowley, A. H.; Harris, P. R.; Jones, R. A. *Organometallics* **1991**, *10*, 652. (o) Kaloyeros, A. E.; Williams, W. S.; Allocca, C. M.; Pollina, D. M.; Girolami, G. S. *Adv. Ceram. Mater.* **1987**, 2, 257. (p) Atwood, D. A.; Cowley, A. H.; Harris, P. R. *Organometallics* **1993**, *12*, 24. (q) Miller, J. E.; Kidd, K. B.; Cowley, A. H. *Chem. Mater.* **1990**, 2, 589. (r) Cowley, A. H.; Jones, R. A.; Nunn, M. *Chem. Mater.* **1990**, 2, 221. (s) Atwood, D. A.; Cowley, A. H.; Jones, R. A. *J. Organomet. Chem.* **1993**, *449*, C1. (t) Atwood, D. A.; Cowley, A. H.; Harris, P. R. *J. Organomet. Chem.* **1993**, *449*, 61. (u) Cowley, A. H.; Jones, R. A.; Harris, P. R. *Angew. Chem.* **1991**, *30*, 1143. (v) Cowley, A. H., Jones, R. A.; Mardones, M. A. *Angew. Chem.* **1990**, *29*, 1409. (w) MacInnes, A. M.; Power, M. B.; Barron, A. R. *Chem. Mater.* **1992**, *4*, 11. (x) Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315. (y) Landry, C. C.; Barron, A. R. *Science* **1993**, *260*, 1653. (z) Power, M. B.; Barron, A. R. *Angew. Chem.* **1991**, *30*, 135.

(5) (a) Glass, A. M. *Science* **1987**, *235*, 1003. (b) *Diluted Magnetic (Semimagnetic) Semiconductors*; Aggarwal, R. L., Furdyna, J. K., von Molner, S., Eds.; Materials Research Society Symposia Proceedings 89; Materials Research Society: Pittsburgh, PA, 1987. (c) Oh, E.; Ramdas, A. K.; Furdyna, J. K. *J. Lumin.* **1992**, *52*, 183.

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genides, generally require high temperatures and are hindered by impurities incorporated due to the high oxophilicity of the rare earth centers.[7] The molecular precursor approach to synthesis of these materials offers some advantages over other routes. The synthesis of precursor complexes to rare earth monochalcogenides, with the elements combined on a molecular level in the correct stoichiometry, might afford the ability to process these materials at much lower temperatures. In addition, the precursor method would produce soluble lanthanide complexes which can be purified by standard organometallic techniques before pyrolytic cleavage. However, reported complexes of the lanthanide metals with heavier chalcogenide ligands (Se, Te) are very few. Some examples exist of stable compounds of trivalent lanthanide ions coordinated by selenium- and tellurium-containing ligands,[3d,8] but divalent lanthanide complexes containing selenolate or tellurolate ligands are far less common.[1n,o,3g] In a recent communication we described the synthesis of the first examples of this new class of compounds, lower chalcogenide complexes of the divalent lanthanide metals, and their conversion to rare earth monochalcogenides.[9] We now describe in detail the syntheses of these and related organometallic precursors to metal chalcogenide phases. The conversion of these precursors to new binary and ternary chalcogenides will be described elsewhere.[10]

Experimental Section

Materials. Alkyl and aryllithium reagents and hydrides were used as obtained from Aldrich as solutions (1−2.5M) in hydrocarbon or ethereal solvents. Sodium dispersion in mineral oil (Aldrich) was washed with pentane under argon prior to use. Elemental chalcogens were obtained from Aldrich as fine powders (60−100 mesh). Magnesium powder, 50 mesh (Aldrich), was activated by the addition of a catalytic amount of anthracene and ethyl bromide to form a catalytic Mg−anthracene system.[11] Metal powders (Yb and Sm, Rhone-Poulenc) were provided packaged under argon; europium chips (Rhone-Poulenc) were packaged in mineral oil and isolated in the drybox by washing with pentane. 2,6-Di-*tert*-butyl-4-methylphenol (Aldrich) was dried under vacuum for several days prior to use. Bromomesitylene, chlorotrimethylsilane, tris(trimethylsilyl)methane, and dibromoethane (Aldrich) were stored over activated molecular sieves in the drybox. $Pb(acac)_2$ (Strem) was dried in vacuo before use. All other reagents were used as received from Aldrich or Strem. THF, toluene, DME, and pentane were dried and freshly distilled from sodium benzophenone ketyl under an argon atmosphere and stored over activated molecular sieves; ethanol was dried over magnesium powder. Deuterated THF (Aldrich) and benzene (MSD Isotopes) were dried over sodium benzophenone ketyl and vacuum distilled. Diethyl ether and diglyme (Aldrich anhydrous grade) were dried for at least 24 h in the drybox over activated sieves. Acetonitrile (Aldrich anhydrous grade) was distilled from calcium hydride and stored over activated sieves in the drybox.

The following compounds were synthesized by literature procedures or modifications of reported procedures: the lanthanide dihalides[12,13] YbI_2THF_3, SmI_2THF_2, EuI_2THF_2, and $YbI_2(diglyme)_2$; $YbCp^*{}_2THF_2$,[14] $Yb[N(TMS)_2]_2DME_2$;[15] $Yb[O(2,6\text{-}^tBu\text{-}4\text{-}MeC_6H_3)]_2THF_3$;[16] $2,4,6\text{-}^tBu_3C_6H_2Br$ (Mes*Br);[17] $Li[Te(2,4,6\text{-}Me_3C_6H_2)]$ (LiTeMes);[18] $Te_2(2,4,6\text{-}Me_3C_6H_2)_2$ (Mes_2Te_2);[18b,c] $K[Te(2,4,6\text{-}Me_3C_6H_2)]$ (KTeMes);[3a] and $(2,4,6\text{-}Me_3C_6H_2)SeH$ (MesSeH).[2b]

Methods. Reactions and manipulations were carried out under argon or nitrogen using standard Schlenk techniques or Braun or Vacuum Atmospheres dryboxes. Electron-impact and chemical ionization mass spectra were obtained on a Kratos MS9/50 spectrometer. Magnetic susceptibility measurements were recorded on a Johnson-Matthey magnetic susceptibility balance operating under the auspices of the Gouy method. χ_M was not corrected for the diamagnetic contributions which varied depending on the ligands present or the number of solvent molecules coordinated.[19]

Electronic spectra were recorded on a Hewlett-Packard 8450A UV/vis spectrophotometer. Elemental analyses were obtained from Oneida Research Services, Whitesboro, NY, or from Analytische Laboratorien, Gummersbach, Germany.

