

Utility of Organosamarium(II) Reagents in the Formation of Polyatomic Group 16 Element Anions: Synthesis and Structure of $[(C_5Me_5)_2Sm]_2(E_3)(THF)$, $[(C_5Me_5)_2Sm(THF)]_2(E)$, and Related Species ($E = S, Se, Te$)¹

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$(C_5Me_5)_2Sm(THF)_2$ reacts with Te and Se in a 2:1 ratio at room temperature in THF to form $[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, **1**, and $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$, **2**, respectively. $(C_5Me_5)_2Sm(THF)_2$ reacts with $Ph_3P=S$ and $Ph_3P=S$ in a 2:1 ratio at room temperature in THF to form **2** and $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$, **3**, respectively. $(C_5Me_5)_2Sm(THF)_2$ reacts with excess Te and Se at room temperature in THF to form $[(C_5Me_5)_2Sm]_2(Se_3)(THF)$, **4**, and $[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_3)(THF)$, **5**. The sulfur analog, $[(C_5Me_5)_2Sm]_2(S_3)(THF)$, **6**, can be prepared from $(C_5Me_5)_2Sm(THF)_2$ and S_8 in a 2:3 ratio. Triselenide **5** can also be prepared from monoselenide **2** and 2 equiv of Se and monotelluride **1** reacts with excess Te to form telluride **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 Te. The trichalcogenides **5** and **6** can be converted back to the monochalcogenides **2** and **3**, respectively, with 2 equiv of PPh_3 . **4** reacts with PMe_3 in THF to form $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-Te_2)$, **8**. X-ray crystallographic studies revealed that **2** and **3** are isostructural and differ from **1** only in that **1** has benzene in the lattice instead of toluene. In each complex, a bent metallocene moiety is attached to one THF ligand and a bridging E group. The Sm–E distances are 2.988(2)/2.987(2) (Te), 2.782(1)/2.779(1) (Se), and 2.663(1)/2.665(1) Å (S) and the Sm–E–Sm angles are 170.2(1) (Te), 169.7(1) (Se), and 170.0(1) (S). The $(Se-Se-Se)^{2-}$ unit in $[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_3)(THF)$, **5**, contains Se–Se distances of 2.377(1) Å and 2.326(1) Å with an angle of 107.7(1)°. The samarium of one of the bent metallocene units in **5** is attached to THF and a bridging selenium atom with a Sm–Se(1) distance of 2.963(1) Å. The other $(C_5Me_5)_2Sm$ unit is 3.007(1) Å from Se(1) and 3.198(1) and 2.917(1) Å, respectively, from Se(2) and Se(3), which are sequentially connected to Se(1). The plane of three selenium atoms forms an angle of 57.9° with the $Sm_2Se(1)$ plane. A mixed Se/Te complex, **7**, was isolated from the reaction of **1** with Se. **7** is analogous to and isostructural with **5** and contains some Te distributed over at least two of the three chalcogen sites in the molecule. In **8**, two bent metallocene units are side on coordinated to a Te_2 unit with a 2.773(1) Å Te–Te bond such that the four C_5Me_5 rings define a square plane. **1** crystallizes from benzene in space group $P2_1/c$ [C_{2h}^5 ; No. 14] with unit cell parameters at 173 K of $a = 10.832(2)$ Å, $b = 15.140(3)$ Å, $c = 32.330(7)$ Å, $\beta = 95.753(16)^\circ$, and $V = 5276(2)$ Å³ with $Z = 4$ for $D_{calcd} = 1.50$ g cm⁻³. Least-squares refinement of the model based on 4479 observed reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final $R_F = 6.0\%$. **2** crystallizes from toluene in space group $P2_1/c$ [C_{2h}^5 ; No. 14] with unit cell parameters at 168 K of $a = 10.8717(13)$ Å, $b = 14.971(2)$ Å, $c = 32.856(5)$ Å, $\beta = 96.055(11)^\circ$, and $V = 5317.8(12)$ Å³ with $Z = 4$ for $D_{calcd} = 1.445$ g cm⁻³. Least-squares refinement of the model based on 5682 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 4.3\%$. **3** crystallizes from toluene in space group $P2_1/c$ [C_{2h}^5 ; No. 14] with unit cell parameters at 168 K of $a = 10.874(4)$ Å, $b = 14.824(4)$ Å, $c = 32.880(11)$ Å, $\beta = 95.82(3)^\circ$, and $V = 5273(3)$ Å³ with $Z = 4$ for $D_{calcd} = 1.398$ g cm⁻³. Least-squares refinement of the model based on 10850 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 4.2\%$. **5** crystallizes from toluene in space group $P2_1/n$ [C_{2h}^5 ; No. 14] with unit cell parameters at 168 K of $a = 15.316(3)$ Å, $b = 16.355(2)$ Å, $c = 23.963(3)$ Å, $\beta = 97.641(11)^\circ$, and $V = 5949.0(13)$ Å³ with $Z = 4$ for $D_{calcd} = 1.542$ g cm⁻³. Least-squares refinement of the model based on 10330 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 6.9\%$. **7** crystallizes from toluene in space group $P2_1/n$ [C_{2h}^5 ; No. 14] with unit cell parameters at 158 K of $a = 15.297(3)$ Å, $b = 16.386(3)$ Å, $c = 24.016(4)$ Å, $\beta = 97.347(14)^\circ$, and $V = 5970.6(17)$ Å³ with $Z = 4$ for $D_{calcd} = 1.525$ g cm⁻³. Least-squares refinement of the model based on 5855 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 7.4\%$. **8** crystallizes from benzene in space group $P2_1/c$ [C_{2h}^5 ; No. 14] with unit cell parameters at 163 K of $a = 13.163(2)$ Å, $b = 10.644(2)$ Å, $c = 15.376(2)$ Å, $\beta = 114.19(11)^\circ$, and $V = 1965.1(5)$ Å³ with $Z = 2$ for $D_{calcd} = 1.854$ g cm⁻³. Least-squares refinement of the model based on 5268 observed reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 3.8\%$.

