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Synthesis of $(O_2CEPh)^{1-}$ Ligands (E = S, Se) by CO_2 Insertion into Lanthanide Chalcogen Bonds and Their Utility in Forming Crystallographically Characterizable Organoaluminum Complexes $[Me_2Al(\mu\text{-}O_2CEPh)]_2$

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CO_2 inserts into the Sm–S and Sm–Se bonds of $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$ (E = S, Se) to form the first crystallographically characterized $(O_2CEPh)^{1-}$ complexes, $[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$. These complexes are structurally analogous to $[(C_5Me_5)_2Sm(\mu\text{-}O_2CR)]_2$ complexes, but they are less soluble. This feature was utilized in the reaction of Me_2AlCl with $[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$, which forms crystallographically characterizable $[Me_2Al(\mu\text{-}O_2CEPh)]_2$ complexes. Such complexes could not be isolated from an analogous carboxylate reaction. $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSePh)]_2$ decarboxylates in THF to form $(C_5Me_5)_2Sm(SePh)(THF)$. The loss of CO_2 rather than COSe with formation of $(C_5Me_5)_2Sm(OPh)(THF)$ was established by $^{13}CO_2$ studies and independent synthesis of $(C_5Me_5)_2Sm(OPh)(THF)$ from $(C_5Me_5)_2Sm[N(SiMe_3)_2]$ and PhOH.

Introduction

The insertion of CO_2 into reactive M−C bonds of electropositive metals has been used for decades to convert alkyl complexes into more stable, tractable carboxylate derivatives.[1−6] Insertion of CO_2 into other types of metal−ligand bonds (M−H, M−N, M−O) has also received considerable attention,[3,6] but to the best of our knowledge there are few reports involving metal−chalcogen bonds, M−E (E = S, Se, Te).[7,8] The only examples of this type of reaction involve CO_2 insertions into uranium−sulfur bonds. The reaction of $(C_5H_5)_3U(S^iPr)$ with CO_2 to form $(C_5H_5)_3U(O_2CS^iPr)$ was reported to be the first insertion of CO_2 into a metal−sulfur bond of any kind.[7] However, this complex could not be isolated in pure form because of facile decarboxylation. Subsequently, the reaction of $(C_5Me_5)_2U(S^tBu)_2$ with CO_2, eq 1, was found to give the first isolatable complex from such a reaction, $(C_5Me_5)_2U(O_2CS^tBu)_2$, which was characterized by analytical and spectroscopic methods.[8]

$$(C_5Me_5)_2U(S^tBu)_2 \xrightarrow{2CO_2} (C_5Me_5)_2U(O_2CS^tBu)_2 \qquad (1)$$

As part of a recent study of the ligand reduction chemistry of the aryl chalcogenide metallocenes $(C_5Me_5)_2Sm(EPh)(THF)$ and $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$ (E = S, Se, Te),[9] we examined the reactivity of these complexes with CO_2 to determine if insertion would occur and be useful in derivatizing Ln−S, Ln−Se, and Ln−Te bonds. We report here the first crystallographically defined details on $(O_2CEPh)^{1-}$ ligands derived from M−E/CO_2 insertion reactions. The utility of the $(O_2CEPh)^{1-}$ ligands in providing crystallizable organoaluminum derivatives is also described, as well as the decarboxylation chemistry of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSePh)]_2$ in THF.

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 were dried by passage through Glasscontour drying columns before use. NMR solvents were dried over NaK, and vacuum transferred before use. NMR spectra were

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recorded with a Bruker DRX 500 MHz system. Infrared spectra were recorded as thin films obtained from deuterotoluene or deuterobenzene on an ASI ReactIR 1000 instrument.[10] $(C_5Me_5)_2Sm(EPh)(THF)$ (E = Se),[9] $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$ (E = S, Se),[9] and $(C_5Me_5)_2Sm[N(SiMe_3)_2]$[11] were prepared as previously described. PhOH was purchased from Aldrich, and was sublimed before use. CO_2 and $^{13}CO_2$ were purchased from Airgas and Cambridge Isotope Laboratories, Inc., respectively. Me_2AlCl (1.0 M in hexanes) was purchased from Aldrich. Complete elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Complexometric analyses were carried out as previously described.[12]