^1H NMR spectra were obtained on either a Bruker WP200 or AM300 spectrometer. $^{13}C\{^1H\}$, $^{125}Te\{^1H\}$, $^{77}Se\{^1H\}$, and $^{171}Yb\{^1H\}$ NMR spectra were obtained on a Bruker AM300 instrument equipped with a 5 mm broad-band probe tuned to frequencies of 75.469, 94.691, 94.691, and 52.523 MHz, respectively. All spectra were run in dry benzene-d_6 or THF-d_8. ^{125}Te resonances were referenced to an external standard consisting of 1.0 *M* solutions of diphenyl ditelluride, Ph_2Te_2, in the appropriate deuterated solvent. The ^{125}Te resonance of this standard appears at +422 ppm downfield from dimethyl telluride ($\delta = 0$ ppm).[20] The $^{77}Se\{^1H\}$ NMR resonances were referenced to 1 M solutions of dimethyl selenide, Me_2Se (Strem), as external standards in either of the two deuterated solvents. $^{171}Yb\{^1H\}$ NMR resonances were referenced to a 1 *M* solution of $YbCp^*{}_2THF_2$ in THF-d_8 as an external standard at 0 ppm.[21] ^{171}Yb T_1 experiments were performed using a solution of mercuric acetate in D_2O to obtain the ^{171}Yb 180° pulse, since the spectrometer frequency of Hg is very similar to that of ^{171}Yb. Once the 180° pulse was determined, 15 trials were run using a 180° composite inversion pulse with the frequency centered on the ^{171}Yb resonance and with delays varying between 0.01 and 2 s. ^{171}Yb $T_2{}^*$ values were approximated from the width of the ^{171}Yb peaks at half height, $\omega_{1/2}$, by the equation $T_2{}^* = (\pi\omega_{1/2})^{-1}$, after the $\omega_{1/2}$ was corrected for line broadening. $Pb(NO_3)_2$ in D_2O (−2961 ppm) at concentrations of 0.71 and 0.65 M was used as an external standard for ^{207}Pb NMR.

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(6) *Handbook of the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L. R., Eds.; North-Holland: Amsterdam, 1979, Vol. 2, Chapter 19; Vol. 4, Chapter 31.

(7) (a) Petzel, T. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 119.(b) Hickey, C. F.; Gibson, U. J. *J. Appl. Phys.* **1987**, *62*, 3912. (c) Nakahara, J. F.; Takeshita, T.; Tschetta, M. J.; Beardry, B. J.; Gschneidner, K. A. *J. Appl. Phys.* **1988**, *63*, 2331.

(8) Selected references: (a) Schumann, H.; Albrecht, I.; Gallagher, M.; Hahn, E.; Janiak, C.; Kolax, C.; Loebel, J.; Nickel, S.; Palamidis, E. *Polyhedron* **1988**, *7*, 2307. (b) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865. (c) Recknagel, A.; Noltmeyer, M.; Stalke, D.; Pieper, U.; Schmidt, H. G.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *411*, 347. (d) Wedlar, M.; Recknagel, A.; Gilje, J. W.; Nottemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1992**, *426*, 295. (e) Edelmann, F. T.; Rieckhoff, M.; Haiduc, I. *J. Organomet. Chem.* **1993**, *447*, 203. (f) Gornitzka, H.; Edelmann, F. T.; Jacob, K. *J. Organomet. Chem.* **1992**, *436*, 325.

(9) Strzelecki, A. R.; Timinski, P. A.; Helsel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159.

(10) Likar, C. L.; Strzelecki, A. R.; Bilder, D. M.; Sutovich, K. J.; Wenslow, R. M.; Mueller, K. T.; Bianconi, P. A. To be submitted for publication.

(11) (a) Bonneman, H.; Bogdanovic, B.; Brinkman, R.; He, D. W.; Splitehoff, B. *Angew. Chem., Int. Ed. Eng.*, **1983**, *22*, 728. (b) Bogdanovic, B.; Liao, S.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* **1984**, *117*, 1378.

(12) Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chim.* **1981**, *5*, 479.

(13) (a) Watson, P. L. *J. Chem. Soc., Chem Commun.* **1980**, 652. (b) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999.

(14) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999.

(15) (a) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271.

(16) Deacon, G. B.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; MacKinnon, P.; Newnham, R. H. *J. Chem. Soc., Chem. Commun.* **1989**, 935.

(17) Betts, E. E.; Barclay, L. R. C. *Can. J. Chem.* **1956**, *33*, 1768.

(18) (a) Engman, L.; Cava, M. P. *Synth. Commun.* **1982**, *12*, 163. (b) Lange, L.; duMont, W. W. *J. Organomet. Chem.* **1985**, *286*, C1. (c) Akiba, M.; Lakshmikanthan, M. V.; Jen, K. Y.; Cava, M. P. *J. Org. Chem.* **1984**, *49*, 4819. (d) Comasseto, J. V. *Phosphorus, Sulfur Silicon* **1992**, *67*, 183.

(19) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, PA, 1977; p 412.

(20) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; Chapter 12.

(21) Avent, A. G.; Edelman, M. A.; Lappert, M. F.; Lawless, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 3423.

Li(2,4,6-$Me_3C_6H_2$) (1, LiMes).[22] A 1.7 M solution of *tert*-butyllithium (55.4 mL, 94.2 mmol) was added via cannula to a solution of bromomesitylene (15.0 g, 75.4 mmol) in 50 mL of diethyl ether at −78 °C. The solution was stirred cold for 2 h and the solvent was removed in vacuo at reduced temperatures. The resulting solid (82.7% yield) was washed with pentane on a fritted funnel to remove excess *tert*-butyllithium or unreacted bromomesitylene. ^{1}H NMR (THF-d_8): 6.43 ppm (2H, aromatic); 2.33 ppm (6H, CH_3); 2.05 ppm (3H, CH_3); coordinated ether sometimes appeared at 3.72 and 1.02 ppm.

Li[Se(2,4,6-$Me_3C_6H_2$)] (2, LiSeMes). Lithium mesitylselenolate was synthesized in a manner analogous to that reported for LiTeMes by the addition of mesityllithium (**1**, 4.0 g, 31.8 mmol) to a THF suspension of selenium powder (2.51 g, 31.8 mmol) at −40 °C. LiSeMes was isolated in 78% yield as a solid following repeated evaporations and triturations with pentane. ^{1}H NMR (THF-d_8): 6.53 ppm (2H, aromatic); 2.33 ppm (6H, *o*-CH_3); 1.99 ppm (3H, *p*-CH_3).

Se_2(2,4,6-$Me_3C_6H_2$)$_2$ (3, Mes_2Se_2). Mes_2Se_2 was prepared following the same procedure used to prepare Mes_2Te_2, using LiSeMes as the starting material. ^{1}H NMR (benzene-d_6): 6.66 ppm (4H, aromatic); 2.30 ppm (6H, *o*-CH_3); 2.03 ppm (3H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): 143.9, 139.2, 129.4, 128.7, 24.4, and 21.0 ppm. ^{77}Se NMR (benzene-d_6): 369.6 ppm.