Introduction

The soluble organometallic Sm(II) complexes $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ generate a variety of unusual transformations with unsaturated organic substrates.^{2–7} Recent studies

of the reactivity of $(C_5Me_5)_2Sm$ with the main group compounds N_2 ,⁸ Ph_3Bi ,⁹ and $n-Bu_3Sb$,¹⁰ which led to complexes of the $(N_2)^{2-}$, $(Bi_2)^{2-}$, and $(Sb_3)^{2-}$ 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 $(C_5Me_5)_2Sm(THF)_2$ 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 E^{2-} complexes ($E = S, Se, Te$) would be expected to be quite stable. For example, the congeneric oxide complex, $[(C_5Me_5)_2Sm]_2(\mu-O)$,¹¹ is readily formed under a variety of conditions and is frequently observed as an end product in $(C_5Me_5)_2Sm$ -based reactions. One would expect that similar samarium complexes could exist for S, Se, and Te. In addition, the ytterbium complexes $[(C_5Me_5)_2Yb]_2(\mu-E)$ can be easily formed from the less reactive Yb(II) reagent $(C_5Me_5)_2Yb(OEt)_2$.¹² Formation of complexes of diatomic $(E_2)^{2-}$ ions are also conceivable in group 16, and the structure of $[(C_5Me_5)_2Yb]_2(\mu-\eta^2:\eta^2-Te_2)$ has been reported.¹³

We report here that organometallic $(E)^{2-}$ complexes can be readily made with $(C_5Me_5)_2Sm(THF)_2$, but that complexes of the polyatomic anions $(E_3)^{2-}$ can also be obtained using the proper conditions. The $(E)^{2-}$ and $(E_3)^{2-}$ complexes can be interconverted and this reaction chemistry can be used to make mixed element polyatomic anions. In addition, the $(E_3)^{2-}$ complexes can be converted to $(E_2)^{2-}$ species under the proper conditions. Complete crystallographic data have been obtained on the $(E)^{2-}$ series of $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$ 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 $(C_5Me_5)_2Sm(THF)_2$ ¹⁸ was prepared according to the literature. S (325 mesh), Se (325 mesh), Te (200 mesh), PPh_3 , $Ph_3P=Se$, and $Ph_3P=S$ (Aldrich) were dried under high vacuum before use. PMe_3 (Aldrich) was used as a 1 M solution in toluene.

$[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, 1. In a glovebox, addition of $(C_5Me_5)_2Sm(THF)_2$ (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 copper brown powder. Crystallization from benzene gave 1 as dark red crystals (91 mg, 85%), which contain one molecule of benzene per molecule of 1. The benzene is not readily removed by drying under high vacuum.

However, 1 can be obtained solvent-free by dissolving the crystalline material in THF and evaporating the solvent. Anal. Calcd for $C_{48}H_{76}O_2TeSm_2$: C, 51.77; H, 6.88; Te, 11.46; Sm, 27.01. Found: C, 51.52; H, 6.63; Te, 11.60; Sm, 27.30. ¹H NMR (C_6D_6 , 25 °C): δ 1.45 (s, 60 H, C_5Me_5), -0.81 (br, 8 H, THF), -1.30 (br, 8 H, THF). ¹³C NMR (C_6D_6 , 25 °C): δ 115.9 (C_5Me_5), 67.8 (THF), 22.5 (THF), 19.8 (C_5Me_5). IR (Nujol): 1169 w, 1063 w, 1031 m, 1025 s, 919 m, 875 s, 725 w, 669 m cm^{-1} . This complex as well as complexes 2-8 is soluble in toluene and THF, but only slightly soluble in hexane.

$[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$, 2. In a glovebox, addition of $(C_5Me_5)_2Sm(THF)_2$ (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. Calcd for $C_{48}H_{76}O_2SeSm_2$: C, 54.14; H, 7.19; Se, 7.41; Sm, 28.25. Found: C, 53.83; H, 6.96; Se, 7.60; Sm, 28.40. ¹H NMR (C_6D_6 , 25 °C): δ 1.44 (s, 60 H, C_5Me_5), -0.89 (br, 8 H, THF), -1.31 (br, 8 H, THF). ¹³C NMR (C_6D_6 , 25 °C): δ 115.7 (C_5Me_5), 66.4 (THF), 21.8 (THF), 19.4 (C_5Me_5). IR (Nujol): 1169 w, 1069 w, 1038 m, 1025 s, 919 m, 875 s, 725 m, 675 w cm^{-1} .

2 can also be prepared from $(C_5Me_5)_2Sm(THF)_2$ and $Ph_3P=Se$ in THF in 60% yield. However, the procedure above is experimentally more convenient, since it is not necessary to separate 2 from the Ph_3P which is formed during the reaction. 2 is also cleanly formed from 5 (see below) and 2 equiv of PPh_3 in THF.

$[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$, 3. In a glovebox, addition of $(C_5Me_5)_2Sm(THF)_2$ (100 mg, 0.09 mmol) in 5 mL of THF to a solution of $Ph_3P=S$ (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. Calcd for $C_{48}H_{76}O_2SSm_2$: C, 56.63; H, 7.52; S, 3.15; Sm, 29.55. Found: C, 56.30; H, 7.34; S, 3.28; Sm, 29.90. ¹H NMR (C_6D_6 , 25 °C): δ 1.42 (s, 60 H, C_5Me_5), -1.00 (br, 8 H, THF), -1.40 (br, 8 H, THF). ¹³C NMR (C_6D_6 , 25 °C): δ 115.5 (C_5Me_5), 66.3 (THF), 22.6 (THF), 19.1 (C_5Me_5). IR (Nujol): 1262 m, 1063 m, 1023 vs, 925 w, 919 w, 875 s, 800 m, 725 w, 669 m, 586 s cm^{-1} . 3 is also cleanly formed from 6 (see below) and 2 equiv of PPh_3 in THF.

$[(C_5Me_5)_2Sm]_2(THF)(Te_3)$, 4. In a glovebox, addition of $(C_5Me_5)_2Sm(THF)_2$ (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. Calcd for $C_{44}H_{68}OTe_3Sm_2$: C, 40.76; H, 5.29; Te, 29.52; Sm, 23.20. Found: C, 40.49; H, 5.13; Te, 29.30; Sm, 23.45. ¹H NMR (C_6D_6 , 25 °C): δ 0.82 (s, 60 H, C_5Me_5), 1.01 (br, 4 H, THF), 1.73 (br, 4 H, THF). ¹³C NMR (C_6D_6 , 25 °C): δ 117.6 (C_5Me_5), 69.1 (THF), 25.5 (THF), 19.9 (C_5Me_5). IR (Nujol): 1263 w, 1163 m, 1063 m, 1025 s, 950 w, 800 m, 725 s, 700 m, 681 w, 669 w cm^{-1} . Also formed in this reaction is a minor byproduct which has a ¹H NMR resonance at 1.18 ppm. This compound is removed at the crystallization step. 4 can also be prepared from 1 and excess Te in THF in 80% yield. However, the procedure above is experimentally more convenient.

