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Inorganic Chemistry Article

Synthesis, Structure, and Ligand-Based Reduction Reactivity of Trivalent Organosamarium Benzene Chalcogenolate Complexes $(C_5Me_5)_2Sm(EPh)(THF)$ and $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$

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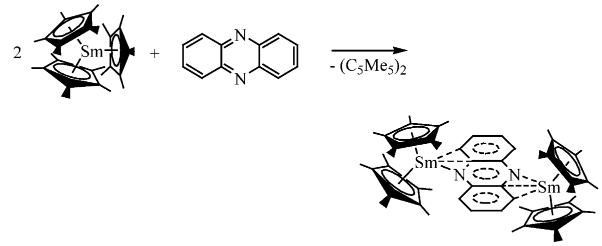
To compare the ligand-based reduction chemistry of $(EPh)^-$ ligands in a metallocene environment to the sterically induced reduction chemistry of the $(C_5Me_5)^-$ ligands in $(C_5Me_5)_3Sm$, $(C_5Me_5)_2Sm(EPh)$ (E = S, Se, Te) complexes were synthesized and treated with substrates reduced by $(C_5Me_5)_3Sm$: cyclooctatetraene; azobenzene; phenazine. Reactions of PhEEPh with $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ produced THF-solvated monometallic complexes, $(C_5Me_5)_2Sm(EPh)(THF)$, and their unsolvated dimeric analogues, $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$, respectively. Both sets of the paramagnetic benzene chalcogenolate complexes were definitively identified by X-crystallography and form homologous series. Only the $(TePh)^-$ complexes show reduction reactivity and only upon heating to 65 °C.

Introduction

The reactivity of the sterically crowded $(C_5Me_5)_3M$ complexes has revealed that when the normally inert $(C_5Me_5)^-$ ligand is placed in sufficiently congested coordination environments, it can function as a one electron reductant according to the half-reaction shown in eq 1.[1,2] This allows trivalent complexes such as $(C_5Me_5)_3Sm$ to function as one-electron reductants as shown in eqs 2−4.[1−3] Although ligand-based reductions have been reported in lanthanide chemistry,[4−16] the $(C_5Me_5)^-$ reductive chemistry is different in that it has only been observed in sterically crowded complexes in which the metal carbon bonds are unusually long. For that reason, this type of reductive process has been called sterically induced reduction (SIR).[17]

$$(C_5Me_5)_3Ln \rightarrow 1e^- + {}^1/_2(C_5Me_5)_2 + [(C_5Me_5)_2Ln]^+ \quad (1)$$

Another ligand that has been shown to do reductive



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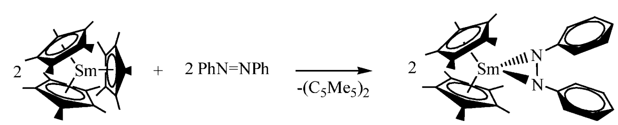

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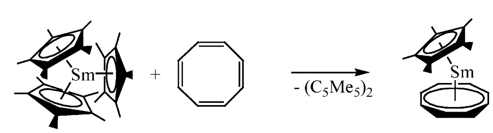

(4)

chemistry in lanthanide complexes is the $(EPh)^-$ group. In a

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series of studies by Brennan and co-workers, the $2(EPh)^-$/PhEEPh redox couple has been shown to reduce elemental chalcogen (E = S) as exemplified in eq 5.[4-16]

$$8Ln(SPh)_3 + 3/4S_8 \xrightarrow{THF} Ln_8S_6(SPh)_{12}(THF)_8 + 6PhSSPh \quad (5)$$

To determine if the ligand-based reductive chemistry observed for $(C_5Me_5)_3Sm$ could be mimicked using the Brennan reductants, $(EPh)^-$, the synthesis of complexes such as $(C_5Me_5)_2Sm(EPh)(THF)$ and $[(C_5Me_5)_2Sm(EPh)]_2$ was of interest. These complexes could be more synthetically accessible than the highly reactive $(C_5Me_5)_3Sm$ (which, for example, ring opens THF[1]) and would provide a new option for reductive lanthanide chemistry with *trivalent* lanthanide metallocene complexes. The desired series of complexes seemed accessible on the basis of the existence of related compounds in the literature such as $(C_5Me_5)_2Yb(SPh)(NH_3)$,[18] $(C_5Me_5)_2Yb(TePh)(NH_3)$,[19] $(C_5Me_5)_2Sm(THF)(TeC_6H_2Me_3$-2,4,6),[20] $(C_5Me_5)_2Sm(THF)(SeC_6H_2(CF_3)_3$-2,4,6),[21] and $[(C_5H_4CMe_3)_2Y(\mu\text{-}SePh)]_2$.[22] Accordingly, we prepared the organosamarium complexes $(C_5Me_5)_2Sm(EPh)(THF)$ and $[(C_5Me_5)_2Sm(EPh)]_2$ (E = S, Se, Te) and report here on their synthesis, structure, and reactivity.

