Utility of Organosamarium(II) Reagents in the Formation of Polyatomic Group 16 Element Anions: Synthesis and Structure of $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\text{E}_3)(\text{THF})_2$, $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\text{E})$, and Related Species (E = S, Se, Te)\(^1\)

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Received March 9, 1994

$[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\mu-\text{Te})$, 1, and $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\mu-\text{Se})$, 2, respectively. $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\mu-\text{P})$, 3, respectively. $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\mu-\text{S})$, 4, and $[(\text{C}_5\text{Me}_5)_2\text{Sm}](\mu-\text{N}^2-\text{Se})_2(\text{THF})$, 5. The sulfur analog, $[(\text{CsMe}_5)_2\text{Sm}]_2(\mu-\text{S})_2(\text{THF})$, 6, can be prepared from $[(\text{CsMe}_5)_2\text{Sm}(\text{THF})]_2$ and $\text{S}_2$ in a 2:3 ratio. Triselenide 5 can also be prepared from monoselenide 2 and 2 equiv of $\text{Se}$ and monotelluride 1 reacts with excess $\text{Te}$ to form tritelluride 4. Both of these reactions occur in THF but not in toluene. Selenium reacts with monotelluride 1 to form a mixture containing a mixed chalcogen complex 7, but this product is not generated from complex 2 by reaction with excess $\text{Te}$. The trichalcogenides 5 and 6 can be converted back to the monochalcogenides 2 and 3, respectively, with 2 equiv of $\text{PPh}_3$. 4 reacts with $\text{PMe}_3$ in THF to form $[(\text{C}_5\text{Me}_5)_2\text{Sm}](\mu-\text{N}^2-\text{Se}-\text{Te})$.

The soluble organometallic Sm(II) complexes $(\text{C}_5\text{Me}_5)_2\text{Sm}$ and $\text{N}_2$, $\text{Pb}_2$, $\text{Bi}_2$, and $\text{n-BS}_2$, which led to complexes of the $(\text{N}_2)_2$, $(\text{Bi}_2)_2$, and $(\text{Sb}_2)_2$ ligands, respectively, suggest that unusual

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Introduction

The soluble organometallic Sm(II) complexes $(\text{C}_5\text{Me}_5)_2\text{Sm}$, $(\text{C}_5\text{Me}_5)_2\text{Sm}$ and $\text{C}_5\text{Me}_5)_2\text{Sm}$ generate a variety of unusual transformations with unsaturated organic substrates.\(^3\) Recent studies of the reactivity of $(\text{C}_5\text{Me}_5)_2\text{Sm}$ with the main group compounds $\text{N}_2$, $\text{Pb}_2$, $\text{Bi}_2$, and $\text{n-BS}_2$, which led to complexes of the $(\text{N}_2)_2$, $(\text{Bi}_2)_2$, and $(\text{Sb}_2)_2$ ligands, respectively, suggest that unusual

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Sm(II) chemistry can be extended to inorganic and organometallic main group substrates as well. In order to determine if (C5Me5)2Sm(THF)2 could assemble and stabilize polyatomic main group element anions in groups other than group 15, we have examined the reactions of this complex with group 16 elements and reagents containing group 16 elements.

Formation of polyatomic species in group 16 with organometallic Sm(II) reagents is challenging since the monoatomic E2- complexes (E = S, Se, Te) would be expected to be quite stable. For example, the congeneric oxide complex, [(C5Me5)2Sm]2O,11 is readily formed under a variety of conditions and is frequently observed as an end product in (C5Me5)2Sn-based reactions. One would expect that similar samarium complexes could exist for S, Se, and Te. In addition, the ytterbium complexes [(C6Me5)2Yb]2(μ-E) can be easily formed from the less reactive Yb(II) reagent (C6Me5)2Yb(OET3).12 Formation of complexes of diatomic (E2)2- ions are also conceivable in group 16, and the structure of [(C5Me5)2Yb]2(μ-S2)2Te2 has been reported.13

We report here that organometallate (E2-) complexes can be readily made with (C5Me5)2Sm(THF)2, but that complexes of the polyatomic anions (E3-)2 can also be obtained using the proper conditions. The (E)2- and (E3-)2 complexes can be interconverted and this reaction chemistry can be used to make mixed element polyatomic anions. In addition, the (E3-)2 complexes can be converted to (E2-)2 species under the proper conditions. Complete crystallographic data have been obtained on the (E)2- series of [(C5Me5)2Sm(THF)2]2(μ-E) complexes, which allows a detailed comparison of group 16-lanthanide bonding parameters, which has not been obtainable with other systems due to lack of suitable crystals.12 In light of recent interest in the synthesis of lanthanide chalcogenide complexes for use as precursors to materials which are dilute magnetic semiconductors, these results provide new opportunities for the formation of suitable mixed-element species.14-16

Experimental Section

The compounds described below were handled under nitrogen with the rigorous exclusion of air and water using Schlenk, high-vacuum, and glovebox (Vacuum Atmospheres HE-553 Dri-Lab) techniques. Solvents were dried and physical measurements were obtained as previously described.17 (C5Me5)2Sm(THF)18 was prepared according to the literature. S (325 mesh), Se (325 mesh), Te (200 mesh), PPh3, Ph3P=Se, and Ph3P=S (Alrich) were dried under vacuum before use. PMe3 (Alrich) was used as a 1 M solution in toluene.