$[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_3)(THF)$, 5. In a glovebox, addition of $(C_5Me_5)_2Sm(THF)_2$ (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 dark red. After 20 min, the reaction mixture was centrifuged and the solvent was removed to give an orange-brown powder. Crystallization from toluene at -35 °C gave 5 as dark red crystals (83 mg, 70%), which contain two molecules of toluene per molecule of 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 0.51, 1.01, 1.14, 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

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crude product follows. Anal. Calcd for $C_{44}H_{68}OSe_3Sm_2$: C, 45.93; H, 5.96; Se, 20.59; Sm, 26.14. Found: C, 45.86; H, 5.87; Se, 20.45; Sm, 25.90. Elemental analysis on the toluene-solvated crystals was also obtained. Anal. Calcd for $C_{38}H_{54}OSe_3Sm_2$: C, 52.18; H, 6.34; Se, 17.74; Sm, 22.53. Found: C, 51.85; H, 6.09; Se, 17.60; Sm, 22.20. 1H NMR (C_6D_6 , 25 °C): δ 0.67 (s, 60 H, C_5Me_5), 0.84 (br, 4 H, THF), 1.23 (br, 4 H, THF). ^{13}C NMR (C_6D_6 , 25 °C): δ 117.1 (C_5Me_5), 69.9 (THF), 24.2 (THF), 19.0 (C_5Me_5). IR (Nujol): 1256 w, 1150 w, 1069 s, 1013 s, 950 w, 913 m, 856 s, 800 m, 725 s, 694 w, 669 m cm^{-1} .

5 can also be prepared from 2 and 2 equiv of Se in THF in 70% yield.

$[(C_5Me_5)_2Sm]_2(S_3)(THF)$, 6. In a glovebox, addition of sulfur (8.5 mg, 0.27 mmol) in 5 mL of THF to a solution of $(C_5Me_5)_2Sm(THF)_2$ (100 mg, 0.18 mmol) in 5 mL of THF caused an instant color change to orange. The solvent was removed by rotary evaporation to give an orange powder. Crystallization from hot hexanes gave 6 as orange crystals (36 mg, 40%). Small amounts of side products in varying ratios were observed at 0.51, 1.01, 1.14, 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 crude product follows. Anal. Calcd for $C_{44}H_{68}OS_3Sm_2$: C, 52.33; H, 6.79; S, 9.52; Sm, 29.78. Found: C, 52.04; H, 6.53; S, 9.30; Sm, 30.10. 1H NMR (C_6D_6 , 25 °C): δ 0.67 (s, 60 H, C_5Me_5), 0.90 (br, 4 H, THF), 1.25 (br, 4 H, THF). ^{13}C NMR (C_6D_6 , 25 °C): δ 116.8 (C_5Me_5), 68.4 (THF), 25.2 (THF), 18.6 (C_5Me_5). IR (Nujol): 1263 m, 1156 w, 1081 m, 1063 m, 1019 s, 975 w, 950 w, 919 w, 869 s, 800 m, 731 vs, 694 s, 663 m cm^{-1} .

$[(C_5Me_5)_2Sm]_2(Se_2Te_2)(THF)$, 7 ($a + b = 3$). In a glovebox, addition of 1 (300 mg, 0.27 mmol) in 5 mL of THF to a vigorously stirred slurry of Se (43 mg, 0.54 mmol) in 5 mL of THF caused a slow color change to dark red. After 14 h, the reaction mixture was centrifuged to remove insoluble material and the solvent was removed to yield an orange powder. The NMR spectra of the reaction mixture showed one primary product (1H NMR (C_6D_6 , 25 °C): δ 0.67 (s, 60 H, C_5Me_5), 0.85 (br, 4 H, THF), 1.25 (br, 4 H, THF). ^{13}C NMR (C_6D_6 , 25 °C): δ 117.1 (C_5Me_5), 68.5 (THF), 25.3 (THF), 18.9 (C_5Me_5)), but 1H NMR shifts consistent with 1 or 2 were also observed. The similarity of the NMR spectra of the primary product and 5 made it impossible to exclude the presence of some 5. Analytical data on the bulk reaction mixture showed that too little Te was present for the sample to be pure $[(C_5Me_5)_2Sm]_2(Se_2Te)(THF)$. Hence, not only did Se add to 1 but it also replaced some of the Te. Crystallization from toluene at -35 °C gave crystals (92 mg) containing dark red 7 which was found to be isostructural with 5.

$[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-Te_2)$, 8. In a glovebox, addition of excess PMe_3 (1 mL of a 1.0 M solution in toluene) to a vigorously stirred solution of $[(C_5Me_5)_2Sm]_2(Se_3)(THF)$ (100 mg, 0.08 mmol) in 5 mL of THF caused an instant color change to darker red. The solvent was removed immediately to give a brown powder. Reaction times of several hours gave the same initially isolated product which exhibited the following NMR spectra: 1H NMR (C_6D_6 , 25 °C): δ 0.71 (s, C_5Me_5), 0.81 (s, C_5Me_5), 2.50 (d, PMe_3). ^{13}C NMR (C_6D_6 , 25 °C): δ 117.6 (C_5Me_5), 115.5 (C_5Me_5), 71.0 (THF), 24.8 (THF), 20.1 (C_5Me_5), 18.8 (C_5Me_5). ^{31}P NMR (C_6D_6 , 25 °C): δ 50.5. This phosphine-containing material is not stable in solution at ambient temperature. Single crystals of phosphine-free 8 were obtained from this 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 P2₁ 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 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 UCLA Crystallographic Computing Package²¹ or the SHELXTL program set.²² The analytical scattering

Table 1. Crystallographic Data on the Monochalcogenides $[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, 1, $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$, 2, and $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$, 3^a

	1	2	3
formula	$C_{48}H_{76}TeSm_2 \cdot C_6H_6$	$C_{48}H_{76}SeSm_2 \cdot C_7H_8$	$C_{48}H_{76}SSm_2 \cdot C_7H_8$
mol wt	1191.5	1156.9	1110.0
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ [C_{2h}^2 ; No. 14]	$P2_1/c$ [C_{2h}^2 ; No. 14]	$P2_1/c$ [C_{2h}^2 ; No. 14]
cell const			
a, Å	10.832(2)	10.8717(13)	10.874(4)
b, Å	15.140(3)	14.971(2)	14.824(4)
c, Å	32.330(7)	32.856(5)	32.880(11)
β , deg	95.753(16)	96.055(11)	95.82(3)
cell vol, Å ³	5276(2)	5371.8(12)	5273(3)
mol/unit cell	4	4	4
D_{calcd} , g cm ⁻³	1.50	1.445	1.398
temp, K	173	168	168
μ_{calcd} , mm ⁻¹	2.79	2.847	2.287
transm coeff, min-max	0.184–0.219	0.3598–0.4571	0.2043–0.2321
R_F , %	6.0	4.3	4.2
R_{wF} , %	6.8	5.1	4.8
GOF	1.49	1.14	1.82

^a Radiation for all structures was Mo K α ; $\lambda = 0.710730$ Å.