$[(C_5Me_5)_2Sm(\mu\text{-}O_2CSPh)]_2$, 1. In an argon-filled glovebox free of coordinating solvents, an orange solution of $[(C_5Me_5)_2Sm(\mu\text{-}SPh)]_2$[9] (31 mg, 0.029 mmol) in benzene-d_6 (1 mL) was added to a J-Young NMR tube. The solution was degassed by three freeze−pump−thaw cycles. The NMR tube was subsequently charged with 1 atm of CO_2 gas. The solution became yellow, and orange crystals suitable for X-ray diffraction were observed after 12 h. Removal of solvent yielded **1** as an orange crystalline powder (31 mg, 94%). ^1H NMR (500 MHz, toluene-d_8): δ 1.44 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 4$ Hz), 4.13 (d, 2H, $^3J_{HH} = 7$ Hz, *o*-H), 5.08 (t, 2H, $^3J_{HH} = 7$ Hz, *m*-H), 5.41 (t, 1H, $^3J_{HH} = 7$ Hz, *p*-H). ^{13}C NMR (125.8 MHz, toluene-d_8): δ 18.8 (C_5Me_5), 116.5 (C_5Me_5), 132.2 (*o*-phenyl), 126.7 (*m*-phenyl), 127.2 (*p*-phenyl); the ipso carbon was not located. IR: 3057w, 2961s, 2918s, 2856s, 2729s, 2235s, 1598s, 1532s, 1475s, 1440s, 1378s, 1262s, 1089s, 1023s, 799s, 741s, 691s, 587w cm^{-1}. Anal. Calcd for $C_{54}H_{70}O_4S_2Sm_2 \cdot 2C_6H_6$: C, 60.78; H, 6.34, S, 4.92; Sm, 23.06. Found: C, 60.75; H, 6.27; S, 4.82; Sm, 22.90.

$[(C_5Me_5)_2Sm(\mu\text{-}O_2CSePh)]_2$, 2. As described for **1**, **2** was obtained as an orange crystalline powder (32 mg, 96%) from $[(C_5Me_5)_2Sm(\mu\text{-}SePh)]_2$[9] (31 mg, 0.025 mmol) in benzene-d_6 (1 mL). Orange crystals suitable for X-ray diffraction were observed after 12 h. ^1H NMR (500 MHz, toluene-d_8): δ 1.40 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 4$ Hz), 4.25 (d, 2H, $^3J_{HH} = 7$ Hz, *o*-H), 5.13 (t, 2H, $^3J_{HH} = 7$ Hz, *m*-H), 5.48 (t, 2H, $^3J_{HH} = 7$ Hz, *p*-H). ^{13}C NMR (125.8 MHz, toluene-d_8): δ 18.6 (C_5Me_5), 116.7 (C_5Me_5), 132.9 (*o*-phenyl), 126.6 (*m*-phenyl), 126.5 (*p*-phenyl); the ipso carbon was not located. IR: 3057w, 2961s, 2910s, 2856s, 2223w, 2181w, 1945w, 1532s, 1475s, 1436s, 1401s, 1378s, 1258s, 1092s, 1065s, 1019s, 842s, 803s, 733s, 691s, 668s, 575w cm^{-1}. Anal. Calcd for $C_{54}H_{70}O_4Se_2Sm_2$: Sm, 26.2. Found: 26.2. ^{13}C-labeled **2**-$^{13}CO_2$ was synthesized in an analogous fashion.

$[Me_2Al(\mu\text{-}O_2CSPh)]_2$, 3. In an argon-filled glovebox free of coordinating solvents, Me_2AlCl (69 μL, 0.746 mmol) was added dropwise to an orange slurry of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSPh)]_2$ (**1**; 214 mg, 0.186 mmol) in toluene (4 mL). A clear red solution immediately formed. After the mixture was stirred overnight, the red solution was evaporated to dryness and yielded a red microcrystalline solid. ^1H NMR spectroscopy showed complete consumption of the starting material and formation of only the previously characterized red complex, $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2AlMe_2$;[13] the spectra also showed resonances for **3**, isolated as described below. The red solid was dissolved in hexane, and cooled to −35 °C. After 2 days, **3** was obtained as colorless crystals (30 mg, 38%). Crystals suitable for X-ray diffraction were grown from hexane at −35 °C. ^1H NMR (500 MHz, benzene-d_6): δ −0.63 (s, 6H, CH_3, $\Delta\nu_{1/2} = 2$ Hz), 6.89 (m, 3H), 7.09 (m, 2H). ^{13}C (125.7 MHz, benzene-d_6): δ −11.5 (CH_3), 129.9 (phenyl), 130.9 (phenyl), 135.5 (phenyl); the ipso carbon was not located. IR: 2961s, 2930s, 2856m, 1613s, 1583s, 1478w, 1444s, 1382s, 1332s, 1262s, 1197s, 1158w, 1092s, 1096s, 1019s, 915w, 861s, 803s, 703s cm^{-1}. Anal. Calcd for $C_{18}H_{22}Al_2O_4S_2$: C, 51.42; H, 5.27; Al, 12.83. Found: C, 51.19; H, 5.36; Al, 12.64.