[(C5Me5)2Sm(THF)2](μ-Te).1 In a glovebox, addition of (C5Me5)2Sm(THF)2 (100 mg, 0.18 mmol) in 5 mL of THF to a slurry of Te (11 mg, 0.09 mmol) in 5 mL of THF caused a slow color change from dark purple to dark red. After 2 h, the solvent was removed to give a brown powder. Crystallization from benzene gave 1 as dark red crystals (91% yield, 85%), which contain one molecule of benzene per molecule of 1. The benzene is not readily removed by drying under high vacuum.

[(C5Me5)2Sm(THF)2](μ-Se).2 In a glovebox, addition of (C5Me5)2Sm(THF)2 (100 mg, 0.18 mmol) in 5 mL of THF to a slurry of Se (7 mg, 0.09 mmol) in 5 mL of THF caused a slow color change to orange. After 20 min, the solvent was removed to give an orange powder. Crystallization from toluene at −35 °C gave 2 as orange crystals (87 mg, 85%), which contain one molecule of toluene per molecule of 2. The toluene is not readily removed by drying under high vacuum. However, by dissolving the crystalline material in THF and evaporating the solvent, we obtained 2 solvent-free. Anal. Calc'd for C51H54O5SeS: C, 40.76; H, 5.29; Sm, 29.52. Found: C, 40.76; H, 5.29; Sm, 29.52. 1H NMR (CD2Cl2, 25 °C): δ 1.42 (s, 60 H, C6Me5), −1.00 (br, 8 H, THF), −1.40 (br, 8 H, THF).

[(C5Me5)2Sm(THF)2](μ-S).3 In a glovebox, addition of (C5Me5)2Sm(THF)2 (100 mg, 0.09 mmol) in 5 mL of THF to a solution of Ph3P=S (26 mg, 0.09 mmol) in 5 mL of THF caused a slow color change to yellow. After 20 min, the solvent was removed to give a yellow powder, which was washed twice with 5 mL of hexanes. Crystallization from hot hexane gave 3 as yellow crystals (59 mg, 65%). Single crystals were obtained from toluene at −35 °C. Anal. Calc'd for C51H54O5SeS: C, 48.76; H, 5.99; Sm, 28.25. Found: C, 48.76; H, 5.99; Sm, 28.25. 1H NMR (CD2Cl2, 25 °C): δ 1.42 (s, 60 H, C6Me5), −1.00 (br, 8 H, THF), −1.40 (br, 8 H, THF).

[(C5Me5)2Sm(THF)2](μ-Ts).4 In a glovebox, addition of (C5Me5)2Sm(THF)2 (100 mg, 0.18 mmol) in 5 mL of THF to a vigorously stirred slurry of excess Te in 5 mL of THF caused a slow color change to dark red. After 14 h, the reaction mixture was centrifuged and the solvent was removed to yield a black powder. Crystallization from toluene at −35 °C gave 4 as black crystals (105 mg, 80%), which contain two molecules of toluene per molecule of 4. The lattice toluene cannot be readily removed under high vacuum, but if the crystalline material is dissolved in toluene and the solvent is removed by rotary evaporation, a toluene-free powder is obtained. Anal. Calc'd for C51H54O5SmTe: C, 40.76; H, 5.29; Sm, 29.52. Found: C, 40.49; H, 5.13; Te, 29.30; Sm, 23.45. 1H NMR (CD2Cl2, 25 °C): δ 0.82 (s, 60 H, C6Me5), 1.01 (br, 4 H, THF), 1.73 (br, 4 H, THF).