Experimental Section

The manipulations described below were performed under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were saturated with UHP grade argon (Airgas) and dried by passage through Glasscontour drying columns before use. NMR solvents were dried over NaK and vacuum transferred before use. NMR spectra were recorded with a Bruker DRX 400 or 500 MHz systems. The ^1H and ^{13}C NMR spectra of the initially isolated powders match the NMR spectra of the isolated crystals for **1**−**6**. Infrared spectra were recorded as thin films obtained from THF-d_8 (**1**−**3**) or C_6D_6 (**4**−**6**) on the silicon window of the probe of an ASI ReactIR 1000 instrument.[23] $(C_5Me_5)_2Sm(THF)_2$,[24] $(C_5Me_5)_2Sm$,[25] and $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$[26] were prepared as previously described. PhSSPh, PhSeSePh, and PhTeTePh were purchased from Aldrich and sublimed before use. KSPh was prepared by the addition of 1 equiv of PhSSPh to 2 equiv of K sand. Stirring overnight yielded a white toluene insoluble material. Complete elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Complexometric metal analyses were carried out in house as previously described.[27]

$(C_5Me_5)_2Sm(SPh)(THF)$, 1. In a nitrogen filled glovebox, PhSSPh (19 mg, 0.088 mmol) in 5 mL of THF was added to a stirring solution of purple $(C_5Me_5)_2Sm(THF)_2$ (100 mg, 0.177 mmol) in 5 mL of THF. A clear orange solution immediately formed. After the mixture was stirred overnight, the orange solution was evaporated to dryness to yield **1** as an orange powder (95 mg, 90%). Crystals of **1** suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution. ^1H NMR (500 MHz, THF-d_8): 1.19 (s, 30H, C_5Me_5, $\Delta\nu_{1/2}$ = 2 Hz), 6.86 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-H), 5.87 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-H), 6.59 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-H). ^{13}C NMR (500 MHz, THF-d_8, 25 °C): δ 17.8 (C_5*Me*$_5$), 116.8 (*C*$_5$Me$_5$), 129.8 (*o*-phenyl), 128.4 (*m*-phenyl), 121.0 (*p*-phenyl). IR: 3057 w, 2961 m, 2907 s, 2856 s, 2725 w, 1660 w, 1579 m, 1532 w, 1475 s, 1436 s, 1378 s, 1262 m, 1162 m, 1085 s, 1046 s, 1023 s, 992 s, 895 m, 822 s, 802 s, 737 s, 694 s, 568 w cm^{-1}. Anal. Calcd for $C_{30}H_{43}OSSm$: Sm, 25.0. Found: Sm, 24.9. Sublimation of **1** at 155 C at 8×10^{-4} Torr afforded **4** in 8% yield (see below).

$(C_5Me_5)_2Sm(SePh)(THF)$, 2. As described for **1**, **2** was obtained as an orange powder (113 mg, 98%) from PhSeSePh (27 mg, 0.088 mmol) and $(C_5Me_5)_2Sm(THF)_2$ (100 mg, 0.177 mmol). Crystals of **2** suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution. ^1H NMR (500 MHz, THF-d_8): 1.18 (s, 30H, C_5Me_5, $\Delta\nu_{1/2}$ = 2 Hz), 7.01 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-H), 6.58 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-H), 6.71 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-H). ^{13}C NMR (500 MHz, THF-d_8): δ 17.8 (C_5*Me*$_5$), 116.7 (*C*$_5$Me$_5$), 133.2 (*o*-phenyl), 128.6 (*m*-phenyl), 122.4 (*p*-phenyl). IR: 3061 w, 2964 m, 2907 s, 2856 s, 2725 w, 1575 s, 1471 s, 1436 s, 1378 m, 1262 m, 1162 m, 1096 s, 1069 s, 1046 s, 1019 s, 818 s, 799 s, 733 s, 694 s, 633 s, 579 w, 555 w, 521 w cm^{-1}. Anal. Calcd for $C_{30}H_{43}OSeSm$: Sm, 23.2. Found: Sm, 23.8.

$(C_5Me_5)_2Sm(TePh)(THF)$, 3. As described for **1**, **3** was obtained as an orange powder (62 mg, 95%) from PhTeTePh (38 mg, 0.094 mmol) and $(C_5Me_5)_2Sm(THF)_2$ (107 mg, 0.19 mmol). Crystals of **3** suitable for X-ray diffraction were grown at 25 °C from a concentrated toluene solution. ^1H NMR (500 MHz, THF-d_8): 1.23 (s, 30H, C_5Me_5, $\Delta\nu_{1/2}$ = 2 Hz), 7.10 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-H), 7.01 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-H), 6.69 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-H). ^{13}C NMR (500 MHz, THF-d_8): δ 18.3 (C_5*Me*$_5$), 116.9 (*C*$_5$Me$_5$), 139.6 (*o*-phenyl), 128.8 (*m*-phenyl), 124.0 (*p*-phenyl). IR: 3053 w, 2957 s, 2922 s, 2856 s, 2725 w, 1942 w, 1876 w, 1799 w, 1741 w, 1660 w, 1571 m, 1471 m, 1436 s, 1378 m, 1262 s, 1096 s, 1061 s, 1015 s, 864 m, 802 s, 725 s, 687 s cm^{-1}. Anal. Calcd for $C_{30}H_{43}OSmTe\cdot1/2THF$: C, 52.38; H, 6.46; Sm, 20.49; Te, 17.39. Found: C, 52.81; H, 6.26; Sm, 20.60; Te, 17.75.