K[Se(2,4,6-$Me_3C_6H_2$)] (4, KSeMes). To a THF (40 mL) solution of dimesityl diselenide (**3**, 5.26 g, 13.3 mmol) was added 1 M potassium tri-*sec*-butylborohydride/THF solution (24.27 g, 26.6 mmol), over a 15 min period. The same isolation procedures reported in the preparation of KTeMes were employed, giving **4** as a white solid in 85.4% yield. ^{1}H NMR (THF-d_8): 6.59 ppm (2H, aromatic); 2.38 ppm (6H, *o*-CH_3); 2.03 ppm (3H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8): 142.7, 141.4, 127.9, 126.9, 28.3, and 21.0 ppm. ^{77}Se NMR (THF-d_8): 26.6 ppm. Anal. Calcd for $C_9H_{11}SeK$: C, 45.54; H, 4.68; Se, 33.29; K, 16.49. Found: C, 45.32; H, 4.84; Se, 32.95; K, 16.20.

(2,4,6-$^t Bu_3C_6H_2$)SeH (5, Mes*SeH). Supermesitylselenol (2,4,6-tri-*tert*-butylphenylselenol) was prepared by a modified literature method for the synthesis of thiols.[23] A Grignard reagent was formed using a slight excess of an activated, catalytic magnesium anthracene reagent (0.176 g Mg, 7.24 mmol) in THF (40 mL). To this reagent was added supermesityl bromide (2.0 g, 6.16 mmol), and the reaction mixture was then stirred for 12 h under argon. Elemental selenium (0.44 g, 5.57 mmol) was then added and the mixture was stirred for a further 12 h, after which time 2.5 N HCl (6 mL) and saturated aqueous NaCl (40 mL) were added. The isolation of the selenol involved ether extraction and drying of the organic layer over $MgSO_4$, followed by solvent evaporation and drying of the solid selenol in vacuo (66% yield). Mass spectrum: calcd *m/z* 326; found *m/z* 326; and a small peak at *m/z* 650 corresponding to the diselenide. A second method for the preparation of **5** was described by Bochmann and co-workers.[2b] The selenol was obtained as a yellow solid. ^{1}H NMR (benzene-d_6): 7.42, 1.64, 1.35, and 1.29 ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6): 152.3, 150.3, 122.9, 119.6, 35.1, 32.2, 31.8, and 31.6 ppm. ^{77}Se NMR(benzene-d_6): 120.7 ppm.

Yb(TeMes)$_2$(solv)$_x$ (6, 7, 8). Method A. KTeMes (2.52 g, 4.19 mmol) was added to $YbBr_2THF_2$ (2.00 g, 8.82 mmol) in 40 mL of THF (YbI_2THF_3 can also be used as the Yb-containing reagent). The reaction proceeded almost immediately upon addition of the potassium salt with complete reaction occurring after stirring for 1 h at room temperature. The reaction mixture was then filtered to remove precipitated KBr, and the THF was removed by evaporation. The resulting orange residue was extracted into 20 mL of toluene, and the solution was again filtered to remove residual KBr. Removal of the toluene in vacuum and recrystallization of the solid residue at −40 °C from a solution of 20 mL THF and 10 mL of pentane gave Yb(TeMes)$_2$(THF)$_x$ (x = 2−3) (**6**) as orange crystals in 85−93% yield (depending on the number of THF molecules coordinated). Recrystallization from THF alone gave even higher yields. Magnetic susceptibility: diamagnetic. Electronic spectrum (THF): λ_{max} = 240 and 260 nm. ^{1}H NMR (THF-d_8): 6.62 ppm (4 H, aromatics); 2.42 ppm (12 H, *o*-CH_3); 2.04 ppm (6 H, *p*-CH_3); 3.58 and 1.73 ppm (THF). $^{13}C\{^1H\}$ NMR (THF-d_8): 145.4, 132.1, 125.5, and 117.9 ppm (aromatics); 33.4 ppm (*o*-CH_3); 20.8 ppm (*p*-CH_3); 68.2 and 26.3 ppm (coordinated THF). ^{125}Te NMR (THF-d_8): −272 ppm. ^{171}Yb NMR (THF-d_8): 527 ppm. Anal. Calcd for $C_{18}H_{22}Te_2Yb{\cdot}2.3OC_4H_8$: Yb, 20.8; Te, 30.7; C, 39.3; H, 4.9. Found: Yb, 20.7; Te, 29.9; C, 39.7; H, 5.3. NMR relaxation times for ^{171}Yb in complex **6**: T_1 = 1.65 s; T_2^* = 0.00834 s.

Method B. Yb[O(2,6-^{t}Bu-4-MePh)]$_2$THF$_3$ (2.00 g, 2.42 mmol) was dissolved in 40 mL of THF, to which solution 2.2 equiv of [TMS]-TeMes (1.70 g, 5.32 mmol) were added. This solution was stirred for 24 h, after which the THF was removed by evaporation, the solid residue was dissolved in toluene, and the solution was concentrated in volume and cooled to −40 °C. Yellow-orange crystals of **6** were produced, which were isolated by filtration and washed with pentane to remove any organics. ^{1}H NMR (THF-d_8): 6.65 ppm (4 H, aromatics); 2.47 ppm (12 H, *o*-CH_3); 2.05 ppm (6 H, *p*-CH_3); 3.58 and 1.72 ppm (THF), and additional peaks at 2.06, 1.42, 1.33, and 0.07 ppm (from Me_3Si-O(2,6-^{t}Bu-4-MePh) impurities). ^{125}Te NMR spectra showed resonances at −276 ppm in THF-d_8 and −280 ppm in benzene-d_6.

Yb(TeMes)$_2$(diglyme)$_2$ (**7**) was synthesized similarly by the addition of a slight excess of 2 equiv of KTeMes (0.88 g, 3.09 mmol) to a THF solution (40 mL) of YbI_2(diglyme)$_2$ (1.00 g, 1.44 mmol) to which a few drops of anhydrous diglyme and a few milliliters of toluene were added. After filtration of the reaction mixture, and removal of the solvent in vaccum, the red solid obtained was dissolved in 30 mL of toluene to which a few drops of diglyme had been added. If all the red complex was not extracted into the toluene solution, a few milliliters of THF were also added. The extract was filtered, concentrated to 15 mL, and cooled to −40 °C to crystallize **7**. Magnetic susceptibility: diamagnetic. ^{1}H NMR (THF-d_8): 6.66 ppm (4 H, aromatics); 2.48 ppm (12 H, *o*-CH_3); 2.09 ppm (6 H, *p*-CH_3); 3.54, 3.45, and 3.26 ppm (diglyme). $^{13}C\{^1H\}$ NMR (THF-d_8): 145.5, 131.9, 125.5, and 118.4 ppm (aromatics); 33.3 ppm (*o*-CH_3); 20.9 ppm (*p*-CH_3); 72.7, 70.7, and 59.4 ppm (coordinated diglyme). ^{125}Te NMR (THF-d_8): −260 ppm. ^{171}Yb NMR (THF-d_8): 430 ppm. Anal. Calcd for $C_{30}H_{50}O_6Te_2Yb$: Yb, 18.5; Te, 27.3; C, 38.5; H, 5.4. Found: Yb, 18.2; Te, 26.6; C, 39.1; H, 5.5. Low temperature ^{125}Te NMR studies are shown in Figure 1. The DME adduct, Yb(TeMes)$_2$(DME)$_2$ (**8**), was prepared by carrying out the synthesis in DME instead of THF. ^{1}H NMR (THF-d_8): 6.62 ppm (4 H, aromatics); 2.29 ppm (12 H, *o*-CH_3); 2.13 ppm (6 H, *p*-CH_3); 3.43 ppm (8H, DME); 3.27 ppm (12H, DME).