[(C5Me5)2Sm(THF)2](μ-Te, μ-Se).5 In a glovebox, addition of (C5Me5)2Sm(THF)2 (100 mg, 0.18 mmol) in 5 mL of THF to a vigorously stirred slurry of excess Se in 5 mL of THF caused an instant color change to orange. After 20 min, the solvent was removed to give an orange powder. Crystallization from toluene at −35 °C gave 5 as dark red crystals (83 mg, 70%), which contain two molecules of toluene per molecule 5. The lattice toluene cannot be readily removed under high vacuum, but if the crystalline material is dissolved in toluene and the solvent is removed by rotary evaporation, a toluene-free powder is obtained. As in the synthesis of 4, side products are formed in this reaction. In this case, several small resonances are observed in the 1H NMR spectrum at δ 0.51, 2.14, 1.18, 1.66, 1.76, and 1.96 ppm, and these impurities are not easily removed by crystallization. In fact, the impurities often are found to be more prevalent in the material which is crystallized. Analytical data on the...
Analytical data on the bulk reaction mixture showed that too little sulfur was added and the reaction mixture was centrifuged to remove excess selenol. Reaction times of several hours in a glovebox caused an instant color change to dark red. After 14 h, the reaction mixture was centrifuged to remove the primary product and [CuH78OSe3Sm2] as orange crystals in 5 mL of THF caused a slow color change to dark red. This phosphine-containing material is not stable in solution at ambient temperature. Single crystals of [CuH78OSe3Sm2] were obtained. Anal. Calcd for C48H176OSe3Sm2: C, 52.18; H, 6.32; Se, 16.8; Sm, 29.5.

**Table 1. Crystallographic Data on the Monochalcogenides**

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* Radiation for all structures was Mo Kα; λ = 0.710 730 Å.

**Table 2. Crystallographic Data on the Polychalcogenides**

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<td>GOF</td>
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* Radiation for all structures was Mo Kα; λ = 0.710 730 Å.

Factors for neutral atoms were used throughout the analysis\(^{23}\) both the real (d(F)) and imaginary (i(F)) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was \(\Sigma[w(Fo^2-Fc^2)]\) where \(w^2\) is defined below. The structures were refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with \(d(C-H) = 0.96\ Å\) and \(U iso = 0.08 Å^2\) except where noted.

\[(CuH78OSe3Sm2)[Te(C7H5)](1)\] and \([(CuH78OSe3Sm2)[Se(C7H5)](2)\] were obtained from the crystalline material after a 2-week period in benzene.

**General Aspects of X-ray Data Collection, Structure Determination, and Refinement for 1-3, 5, 7, and 8.** In each case a crystal was immersed in Paratone-D oil (Exxon lube oil additive) under nitrogen and then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex P2 or a Siemens P3 diffractometer (Siemens R3m/V System) which is equipped with a modified LT-1 or LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out using standard techniques similar to those of Churchill.\(^{20,21}\) Details are given in Tables 1 and 2. All data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. All crystallographic calculations were carried out using either our locally modified version of the UCLLA Crystallographic Computing Package\(^{22}\) or the SHELXTL program set.\(^{23}\) The analytical scattering

(21) UCLLA Crystallographic Computing Package; University of California: Los Angeles, CA, 1981. Strouse, C. Personal communication.
Variables (anisotropic Sm and Se) refined against those 5855 data with
systematic absences consistent with space group P2\_1/c
[C\_2\_\bar{1} No. 14]. For least-squares analysis, \( w^{-1} = \sigma^2(F_0^2) + 0.00013 \)
the structure was solved by direct methods (SHELXTL). There
is a molecule of toluene present in the asymmetric unit. Refinement
of positional and thermal parameters led to convergence with \( R_F = 4.3\% 
\), \( R_w = 5.1\% 
\), and GOF = 1.14 for 541 variables refined against those
5682 data with \( |F_o| > 3.0 |\sigma(F_o)| \). A final difference-Fourier synthesis yielded
\( \sigma_{(max)} = 0.62 \text{ e}^{-3} \).

\( ([\text{CMe}_5\text{Sm}]_2\text{Sm(THF)}_2)_{10}^{-1} \text{(µ-S)}_3 \). A total of 13 309 data were collected
on a yellow crystal of approximate dimensions 0.50 × 0.50 × 0.50 mm
at 168 K. Systematic absences were consistent with space group P2\_1/c
[C\_2\_\bar{1} No. 14]. For least-squares analysis, \( w^{-1} = \sigma^2(F_0^2) + 0.00003 \)
\( |F_o| > 3.0 |\sigma(F_o)| \). A final difference-Fourier synthesis yielded
\( \sigma_{(max)} = 0.70 \text{ e}^{-3} \).

Results

Synthesis. The divalent organosamarium complex (C\_2\_Me\_5\text{Sm})
- Sm(THF), reacts readily with Te, Se, P\_Ph\_3, and P\_Ph\_3=S in hexanes, toluene, and THF to form trivalent organometallic
products. In general, the rate of reaction of the chalcogenides is
S > Se > Te. These reactions generate several different series of
congeneric sulfur, selenium, and tellurium products depending
on the stoichiometry, reaction time, and absence or presence of
THF. We report here on the THF solvates, (C\_2\_Me\_5\text{Sm(THF)}_2)_2(µ-E), 1-3,
and (C\_2\_Me\_5\text{Sm})_2(E)_2(THF), 4-6 (E =
Te, Se, S), which are the main products most readily obtained
in good yield and purity from (C\_2\_Me\_5\text{Sm(THF)}_2). We also describe the
(E\_3\_S\_3)-complex (C\_2\_Me\_5\text{Sm})_2(S)[µ-\text{µ-µ}-\text{Te}]
for which analogous sulfur and selenium complexes have not been isolated.
It is likely from the side products observed in these reactions that other series of products also are formed in these systems, but
they have not been pursued at this time.