Table 2. Crystallographic Data on the Polychalcogenides $[(C_5Me_5)_2Sm]_2(\mu-\eta^1-\eta^2-Se_3)(THF)$, 5, and $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-Te_2)$, 8^a

	5	8
formula	$C_{44}H_{68}OSe_3Sm_2 \cdot 2.5(C_7H_8)$	$C_{40}H_{60}Te_2Sm_2$
mol wt	1380.9	1096.8
crystal syst	monoclinic	monoclinic
space group	$P2_1/n$ [C_{2h}^2 ; No. 14]	$P2_1/c$ [C_{2h}^2 ; No. 14]
cell const		
a, Å	15.316(3)	13.163(2)
b, Å	16.355(2)	10.644(2)
c, Å	23.963(3)	15.376(2)
β , deg	97.641(11)	114.191(11)
cell vol, Å ³	5949.0(13)	1965.1(5)
mol/unit cell	4	2
D_{calcd} , g cm ⁻³	1.542	1.854
temp, K	168	163
μ_{calcd} , mm ⁻¹	3.651	4.455
transm coeff, min-max	0.2244–1.0000	0.1992–0.9734
R_F , %	6.9	3.8
R_{wF} , %	6.9	5.2
GOF	1.74	1.71

^a Radiation for all structures was Mo K α ; $\lambda = 0.710730$ Å.

factors for neutral atoms were used throughout the analysis;²³ both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where w^{-1} 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 $U(iso) = 0.08$ Å² except where noted.

$[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, 1. A total of 7684 data were collected on a red/orange crystal of approximate dimensions $0.15 \times 0.20 \times 0.45$ mm at 173 K. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 ; No. 14] is therefore uniquely defined. For least-squares analysis, w^{-1} was $\sigma^2(|F_o|) + 0.0008(|F_o|)^2$. The structure was solved by direct methods (MITHRIL).²⁴ There is one molecule of benzene present in the asymmetric unit. Refinement of positional and thermal parameters led to convergence with $R_F = 6.0\%$, $R_{wF} = 6.8\%$, and $GOF = 1.49$ for 532 variables refined against those

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(21) *UCLA Crystallographic Computing Package*; University of California: Los Angeles, CA, 1981. Strouse, C. Personal communication.

(22) Sheldrick, G. M., Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1990.

(23) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands 1992; Vol. C.

(24) Gilmore, C. J. MITHRIL, A Computer Program for the Automated Solution of Crystal Structures from X-ray Data. University of Glasgow.

4479 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features; $\rho(\max) = 1.28 \text{ e } \text{Å}^{-3}$.

$[(C_5Me_5)_2Sm(THF)_2(\mu-Se)]_2$, 2. A total of 7743 data were collected on a pale gold crystal of approximate dimensions $0.13 \times 0.24 \times 0.33 \text{ mm}$ at 168 K. Systematic absences were consistent with space group $P2_1/c$ [C_{2h}^2 ; No. 14]. For least-squares analysis, w^{-1} was $\sigma^2(|F_o|) + 0.0010 \cdot (|F_o|)^2$. 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 $R_F = 4.3\%$, $R_{wF} = 5.1\%$, 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 $\rho(\max) = 0.62 \text{ e } \text{Å}^{-3}$.

$[(C_5Me_5)_2Sm(THF)_2(\mu-S)]_2$, 3. A total of 13 309 data were collected on a yellow crystal of approximate dimensions $0.50 \times 0.50 \times 0.50 \text{ mm}$ at 168 K. Systematic absences were consistent with space group $P2_1/c$ [C_{2h}^2 ; No. 14]. For least-squares analysis, w^{-1} was $\sigma^2(|F_o|) + 0.0003 \cdot (|F_o|)^2$. It was expected that the complex was isostructural with the Se analog. The atomic coordinates from the Se complex were used as the starting model for the present study. There is one molecule of toluene present in the asymmetric unit. Full-matrix least-squares refinement of positional and thermal parameters led to convergence with $R_F = 4.2\%$, $R_{wF} = 4.8\%$, and $GOF = 1.82$ for 541 variables refined against those 10 850 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis yielded $\rho(\max) = 0.70 \text{ e } \text{Å}^{-3}$.

$[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_3)(THF)$, 5. A total of 14 749 data were collected on a red crystal of approximate dimensions $0.37 \times 0.43 \times 0.50 \text{ mm}$ at 168 K. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ [C_{2h}^2 ; No. 14], is therefore uniquely defined. All crystallographic calculations were carried out as described above for 1. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0005 \cdot (|F_o|)^2$. The structure was solved by direct methods (SHELXTL). There are 2.5 molecules of toluene present in the asymmetric unit. The toluene molecule defined by atoms C(51)–C(57) was fixed as a rigid group during refinement because of disorder which could not be accurately modeled. The toluene molecule (C(71)–C(73)) is located about an inversion center (0, 0, 0). The methyl carbon was observed in a difference map but was disordered over several sites. This atom was not included in the refinement since no satisfactory disorder model could be determined. This toluene molecule exhibits high thermal motion and discrepancies in distances and angles. The hydrogen atoms associated with the above two toluene molecules were not included in the refinement. Refinement of positional and thermal parameters led to convergence with $R_F = 6.9\%$, $R_{wF} = 6.9\%$, and $GOF = 1.74$ for 542 variables refined against those 10 330 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis yielded $\rho(\max) = 3.95 \text{ e } \text{Å}^{-3}$ at a distance of 1.05 Å from Se(2).

$[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_2Te_1)(THF)$, 7. A total of 8197 data were collected on a dark red crystal of approximate dimensions $0.23 \times 0.33 \times 0.40 \text{ mm}$ at 158 K. The complex was isostructural with 5, and refinement of the model including treatment of the disordered toluene molecules was carried out as described for 5. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.003 \cdot (|F_o|)^2$. Several models involving disorder of Te over the three possible chalcogen positions were examined but were not found to be better than refinement with all of the chalcogens as Se. This refinement gives a structure with a Se(1)–Se(2) distance 0.08 Å longer than expected for a homogeneous system and equivalent isotropic temperature parameters for Se(1) and Se(2) (0.03 Å²) which are probably lower than expected (Se(3) has 0.049 Å²). At convergence $R_F = 7.4\%$, $R_{wF} = 7.6\%$, and $GOF = 2.39$ for 282 variables (anisotropic Sm and Se) refined against those 5855 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis yielded $\rho(\max) = 4.86 \text{ e } \text{Å}^{-3}$ at a distance of 1.04 Å from Se(2).