$[(C_5Me_5)_2Sm(\mu\text{-}SPh)]_2$, 4. In an argon-filled glovebox free of coordinating solvents, PhSSPh (55 mg, 0.25 mmol) in toluene (2 mL) was added slowly to a stirring green solution of $(C_5Me_5)_2Sm$ (211 mg, 0.50 mmol) in toluene (5 mL). The solution immediately turned dark red. After the reaction mixture was stirred overnight, the solvent was removed by rotary evaporation to yield **4** as a red orange crystalline powder (258 mg, 97%). Crystals of **4** suitable for X-ray diffraction were grown at −35 °C from a concentrated

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Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2Sm(EPh)(THF)$ Complexes **1**−**3**

	1	**2**	**3**
empirical formula	$C_{30}H_{43}OSmS$	$C_{30}H_{43}OSmSe$	$C_{30}H_{43}OSmTe$
fw	602.05	648.95	697.59
temp (K)	163(2)	168(2)	163(2)
cryst system	orthorhombic	orthorhombic	orthorhombic
space group	Pbca	Pbca	Pbcn
a (Å)	17.5355(6)	17.3589(17)	18.3046(17)
b (Å)	15.1031(5)	15.2692(15)	17.2195(16)
c (Å)	21.2702(7)	21.463(2)	18.1750(17)
V (Å^3)	5633.2(3)	5689.0(10)	5728.7(9)
Z	8	8	8
ρ_{calcd} (Mg/m^3)	1.420	1.515	1.618
μ (mm^{-1})	2.178	3.363	3.067
R1 [$I > 2.0\sigma(I)$]^a	0.0400	0.0369	0.0184
wR2 (all data)^a	0.0977	0.1032	0.0442

^{a} Definitions: $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

toluene solution. ^{1}H NMR (400 MHz, C_6D_6): (s, C_5Me_5, $\Delta\nu_{1/2}$ = 10 Hz). Aryl resonances could not be located. ^{13}C NMR (500 MHz, C_6D_6): δ 23.4 (C_5*Me*$_5$), 116.8 (*C*$_5$Me$_5$). IR: 3057 w, 2961 s, 2910 s, 2865 s, 2729 w, 1660 w, 1579 m, 1475 s, 1436 s, 1378 m, 1332 w, 1262 s, 1085 s, 1023 s, 799 s, 737 s, 694 s, 586 w cm^{-1}. Anal. Calcd for $C_{52}H_{70}S_2Sm_2$: C, 58.92; H, 6.66; S, 6.05; Sm, 28.37. Found: C, 59.70; H, 6.62; S, 5.40; Sm, 27.60. Addition of THF to **4** afforded **1** in quantitative yield. Complex **4** can also be made from a trivalent precursor. In an NMR tube, $[(C_5Me_5)_2Sm][(\mu\text{-Ph})_2BPh_2]$ (11 mg, 0.015 mmol) dissolved in C_6D_6 was added to KSPh (3 mg, 0.022 mmol). ^{1}H NMR spectroscopy showed complete consumption of $[(C_5Me_5)_2Sm][(\mu\text{-Ph})_2BPh_2]$ with the formation of **4** in 1 h.

$[(C_5Me_5)_2Sm(\mu\text{-SePh})]_2$, 5. As described for **4**, **5** was obtained as an orange crystalline powder (239 mg, 98%) from PhSeSePh (66 mg, 0.21 mmol) and $(C_5Me_5)_2Sm$ (178 mg, 0.42 mmol). Crystals of **5** suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution. ^{1}H NMR (500 MHz, C_6D_6): δ 1.33 (s, C_5*Me*$_5$, $\Delta\nu_{1/2}$ = 10 Hz). Aryl resonances could not be located even at low temperature (200 K). ^{13}C NMR (500 MHz, C_6D_6): δ 23.4 (C_5*Me*$_5$), 116.7 (*C*$_5$Me$_5$). IR: 3061 m, 2961 s, 2910 s, 2856 s, 1575 s, 1471 s, 1436 s, 1378 m, 1262 m, 1096 m, 1069 s, 1023 s, 802 s, 733 s, 690 s, 663 s cm^{-1}. Anal. Calcd for $C_{52}H_{70}Se_2Sm_2$: Sm, 26.1. Found: Sm, 26.2. Addition of THF to **5** afforded **2** in quantitative yield.