$[Me_2Al(\mu\text{-}O_2CSePh)]_2$, 4. As described for **3**, **4** was obtained from Me_2AlCl (64 μL, 0.692 mmol) and $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSePh)]_2$ (**2**; 215 mg, 0.173 mmol) in toluene (4 mL). ^1H NMR spectroscopy showed complete consumption of the starting material and formation of only the previously characterized $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2AlMe_2$[13] and resonances for **4** isolated as described below. The red solid was dissolved in hexane, and cooled to −35 °C. After 2 days, **4** was obtained as colorless crystals (37 mg, 42%). Crystals suitable for X-ray diffraction were grown from hexane at −35 °C. ^1H NMR (500 MHz, benzene-d_6): δ −0.67 (s, 6H, $\Delta\nu_{1/2} = 2$ Hz), 6.90 (m, 3H), 7.22 (m, 2H). ^{13}C NMR (125.7 MHz, benzene-d_6): δ −11.2 (CH_3), 130.1 (phenyl), 130.4 (phenyl), 136.6 (phenyl); the ipso carbon was not located. IR: 2930s, 2895m, 2853w, 1606s, 1567s, 1478m, 1440s, 1339s, 1289s, 1262s, 1200s, 1158w, 1092s, 1019s, 911w, 803s, 703s cm^{-1}. Anal. Calcd for $C_{18}H_{22}Al_2O_4Se_2$: C, 42.04; H, 4.31; Se, 30.72; Al, 10.49. Found: C, 41.89; H, 4.26; Se, 30.25; Al, 10.63.

$(C_5Me_5)_2Sm(OPh)(THF)$, 5. In a nitrogen-filled glovebox, PhOH (22 mg, 0.231 mmol) in 3 mL of THF was added dropwise to a stirred solution of orange $(C_5Me_5)_2Sm[N(SiMe_3)_2]$[11] (134 mg, 0.230 mmol) in THF (5 mL). A clear yellow solution immediately formed. After the mixture was stirred overnight, the yellow solution was evaporated to dryness to yield **5** as a yellow powder (131 mg, 97%). Crystals of **5** suitable for X-ray diffraction were grown at −35 °C from a concentrated hexane solution. ^1H NMR (500 MHz, THF-d_8): δ 1.25 (s, 30H, C_5Me_5, $\Delta\nu_{1/2} = 2$ Hz), 7.12 (t, 1H, $^3J_{HH} = 7$ Hz, *p*-H), 7.15 (d, 2H, $^3J_{HH} = 7$ Hz, *o*-H), 7.27 (t, 2H, $^3J_{HH} = 7$ Hz, *m*-H). ^{13}C NMR (125.7 MHz, THF-d_8): δ 17.8 (C_5Me_5), 115.4 (C_5Me_5), 115.9 (*p*-phenyl), 119.4 (*o*-phenyl), 131.0 (*m*-phenyl); the ipso carbon was not located. IR: 2964s, 2907s, 2856s, 1590s, 1486s, 1444s, 1378w, 1293s, 1258s, 1162s, 1092s, 1065s, 1019s, 861s, 826s, 803s, 757s, 695s cm^{-1}. Anal. Calcd for $C_{30}H_{43}O_2Sm$: C, 61.49; H, 7.40; Sm, 25.66. Found: C, 61.21; H, 7.29; Sm, 25.40.

Reaction of 2-$^{13}CO_2$ + THF. THF-d_8 (1 mL) was condensed into a J-Young tube containing $[(C_5Me_5)_2Sm(\mu\text{-}O_2{}^{13}CSePh)]_2$ (15 mg, 0.012 mmol) at −196 °C, and the J-young tube was sealed. As the tube warmed to room temperature, bubbles were observed. The ^1H and ^{13}C NMR spectra of the orange solution showed complete consumption of the starting material and formation of $(C_5Me_5)_2Sm(SePh)(THF)$ in approximately 80% yield. Free $^{13}CO_2$ was observed at 126.1 ppm.

X-ray Data Collection, Structure Solution, and Refinement of 1. A yellow crystal of approximate dimensions 0.07 mm × 0.15 mm × 0.32 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[14] 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). The raw frame data were processed using SAINT[15] and SADABS[16] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[17] program. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later