$[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-Te_2)$, 8. A total of 6271 data were collected on a dark red crystal of approximate dimensions $0.27 \times 0.42 \times 0.50 \text{ mm}$ at 163 K. Systematic absences were consistent with space group $P2_1/c$ [C_{2h}^2 ; No. 14]. For least-squares analysis w^{-1} was $\sigma^2(|F_o|) + 0.0005 \cdot (|F_o|)^2$. The structure was solved via an automatic Patterson routine (SHELXTL). The molecule is a dimer located on an inversion center at (0, 0, 0). Refinement of positional and thermal parameters led to convergence with $R_F = 3.8\%$, $R_{wF} = 5.2\%$, and $GOF = 1.71$ for 200 variables refined against those 5268 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis yielded $\rho(\max) = 2.75 \text{ e } \text{Å}^{-3}$ at a distance of 0.78 Å from Sm(1).

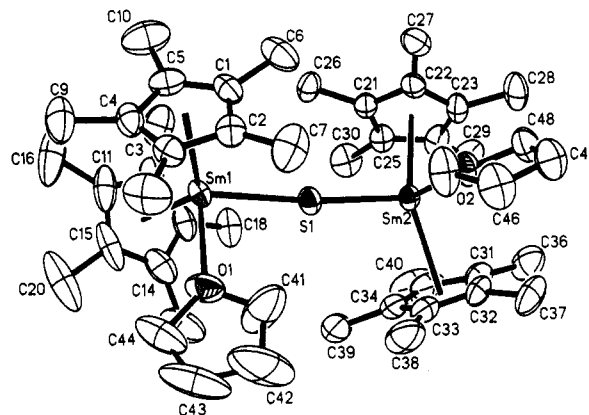
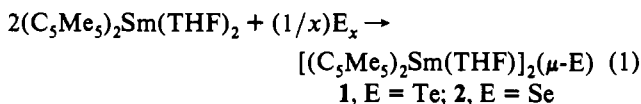


Figure 1. Thermal ellipsoid plot for $[(C_5Me_5)_2Sm(THF)_2(\mu-S)]_2$, 3, drawn at the 50% probability level with numbering identical with that for $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$, 2, and $[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, 1.

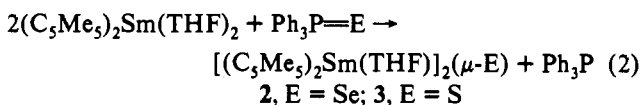
Results

Synthesis. The divalent organosamarium complex $(C_5Me_5)_2Sm(THF)_2$ reacts readily with Te, Se, S, $Ph_3P=Se$, and $Ph_3P=S$ 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, $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$, 1–3, and $[(C_5Me_5)_2Sm(E_3)(THF)]_2$, 4–6 (E = Te, Se, S), which are the main products most readily obtained in good yield and purity from $(C_5Me_5)_2Sm(THF)_2$. We also describe the $(E_2)^{2-}$ complex $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-Te_2)$ 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.

$[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$, 1–3. The reaction of 2 equiv of $(C_5Me_5)_2Sm(THF)_2$ with a slurry of 1 equiv of Te or Se generates the monochalcogenide complexes $[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, 1, and $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$, 2, in 65–85% yield according to eq 1. 2 can also be prepared from triphenylphosphine selenide



in THF as shown in eq 2, and this is the best way to make the



sulfur analog $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$, 3. Equation 2 requires an extra separation step (a wash) to remove the PPh_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 $[(C_5Me_5)_2Sm]_2(E_3)(THF)$, 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, 1 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 isostructural, and the X-ray crystal structure of 1 differs only in

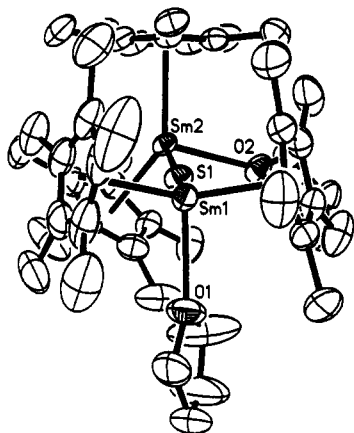
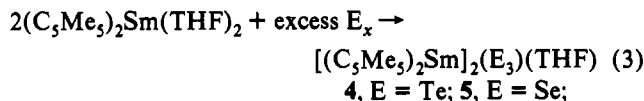


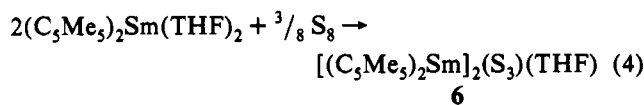
Figure 2. End view of $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$, 3.

that it has benzene in the lattice instead of toluene. The 1H NMR shifts of 1–3, δ 1.45, 1.44, and 1.42, respectively, are remarkably similar to the δ 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 δ 0.06 ppm shift of the unsolvated oxide, $[(C_5Me_5)_2Sm]_2(\mu-O)$.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}

$[(C_5Me_5)_2Sm]_2(E_3)(THF)$, 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, $[(C_5Me_5)_2Sm]_2(Se_3)(THF)$, 4, can be isolated in 80% yield as a black powder according to eq 3. The dark red



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.



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 1H 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 1H NMR shifts for 4–6 fall in a narrow δ 0.67–0.82 range in which the tellurium complex is most downfield and the sulfur complex most upfield.

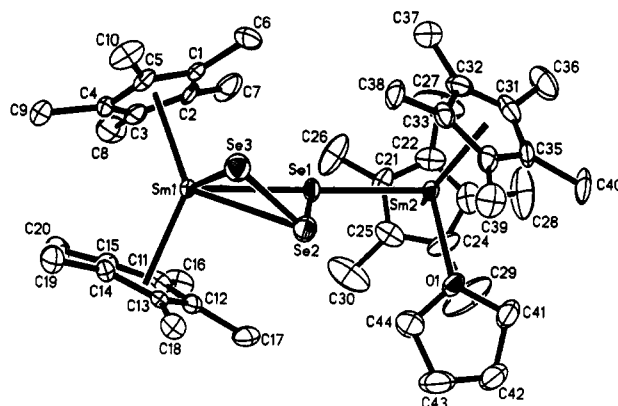


Figure 3. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_3)(THF)$, 5, drawn at the 50% probability level.

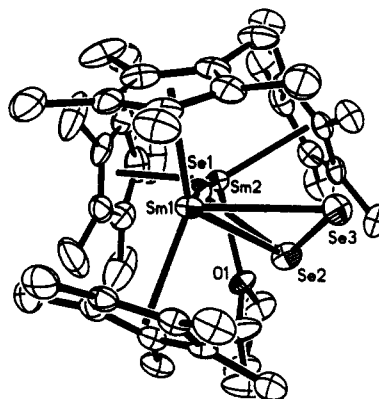
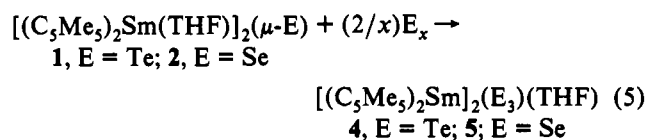


Figure 4. End view of $[(C_5Me_5)_2Sm]_2(\mu-\eta^1:\eta^3-Se_3)(THF)$, 5.