$[(C_5Me_5)_2Sm(\mu\text{-TePh})]_2$, 6. As described for **4**, **6** was obtained as a dark orange crystalline powder (251 mg, 99%) from PhTeTePh (83 mg, 0.20 mmol) and $(C_5Me_5)_2Sm$ (170 mg, 0.40 mmol). Crystals of **6** suitable for X-ray diffraction were grown at 25 °C from a concentrated toluene solution. ^{1}H NMR (500 MHz, C_6D_6): δ 1.34 (s, C_5Me$_5$, $\Delta\nu_{1/2}$ = 10 Hz). Aryl resonances could not be located. ^{13}C NMR (500 MHz,C_6D_6): δ 23.4 (C_5*Me*$_5$), 116.9 (*C*$_5$Me$_5$). IR: 3065 w, 2961 s, 2910 s, 2856 s, 2737 w, 1656 w, 1613 w, 1571 m, 1471 m, 1436 s, 1378 m, 1328 w, 1262 s, 1096 s, 1061 s, 1015 s, 802 s, 725 s, 687 s, 579 w, 552 w cm^{-1}. Anal. Calcd for $C_{52}H_{70}Te_2Sm_2$: Sm, 24.0. Found: Sm, 24.1. Addition of THF to **6** afforded **3** in quantitative yield.

Reaction of 6 with $C_{12}H_8N_2$. The ^{1}H NMR spectrum of **6** (13 mg, 0.011 mmol) in C_6D_6 (1 mL) containing phenazine (19 mg, 0.011 mmol) showed resonances only for orange **6** after 12 h. After the mixture was heated at 65 °C overnight, the ^{1}H and ^{13}C NMR spectra of the dark brown mixture showed consumption of starting materials and the formation of $[(C_5Me_5)_2Sm]_2[(C_{12}H_8N_2)]$[28] and PhTeTePh.

Reaction of 3 with PhN═NPh. The ^{1}H NMR spectrum of **3** (11 mg, 0.015 mmol) in C_6D_6 (1 mL) containing PhNNPh (3 mg, 0.016 mmol) showed resonances only for orange **3** after 12 h. After the mixture was heated at 65 °C overnight, the ^{1}H and ^{13}C NMR spectra of the dark green mixture showed consumption of starting materials and the formation of $(C_5Me_5)_2Sm(N_2Ph_2)(THF)$[29] and PhTeTePh.

X-ray Data Collection, Structure Solution, and Refinement of 2. An orange crystal of approximate dimensions 0.23 × 0.24 × 0.25 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[30] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). Details are given in Table 1. The raw frame data were processed using SAINT[31] and SADABS[32] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[33] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbca* which was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[34] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The carbon atoms of the THF ligand were disordered and included using multiple components with partial site occupancy factors. At convergence, wR2 = 0.1032 and GOF = 1.126 for 294 variables refined against 6961 data. As a comparison for refinement on F, R1 = 0.0369 for those 5141 data with $I > 2.0\sigma(I)$. Structural data on **1** and **3**−**6** were collected similarly. Details are given in Tables 1 and 2 and in the Supporting Information.

Results

Synthesis. $(C_5Me_5)_2Sm(EPh)(THF)$, 1−3. In analogy to the reactions of $(C_5Me_5)_2YbL_x$ complexes with PhEEPh (E = S, Se, Te),[18,19] 2 equiv of divalent $(C_5Me_5)_2Sm(THF)_2$[24] react with 1 equiv of PhEEPh (E = S, Se, Te) in THF to produce orange crystalline products, **1**−**3**, respectively, in

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Table 2. X-ray Data Collection Parameters for $[(C_5Me_5)_2Sm]_2(\mu\text{-EPh})_2$ Complexes **4**−**6**

	4	**5**	**6**
empirical formula	$C_{52}H_{70}S_2Sm_2{\cdot}2C_7H_8$	$C_{52}H_{70}Se_2Sm_2{\cdot}2C_7H_8$	$C_{52}H_{70}Sm_2Te_2$
fw	1244.17	1337.97	1250.98
temp (K)	163(2)	163(2)	193(2)
cryst system	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Pca2_1$
a (Å)	10.3682(12)	10.3260(4)	23.132(2)
b (Å)	10.5399(12)	10.6832(4)	10.2800(11)
c (Å)	14.7518(16)	14.8928(7)	20.361(2)
α (deg)	69.395(2)	111.0120(10)	90
β (deg)	76.742(2)	98.1180(10)	90
γ (deg)	83.724(2)	97.3330(10)	90
V (Å^3)	1468.0(3)	1489.77(11)	4841.7(9)
Z	1	1	4
ρ_{calcd} (Mg/m^3)	1.407	1.491	1.716
μ (mm^{-1})	2.090	3.211	3.615
R1 $[I > 2.0\sigma(I)]^a$	0.0238	0.0314	0.0172
wR2 (all data)^a	0.0639	0.0812	0.0416

[a] Definitions: $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

high yields. **1**−**3** were characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis and were completely identified by X-ray crystallography, eq 6, Figure 1. The complexes have similar ^{1}H NMR C_5Me_5 resonances: 1.19, 1.18, and 1.23 ppm for **1**−**3**, respectively. The ^{13}C NMR C_5Me_5 signals are consistent with Sm^{3+},[35] and the IR spectra are nearly superimposable.