Yb(SeMes)$_2$(solv)$_2$ (9, 10). KSeMes (**4**, 1.53 g, 6.45 mmol) was added to a THF solution (40 mL) of $YbBr_2THF_2$ (1.50 g, 3.14 mmol) or YbI_2THF_3 (2.02 g, 3.14 mmol) and the solution was stirred for 1−2 h. The reaction mixture was then filtered to remove precipitated potassium salts, the salts were washed several times with 15 mL of THF, and the THF was evaporated from the combined washings and reaction mixture. The solid residue was again extracted into 30 mL of THF and filtered, and the THF solution was concentrated in volume to 15 mL under vacuum. Yb(SeMes)$_2$THF$_2$ (**9**) was isolated as yellow crystals in 85% yield by addition of pentane and cooling to −40 °C. Magnetic susceptibility: diamagnetic. ^{1}H NMR (THF-d_8): 6.60 ppm (4 H, aromatics); 2.36 ppm (12 H, *o*-CH_3); 2.05 ppm (6 H, *p*-CH_3); 3.58 and 1.72 ppm (THF). $^{13}C\{^1H\}$ NMR (THF-d_8): 141.7, 139.5, 129.9, and 127.0 ppm (aromatics); 27.7 ppm (*o*-CH_3); 20.9 ppm (*p*-CH_3); 68.2 and 26.4 ppm (coordinated THF). ^{77}Se NMR (THF-d_8): 57.8 ppm. Anal. Calcd for $C_{26}H_{38}O_2Se_2Yb$: Yb, 24.3; Se, 22.1; C, 43.8; H, 5.4. Found: Yb, 24.0; Se, 22.4; C, 40.4; H, 4.8.

Yb(SeMes)$_2$DME$_2$ (**10**) was prepared by addition of a solution of 2.2 equiv of MesSeH (0.68 g, 3.42 mmol) in pentane (10 mL) to a DME solution (25 mL) of Yb[N(TMS)$_2$]$_2$DME$_2$ (1.05 g, 1.55 mmol) at −40 °C. After 1 h of stirring at −40 °C, the reaction mixture was filtered with a frit which had been cooled to −40 °C in a freezer, isolating **10** as a yellow-orange solid in 59% yield. More product could be obtained by evaporation of the pentane/DME solvent from the filtrate and recrystallization of the solid residue from 50 mL of pentane at −40 °C. The reaction proceeded rapidly upon addition of the selenol, as evidenced by the disappearance of the Yb(II) amide observed upon stirring for 5 min. Some soluble, paramagnetic substance was often observed in the measurement of magnetic susceptibilities. ^{1}H NMR

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(22) (a) Zigler, S. S.; Johnson, L. M.; West, R. *J. Organomet. Chem.* **1987**, *341*, 187. (b) Sharp, P. R.; Astruc, D.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *182*, 477.

(23) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050.

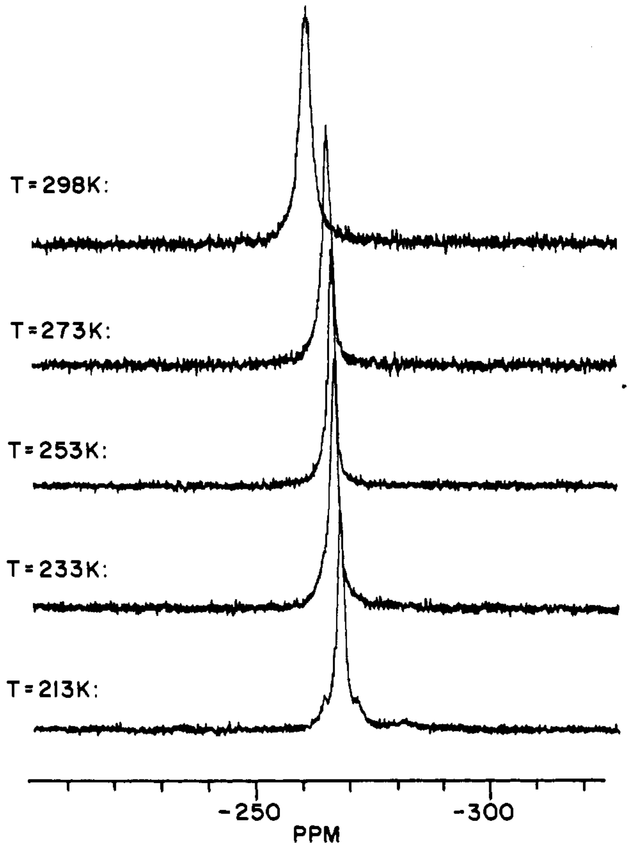

Figure 1. Low temperature ^{125}Te NMR studies on Yb(TeMes)$_2$diglyme$_2$ in THF-d_8. Conditions: spectrometer frequency = 94.691 MHz; relaxation delay = 0.1 s.

Table 1. Magnetic Susceptibility Data for Paramagnetic Lanthanide Chalcogenolate Complexes

complex	χ_g (cgsu)	χ_M (cgsu)	$\mu_{eff}{}^a$ (μ_B)
Sm(TeMes)$_2$THF$_2$	5.00×10^{-6}	3.94×10^{-3}	3.06
Sm(SeMes)$_2$THF$_2$	6.09×10^{-6}	4.21×10^{-3}	3.17
Eu(TeMes)$_2$THF$_2$	2.57×10^{-5}	2.03×10^{-2}	6.95
Eu(SeMes)$_2$THF$_2$	3.90×10^{-5}	2.70×10^{-2}	8.02

[a] μ_{eff} values not corrected for diamagnetic contributions associated with ligands about the metal center.

(THF-d_8): 6.57 ppm (4 H, aromatics); 2.37 ppm (12 H, *o*-CH$_3$); 2.02 ppm (6 H, *p*-CH$_3$); 3.43 (8H, DME) and 3.27 ppm (12H, DME). ^{13}C{^{1}H} NMR (THF-d_8): 141.6, 139.4, 129.4, and 126.7 ppm (aromatics); 27.8 and 20.8 ppm (*o*- and *p*-CH$_3$); 72.3 and 59.0 ppm (coordinated DME). ^{77}Se NMR (THF-d_8): 33.2 ppm. ^{171}Yb NMR (THF-d_8): 518 ppm.