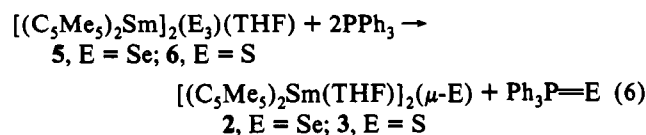
Neither the 1H NMR nor the ^{13}C NMR spectra of 4–6 show the asymmetry observed in the solid state. The NMR spectrum of the triselenide 5 was examined at low temperature ($-40^\circ C$) and showed broadening of the C_5Me_5 signal, but resolution into two peaks was not achieved. No ^{77}Se NMR signal 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



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 mono-telluride 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



since formation of " $Te=PPh_3$ " is less favored. Since $Te=PMe_3$ is known, the more reactive PMe_3 was substituted for PPh_3 in the

(25) Evans, W. J.; Gonzales, S. G. *J. Organomet. Chem.*, in press.
(26) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* 1993, 12, 2618–2633 and references therein. Recknagel, A.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* 1991, 410, 53–61.

(27) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* 1987, 326, 299–306.

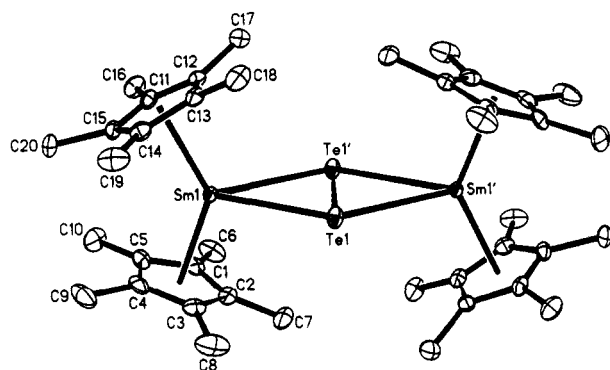
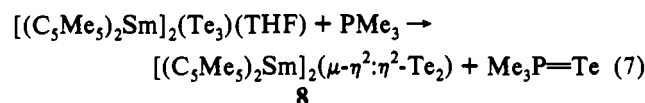


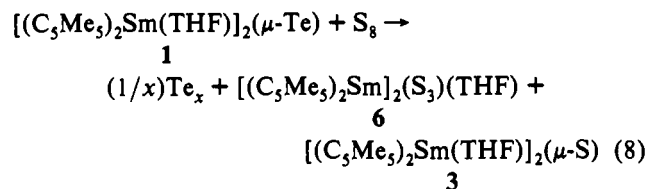
Figure 5. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-Te_2)$, **8**, drawn at the 50% probability level.

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

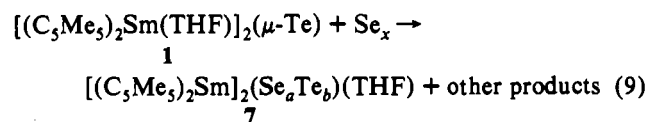
Synthesis of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-Te_2)$, **8.** Addition of PMe_3 to $[(C_5Me_5)_2Sm]_2(Te_3)(THF)$ causes a major change in the NMR spectrum of **4**. The initially formed product contains phosphine resonances in the NMR, but is too unstable in solution to definitively characterize. Attempts at crystallizing this initial product produced crystals of the phosphine-free complex $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-Te_2)$, **8**, according to eq 7. Complex **8** was identified by X-ray crystallography, Figure 5.



Mixed Chalcogenides, $[(C_5Me_5)_2Sm]_2(E_aE'_b)(THF)$ ($a + b = 3$). Equation 5 presents the opportunity to form mixed chalcogenide complexes by adding 2 equiv of E' to a $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$ 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 other chalcogens. Hence, the reaction of sulfur with **1** forms elemental tellurium and the monosulfide, **3**, mixed with a small amount of the trisulfide, **6** (eq 8). Relatively unreactive Te does



not react with either **2** or **3**. However, addition of intermediate Se with the less reactive Te complex **1** forms a mixed chalcogenide complex, $[(C_5Me_5)_2Sm]_2(Se_aTe_b)(THF)$, **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 $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$ and $[(C_5Me_5)_2Sm]_2(Se_3)(THF)$, 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

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(THF)]_2(\mu-Te)$, **1**, $[(C_5Me_5)_2Sm(THF)]_2(\mu-Se)$, **2**, and $[(C_5Me_5)_2Sm(THF)]_2(\mu-S)$, **3**

	1	2	3
Sm(1)–E(1)	2.998(2)	2.782(1)	2.663(1)
Sm(2)–E(1)	2.987(2)	2.779(1)	2.665(1)
Sm(1)–O(1)	2.475(9)	2.482(7)	2.498(4)
Sm(2)–O(2)	2.486(12)	2.473(5)	2.475(3)
Sm–C(C_5Me_5) (avg)	2.746(7)	2.755(4)	2.762(5)
Sm(1)–E(1)–Sm(2)	170.2(1)	169.7(1)	170.0(1)

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 $(C_5H_5)_2TiSe_xS_{5-x}$ system.³⁰

Structure. $[(C_5Me_5)_2Sm(THF)]_2(\mu-E)$, **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 $(C_5Me_5)_2Sm$ complexes. The (ring centroid)–Sm–(ring centroid) angles, the average Sm–C(C_5Me_5) distances, and the Sm–O(THF) distances are all in the normal range.³¹

The Sm–E distances follow a progression consistent with the differences in the radii of the chalcogens. 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 Te^{2-} is 0.23 Å larger than Se^{2-} , which is 0.14 Å larger than S^{2-} .

The data on **2** also match those found in $[(C_5Me_5)_2Yb]_2(\mu-Se)$:¹² eight-coordinate Sm(III) is 0.154 Å larger than seven-coordinate Yb(III),³² the Sm–C(C_5Me_5) average is 0.146 Å larger, and the Sm–Se distance is 0.159 Å larger. However, comparisons with the oxide complex, $[(C_5Me_5)_2Sm]_2(\mu-O)$,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 $[(C_5Me_5)_2Sm]_2(\mu-O)$ ¹¹ does not match the 0.44-Å difference in S^{2-} and O^{2-} 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 $[(C_5Me_5)_2Sm]_2(\mu-O)$ 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 $(C_5Me_5)_2Sm(THF)(TeC_6H_2Me_3-2,4,6)$ ³³ (3.088(2) Å), $(C_5Me_5)_2Sm(THF)[SeC_6H_2(CF_3)_3-2,4,6]$ ³³ (2.919(1) Å), and $(C_5Me_5)_2Sm(S_2CNMe_2)$ ³³ (2.808(2) Å). The Sm–E distances in **1–3** are short compared to these other distances although in each case trivalent, eight coordinate $(C_5Me_5)_2Sm$ complexes are involved. Similarly, the Sm–E distances in **1–3** are shorter than would be expected compared to metal chalcogen distances in eight-coordinate $(C_5Me_5)_2Yb(S_2CNEt_2)$ (2.70(1) Å),³⁴ in eight-coordinate $(C_5Me_5)_2Lu(\mu-SCMe_3)_2Li(THF)_2$ (2.716(3) Å),³⁵ in eight-coordinate $(C_5Me_5)_2Yb(SPh)(NH_3)$ (2.675(5) Å),³⁶ in eight-coordinate $(C_5Me_5)_2Yb(TePh)(NH_3)$