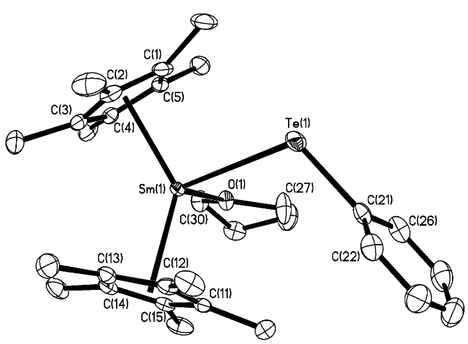
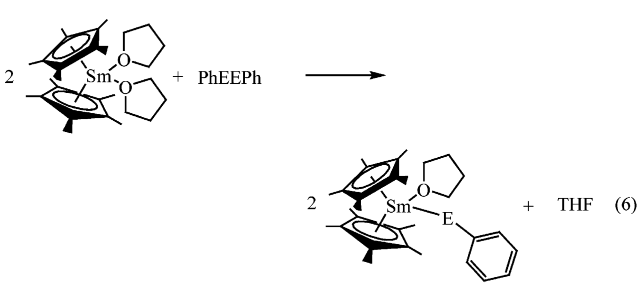


Figure 1. Molecular structure of $(C_5Me_5)_2Sm(TePh)(THF)$, **3**, with thermal ellipsoids drawn at the 50% probability level.



(6)

E = S, **1**; Se, **2**; Te, **3**

$[(C_5Me_5)_2Sm(\text{-EPh})]_2$, 4−6. Reaction of 2 equiv of unsolvated $(C_5Me_5)_2Sm$[25] with 1 equiv of PhEEPh (E = S, Se, Te) in toluene produces dark red (E = S, **4**) and dark orange (E = Se, **5**; E = Te, **6**) crystalline products in high yields, eq 7, Figure 2. Like **1**−**3**, the ^{1}H NMR C_5Me_5 resonances for **4**−**6** are similar: 1.37, 1.33, and 1.34 ppm, respectively. The complexes exhibit broader line widths for the $(C_5Me_5)^-$ resonances (∼10 Hz) compared to **1**−**3** (∼2 Hz). A trivalent oxidation state is again indicated by the ^{13}C NMR spectra, and the IR spectra are very similar. Addition of THF to **4**−**6** generates **1**−**3** quantitatively. Attempts to form **4** by desolvation of **1** under vacuum gave very low yields.

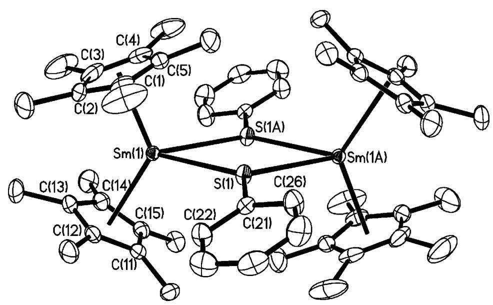
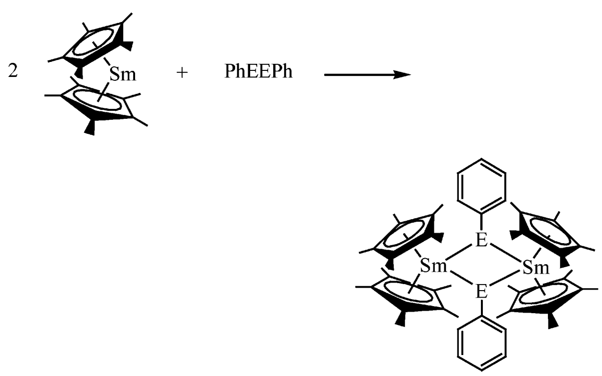


Figure 2. Molecular structure of $[(C_5Me_5)_2Sm(SPh)]_2$, **4**, with thermal ellipsoids drawn at the 50% probability level.



(7)

E = S, **4**; Se, **5**; Te, **6**

$[(C_5Me_5)_2SmSPh]_2$, **4**, was also prepared via a trivalent route using the reaction of $[(C_5Me_5)_2Sm][(\mu\text{-Ph})_2BPh_2]$ and KSPh, prepared from K and PhSSPh, as shown in eq 8.

The loosely ligated complex, $[(C_5Me_5)_2Sm][(\mu\text{-Ph})_2BPh_2]$, has previously been shown to be a good precursor to $(C_5Me_5)_2SmX$ products in reactions with MX salts (M = K, Li; X = C_5Me_5,[26] CH_2Ph, Me, CH_2SiMe_3, and Ph[36]).

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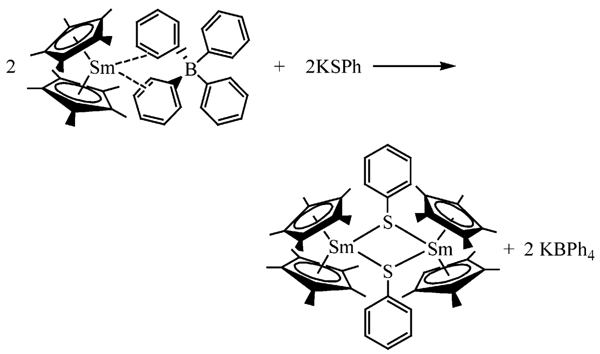

(8)