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Table 1. X-ray Data Collection Parameters for $[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$ (E = S, **1**; E = Se, **2**)

empirical formula	$C_{54}H_{70}O_4S_2Sm_2{\cdot}2(C_6H_6)$ **1**	$C_{54}H_{70}O_4Se_2Sm_2{\cdot}2(C_6H_6)$ **2**
fw	1304.14	1397.94
T (K)	163(2)	163(2)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.0448(8)	10.0816(9)
b (Å)	11.3453(9)	11.4143(10)
c (Å)	14.8839(12)	14.9377(12)
α (deg)	71.0950(10)	71.1060(10)
β (deg)	73.9510(10)	73.6160(10)
γ (deg)	69.1850(10)	69.2800(10)
V ($Å^3$)	1474.8(2)	1493.6(2)
Z	1	1
ρ_{calcd} (Mg/m^3)	1.468	1.554
μ (mm^{-1})	2.089	3.211
R1 [$I > 2.0\sigma(I)$][a]	0.0189	0.0176
wR2 (all data)[a]	0.0467	0.0437

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

Table 2. X-ray Data Collection Parameters for $[Me_2Al(\mu\text{-}O_2CEPh)]_2$ (E = S, **3**; E = Se, **4**) and $(C_5Me_5)_2Sm(OPh)(THF)$, **5**

empirical formula	$C_{18}H_{22}Al_2O_4S_2$ **3**	$C_{18}H_{22}Al_2O_4Se_2$ **4**	$C_{30}H_{43}O_2Sm$ **5**
fw	420.44	514.24	585.99
T (K)	163(2)	163(2)	163(2)
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	7.3848(7)	7.5821(8)	9.6264(10)
b (Å)	7.8025(7)	7.8593(9)	17.0880(18)
c (Å)	9.7743(9)	9.7855(11)	17.0045(18)
α (deg)	95.896(2)	95.797(2)	90
β (deg)	90.289(2)	90.635(2)	102.183(2)
γ (deg)	108.727(2)	109.368(2)	90
V ($Å^3$)	530.12(8)	546.69(10)	2734.2(5)
Z	1	1	4
ρ_{calcd} (mg/m^3)	1.317	1.562	1.424
μ (mm^{-1})	0.353	3.481	2.171
R1 [$I > 2.0\sigma(I)$][a]	0.0288	0.0208	0.0209
wR2 (all data)[a]	0.0777	0.0508	0.0535

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

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[18] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference Fourier map and refined (*x*, *y*, *z* and U_{iso}). The molecule was a dimer, and was located about an inversion center. There were two molecules of benzene solvent present per dimeric formula unit. At convergence, wR2 = 0.0467 and GOF = 1.063 for 498 variables refined against 6877 data points. As a comparison for refinement on *F*, R1 = 0.0189 for those 6431 data points with $I > 2.0\sigma(I)$. See Table 1 for parameters related to **1** and **2**.

X-ray Data Collection, Structure Solution, and Refinement of 2. A yellow crystal of approximate dimensions 0.11 mm × 0.32 mm × 0.32 mm was handled as was described for **1**. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The molecule was a dimer, and was located about an inversion center. There were two molecules of benzene solvent present per dimeric formula unit. At convergence, wR2 = 0.0437 and GOF = 1.050 for 498 variables refined against 6953 data points. As a comparison for refinement on *F*, R1 = 0.0176 for those 6637 data points with $I > 2.0\sigma(I)$.

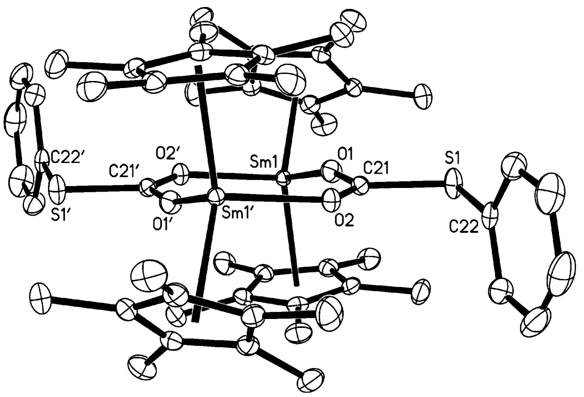

Figure 1. Molecular structure of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSPh)]_2$, **1**, with thermal ellipsoids drawn at the 50% probability level. $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSePh)]_2$, **2**, is isomorphous.

X-ray Data Collection, Structure Solution, and Refinement of 3. A colorless crystal of approximate dimensions 0.15 mm × 0.20 mm × 0.21 mm was handled as was described for **1**. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The molecule was located about an inversion center. At convergence, wR2 = 0.0777 and GOF = 1.027 for 162 variables refined against 2495 data points. As a comparison for refinement on *F*, R1 = 0.0288 for those 2138 data points with $I > 2.0\sigma(I)$. See Table 2 for parameters relating to **3**, **4**, and **5**.