(2(C\_5\_Me\_3\text{Sm(THF)}_2) + (1/x)E) \rightarrow
\text{(C\_5\_Me\_3\text{Sm(THF)}_2)(µ-E)}_2
\text{(µ-Se)}_2, 2, and (C\_5\_Me\_3\text{Sm(THF)}_2)(µ-Se) \text{Te}, 1.

in THF as shown in eq 2, and this is the best way to make the
2(C\_5\_Me\_3\text{Sm(THF)}_2) + \text{Ph}_3\text{P}= \text{E} \rightarrow
\text{(C\_5\_Me\_3\text{Sm(THF)}_2)(µ-E) + \text{Ph}_3\text{P}(2)} \text{E = Se; 3, E = S}
sulfur analog ([C\_5\_Me\_3\text{Sm(THF)}_2](µ-S)) \text{3}. Equation 2 requires
an extra separation step (a wash) to remove the P\_Ph\_3 byproduct,
but it is a more effective method to get exact stoichiometries in
small scale reactions since the molecular weight of the chalcogenide
reagent is much higher. If the stoichiometries are not
exact such that an excess of the chalcogenide is present, formation of
the trichalcogenide dianion complexes ([C\_5\_Me\_3\text{Sm}]_2(E\_2))-
(THF)_2, 4-6 (see below) can occur. This is most often a problem in
the sulfur and selenium reactions since these take place most rapidly.
The tellurium reaction is slow enough that, even in the
presence of excess tellurium, I can be isolated free of 4 by
conducting the reaction for less than 20 min.

The products 1-3 were characterized by NMR and IR
spectroscopy and elemental analysis and were identified by X-ray
crystallography. Complexes 2 and 3 (Figures 1 and 2) are
isomorphous, and the X-ray crystal structure of 1 differs only in

\( \text{Figure 1. Thermal ellipsoid plot for } ([\text{CMe}_5\text{Sm(THF)}_2]\text{(µ-S)}_3, 3, drawn
at the 50% probability level with numbering identical with that for } ([\text{CMe}_5-
\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 2, and ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 1.

\text{Figure 2. Thermal ellipsoid plot for } ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 2,
and ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 1.

\text{Figure 3. Thermal ellipsoid plot for } ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 2,
and ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 1.

\text{Figure 4. Thermal ellipsoid plot for } ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 2,
and ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 1.

\text{Figure 5. Thermal ellipsoid plot for } ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 2,
and ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 1.

\text{Figure 6. Thermal ellipsoid plot for } ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 2,
and ([\text{CMe}_5\text{Sm(THF)}_2]_{10}^{-1}(\text{µ-Se})_2, 1.
that it has benzene in the lattice instead of toluene. The \(^1\)H NMR shifts of 1–3, \(\delta 1.45, 1.44,\) and 1.42, respectively, are remarkably similar to the \(\delta 1.41\) ppm shift of the oxide analog \([(C_5Me_5)_2Sm(THF)]_2(\mu-O))\). 9,25 This shift is significantly different from the \(\delta 0.06\) ppm shift of the unsolvated oxide, \([(C_5Me_5)_2Sm]\)(\(\mu-O))\).11 The colors of 1–3 change from red to orange to yellow, respectively, and the lowest molecular weight member of the series, \([(C_5Me_5)_2Sm(THF)]_2(\mu-O))\), is bright yellow. Trivalent samarium complexes are typically yellow or orange, but a growing number of red species have been identified when ligands are present which can be involved in charge transfer with the metal center.3,7,8,26

\[
[(C_5Me_5)_2Sm(E_2)](THF), 4–6.
\]

The reaction of \((C_5Me_5)_2Sm(THF)_2\) with excess tellurium in THF for short time periods forms 1 as described above. However, after 1 h another product begins to appear in the NMR spectra of the reaction mixture, and after 14 h, \([(C_5Me_5)_2Sm]_2(Te_3)(THF), 4\), can be isolated in 80% yield as a black powder according to eq 3. The dark red

\[
2(C_5Me_5)_2Sm(THF)_2 + \text{ excess } E_x \rightarrow

[(C_5Me_5)_2Sm]_2(E_x)(THF) \tag{3}
\]

selenium analog 5 can be prepared similarly using excess selenium, but in this case the reaction requires only 20 min. To cleanly obtain the yellow sulfur analog \([(C_5Me_5)_2Sm]_2(\mu-S_3)(THF), 6\), a 3:2 S:Sm stoichiometry must be used and the reaction must be stopped immediately after the reagents have been mixed (eq 4). Longer reaction times in the Se and S reactions or the presence of excess sulfur give complicated mixtures of products.