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Table 4. Selected Bond Distances (Å) and Angles (deg) for [(C₅Me₅)₂Sm]₂(μ-η¹:η³-Se₃)(THF), **5**

Sm(1)–Se(1)	3.007(1)	Sm(1)–Se(3)	2.917(1)
Sm(2)–O(1)	2.456(6)	Se(2)–Se(3)	2.326(1)
Sm(1)–Se(2)	3.198(1)	Se(1)–Se(2)	2.377(1)
Sm(1)–C(av)	2.73(2)	Sm(2)–C(av)	2.72(1)
Se(1)–Sm(1)–Se(2)	44.9(1)	Se(1)–Sm(1)–Se(3)	79.7(1)
Se(2)–Sm(1)–Se(3)	44.4(1)	Se(1)–Sm(1)–Cnt(1)	106.2
Se(2)–Sm(1)–Cnt(1)	130.3	Se(3)–Sm(1)–Cnt(1)	101.6
Se(1)–Sm(1)–Cnt(2)	111.7	Se(2)–Sm(1)–Cnt(2)	96.2
Se(3)–Sm(1)–Cnt(2)	111.0	Cnt(1)–Sm(1)–Cnt(2)	133.2
Se(1)–Sm(2)–O(1)	96.9(1)	Se(1)–Sm(2)–Cnt(3)	100.5
Se(1)–Sm(2)–Cnt(4)	110.3	O(1)–Sm(2)–Cnt(3)	103.6
O(1)–Sm(2)–Cnt(4)	105.1	Cnt(3)–Sm(2)–Cnt(4)	134.4
Sm(2)–Se(1)–Se(2)	103.2(1)	Sm(1)–Se(2)–Se(1)	63.3(1)
Sm(1)–Se(2)–Se(3)	61.4(1)	Se(1)–Se(2)–Se(3)	107.7(1)
Sm(1)–Se(3)–Se(2)	74.2(1)		

(3.039(1) Å),³⁷ in seven-coordinate La[TeSi(SiMe₃)₃]₃(dmpe)₂ (3.16(1) Å),¹⁵ and in five-coordinate Ce₅Te₃[TeSi(SiMe₃)₃]₉ (3.026(3) Å),¹⁵ 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 chalcogens along with conjecture about how the linearity relates to π bonding and steric demands.^{12,38} The closest samarium analog to 1–3 is [(C₅Me₅)₂Sm]₂(μ-O)¹¹ which has a precisely linear 180° Sm–E–Sm angle. In comparison, the solvated cerium oxide [(C₅Me₅)₂Ce(THF)]₂(μ-O)³⁹ has a Ce–O–Ce angle of 175.9(2)°. In the actinide sulfide complex [(C₅H₄Me)₃U]₂(μ-S),³⁸ 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)° angle in [(C₅Me₅)₂Yb]₂(μ-Se).¹² Interestingly, the Ln–E–Ln angles in 1–3 do not change as the chalcogen is varied. The (ring centroid)–Ln–(ring centroid) angles, which are usually sensitive to the steric bulk of the remaining ligands, are also very similar in this series. This suggests that steric factors in this set of structures are similar despite the difference in chalcogen. The linearity seen in [(C₅Me₅)₂Sm]₂(μ-O) may arise due to the necessity to arrange the four C₅Me₅ rings in a sterically efficient tetrahedral arrangement (which requires a 180° Sm–O–Sm angle). This preferred tetrahedral arrangement of four C₅Me₅ rings has been seen in a variety of bimetallic samarium complexes containing small bridging ligands,⁴⁰ e.g. [(C₅Me₅)₂Sm]₂(μ-N₂),⁸ [(C₅Me₅)₂Sm]₂(μ-H)₂,^{40b} and [(C₅Me₅)₂Sm]₂(μ-NHNH),^{40c} and as described above, the Sm–O bonds in that complex are rather short. In 1–3, the presence of THF on each (C₅Me₅)₂Sm moiety distorts the four C₅Me₅ rings from the tetrahedral arrangement as shown in the view down the Sm–Sm vector in Figure 2. The need for a linear Sm–E–Sm angle is not as great and the observed angles result.

[(C₅Me₅)₂Sm]₂(μ-η¹:η³-Se₃)(THF), **5**. As shown in Figures 3 and 4, complex **5** contains two distinct types of samarium atoms. Sm(1) is formally nine coordinate and Sm(2) is formally eight coordinate. Sm(2) has a local environment much like that of the samarium atoms in 1–3 and its 2.72(1)-Å Sm–C(C₅Me₅) average distance and 2.456(6)-Å Sm–O(THF) bond are very similar to those in the monoselenide **2**. Although of higher formal coordination number, Sm(1) has a comparable Sm–C(C₅Me₅) average distance, 2.73(2) Å. However, the Sm–Se distances in

Table 5. Selected Bond Distances (Å) and Angles (deg) for [(C₅Me₅)₂Sm]₂(μ-η²:η²-Te₂), **8**, [(C₅Me₅)₂Yb]₂(μ-η²:η²-Te₂), **10** and [(C₅Me₅)₂Sm]₂(μ-η²:η²-Bi₂), **11**

	8	10	11
Sm–E	3.213(1) 3.204(1)	3.1513(9) 3.1598(7)	3.265(1) 3.283(1) 3.291(1) 3.311(1)
E–E	2.773(1)	2.7686(11)	2.851(1)
Sm–C(av)	2.710(15)	2.626	2.72(2)
Cnt–Sm–Cnt	138.8	133.32	134.4
Sm–E–E	64.2(1) 64.6(1)	63.82(2) 64.14(2)	64.7(1) 64.9(1) 63.7(1) 63.9(1)
Sm–E–Sm	128.8(1)	127.96(2)	129.6(1) 127.6(1)
E–Sm–E	51.2(1)	52.04(2)	51.2(1) 51.6(1)

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 2.917(1) Å for Se(3). Therefore, the (Se₃)²⁻ ion appears to be less closely associated with the (C₅Me₅)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 (C₅Me₅)₂Sm(THF)[SeC₆H₂(CF₃)₃]-2,4,6].³³