X-ray Data Collection, Structure Solution, and Refinement of 4. A colorless crystal of approximate dimensions 0.09 mm × 0.27 mm × 0.50 mm was handled as was described for **1**. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The molecule was located about an inversion center. At convergence, wR2 = 0.0508 and GOF = 1.040 for 162 variables refined against 2613 data points. As a comparison for refinement on *F*, R1 = 0.0208 for those 2451 data points with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution, and Refinement of 5. A yellow crystal of approximate dimensions 0.18 mm × 0.32 mm × 0.39 mm was handled as described for **1**. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$, which was later determined to be correct. At convergence, wR2 = 0.0535 and GOF = 1.083 for 439 variables refined against 6666 data points. As a comparison for refinement on *F*, R1 = 0.0209 for those 6064 data pointswith $I > 2.0\sigma(I)$.

Results and Discussion

$[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$ (E = S, 1; E = Se, 2). Reaction of $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$ (E = S, Se) with 1 atm of CO_2 in benzene-d_6 produced the orange crystalline products **1** and **2** for S and Se, respectively, in high yields. The ^1H and ^{13}C NMR data in each case showed a single C_5Me_5 resonance in the typical region for trivalent metallocenes. X-ray quality crystals of both compounds were obtained directly from the reaction mixtures and provided crystallographic confirmation, Figure 1, of CO_2 insertion according to eq 2.

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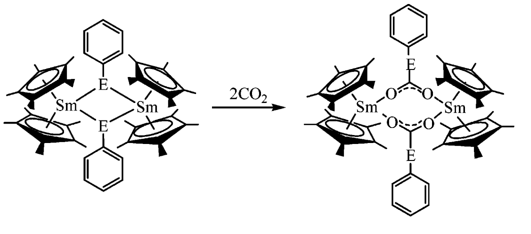
(15) *SAINT Software Users Guide*, version 6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

(16) Sheldrick, G. M. *SADABS*, version 2.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.

(17) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.

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



(2)

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

Complex **2** can also be obtained in high yield from the THF-solvated precursor, $(C_5Me_5)_2Sm(SePh)(THF)$, under 1 atm of CO_2 in benzene.

$[(C_5Me_5)_2Sm(\mu\text{-}TePh)]_2$ appears to react similarly with CO_2, but crystallographic confirmation of the product has not yet been obtained. The product does have a single C_5Me_5 ^1H NMR resonance at 1.41 ppm that is similar to those of **1** and **2** in toluene, at 1.44 and 1.40 ppm, respectively. Attempts to make a mixed chalcogenide analogue from $[(C_5Me_5)_2Sm(\mu\text{-}SPh)]_2$ and$[(C_5Me_5)_2Sm(\mu\text{-}TePh)]_2$ gave crystals of $[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$ that were isomorphous with **1** and **2** and that refined with site occupancy factors for E of 90% for S and 10% for Te.

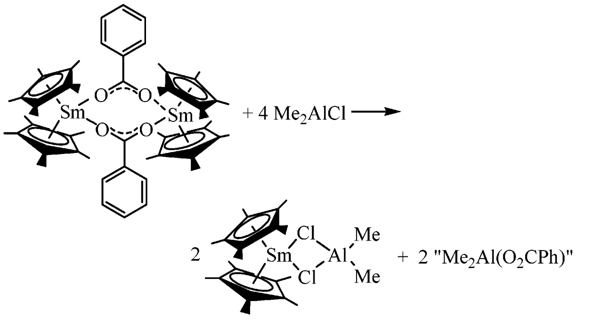
As shown in Figure 1, both **1** and **2** have a square planar arrangement of $(C_5Me_5)^{1-}$ ring centroids that is typical of metallocenes bridged by large groups.[19−21] Perpendicular to the plane of the four $(C_5Me_5)^{1-}$ ring centroids is an eight-membered $\overline{\text{SmOC(E)OSmOC(E)O}}$ ring. These atoms are coplanar within 0.12 Å in **1** and **2**. The aryl rings attached to the chalcogen have a trans arrangement with respect to each other. The overall structure is similar to that of the benzylcarboxylate $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCH_2Ph)]_2$, **6**, obtained by insertion of CO_2 into the Sm−benzyl bond in $(C_5Me_5)_2Sm(CH_2Ph)$.[21] In this sense, the S and Se atoms of **1** and **2** are analogous to the CH_2 unit in **6**. Because of the larger sizes of S and Se, the attached phenyl rings are farther from the $Sm_2(\mu\text{-}O_2CR)_2$ cores. In this regard, the $(O_2CEPh)^{1-}$ ligands may be valuable for the construction of bimetallic lanthanide complexes that keep C−H bonds distant from the metals, a desirable feature in terms of fluorescence quenching.[22] The Sm···Sm distances in **1** and **2** are 5.565 and 5.604 Å, respectively, compared to 5.034 and 5.231 Å in the $[(C_5Me_5)_2Sm(\mu\text{-}EPh)]_2$ precursors.[9]

The 1.242(2)−1.258(2) Å C(21)−O(1) and C(21)−O(2) distances (see Table 3) in **1** and **2** indicate a delocalized structure for the carboxylate portion of the $(O_2CEPh)^{1-}$ ligands. The 1.792(2) and 1.947(2) Å C(21)−E distances in **1** and **2**, respectively, are in the single-bond range.[23] The O_2C−E−C(ipso carbon) angles of 104.19(9) and 102.05(7)° in **1** and **2**, respectively, are consistent with sp^3 hybridization around E.