\[
2(C_5Me_5)_2Sm(THF)_2 + \frac{3}{2} S_8 \rightarrow

[(C_5Me_5)_2Sm]_2(S_8)(THF) \tag{4}
\]

Complexes 4–6 were characterized by elemental analysis and NMR and IR spectroscopy, and 5 was definitively identified by X-ray crystallography (Figures 3 and 4). The \(^1\)H NMR spectra of the complexes initially isolated from reactions 3 and 4 indicated the presence of four THF molecules per formula unit. Drying these crude products under high vacuum overnight did not remove the THF. However, dissolving the complexes in toluene and removing the solvent gave analytically pure monosolvated 4–6.

As in the series 1–3, there is a progressive deepening of color as the chalcogenide group is descended. The \(^1\)H NMR shifts for 4–6 fall in a narrow \(\delta 0.67–0.82\) range in which the tellurium complex is most downfield and the sulfur complex most upfield.

Neither the \(^1\)H NMR nor the \(^{13}\)C NMR spectra of 4–6 show the asymmetry observed in the solid state. The NMR spectrum of the triselenide 5 was examined at low temperature (–40 °C) and showed broadening of the \(C_5Me_5\) signal, but resolution into two peaks was not achieved. No \(^{77}\)Se NMR signal was observed for 5, presumably due to the paramagnetism of the Sm\(^{3+}\) centers.27

Interconversion of 4–6 with 1–3. Complexes 4 and 5 can be generated in THF from 1 and 2 by adding an excess of Te or 2 equiv of Se, respectively, as shown in eq 5. Interestingly, the

\[
[(C_5Me_5)_2Sm(THF)]_2(\mu-E) + (2/x)E_x \rightarrow

1, E = Te; 2, E = Se
\]

formation of 4 from 1 or from \((C_5Me_5)_2Sm(THF)_2\) with excess tellurium proceeds only in THF, but not in toluene. In toluene, the \((C_5Me_5)_2Sm(THF)_2\)/excess Te reaction stops at the monosolvate 1. The sulfur analog of reaction 5, i.e., a reaction starting with 3, produces such a complicated product mixture that this is not a useful route to 6.

Conversion of 5 and 6 to 2 and 3 can be accomplished in high yield by addition of two equiv of PPh\(_3\) to the trichalcogenides (eq 6). In this case, the analogous tellurium reaction failed, perhaps

\[
[(C_5Me_5)_2Sm(THF)]_2(\mu-E) + 2PPh_3 \rightarrow

5, E = Se; 6, E = S
\]

since formation of "Te=PPh\(_3\)" is less favored. Since Te=PMMe\(_3\) is known, the more reactive PMMe\(_3\) was substituted for PPh\(_3\) in the

teuor version of reaction 6 with the result described in the next section.

**Synthesis of [(C5Mes)2Sm]2(μ-η5:η4:η3:Te5).** Addition of PMe3 to [(C5Mes)2Sm]2(Te5) (THF) causes a major change in the NMR spectrum of 4. The initially formed product contains phosphine resonances in the NMR, but is too unstable in solution to definitively characterize. Attempts at crystalizing this initial product produced crystals of the phosphine-free complex [(C5Mes)2Sm]2(μ-η5:η4:η3:Te5), 8, according to eq 7. Complex 8 was identified by X-ray crystallography, Figure 5.

\[
\begin{align*}
[(C5Mes)2Sm]2(THF) + PMe3 \rightarrow & \ 
[(C5Mes)2Sm]2(\mu-\eta^5:\eta^4:\eta^3:Te^5) + Me_3P=Te \\
8
\end{align*}
\]

**Mixed Chalcogenides, [(C5Mes)2Sm]2(E=E′)2(THF) (a + b = 3).** Equation 5 presents the opportunity to form mixed chalcogenide complexes by adding 2 equiv of E′ to a [(C5Mes)2Sm](THF)]2(μ-E) complex. Not every permutation of this reaction is successful, however, due to the difference in reactivities of the chalcogenides. Highly reactive sulfur completely replaces the elemental tellurium and the monosulfide, 3, mixed with a small amount of the trisulfide, 6, (eq 8). Relatively unreactive Te does

\[
\begin{align*}
[(C5Mes)2Sm(THF)]2(\mu-Te) + S_2 \rightarrow & \ 
1 \\
\frac{1}{2}Te_2 + [(C5Mes)2Sm]2(S_2)(THF) + & \ 
6 \\
[(C5Mes)2Sm(THF)]2(\mu-S) \ (8)
\end{align*}
\]