Sm(TeMes)$_2$THF$_2$ (11). KTeMes (1.12 g, 1.82 mmol) was added to a THF solution (40 mL) of SmI$_2$THF$_2$ (1.00 g, 3.92 mmol), and the reaction was complete after an hour of stirring at room temperature. Workup following the same procedure as that described for **6**, Method A, gave Sm(TeMes)$_2$THF$_2$ (**11**) as a dark green solid in 67% yield. Magnetic susceptibility is shown in Table 1. ^{1}H NMR (THF-d_8): 7.51 ppm (4 H, aromatics); 4.45 ppm (12 H, *o*-CH$_3$); 1.46 ppm (6 H, *p*-CH$_3$); 3.61 and 1.76 ppm (THF). ^{13}C{^{1}H} NMR (THF-d_8): 133.4, 130.7, and 121.4 ppm (aromatics, ipso missing); 41.6 ppm (*o*-CH$_3$); 21.7 ppm (*p*-CH$_3$); 68.0 and 22.5 ppm (coordinated THF). Anal. Calcd for $C_{26}H_{38}O_2Te_2Sm$: Sm, 19.1; Te, 32.4; C, 39.6; H, 4.9. Found: Sm, 19.1; Te, 31.8; C, 40.2; H, 4.4.

Sm(SeMes)$_2$THF$_2$ (12). KSeMes (**4**, 2.27 g, 9.57 mmol) was added to SmI$_2$THF$_2$ (2.50 g, 4.56 mmol) in anhydrous THF (40 mL). The reaction proceeded almost immediately upon addition of the potassium salt; the reaction mixture was then stirred between 1 and 2 h. Compound **12** was isolated as a dark green solid in 69% yield, assuming two THF molecules coordinated. Isolation of the complex was accomplished by the same method used in the preparation of **9**. Magnetic susceptibility is shown in Table 1. ^{1}H NMR (THF-d_8): 6.93 ppm (4 H, aromatics); 2.66 ppm (12 H, *o*-CH$_3$); 1.27 ppm (6 H, *p*-CH$_3$); 3.58 and 1.75 ppm (THF). ^{13}C{^{1}H} NMR (THF-d_8): 137.2, 122.3, and 120.7 ppm (aromatics, ipso missing); 46.1 ppm (*o*-CH$_3$); 24.2 ppm (*p*-CH$_3$); 68.0 and 25.8 ppm (coordinated THF). Anal. Calcd for $C_{26}H_{38}O_2Se_2Sm$: Sm, 21.8; Se, 22.9; C, 43.8; H, 5.4. Found: Sm, 20.5; Se, 21.9; C, 39.4; H, 4.3.

Eu(TeMes)$_2$THF$_2$ (13). KTeMes (1.09 g, 3.82 mmol) was added to EuI$_2$THF$_2$ (1.00 g, 1.82 mmol) in anhydrous THF (40 mL). The reaction mixture was stirred for approximately 1 h, after which it was filtered and the solvent was removed under vacuum. The solid residue was extracted into a solution of 40 mL of toluene and 10 mL of THF, and the solution was filtered to remove any excess potassium iodide, after which the solvent was again removed under vacuum. Recrystallization of the solid residue at −40 °C from a solution of 20 mL of THF and 10 mL of pentane gave **13** as an yellow-orange solid in 71% yield, assuming two THF molecules coordinated. Magnetic susceptibility is shown in Table 1. Anal. Calcd for $C_{26}H_{42}O_4Te_2Eu$: Eu, 18.4; Te, 30.9; C, 37.8; H, 5.1. Found: Eu, 19.0; Te, 31.5; C, 38.2; H, 5.2.

Eu(SeMes)$_2$THF$_2$ (14). KSeMes (**4**, 0.45 g, 1.91 mmol) was added to EuI$_2$THF$_2$ (0.50 g, 0.91 mmol) in anhydrous THF (40 mL). The reaction mixture was stirred for 1 to 2 h, after which time Eu(SeMes)$_2$THF$_2$ (**14**) was isolated using the same procedures described in the synthesis of **9**. Compound **14** was isolated as a bright yellow solid in 70% yield, considering two THF molecules coordinated. Magnetic susceptibility is shown in Table 1. Anal. Calcd for $C_{26}H_{38}O_2Se_2Eu$: Eu, 22.0; Se, 22.8; C, 45.1; H, 5.5. Found: Eu, 25.6; Se, 20.3; C, 41.0; H, 4.3.

Yb(SeMes*)$_2$DME (15). Mes*SeH (0.33 g, 0.49 mmol) was added to Yb[N(TMS)$_2$]$_2$DME$_2$ (0.33 g, 1.02 mmol) in an anhydrous DME/pentane solution (20 mL of each). The reaction mixture was stirred for 1−24 h and then filtered on a frit cooled to −40 °C to isolate **15** as a yellow solid in 38% yield, considering one DME molecule coordinated. More product could be crystallized from a 40 mL pentane solution at −40 °C. ^{1}H NMR (benzene-d_6): 7.53 ppm (4 H, aromatics); 2.22 ppm (36 H, *o*-^{t}butyl); 1.43 ppm (18 H, *p*-^{t}butyl); 3.22 and 3.11 ppm (DME). ^{13}C{^{1}H} NMR (benzene-d_6): 152.6, 141.7, 138.2, and 120.7 ppm (aromatics); 39.8, 34.8, 32.2, and 32.0 ppm (*o*- and *p*-^{t}butyl); 71.4 and 58.8 ppm (coordinated DME). ^{77}Se NMR: 196 ppm. Anal. Calcd for $C_{40}H_{68}O_2Se_2Yb$: Yb, 19.0; Se, 17.3; C, 52.7; H, 7.5. Found: Yb, 18.6; Se, 17.3; C, 49.5; H, 7.1.

Sn(TeMes)$_4$ (16). SnCl$_2$ (0.32g, 1.7 mmol) or SnBr$_2$ (0.48g, 1.7 mmol) was added to a solution of KTeMes (1.00g, 3.5 mmol) in 50 mL of THF. This solution was stirred for 6−12 h with exclusion of light, followed by removal of solvent in vacuo. The resulting red-black solid was dissolved in toluene (200 mL), and the solution was filtered to remove black solid. Removal of the solvent in vacuo followed by washing with 50 mL of pentane gave **16** as a dark red solid in 50% yield. ^{1}H NMR (THF-d_8): 2.25 ppm (*p*-CH$_3$); 2.40 ppm (*o*-CH$_3$); 6.92 ppm (arom). ^{125}Te NMR (THF-d_8): 49.8 ppm. Anal. Calcd for Sn(TeMes)$_4$: Sn, 10.73; Te, 46.15; C, 39.10; H, 4.01. Found: Sn, 10.80; Te, 45.9; C, 38.89; H, 4.05.

Pb(SeMes)$_2$ (17). MesSeH (1.03g, 5.17 mmol) was added to Pb(acac)$_2$ (1.00g, 2.47 mmol) in 100 mL of THF. After stirring for 1 h, the reaction mixture was filtered and the solvent was evaporated under vacuum to near dryness. Addition of 50 mL of pentane followed by filtration led to the collection of 1.49 g (70% yield) of **17** as an orange solid that was slightly soluble in THF. ^{1}H NMR (THF-d_8): 6.77 ppm (arom); 2.44 ppm (*o*-CH$_3$); 2.19 ppm (*p*-CH$_3$). ^{77}Se NMR (THF-d_8): 50.5 ppm. ^{13}C{^{1}H} NMR (THF-d_8): 143.6, 135.1, 130.5, and 128.2 ppm (aromatics); 26.7 ppm (*o*-CH$_3$); 20.91 ppm (*p*-CH$_3$). ^{207}Pb NMR-(THF-d_8): (PEt$_3$ added to increase solubility) 2815 ppm (broad) and 3394 ppm (sharp). Anal. Calcd for Pb(SeMes)$_2$: Pb, 34.33; Se, 26.2; C, 35.82; H, 3.67. Found: Pb, 34.15; Se, 25.7; C, 35.49; H, 3.86.