$[Me_2Al(\mu\text{-}O_2CEPh)]_2$ (E = S, 3; E = Se, 4). The fact that **1** and **2** readily crystallized from the reaction mixture suggested that the $(O_2CEPh)^{1-}$ ligands could be useful in providing less soluble, more crystalline forms of complexes analogous to carboxylates. This was tested with the analogue of the reaction shown in eq 3. Equation 3 was studied as a model for the activation of lanthanide carboxylates with alkyl aluminum reagents to make catalysts for the polymerization of isoprene to high *cis*-1,4-polyisoprene.[13] Unfortunately, even in this carboxylate model system, the aluminum byproduct could not be fully characterized, in part because of its high solubility.

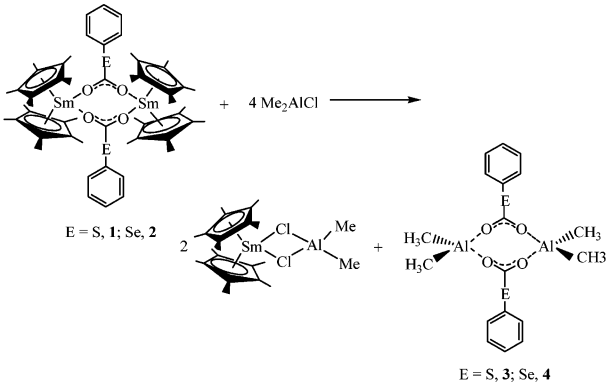
Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(\mu\text{-}O_2CEPh)]_2$ (E = S, **1**; E = Se, **2**)

	1	**2**
Sm(1)−O(1)	2.3286(13)	2.3307(13)
Sm(1)−O(2′)	2.3771(13)	2.3812(12)
Sm(1)−Cnt1	2.427	2.425
Sm(1)−Cnt2	2.442	2.440
E(1)−C(22)	1.778(2)	1.9153(19)
E(1)−C(21)	1.7916(18)	1.9472(17)
O(1)−C(21)	1.258(2)	1.251(2)
Cnt1−Sm(1)−O(1)	106.4	106.4
Cnt2−Sm(1)−O(1)	107.5	107.6
Cnt1−Sm(1)−Cnt2	133.4	133.6
O(1)−Sm(1)−O(2′)	85.84(5)	82.33(5)
C(21)−O(1)−Sm(1)	163.89(13)	164.80(12)
O(2)−C(21)−O(1)	127.61(17)	128.62(16)
O(1)−C(21)−E(1)	111.82(14)	111.20(12)
C(22)−E(1)−C(21)	104.19(9)	102.05(7)



(3)

To determine if the reduced solubility of $(O_2CEPh)^{1-}$ complexes could help in this case, we examined the analogous reaction of **1** and **2** with Me_2AlCl. This reaction produced the expected organosamarium product, $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2AlMe_2$, analogous to that in eq 3. However, in this case the organoaluminum byproducts, $[Me_2Al(\mu\text{-}O_2CEPh)]_2$ (E = S, **3**; E = Se, **4**), could be isolated as colorless crystals and fully characterized (eq 4). Cooling the reaction mixtures to −35 °C allowed for the separation of **3** and **4** from $(C_5$-



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

E = S, **3**; Se, **4**

(4)

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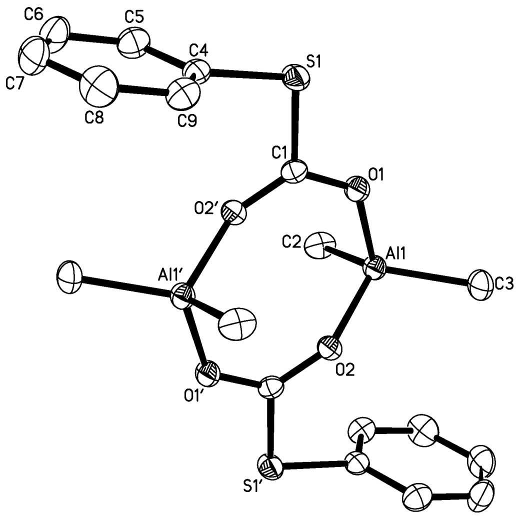