not react with either 2 or 3. However, addition of intermediate Se with the less reactive Te complex 2 forms a mixed chalcogenide complex, [(C5Mes)2Sm]2(Se2Te5) (THF) 7, which retains some tellurium according to eq 9. Unfortunately, formation of 7 is accompanied by formation of other products as well as some elemental tellurium. The NMR data and mass balance are consistent with the formation of some [(C5Mes)2Sm(THF)]2(μ-Se) and [(C5Mes)2Sm]2(Se2Te5) (THF), but the NMR spectrum of these species are too similar to those of the related tellurium and mixed chalcogenide analogs to be definitive. Complex 7 was identified by X-ray crystallography as a trichalcogenide isostructural with 5, but disorder in the positions of the chalcogenides prevented a definitive assignment of a and b from the crystallographic data. Indeed, the single crystal may contain a mixture of trichalcogenide complexes. 28 Displacement of one chalcogen for another is well established in group 16 chemistry, 29 and disorder in mixed chalcogenide complexes was previously observed in the (C5H5)2TiSe2S2 system. 30

**Structure. [(C5Mes)2Sm(THF)]2(μ-E), 1–3.** Complexes 2 and 3 are isostructural and differ from 1 only in that 1 has benzene in the lattice instead of toluene. The numbering shown in Figure 1 for 3 is the same as for 2 and 1, and Table 3 shows how the metrical parameters for these complexes compare. The formally eight-coordinate local environment around each samarium atom is typical for trivalent (C5Mes)2Sm complexes. The (ring centroid)–Sm–(ring centroid) angles, the average Sm–C(C5Mes) distances, and the Sm–O(THF) distances are all in the normal range. 31

The Sm–E distances follow a progresson consistent with the differences in the radii of the chalcogenes. Hence, using averages, the Sm–Te distance in 1 is 0.20 Å larger than the Sm–Se distance in 2 which is in turn 0.12 Å larger than the Sm–S distance in 3. In comparison according to Shannon, 32 Te2+ is 0.23 Å larger than Se2+, which is 0.14 Å larger than S2-.

The data on 2 also match those found in [(C5Mes)2Yb]2(μ-Se), 32 eight-coordinate Sm(III) is 0.154 Å larger than seven-coordinate Yb(III), 32 the Sm–C(C5Mes) average is 0.16 Å larger, and the Sm–Se distance is 0.159 Å larger. However, comparisons with the oxide complex, [(C5Mes)2Sm]2(μ-O), 11 do not match as well. The 0.57-Å difference between the Sm–S bond distance in 3 and the 2.094(1)-Å Sm–O distance in [(C5Mes)2Sm]2(μ-O) 11 does not match the 0.44-Å difference in S2- and O2- radii even after the 0.059-Å difference in Sm(III) radii for 7- and 8-coordination is taken into account. The Sm–O distance in [(C5Mes)2Sm]2(μ-O) was considered to be unusually short when it was first reported and the data in this paper continue to support this assessment.

The Sm–E distances in 1–3 can also be compared with the Sm–E distances in (C5Mes)2Sm(TeCsH2Me3-2,4,6)2 (3.086(2) Å), (C5Mes)2Sm(THF)(SeCsH2(CF3))2 and (C5Mes)2Sm(μ-Se)2(THF) (2.808(2) Å). The Sm–E distances in 1–3 are shorter compared to these other distances although in each case trivalent, eight coordinate (C5Mes)2Sm complexes are involved. Similarly, the Sm–E distances in 1–3 are shorter than those expected to be compared to metal chalcogenide distances in eight-coordinate (C5Mes)2Yb(S2CNEt3)2 (2.70(1) Å), 34 in eight-coordinate (C5Mes)2Yb(S2CNEt3)2(μ-Se) (2.716(3) Å), 35 in eight-coordinate (C5Mes)2Yb(S2)2PH(S)(NH2)2 (2.675(5) Å), 36 in eight-coordinate (C5Mes)2Yb(THF)2(NH2)2.
Table 4. Selected Bond Distances (Å) and Angles (deg) for [(CsMes)2Sm]2[(μ-η2-p3-Se)2] (THF), 5