Structure. Monometallic Solvates, 1−3. Complexes **1**−**3** have the familiar structure of $(C_5Me_5)_2LnXL$ complexes (X = anion; L = neutral ligand) in which the two $(C_5Me_5)^-$ ring centroids and the $(EPh)^-$ and THF ligands roughly define a distorted tetrahedron around the Sm^{3+} center. As shown in Table 3, the metrical parameters associated with the $[(C_5Me_5)_2Sm]^+$ fragment are normal as are the Sm−O(THF) distances.[37] As expected, the Sm−E distances gradually increase from **1** to **3**, i.e., S to Se to Te: 2.7605(12), 2.8837(6), and 3.1279(3) Å, respectively. In comparison, Shannon radii show that S^{2-} is 0.14 Å smaller than Se^{2-} which is 0.23 Å smaller than Te^{2-}.[38] Compared to the Yb−Se and Yb−Te distances in eight-coordinate $(C_5Me_5)_2Yb(SPh)(NH_3)$ (2.670(3) Å),[18] $(C_5H_5)_2Yb(SC_6H_2(CF_3)_3$-2,4,6)(THF) (2.639(3) Å) and $(C_5Me_5)_2Yb(TePh)(NH_3)$ (3.039(1) Å),[19] these distances are in the expected range considering that the effective ionic radius of eight-coordinate Sm^{3+} is 0.094 Å larger than that of eight-coordinate Yb^{3+}.[38]

The Sm−E−C (ipso) angles in **1**−**3** decrease from S to Se to Te with values of 120.82(17), 118.51(14), and 112.49(6)°, respectively. Other lanthanide metallocene chalcogenides show similar angles: $(C_5H_5)_2Yb(SC_6H_2(CF_3)_3$-2,4,6)(THF),[21] $(C_5Me_5)_2Sm(SeC_6H_2(CF_3)_3$-2,4,6)(THF),[20] and $(C_5Me_5)_2Sm(TeC_6H_2Me_3$-2,4,6)(THF)[20] have angles of 121.2(1), 126.4(1), and 123.5(3)°, respectively. Although the oxygen donor atom of the THF is located symmetrically between the two $(C_5Me_5)^-$ rings, as evidenced by similar 103.7−106.1° (C_5Me_5 ring centroid)−Sm−O angles, the $(EPh)^-$ ligands are not. The C(1)−C(5) ring centroid)−Sm−E angles are 99.5−100.0°, whereas the (C(11)−C(15) ring centroid)−Sm−E angles are 113.1−114.8°. This difference, which puts the E atom closer to the C(1)−C(5) ring, apparently minimizes steric crowding between the phenyl ring and the C(11)−C(15) ring.

Unsolvated Bimetallic Complexes, 4−6. In the absence of a coordinating solvent, the $(C_5Me_5)_2Sm(EPh)$ units dimerize in the solid state to achieve the common eight-coordinate lanthanide metallocene structure. As in compounds **1**−**3**, the two $(C_5Me_5)^-$ rings and two $(EPh)^-$ ligands in **4**−**6** roughly define a distorted tetrahedral arrangement around each of the Sm^{3+} centers. The 128.6−132.7° (C_5Me_5 ring centroid)−Sm−(C_5Me_5 ring centroid) angles in **4**−**6** are numerically smaller than the 133.7−135.2° range in the solvated analogues **1**−**3**, but the difference is not large. The Sm−C(C_5Me_5) distances, 2.688(3)−2.733(3)°, are in the normal range.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(EPh)(THF)$ Complexes **1**−**3**

	1	**2**	**3**
E	S	Se	Te
Sm(1)−O(1)	2.445(3)	2.443(3)	2.4490(15)
Sm(1)−E(1)	2.7605(12)	2.8837(6)	3.1279(3)
Sm(1)−Cnt1	2.442	2.448	2.448
Sm(1)−Cnt2	2.452	2.445	2.445
E(1)−C(21)	1.759(5)	1.913(4)	2.127(2)
Cnt1−Sm(1)−E(1)	99.5	98.7	100.0
Cnt2−Sm(1)−E(1)	114.4	114.8	113.1
Cnt1−Sm(1)−Cnt2	133.7	134.1	135.2
C(21)−E(1)−Sm(1)	120.82(17)	118.51(14)	112.49(6)
Cnt1−Sm(1)−O(1)	104.6	105.7	104.1
Cnt2−Sm(1)−O(1)	106.1	105.1	103.7
O(1)−Sm(1)−E(1)	89.72(9)	89.35(8)	92.51(4)

The arrangement of the $(EPh)^-$ ligands in the dimers is quite symmetrical. In **4** and **5**, the Sm_2E_2 rings are perfectly planar and in **6** only a 0.014 2 Å deviation from planarity is observed in the Sm_2Te_2 ring. The Sm−E and Sm−E′ distances are equal within 0.01 Å in each compound. Since there are two $(EPh)^-$ ligands in the coordination sphere of each metal in **4**−**6**, it is more difficult to orient the $(EPh)^-$ ligands asymmetrically to avoid the $(C_5Me_5)^-$ rings as in **1**−**3**. Nevertheless, as in **1**−**3**, the (C_5Me_5 ring centroid)−Sm−donor atom angles fall into two ranges: (C(1)−C(5) ring centroid)−Sm−E and (C(1)−C(5) ring centroid)−Sm−E′ are 105.3−109.8°, and the corresponding angles involving C(11)−C(15) are 112.8−116.5°. The E to E′ distances, 3.024, 3.114, and 3.449 Å for **4**−**6**, respectively, are outside the usual range of E−E bond lengths.[9,13,39]