Figure 2. Molecular structure of $[Me_2Al(\mu\text{-}O_2CSPh)]_2$, **3**, with thermal ellipsoids drawn at the 50% probability level. $[Me_2Al(\mu\text{-}O_2CSePh)]_2$, **4**, is isomorphous.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Me_2Al(\mu\text{-}O_2CEPh)]_2$ (E = S, **3**; E = Se, **4**)

	3	**4**
Al(1)−O(1)	1.8570(10)	1.8595(13)
Al(1)−O(2)	1.8255(10)	1.8290(12)
Al(1)−C(3)	1.9400(16)	1.9374(19)
Al(1)−C(2)	1.9566(16)	1.959(2)
S(1)−C(1)	1.7548(13)	1.9017(16)
S(1)−C(4)	1.7767(14)	1.9193(16)
O(1)−C(1)	1.2642(16)	1.2646(19)
O(2)−C(1′)	1.2585(15)	1.2564(19)
O(2)−Al(1)−O(1)	101.93(4)	101.58(5)
O(1)−Al(1)−C(3)	106.20(6)	105.67(8)
O(1)−Al(1)−C(2)	106.91(6)	106.99(8)
C(3)−Al(1)−C(2)	124.45(8)	124.55(10)
C(1)−E(1)−C(4)	102.27(6)	99.43(7)
C(1)−O(1)−Al(1)	128.43(9)	128.96(11)
O(1)−C(1)−E(1)	114.07(10)	114.18(11)

$Me_5)_2Sm(\mu\text{-}Cl)_2AlMe_2$ in each case. Complexes **3** and **4** were characterized by elemental analysis and ^1H NMR, ^{13}C NMR, and IR spectroscopy. They were completely identified by X-ray crystallography (Figure 2).

Complexes **3** and **4** are isomorphous and dimeric in the solid state. As in **1** and **2**, the phenyl groups adopt a trans orientation with respect to each other. The bond distances and angles in **3** and **4** are similar to those in $[Me_2Al(\mu\text{-}O_2CN^iPr_2)]_2$ (see Table 4).[24] The O−Al−O and C(Me)−Al−O angles fall into the narrow range 101.58(5)−108.20(8)°, whereas the C1−E−C4 angles, 102.27(6)° for **3** and 99.43(7)° for **4**, are similar to those of the analogues in **1** and **2**.

Decarboxylation of 2. Although $[(C_5Me_5)_2Sm(\mu\text{-}O_2CSePh)]_2$, **2**, can be synthesized from the THF solvate $(C_5Me_5)_2Sm(SePh)(THF)$ in benzene, dissolving **2** in THF generates a gas and a product that has the same ^1H NMR spectrum as $(C_5Me_5)_2Sm(SePh)(THF)$. If this reaction was analogous to the decarboxylation of $(C_5H_5)_3U(O_2CS^iPr)$ that prevented its isolation,[7] the products of the decomposition would be as shown in eq 5.

$$\underset{\mathbf{2}}{[(C_5Me_5)_2Sm(\mu\text{-}O_2SePh)]_2} \xrightarrow{THF} 2(C_5Me_5)_2Sm(SePh)(THF) + 2CO_2 \quad (5)$$

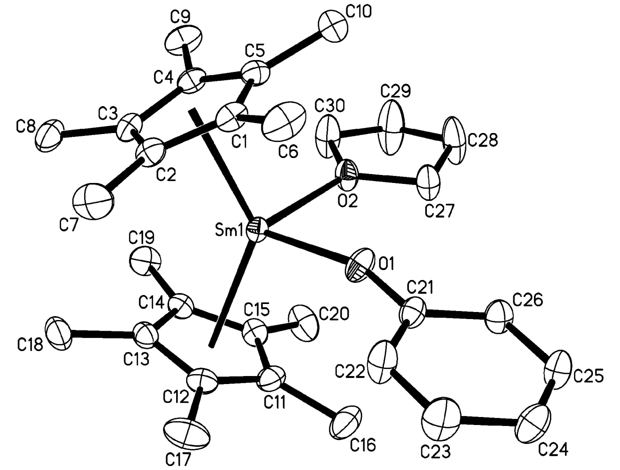
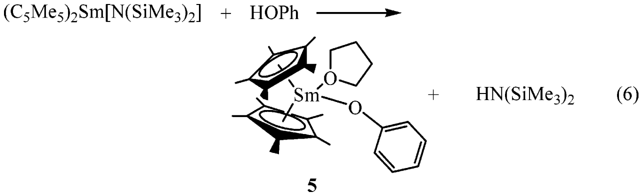


Figure 3. Molecular structure of $(C_5Me_5)_2Sm(OPh)(THF)$, **5**, with thermal ellipsoids drawn at the 50% probability level.