Results/Discussion

Synthetic Approaches to Lanthanide Chalcogenolate Complexes. Due to the possible advantages associated with a molecular precursor synthetic approach, many reports have appeared demonstrating its utility in the preparation of semiconductor materials and ceramics. Many of these reports have explored the use of metal-organic species to synthesize III–V or II–VI semiconducting materials,[1-4] such as GaAs, InP, HgTe, CdSe, and CdTe, by a chemical vapor deposition approach or by the thermal decomposition of a solid molecular precursor. There have also been many reports involving the syntheses of heavy transition metal thiolate, selenolate and tellurolate complexes, which are precursors via similar routes to II–VI materials. Steigerwald[1] reported the synthesis of zinc, cadmium, and mercury selenolate and tellurolate complexes of the general formula $M(QPh)_2$, where M = Zn, Cd, and Hg; Q = Se, and Te; and Ph = phenyl. These compounds were synthesized by a variety or routes, such as the reaction of the dialkylmetal complex with 2 equiv of the selenol,[1h,i] the metathesis or transmetalation route involving the reaction of the metal chloride with the lithium salt of the phenyltellurolate anion,[1a] or the oxidation of the metal upon reaction with the ditelluride.[1b] Soluble, solvent-free II–VI precursors have been developed for group 12 metals by using bulkier organic groups on the selenolate or tellurolate ligand.[1] Arnold,[3] using a temperature stable tellurol containing the bulky tris(trimethylsilyl)silyl group, has synthesized soluble, stable tellurolate complexes of Zn, Cd, and Hg, and of group 4 metals. Isolation[2] of soluble, low-coordinate cadmium mesityl or supermesityl selenolate and tellurolate complexes has also been reported.

Preparation of Divalent Lanthanide Chalcogenolate Complexes: Method A. For some of the group 12 metals, oxidation of the zerovalent metal with a ditelluride was found to be a successful route to divalent tellurolate complexes.[1b] No such reactivity was observed for ytterbium; when Yb metal was stirred in a THF solution of diphenyldiselenide or ditelluride, no reaction occurred, even after sonication. A transmetalation route, Method A, shown in eq 1, was more successful; lanthanide dihalides were treated with 2 equiv of the potassium salt of the bulky arylchalcogenolate ligand. The driving force in this reaction is the precipitation of the alkali metal halide byproduct from solution. The resulting complexes contain two anionic chalcogenide ligands bonded to the divalent metal center. Performing the syntheses in coordinating solvents such as THF or DME provided soluble, monomeric, or low nuclearity complexes.

$$\mathrm{LnX_2THF}_y + 2\mathrm{MQR} \xrightarrow{\text{solvent}} \mathrm{Ln(QR)_2(solv)}_y + 2\mathrm{MX} \qquad (1)$$

$$\mathrm{Ln = Yb, Sm, Eu;\ M = K;\ X = Br, I;}$$
$$\mathrm{Q = Se, Te;\ R = Mes, Mes^*}$$

A critical factor in the success of these syntheses is the complete exclusion of lithium, sodium, and chloride ions from the reaction mixture. Although reactions similar to those shown in eq 1 which utilize these ions do give divalent lanthanide chalcogenolate complexes, no method of purification which was attempted (including variation of the reaction solvent, extensive extraction of the products, addition of nitrogen, phosphorus, or oxygen donor ligands to the reaction mixtures, and increasing the complexes' steric saturation) was successful in removing all the lithium or sodium halide byproducts from the lanthanide complexes. These alkali metal halide contaminated materials were often isolated as oils or insoluble solids. Potassium bromide and iodide, conversely, are much more insoluble in THF or DME than lithium and sodium halides, and precipitate readily from the reaction mixture, thus driving the reaction to completion. Simple extraction of the products into toluene and filtration removes any remaining potassium salts and gives analytically pure complexes after recrystallization. The steric bulk provided by the mesityl ligand also contributes significantly to the success of this synthetic route: analogous reactions using the potassium salts of phenylselenolate and -tellurolate ligands gave lanthanide complexes, for the most part insoluble, from which the alkali metal halide side products again could not be removed.

Characterization of Chalcogenolate Complexes Obtained by Method A. This synthetic procedure proved useful in the preparation of precursors containing Yb, Sm, and Eu bonded to organoselenolate or tellurolate ligands, of the general formula $\mathrm{Ln(QR)_2THF}_x$ ($x = 2-3$). Characterization of these complexes, accomplished by magnetic measurements, elemental analysis and multinuclear NMR techniques, confirmed their formulation and suggested that these complexes are structurally analogous to the homoleptic chalcogenide complexes of the group 12 metals.[1-3]

The ytterbium(II) complexes were studied extensively by multinuclear NMR to gain structural information. Elemental analysis of $\mathrm{Yb(TeMes)_2(THF)}_x$ (**6**) showed a 1:2 metal to tellurolate ligand ratio, and between 2.3 and 2.4 THF molecules either coordinated to the complex or crystallized in the lattice. Complex **6** is a diamagnetic orange solid under argon but quickly oxidizes upon exposure to air, as evidenced by a color change to a red-brown solid and the development of a magnetic moment typical of Yb(III). The electronic spectrum of **6** in THF shows absorption maxima at 240 and 260 nm, which change upon exposure to air to 240 and 295 nm. Although single crystals of **6** can be grown from THF or THF/toluene at −40 °C, their extreme air, moisture, and temperature sensitivity prevented crystallographic characterization other than the determination of their unit cell.[24] This was the case for all the divalent lanthanide complexes synthesized. Multinuclear NMR studies were therefore initiated on the Yb(II) complexes to obtain structural information; observation of ^{1}H, ^{13}C, ^{125}Te, and ^{171}Yb NMR resonances is possible. ^{125}Te NMR is known to be very sensitive to ligand environment,[20] and its very large chemical shift range provided additional structural information. In a concentrated THF-d_8 solution of **6**, for example, a single resonance is observed at −272 ppm. This chemical shift is far upfield from organotellurium compounds and is characteristic of metal tellurolates, but is shifted approximately 26 ppm downfield from the potassium tellurolate used as a reagent in the synthesis of **6**. The single ^{125}Te NMR resonance observed suggested one tellurium ligand environment and therefore a very symmetrical and possibly monomeric structure for the complex. An alternative interpretation of the results is that ligand exchange among different environments is rapid on the NMR time scale, resulting in a single broad averaged resonance. The resonance was somewhat broad with a peak width at half height, $\omega_{1/2}$, of 117 Hz; this width could also be due to short T_2 relaxation times caused by steric constraints and rigidity about the very crowded Yb(II) metal center. Low temperature ^{125}Te NMR studies were initiated to distinguish among these possibilities. Complex **6**, however proved to be too insoluble in THF below 0 °C to obtain ^{125}Te spectra, so the more soluble diglyme adduct $\mathrm{Yb(TeMes)_2(diglyme)_2}$ (**7**) was prepared by recrystallization of **6** from toluene to which a few drops of diglyme were added. Elemental analysis of **7** again confirmed the 1:2 metal to tellurolate ligand ratio, and indicated that two diglyme molecules were coordinated per Yb(II) center. Complex **7**, like **6**, shows one ^{125}Te NMR resonance in THF-d_8 at −260 ppm; a single ^{171}Yb NMR