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm(1)-Se(1)</td>
<td>3.007(1)</td>
</tr>
<tr>
<td>Sm(2)-O(1)</td>
<td>2.456(6)</td>
</tr>
<tr>
<td>Sm(1)-Se(2)</td>
<td>3.198(1)</td>
</tr>
<tr>
<td>Sm(1)-C(THF)</td>
<td>2.73(2)</td>
</tr>
<tr>
<td>Se(1)-Sm(1)-Se(2)</td>
<td>44.9(1)</td>
</tr>
<tr>
<td>Se(2)-Sm(1)-Cnt(3)</td>
<td>106.2</td>
</tr>
<tr>
<td>Se(1)-Sm(1)-Cnt(1)</td>
<td>101.6</td>
</tr>
<tr>
<td>Se(1)-Sm(1)-Cnt(2)</td>
<td>96.2</td>
</tr>
<tr>
<td>Se(3)-Sm(1)-Cnt(2)</td>
<td>111.0</td>
</tr>
<tr>
<td>Cnt(1)-Sm(1)-Cnt(3)</td>
<td>133.2</td>
</tr>
<tr>
<td>Sm(1)-Se(2)-O(1)</td>
<td>96.9(1)</td>
</tr>
<tr>
<td>Sm(1)-Se(2)-Cnt(3)</td>
<td>100.5</td>
</tr>
<tr>
<td>Se(1)-Sm(2)-Cnt(4)</td>
<td>110.3</td>
</tr>
<tr>
<td>Cnt(2)-Sm(2)-Cnt(4)</td>
<td>134.4</td>
</tr>
<tr>
<td>Sm(2)-Se(2)-Se(3)</td>
<td>103.2(1)</td>
</tr>
<tr>
<td>Sm(1)-Se(3)-Se(3)</td>
<td>64.1(4)</td>
</tr>
<tr>
<td>Sm(1)-Se(3)-Se(3)</td>
<td>71.7(2)</td>
</tr>
</tbody>
</table>

(3.039(1) Å), in seven-coordinate La[TeSi(SiMe3)3]2(dmpe)2(3.16(1) Å), and in five-coordinate Ce7Te6[Te2(SiMe3)3]5(3.026(3) Å), although the latter two structures are sufficiently different from 1-3 to make direct comparison more difficult.

There has been considerable interest in the Ln-E-Ln angles in f-element complexes containing bridging chalcogen atoms along with conjecture about how the linearity relates to π bonding and steric demands. The closest samarium analog to 1-3 is [Sm2Se4]4- which has a precisely linear Sm-Se-Se angle. In comparison, the solvated cerium oxide [Ce2Se4]2+(THF)- has a Ce-O-Ce angle of 175.9(2)°. In the actinide sulfide complex [C2H2N2O5]2(μ-O)3, a M-E-M angle of 164.9(4)° was observed.

The 169.7(1)-170.2(5)° Ln-E-Ln angles in 1-3 are not as linear as the lanthanide oxides just described and match the 171.09(6)° O angle in [(CsMes)2Yb]2(p-Se). Interestingly, the Sm-Se distances in 5 are much longer than the 2.782(1)- and 2.779(1) Å distances in 2. The Sm(2)-Se(1) distance, which should be most similar since it is similarly coordinated, is 2.963(1) Å. Such a long Sm-(μ-E) distance might be expected to generate a shorter distance on the other side of the bridge, but the Sm(1)-Se(1) distance is also long, 3.007(1) Å. The other Sm(1)-Se distances are also in this range, 3.198(1) Å for Se(2) and 3.265(1) Å for Se(3). Therefore, the Sm-Se(2) distance is less closely associated with the (CsMes)2Sm units in 5 compared to 2. The Sm-Se distances are even longer than the 2.919(1) Å distance in the sterically crowded complex [(CsMes)2Sm]2(THF)[Se2C6H4(CF3)2-2,4,6]33.

The Sm-Se(3) bond in 5 is a Se(3)-Sm distance of 2.377(1) Å, a Sm-Se(1) distance of 2.326(1) Å, and a Sm-Se(2) distance of 107.7(1)°. Both the Se-Se distances and the Se-Se angle are comparable to the 2.35(6)-2.383(7) Å-Se-Se single bond distances and 102-110° angles found in a variety of solid-state materials: K2Se4 (2.383(7) Å; 102.5° Se-Se-Se angle), Rb2Se4 (2.383(7) Å; 103.1(3)°), Cs2Se4 (2.35(1) Å; 103.6(5)°), and Ba2Se4 (2.40(5) Å; 103(3)°) as well as those in trigonal selenium4 (2.373(5) Å; 103.1(2)°), a selenium4 (2.34(2) Å) and amorphous selenium4 (2.33 Å). A Sm-Se(2) distance of a (Se3)2- anion in a molecular complex is the structure of [Ni2Se6(S4C2)4(S4C4)4] which contains (Se3)2- anions bridging two nickel atoms in the corner of a NiSe6 cube of tetrahedral symmetry.48 These (Se3)2- anions have Se-Se distances ranging from 2.231(9) to 2.343(6) Å (2.319(9) Å average) and Se-Se angles ranging from 101.9(2) to 105.0(3)° (103.9(3)° average).

