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Metal Vapor Synthesis of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_4Et)_2Sm(THF)_2$ and Their Reactivity with Organomercurial Reagents. Synthesis and X-ray Structural Analysis of $(C_5Me_5)_2Sm(C_6H_5)(THF)$[†]

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The reaction of samarium metal vapor with hexane solutions of C_5Me_5H and C_5Me_4EtH at −110 to −125 °C followed by suitable workup gives $(C_5Me_5)_2Sm$ and $(C_5Me_4Et)_2Sm$, respectively, as well as products which dissolve in THF to give $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_4Et)_2Sm(THF)_2$, respectively. Evidence is found for hydride- and nitrogen-containing intermediates that decompose to the above compounds upon workup. $(C_5Me_5)_2Sm(THF)_2$ reacts with $Hg(C_6H_5)_2$ to form $(C_5Me_5)_2Sm(C_6H_5)(THF)$ that has been characterized by X-ray crystallography. The phenyl complex crystallizes in space group $P2_1/c$ with unit-cell dimensions $a = 9.680$ (5) Å, $b = 17.291$ (7) Å, $c = 17.140$ (7) Å, $\beta = 103.78$ (4)°, and $Z = 4$ for $D_{calcd} = 1.36$ g cm^{-3}. Least-squares refinement on the basis of 3308 observed reflections led to a final R value of 0.034. The two C_5Me_5 ring centroids, the phenyl carbon attached to Sm, and the THF oxygen describe a distorted tetrahedral structure around Sm in a structure typical of bent metallocene derivatives. Average Sm–C(ring) distances are 2.73 (1) and 2.745 (9) Å, the Sm–C(phenyl) distance is 2.511 (8) Å, and the Sm–O(THF) distance is 2.511 (4) Å.

For many years, the organometallic chemistry of the lanthanide elements centered almost entirely on the +3 oxidation state.[2] Several years ago we initiated an investigation of the low oxidation state chemistry of the lanthanides in efforts to develop a more extensive chemistry for these elements.[3–7] Since then, low-valent lanthanide chemistry has become a very active area[8–12] and numerous reports have appeared on both divalent complexes and the formally zerovalent elemental metals. This paper spans both areas. We report here some reactions of elemental samarium in the vapor state with substituted cyclopentadienes that provide some of the most reactive divalent organolanthanide complexes known. The utility of these divalent species in generating trivalent samarium complexes is presented as well as an X-ray crystal structure of one of these trivalent products. A preliminary report of the synthesis of one divalent product has appeared.[5]

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations of these compounds were conducted under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques.

Materials. Pentane and hexane were washed with sulfuric acid, washed with H_2O, dried over $MgSO_4$, heated to reflux over $LiAlH_4$, and vacuum transferred. Toluene and THF were distilled from potassium benzophenone ketyl. THF-d_8 and benzene-d_6 were vacuum transferred from potassium benzophenone ketyl. Samarium ingots were obtained from Research Chemicals (Phoenix, AZ) and filed to a silvery finish in the glovebox prior to use. C_5Me_5H was either made by literature methods[13] or purchased (Aldrich). C_5Me_4EtH was made according to the literature.[14a] Both types of cyclopentadienes were dried over activated 3A molecular sieves and degassed by dynamic vacuum transfer through a trap before use. Diphenylmercury was purchased from Strem and used as received. Trimethylchlorosilane was dried over 4A molecular sieves and degassed by vacuum transfer. *n*-Butyllithium in hexane was purchased from Aldrich.

Physical Measurements. Infrared spectra were obtained as Nujol mulls between NaCl plates in a Barnes Engineering Pres-Lok holder or as KBr pellets in a KBr press sealed from the atmosphere by O-rings and two NaCl plates. The IR spectra were recorded on a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were obtained on a Bruker HX270 spectrometer. ^{13}C NMR

[†] This paper is dedicated in memory of Earl L. Muetterties, who, in addition to being an outstanding scientist and teacher, was a remarkable human being and an inspiration to all who knew him well.