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[24] Unit cell for **17** ($\mathrm{YbTe_2C_{27.2}H_{40.4}O_{2.3}}$): space group *Pbcn* with a = 11.78 Å, b = 11.61 Å, c = 14.30 Å, and V = 1957 Å^3.

resonance (see below) is seen at 430 ppm. The ^{125}Te peak was again quite broad. Variable-temperature ^{125}Te NMR studies on **7** in THF-d_8 (Figure 1) were carried out from +25 to −80 °C, at which temperature the complex became too insoluble to observe an NMR signal. These spectra show a small temperature-dependent ^{125}Te chemical shift for **7**, but only one ^{125}Te resonance, even at −60 °C. The resonance narrows slightly as the temperature is lowered, and coupling to the spin $^1/_2$ Yb center ($J_{\mathrm{Te-Yb}}$ = 758 Hz) appears at −60 °C. A very low intensity ^{125}Te resonance at ≈−279 ppm is also observed, the result of ligand exchange that is sufficiently slow at −60 °C to allow the observation of two ^{125}Te resonances. The chemical shift difference of these two peaks is attributed to solvent effects arising from varying numbers of diglyme molecules in the coordination spheres of different Yb(II) centers. It is less likely to arise from a dimeric structure containing both bridging and terminal tellurolate ligands because the resonances should be more equal in magnitude or present in small whole number ratios in such a structure. These data therefore suggest that complexes **6** and **7** are monomeric in solution, and that the broadness of their ^{125}Te NMR resonances is the result of short T_2 relaxation times.

^{171}Yb NMR[22] confirmed the structural information of the ^{125}Te NMR spectra. The observation of a ^{171}Yb NMR resonance for a complex confirms the divalent oxidation state. A THF-d_8 solution of **6** displays a single resonance at +527 ppm relative to YbCp$_2$*, indicating one type of Yb(II) environment present in solution. Measurements of the ^{171}Yb relaxation times of the complex were performed to confirm the suggestion of the ^{125}Te NMR spectra that the steric saturation of the complex causes greater rigidity in the complex and affects its relaxation times, giving broadened NMR peaks. The method utilized to obtain the T_1 involved obtaining 15 spectra using a 180° composite inversion pulse and varying the delay between 0.001 and 2 s. The T_1 value obtained from this data for **6** was 1.65 s, while the T_2*, obtained from $\omega_{1/2}$, was found to be 0.00834 s. Since the T_1 for small molecules usually approximately equals T_2*, the disproportion between these two relaxation times in **6** confirms its unusual rigidity and the suggestion that its ^{125}Te NMR resonances are broadened by the consequent short T_2* and not by rapid exchange of ligand environments.

Characterization of Yb(SeMes)$_2$THF$_2$ (**9**) and Yb(SeMes)$_2$DME$_2$ (**10**), the selenolate complexes analogous to **6**, **7**, and **8**, was similarly carried out by elemental analysis, magnetic measurements, and multinuclear NMR. Analysis of **9** shows a Yb to Se ratio of 1:2; ^{1}H NMR integration of **9** and **10** show selenolate ligands and two solvent molecules to be coordinated to each metal; magnetic susceptibility measurements show the complexes to be diamagnetic. The selenolate complexes are much less soluble than the tellurolates, a characteristic which was found to be general for all the divalent lanthanides used. This lowered solubility could arise from the smaller atomic radius of selenium, which would contract the coordination sphere and sterically saturate the Yb to a greater degree than is seen in the tellurolate complexes, or the complexes could be dimeric, as is seen in analogous cadmium selenolate complexes.[2] The selenolate complexes are soluble, however, and are isolated free of alkali metal halide salts as demonstrated by elemental analysis. ^{1}H, ^{13}C, and ^{77}Se NMR data for the THF adduct **9** were acquired; due to the decreased solubility of **9**, a solution concentrated enough to allow ^{171}Yb NMR to be acquired could not be made. A single resonance is observed in the ^{77}Se NMR spectrum of **9** at +57.8 ppm (Figure 2), characteristic of metal-bonded selenolate ligands. The peak was quite broad, with a $\omega_{1/2}$ value of approximately 62 Hz. These data correspond with that obtained for the tellurolate analogues, suggesting that the selenolates may also be monomeric in solution. The absence in the ^{77}Se NMR spectrum of **9** of the sharp downfield resonance characteristic of dimesityl diselenide or other organoselenium compounds indicates that no unwanted side reactions or oxidation to Yb(III) has occurred.

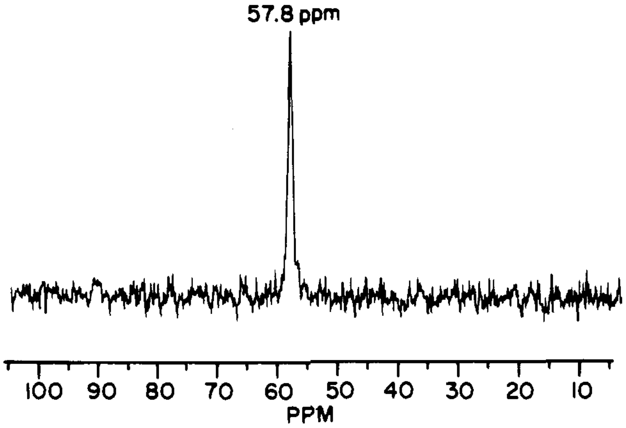

Figure 2. ^{77}Se NMR spectrum of Yb(SeMes)$_2$THF$_2$ in THF-d_8. Conditions: spectrometer frequency = 57.240 MHz; relaxation delay = 0.1 s; number of scans = 10 142; $\omega_{1/2}$ ≈ 110 Hz.