However, since the lanthanides are highly oxophilic, it is possible that COSe was lost and $(C_5Me_5)_2Sm(OPh)(THF)$ was the byproduct. This would require that the ^1H NMR spectrum of $(C_5Me_5)_2Sm(OPh)(THF)$ be identical to that of $(C_5Me_5)_2Sm(SePh)(THF)$.

To rule out the formation of $(C_5Me_5)_2Sm(OPh)(THF)$, we synthesized this complex independently. Reaction of $(C_5Me_5)_2Sm[N(SiMe_3)_2]$[11] with PhOH produced a yellow crystalline product in high yield. $(C_5Me_5)_2Sm(OPh)(THF)$, **5**, was characterized by elemental analysis and ^1H NMR, ^{13}C NMR, and IR spectroscopy. It was completely identified by X-ray crystallography (eq 6; Figure 3). The complex has a ^1H NMR C_5Me_5 resonance at 1.25 ppm that is similar to those of the previously characterized complexes $(C_5Me_5)_2Sm(EPh)(THF)$ (E = S, Se, Te; 1.19, 1.18, and 1.23 ppm, respectively).[9] However, the NMR spectrum of the product of eq 6 was distinct from that of $(C_5Me_5)_2Sm(SePh)(THF)$.



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Further confirmation that **2** decomposed in THF by loss of CO_2 was obtained by synthesis of the carbon-labeled analogue $[(C_5Me_5)_2Sm(\mu\text{-}O_2{}^{13}CSePh)]_2$. Addition of this complex to THF-d_8 generated an organolanthanide product with ^1H and ^{13}C NMR spectra consistent with $(C_5Me_5)_2Sm(SePh)(THF)$ as well as a ^{13}C NMR peak at 126.1 ppm, which matches the resonance of free $^{13}CO_2$ at 1 atm in THF-d_8 (eq 7).

$$[(C_5Me_5)_2Sm(\mu\text{-}O_2{}^{13}CSePh)]_2 \xrightarrow{THF} 2(C_5Me_5)_2Sm(SePh)(THF) + 2{}^{13}CO_2 \quad (7)$$

The structure of $(C_5Me_5)_2Sm(OPh)(THF)$ is not isomorphous with those of the $(C_5Me_5)_2Sm(EPh)(THF)$ complexes.[9]

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Table 5. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(OPh)(THF)$, **5**

Sm(1)−O(1)	2.1645(14)
Sm(1)−O(2)	2.4729(15)
Sm(1)−Cnt1	2.453
Sm(1)−Cnt2	2.445
O(1)−C(21)	1.345(2)
Cnt1−Sm(1)−O(1)	107.3
Cnt2−Sm(1)−O(1)	106.8
Cnt1−Sm(1)−Cnt2	135.0
C(21)−O(1)−Sm(1)	160.66(15)
Cnt1−Sm(1)−O(2)	103.9
Cnt2−Sm(1)−O(2)	104.7
O(1)−Sm(1)−O(2)	89.73(6)

The metallocene parts of all four of these complexes are similar: a 135.0° (C_5Me_5 ring centroid)−Sm−(C_5Me_5 ring centroid) angle vs 133.7−135.2° and a 2.453 Å Sm−centroid distance vs 2.442−2.452 Å.

The Sm−O(OPh) distance of 2.164(1) Å (see Table 5) is much shorter than that of the Sm−E(EPh) analogues (2.760(1)−3.1239(3) Å), as expected on the basis of the sizes of the donor atoms.[25] The Sm−O(THF) distance of 2.473(2) Å in **5** may be slightly longer than that in the analogues (2.443(3)−2.449(2) Å) as a consequence of **5** having more steric bulk close to the metal. The main difference in the structure of **5** is the 160.7(2)° Sm−O−C(ipso) angle. The analogous angles in the S, Se, and Te complexes are much more acute: 120.8(2), 118.5(1), and 112.49(6)°, respectively. Another difference in **5** is that the $(OPh)^{1-}$ ligand is symmetrically positioned between the rings with 106.8 and 107.3° (C_5Me_5 ring centroid)−Sm−O(1) angles. In the S, Se, and Te analogues, these two angles differ by 13−16°.

Conclusion

CO_2 insertion reactions can be used to derivatize aryl chalcogenide ligands and provide $(O_2CEPh)^{1-}$ ligands. These groups readily form crystallographically characterizable complexes with lanthanide metallocenes that decarboxylate in THF. Complexation of the $(O_2CEPh)^{1-}$ ligands to a dimethylaluminum fragment gives a dimeric complex that is fully characterizable by X-ray crystallography, in contrast to the more soluble carboxylate analogue.

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Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure solution, and refinement of compounds **1**−**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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