The (Se₃)²⁻ ion in this complex has a Se(1)–Se(2) distance of 2.377(1) Å, a Se(2)–Se(3) distance of 2.326(1) Å, and a Se–Se–Se angle of 107.7(1)°. Both the Se–Se distances and the Se–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: K₂Se₃⁴¹ (2.383(2) Å; 102.5° Se–Se–Se angle), Rb₂Se₃⁴² (2.383(7) Å; 103.1(3)°), Cs₂Se₃⁴² (2.358(1) Å; 103.6(5)°), and BaSe₃⁴³ (2.40(5) Å; 110(3)°) as well as to those in trigonal selenium⁴⁴ (2.373(5) Å; 103.1(2)°), α-selenium⁴⁵ (2.34(2) Å) and amorphous selenium⁴⁶ (2.33 Å). A rare case⁴⁷ of a (Se₃)²⁻ anion in a molecular complex is the structure of [Ni₄Se₄(Se₃)₅(Se₄)]⁴⁻ which contains (Se₃)²⁻ anions bridging two nickel atoms in the corner of a Ni₄Se₄ 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–Se angles ranging from 101.9(2) to 105.0(3)° (103.9(3)° average).

[(C₅Me₅)₂Sm]₂(μ-η²:η²-Te₂), **8**. Although complex **8** is similar in composition to both [(C₅Me₅)₂Yb]₂(μ-η²:η²-Te₂), **10**,¹³ and [(C₅Me₅)₂Sm]₂(μ-η²:η²-Bi₂), **11**,⁹ it is isostructural 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.⁴⁰ The 2.773(1)- and 2.7686(11)-Å Te–Te distances in **8** and **10**, respectively, are equivalent and are in the single bond range found in {Ni[MeC(CH₂PPh₂)₃]₂(μ-η²:η²-Te₂)(THF)₂

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(2.802(1) Å),⁴⁸ [Mo₄Te₁₆(ethylenediamine)₄]²⁻ (2.841(2) Å),⁵⁰ and (Ph₄P)₂[(Fe₄Te₄(CO)₁₀]₂(Te₂)] (2.829(2) Å),⁵¹ but they are longer than the Te–Te bonds in PhTe₂Ph (2.712(2) Å),⁵² [MeC(CH₂PPh₂)₃]₂NiTe₂ (2.665(2) Å), and [PhP(CH₂CH₂PPh₂)₂]₂NiTe₂ (2.668(1) Å).⁵³ The 2.710(15)-Å Sm–C(C₅Me₅) ring average in **8** compares well with the 2.626(16)-Å distance in **10** after the 0.094-Å difference in radii is taken into account.³² The 3.213(1)- and 3.204(1)-Å Sm–Te distances in **8** are slightly shorter than would be expected compared to the 3.1513(9)- and 3.1598(7)-Å distances in **10** considering the difference in metallic radii, but the metal–ligand angles are all very similar. The main differences between **8** and **11** are longer Sm–Bi distances (3.29(2) Å) due to the larger size of bismuth.

Discussion

As anticipated, the formation of organosamarium complexes containing the E²⁻ ion is facile. Consistent with the strong reduction potential of Sm(II)² and the previously reported chalcogen chemistry of the weaker reductant (C₅Me₅)₂Yb(OEt₂),¹² (C₅Me₅)₂Sm(THF)₂ is readily oxidized by Te, Se, S, Ph₃P=Se, and Ph₃P=S to form (E²⁻)-containing species. The relative reactivity of S > Se > Te is also quite normal.

However, in contrast to the ytterbium species, [(C₅Me₅)₂Yb]₂(μ-E), the samarium complexes are isolated as mono-THF solvates, [(C₅Me₅)₂Sm(THF)]₂(μ-E), **1–3**. This is consistent with the larger size of samarium. The samarium and ytterbium systems also differ in that all three organosamarium complexes could be crystallographically characterized. With ytterbium, only the selenide provided X-ray quality crystals despite attempts to get metrical data on the entire series. This is consistent with the previously observed flexibility of the (C₅Me₅)₂Sm unit in providing stable, crystallographically-characterizable structures with a variety of different, but closely related coordination environments.^{52–54} As expected, the samarium reactions are more facile than the ytterbium syntheses. Hence, [(C₅Me₅)₂Yb]₂(μ-S) was prepared from Ph₃Ph=S in toluene at reflux for 5 h and could not be obtained from the reaction of (C₅Me₅)₂Yb(OEt₂) with elemental sulfur, whereas (C₅Me₅)₂Sm(THF)₂ reacts with sulfur upon mixing at ambient temperature.

Given that the monochalcogenides, **1–3**, readily form, it was pleasantly surprising to find that the existence of **1–3** did not

preclude the isolation of organosamarium complexes of polyatomic anions of group 16. Hence, the (C₅Me₅)₂Sm unit is able to coordinate and stabilize the trichalcogenide dianions, (E₃)²⁻ as well as the previously identified (Te₂)²⁻ ion. Soluble molecular complexes of (E₃)²⁻ anions are rare.⁴⁷ Solid state salts of (E₃)²⁻ anions are known in K₂Se₃,⁴¹ Rb₂Se₃,⁴² Cs₂Se₃,⁴³ BaSe₃,⁴³ and K₂Te₃⁵⁷ but require rather severe synthesis conditions, e.g. reaction of the elemental chalcogen and the metals at 500–700 °C, reactions in NH₃(l) under pressure at 150–327 °C, or reaction in ethylenediamine in the presence of crypt.⁵⁸ The (E₃)²⁻ anions in [Ni₄Se₄(Se₃)₅(Se₄)]⁴⁻ are an exception.⁴⁸

The formation of the trichalcogenide ions from the E²⁻ complexes has ample precedent in the chemistry of chalcogen anions, which react with the elements to make longer chain anions^{47,59} and in the formation of (Te₃)²⁻ from Te and K₂Te.⁵⁸ Given the extensive chemistry of chalcogenide anions and the variety of structures that have been observed,^{47,60} an extensive series of [(C₅Me₅)₂Sm]_xE_y(THF)_z complexes could exist. It is interesting to note that the values x = 2, y = 1–3, and z = 1–2 appear to be preferred in this system. Hence, both synthetically and structurally, the (C₅Me₅)₂Sm moiety is flexible but somewhat selective in the manipulation of group 16 anionic species.

Conclusion

This study shows that the (C₅Me₅)₂Sm unit is capable of assembling polyatomic anions in groups other than group 15. Despite the tendency to form E²⁻ 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 (E₃)²⁻ ions appear to be particularly favored in this organosamarium system. It is difficult to assess how much the coordination environment provided by (C₅Me₅)₂Sm 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.

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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.

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