Samarium(II) and europium(II) complexes of the mesityl selenolate and tellurolate ligands show properties analogous to the Yb(II) congeners; Sm(II) proved to be more difficult to work with because of its larger size and less stable divalent oxidation state. Sm(TeMes)$_2$(THF)$_2$ (**11**), synthesized by Method A, shows a net effective magnetic moment of 3.06 B.M. (Table 1), somewhat low for Sm(II) species but not corrected for diamagnetic contributions from the attached ligands. Elemental analysis, however, confirmed the stoichiometry of the complex, and the expected drop in magnetic susceptibility occurred upon exposure to air (χ_g drops from 5.00 × 10^{-6} to 1.27 × 10^{-6} cgsu, corresponding to oxidation from a 4f^6 to a 4f^5 configuration).[3g] Elemental analysis and magnetic measurements similarly confirm the stoichiometry and oxidation state of the selenolate complex Sm(SeMes)$_2$(THF)$_2$, **12**. The insolubility of the complex made it more difficult to purify, a fact reflected by the difficulty in obtaining a good elemental analysis. NMR studies, limited to ^{1}H and ^{13}C NMR spectra due to the paramagnetic samarium nucleus, show peaks which are broadened and shifted compared to the spectra recorded for the diamagnetic ytterbium analogues. The ^{1}H NMR spectrum of **11** shows resonances at 7.51, 4.45, and 1.46 ppm arising from the mesityl group, and at 3.61 and 1.76 ppm from coordinated THF. The proton-decoupled ^{13}C NMR spectra shows broadened resonances at 133.4, 130.7, and 121.4 ppm corresponding to the aromatic carbons with the ipso carbon missing due to its close vicinity to the paramagnetic Sm(II) center. The *o*-CH$_3$ groups give rise to a broad resonance at 41.6 ppm and the resonance of the *p*-CH$_3$ group is hidden beneath that of THF-d_8 at 21.7 ppm. Resonances due to coordinated THF appear at 68.0 and 22.5 ppm. The ^{1}H and ^{13}C NMR spectra of **12** are virtually identical to those of **11**. The spectra therefore correspond to those seen for the Yb analogues, suggesting one type of ligand environment in the Sm complexes. Eu(TeMes)$_2$THF$_2$ (**13**) and Eu(SeMes)$_2$THF$_2$ (**14**) were similarly characterized by elemental analysis and magnetic measurements, which confirmed their stoichiometry and oxidation states. The high magnetic moment of europium(II) rendered NMR studies ineffective: the ^{1}H NMR spectrum of **13**, for example, displays only broad and unresolved resonances at 3.49, 1.58, 0.06, and −2.19 ppm, attributed to the ligands and coordinated solvent.

Preparation of Divalent Lanthanide Chalcogenolate Complexes by Method B; Other Attempted Synthetic Routes. Since Method A, the transmetalation route to divalent lanthanide chalcogenolate complexes, gave rise to potentially troublesome alkali metal halide side products, several other synthetic pathways to these complexes which did not involve alkali metal salts were investigated. One such pathway, Method B, involved the reaction of divalent lanthanide amide complexes with organoselenols (eq 2), an analogue of the method used successfully for the synthesis of group 12 chalcogenolate complexes.[2a,3c] This method proved successful for the synthesis of $Yb(SeMes)_2DME_2$ (**10**), and $Yb(SeMes^*)_2DME$ (**15**): a slight excess of mesitylselenol or supermesitylselenol added to cooled pentane/DME solutions of $Yb[N(TMS)_2]_2DME_2$ gave the Yb(II) selenolates. Again, elemental analysis, magnetic measurements, and multinuclear NMR were used to characterize the products. For complex **10**, however, the ^{77}Se and ^{171}Yb NMR resonances are significantly broader than those of the Yb(II) selenolate complexes produced by Method A. Also, the ^{1}H NMR spectrum of **10** displays some broad peaks characteristic of paramagnetic Yb(III) species, and magnetic susceptibility measurements show the complex to be slightly paramagnetic. The NMR data suggest that a Yb(II) selenolate complex is the primary species formed by this method but that oxidation of the Yb(II) by the acidic selenol to give Yb(III) impurities is also occurring. The degree of oxidation is much more pronounced when tellurols are used, or when the synthesis of Sm(II) complexes is attempted, making this synthetic route to divalent lanthanide chalcogenide complexes much inferior to Method A. Another synthetic route to these complexes which was attempted was the reaction of lanthanide(II) alkoxides or aryloxides with the trimethylsilylated derivatives of the tellurolate ligand (eq 3). The driving force of these reactions would be the formation of a strong silicon−oxygen bond in the form of a silylether. Although these reactions did give the divalent tellurolates as products, the silyl ether byproduct proved difficult to remove, as it appeared to either coordinate to or cocrystallize with the lanthanide complexes. Therefore, the reaction of the lanthanide dihalides with the potassium salts of the chalcogenolate ligands (Method A) became the method of choice in the preparation of divalent lanthanide chalcogenolate complexes in high yield and purity.

$$Yb[N(TMS)_2]_2DME_2 + 2RSeH \xrightarrow{DME} Yb(SeR)_2DME_x + 2HN(TMS)_2 \quad (2)$$

$$R = \text{mesityl, supermesityl}$$

$$Ln(OR)_2THF_x + 2TMSTeMes \xrightarrow{THF} Ln(TeMes)_2THF_x + 2TMS{-}O{-}R \quad (3)$$

$$Ln = Yb, Sm; TMS = (CH_3)_3Si; R = \text{alkyl or aryl}$$

Preparation of group 14 chalcogenolate complexes[25] has been investigated to provide precursors to IV−VI semiconductors that can be copyrolyzed with the lanthanide chalcogenide precursors to produce diluted magnetic semiconductors. These precursors must have similar solubility to the lanthanide chalcogenide precursors so that intimate mixing occurs before pyrolysis.[10]

The primary difficulty in preparing chalcogenide complexes of the group 14 elements is that the metal centers are easily reduced to the metal by the potassium chalcogenides. Attempts to produce $Pb(SeMes)_2$ (**17**) or $Pb(TeMes)_2$ by reaction of lead chloride with KSeMes or KTeMes in THF generally led to complete reduction to elemental lead. Reaction of lead acetylacetonate with the selenol, however, produces the lead selenide precursor **17** in a high yield with no recovery of elemental lead. This precursor is soluble in THF and has proven useful in combination with the lanthanide selenide precursors. Reaction of $SnCl_2$ with KTeMes led to the isolation of a highly soluble solid which on analysis was found to be $Sn(TeMes)_4$ (**16**). This tin tellurolate has been found to be a precursor to SnTe, not $SnTe_2$.[10]

Conclusions. The syntheses of the first examples of a new class of compounds, lower chalcogenide complexes of the divalent lanthanide metals, has been achieved by transmetalation reactions employing lanthanide dihalides and potassium salts of arylchalcogenolate ligands. Crucial to the success of these syntheses are exclusion of light alkali metal ions and the use of sterically demanding mesityl or supermesityl substituents on the chalcogenide element. Related group 12 and 14 chalcogenolate complexes can be prepared by a similar route or by reaction of appropriate precursors with selenols. These syntheses produce chalcogenolate complexes in high yield and sufficient purity to act as organometallic precursors to metal chalcogenide phases; the conversion of the precursors to solid state phases will be described in subsequent publications.

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[25] (a) Bahr, S.; Boudjouk, P.; McCarthy, G. J. *Chem. Mater.* **1992**, *4*, 383. (b) Harrison, P. G.; Stobart, S. R. *Inorg. Chim. Acta* **1973**, *7*, 306. (c) Shaw, R. A.; Woods, M. *J. Chem. Soc. A* **1971**, 1569. (d) Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 8214.