The coordination around the E donor atoms is nearly trigonal planar with angles that sum to near 360°: 359.7, 358.5, and 357.0° for **4**−**6**, respectively. This is similar to the structures of $[Sm(\mu\text{-}SPh)(C_8H_8)(THF)_2]_2$,[40] $[Sm(\mu\text{-}SePh)(C_8H_8)(THF)_2]_2$,[41] and $\{Sm[\mu\text{-}S(C_6H_2{}^iPr\text{-}2,4,6)](C_8H_8)(THF)\}_2$,[40] whose analogous angles sum to 359.1, 354.0, and 359.3°, respectively. In contrast, $[(Me_3CC_5H_4)_2Ce(\mu\text{-}SCHMe_2)]_2$ and $[(C_5H_5)_2Yb(\mu\text{-}SCH_2CH_2Me)]_2$ have angles that sum to 348 and 326.8°, respectively.[42,43]

The Sm−E distances increase in the order S, Se, and Te for **4**−**6**, 2.9341(6), 3.0478(4), and 3.2627(4) Å, respectively (Table 4). These distances are all longer than the Sm−E distances in **1**−**3** as is common for bridging versus terminal ligation. These Sm−E distances are similar to the 2.914(8) and 3.095(2) Å Sm−E lengths in $[Sm(\mu\text{-}SPh)(C_8H_8)(THF)_2]_2$ and $[Sm(\mu\text{-}SePh)(C_8H_8)(THF)_2]_2$, respectively, compounds which also have planar Sm_2E_2 units.[40,41]

Reactivity. Complexes **1**−**6** were combined with three of the substrates reduced by $(C_5Me_5)_3Sm$ to see if similar

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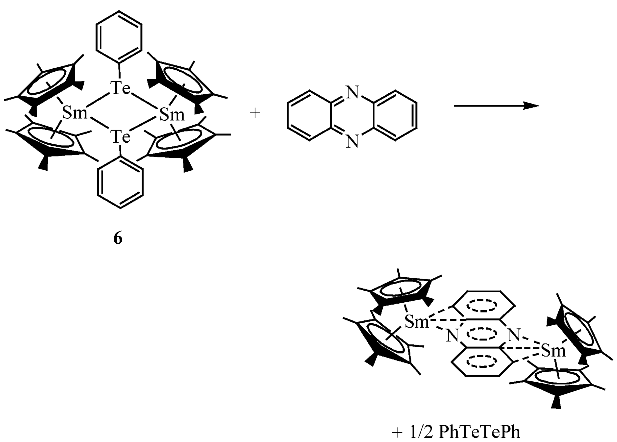
Table 4. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm_2(\mu\text{-EPh})]_2$ Complexes **4**−**6**

	4	**5**	**6**
E	S	Se	Te
Sm(1)−E(1)	2.9341(6)	3.0478(4)	3.2627(4)
Sm(1)−E(1)	2.9388(6)	3.0558(4)	3.2606(3)
E(1)−C(21)	1.765(2)	1.912(3)	2.130(3)
Sm(1)−Cnt1	2.429	2.427	2.437
Sm(1)−Cnt2	2.464	2.456	2.438
E(1)−Sm(1)−E(1)	61.99(2)	62.017(11)	63.844(7)
Cnt1−Sm(1)−E(1)	106.7	105.3	112.8
Cnt2−Sm(1)−E(1)	116.4	116.5	106.9
Cnt1−Sm(1)−E(1)	108.5	109.8	106.8
Cnt2−Sm(1)−E(1)	115.5	113.0	113.2
Cnt1−Sm(1)−Cnt2	128.6	130.1	132.7
C(21)−E(1)−Sm(1)	124.82(8)	123.73(10)	118.81(8)
Sm(1)−E(1)−Sm(1)	118.01(2)	117.983(11)	116.151(9)

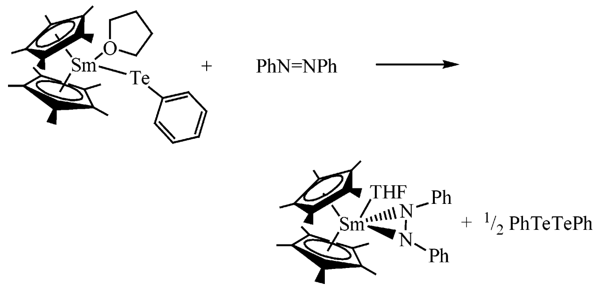
reduction chemistry would result. The reduction potentials of C_8H_8 (−1.83 and −1.99 V vs SCE),[44] azobenzene (−1.35 to −1.41 V and −1.75 to −2.03 V vs SCE),[45] and phenazine (−0.364 V vs SCE)[46] provided a range of opportunities for reduction. In contrast to $(C_5Me_5)_3Sm$, eqs 2−4, no reaction was observed between **1**−**6** and any of these substrates at room temperature. Only upon heating to 65 °C was reactivity observed and then only with the more easily reduced azobenzene and phenazine. C_8H_8 did not react with **1**−**6** even after heating at 65 °C overnight.