The Sm-Se bond distances and 102-110° angles in 5 are similar in comparison to both [(CsMes)2Yb]2(μ-η2-p3-Se)2, 10,13 and [(CsMes)2Sm]2(μ-η2-p3-Se)2, 11,11 it is isoskeletal with neither. However, the three structures are all very similar as shown in Table 5. The two bent metallocenes in each complex are oriented as shown in Figure 5 such that the four pentamethylcyclopentadienyl ring centroids describe a square plane rather than a tetrahedron.46 The 2.773(1)- and 2.7686(1) Å-Se-Se distances in 8 and 10, respectively, are equivalent and are in the single bond range found in [Ni2(Me4C6H6P(SiMe3)3)4]2(μ-η2-p3-Se)2(THF).

| Table 5. Selected Bond Distances (Å) and Angles (deg) for [(CsMes)2Sm]2[(μ-η2-p3-Se)2]8, [(CsMes)2Yb]2[(μ-η2-p3-Se)2]10, and [(CsMes)2Sm]2[(μ-η2-p3-Se)2]11 |
|-----------------|-----------------|-----------------|
| Sm-E            | 3.213(1)        | 3.265(1)        |
| Sm-Cnt          | 2.773(1)        | 2.7686(1)       |
| Sm-Cnt          | 2.710(15)       | 2.72(2)         |
| Sm-Cnt          | 138.8           | 134.4           |
| Sm-Cnt          | 129.0(2)        | 129.6(1)        |
| Sm-Cnt          | 126.7(1)        | 126.7(1)        |
| Sm-Cnt          | 51.2(1)         | 50.2(4)         | 51.2(1)         | 51.6(1)         |


pleasantly surprising to find that the existence of elemental sulfur, whereas \((C_{5}Me_{5})_{2}S\) reacts with sulfur upon mixing at ambient temperature.

As expected, the samarium reactions are more facile and could form \((E^{2-})^{-}\)-containing species. The relative reactivity of \(S > Se > Te > Bi\) is also quite normal.

However, in contrast to the ytterbium species, \((C_{5}Me_{5})_{2}Yb\)(OEt)\(2\), the samarium complexes are isolated as mono-THF solvates, \((C_{5}Me_{5})_{2}Sm(THF)\)2, \((C_{5}Me_{5})_{2}Sm(TeF)\)2 readily oxidized by Te, Se, S, \(PPh_{3} = Se\), and \(PPh_{3} = S\) to form \((E^{2-})^{-}\)-containing species. This is consistent with the larger size of bismuth.

Given that the monochalcogenides, \((C_{5}Me_{5})_{2}Yb\)(OEt)\(2\), the samarium complexes are isolated as mono-THF solvates, \((C_{5}Me_{5})_{2}Sm(THF)\)2, \((C_{5}Me_{5})_{2}Sm(TeF)\)2 readily oxidized by Te, Se, S, \(PPh_{3} = Se\), and \(PPh_{3} = S\) to form \((E^{2-})^{-}\)-containing species. The relative reactivity of \(S > Se > Te > Bi\) is also quite normal.

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Discussion

As anticipated, the formation of organosamarium complexes containing the \(E^{2-}\) ion is facile. Consistent with the strong reduction potential of \(Sm(II)^{2+}\) and the previously reported chalcogen chemistry of the weaker reductant \((CsMe_{5})_{2}Yb(THF)\), stable, crystallographically-characterizable structures with a variety of different, but closely related coordination environments appear to be preferred in this organosamarium system. Hence, both synthetically and structurally, the \((C_{5}Me_{5})_{2}Sm\) moiety is flexible but somewhat selective in the manipulation of group 16 anionic species.

Conclusion

This study shows that the \((C_{5}Me_{5})_{2}Sm\) unit is capable of assembling polyatomic anions in groups other than group 15. Despite the tendency to form \(E^{2-}\)-anions with group 16 elements, polyatomic anions can be formed under the appropriate conditions. Although these reactions clearly can give a variety of products depending on reaction conditions, preferences for certain types of complexes exist and the \((E^{2-})^{-}\)-ions appear to be particularly favored in this organosamarium system. It is difficult to assess how much the coordination environment provided by \((C_{5}Me_{5})_{2}Sm\) units influences this preference until a wider range of complexes is available. However, the facile interconversions of the mono- and trichalcogenides indicates that the special properties of the organosamarium moieties should provide new ways for controlled manipulation of group 16 anions.

Acknowledgment. We thank the National Science Foundation for support for this research and the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie, Germany, for the award of a Liebig fellowship (to G.W.R.).

Supplementary Material Available. Text detailing the crystal structure determination, tables of crystal data, positional parameters, bond distances and angles, and thermal parameters, and ORTEP drawings of 1-3, 5, 7, and 8 (105 pages). Ordering information is given on any current masthead page.