In the case of phenazine, a clean reduction was observed only with **6** at 65 °C. Hence, reaction of 1 equiv of $[(C_5Me_5)_2Sm(TePh)]_2$ with 1 equiv of $C_{12}H_8N_2$ in C_6D_6 at 65 °C overnight produces in quantitative yield a dark brown mixture containing only previously characterized $[(C_5Me_5)_2Sm]_2[(C_{12}H_8N_2)]$[28] and PhTeTePh identified by ^1H and ^{13}C NMR spectroscopy. This transformation, eq 9, is analogous to the $(C_5Me_5)_3Sm$ reaction, eq 2, above. In contrast, no reaction between **1**−**5** and phenazine was observed at 65 °C.



(9)

In the azobenzene case, again it is a tellurium complex which gives a clean reduction, but in this case it is the THF solvate. Reaction of 1 equiv of $(C_5Me_5)_2Sm(TePh)(THF)$, **3**, with 1 equiv of PhN═NPh in C_6D_6 at 65 °C produces a dark green mixture in quantitative yield containing only the previously characterized $(C_5Me_5)_2Sm(N_2Ph_2)(THF)$[29] and PhTeTePh identified by ^1H and ^{13}C NMR spectroscopy, eq 10. Reactions of **1**, **2**, and **4**−**6** under the same conditions leave significant amounts of starting material and no evidence of formation of PhEEPh.



(10)

Discussion

The syntheses in eqs 6−8 provide two series of homologous samarocene benzene chalcogenolate complexes for comparisons of structure and reactivity. The progression of structural features moving from S to Se to Te in each case follows the typical periodic trends of these elements.

In contrast to the highly reactive $(C_5Me_5)_3Sm$, the chalcogenides **1**−**6** have limited reductive reactivity with C_8H_8, azobenzene, and phenazine. Only the tellurium complexes react and only at elevated temperature with the most easily reduced substrates. In contrast, $(C_5Me_5)_3Sm$ reduces each of the substrates at room temperature. Although these $(TePh)^-$ complexes show some ligand-based reduction analogous to the $(C_5Me_5)^-/(C_5Me_5)$ reactions, the level of reactivity is much lower.

The reason that the THF solvate, **3**, is the reactive species with azobenzene and the unsolvated dimer, **6**, is the reactive species with phenazine is not clear. Since both reactions involve $2TePh^-$/PhTeTePh reduction in benzene, both **3** and **6** could be expected to react with each substrate. In general, in comparisons of the reactivity of solvated and unsolvated samarium metallocene complexes, the unsolvated complexes are the more reactive. This certainly applies to $(C_5Me_5)_2Sm(THF)_2/(C_5Me_5)_2Sm$ and the $(C_5Me_5)_2SmR(THF)/[(C_5Me_5)_2SmR]_x$ pairs for R = Me,[47,48] C_6H_5,[36,49] and $CH_2C_6H_5$.[36,48]

The observation that the $(TePh)^-$ complexes are more reducing than the $(SePh)^-$ and $(SPh)^-$ species is consistent with the expectation that the Sm−Te bonds are the weakest of these three Sm−chalcogen linkages and $(TePh)^-$ is expected to be the most reducing $(EPh)^-$ anion (cf. I^- vs Br^- vs Cl^-). However, as amply shown by electrochemical studies, the $(EPh)^-$/PhEEPh redox couple is system dependent and should not be rationalized so simply. For example, electrochemical studies of PhSSPh and PhSeSePh by Dessy provided reduction potentials of −1.6 and −0.9 V vs Ag/$AgNO_3$, respectively, but the reductions were irreversible.[50] Subsequent studies by Ludvik and Nygard on these com-

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pounds[51] and PhTeTePh indicated that the sulfur compound differed mechanistically from the Se and Te reactions and the formation of mercury products was an issue. The first reduction waves for PhSeSePh and PhTeTePh were observed at −0.335 and −0.345 V vs SCE, respectively. A further complication is that elevated temperatures are needed for **3** and **6** to react.

In any case, the low reactivity of the $(EPh)^-$ ligands in ligand-based reduction via the $2(EPh)^-$/PhEEPh couple emphasizes the special nature of the $(C_5Me_5)_3Ln$ complexes in which $(C_5Me_5)^-/(C_5Me_5)$ processes are facile. Clearly sterically induced reduction with $(C_5Me_5)^-$ is a more effective method to bring reductive chemistry to redox-inactive lanthanides in bis(pentamethylcyclopentadienyl) complexes.

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Conclusion

The use of both Sm^{2+} and Sm^{3+} starting materials has allowed for the synthesis and characterization of new trivalent samarocene benzene chalcogenolate complexes for the evaluation of $(EPh)^-$ ligand-based reductions. In contrast to the sterically crowded $(C_5Me_5)_3Sm$, these benzene chalcogenolates are not reactive reductants. Only at 65 °C with easily reduced substrates do the $(TePh)^-$ complexes provide reductive chemistry and formation of PhTeTePh.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure solution, and refinement of compounds **1**−**6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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