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Table I. Effect of Temperature and Concentration on the ^{1}H NMR Chemical Shift of $(C_5Me_5)_2Sm(THF)_2$ (ppm)

temp, °C	concn, mol/L	C_5Me_5	$\overline{\mathit{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathit{CH}_2\mathrm{O}}$	$\overline{\mathrm{CH}_2\mathit{CH}_2\mathit{CH}_2\mathrm{CH}_2\mathrm{O}}$
20	0.0736	2.30	15.13	5.16
10	0.0736	2.25	13.87	5.54
0	0.0736	2.19	12.76	6.15
−10	0.0736	2.08	9.76	6.76
−20	0.0736	2.04	*a*	7.30
−30	0.0736	2.03	*a*	7.90
−40	0.0736	2.04	*a*	8.42
−50	0.0736	2.06	*a*	8.90
−60	0.0736	2.10	*a*	9.76
−70	0.0736	2.15	*a*	10.94
−80	0.0736	2.22	*a*	11.90
−90	0.0736	2.33	*a*	12.76
26	0.022	2.90	15.49	*a*
26	0.038	2.62	16.34	3.52
26	0.058	2.58	18.17	3.95

[a] Too broad to observe.

spectra were obtained on a Bruker HE90 spectrometer. NIR spectra were recorded in 2-mm cells on a Cary 14 spectrometer. Magnetic susceptibilities were measured on the Bruker HX270 by the method of Evans.[15] Gas chromatography for H_2, HD, and D_2 in gas samples was done on a 6 ft by $^1/_8$ in. 40/60 mesh 5A molecular sieves column (activated at 300 °C under He) at −160 °C in a Varian Aerograph GC. Gas chromatography for H_2 and N_2 was conducted on a 6 ft long by $^1/_4$ in. 5A molecular sieves column at 35 °C in a HP3850A GC. Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany. Complexometric analyses were obtained as previously described.[16]

Metal Vapor Reactor. The reactor and its method of operation have been previously described.[4]

$(C_5Me_5)_2Sm(THF)_2$. In a typical reaction, Sm metal (4.60 g, 30.6 mol) was vaporized into a 0.246 M C_5Me_5H/hexane solution (5.42 g, 39.9 mmol, in 162 mL) in a rotary metal vapor reactor equipped with a 2-L reactor bottom kept at −123 °C over the course of 15 min. This generated a yellow, then green, and finally black matrix. At this point, the reactor rotation rate was slowed to $6^1/_2$ from 7 on the Büchi scale and the matrix was allowed to melt (bath temperature −115 to −117 °C). After the reaction was continued for an additional 25 min under these conditions, the power was turned off and the reactor was evacuated until a pressure of (8–9) × 10^{-4} torr was achieved. The reactor was warmed to room temperature with a water bath and brought into the drybox. The reaction mixture was filtered through a large, fine porosity frit to give a green filtrate (see next section) and a black solid. Successive extractions of the solid with toluene and THF gave the crude product as a purple-brown, THF-soluble material, I. Anal. Calcd for $SmC_{18}H_{32}O_2$ (i.e., $(C_5Me_5)SmH(THF)_2$): Sm, 34.98; C, 50.30; H, 7.26; O, 7.44. Found: Sm, 35.09; C, 50.28; H, 7.26; O, 7.37 (by difference). Deuterolysis of I gave 0.85 mol/g atm of Sm of gas which was a mixture of HD and D_2 in a 1.9:1 ratio. Calcd for $(C_5Me_5)SmH(THF)_2$: 1.5 mol/g atm of Sm; HD/D_2 = 2:1. Magnetic susceptibility: $\chi_M^{296K} = 3400 \times 10^{-6}$ (cf. 4800×10^{-6} ($\mu = 3.4$) to 5400×10^{-6} ($\mu = 3.6$) for a typical Sm^{2+} species). Recrystallization of I from THF at −78 °C gave purple crystalline material that contained ca. 29% Sm and reacted with D_2O to form a 1:1 mixture of HD/D_2. Further handling in THF lowers the percent of Sm and the amount of HD generated by a sample. A second recrystallization of I generated purple crystals of $(C_5Me_5)_2Sm(THF)_2$, II (2.1 g, 3.7 mmol).[17] X-ray quality crystals were obtained by slowly cooling a THF solution to −47 °C. An X-ray crystal structure study[5] confirmed the formula. Complexometric Anal. Calcd for $SmC_{28}H_{46}O_2$: Sm, 26.61. Found: Sm, 26.1. Magnetic susceptibility: $\chi_M^{296K} = 5390 \times 10^{-6}$; $\mu_{eff} = 3.6\ \mu_B$. D_2O decomposition: II (18.8 mg, 0.03 mmol) reacted with D_2O to produce a gas that was identified by GC as pure D_2 (0.014 mmol, 93%). IR (KBr): 3100–2725 s, 2705 w, 1440 s, 1370 w, 1240 m, 1210 w, 1080 s, 1040 s, 950 w, 895 s, 795 m cm^{-1}. ^{1}H NMR (18.8 mg/mL; 0.033 M in C_6D_6 at 23 °C): δ 2.45 (C_5Me_5), 4.4 (THF), 18 (THF). Table I presents some data on the concentration and temperature dependence of the ^{1}H NMR signals of II. ^{13}C NMR (0.054 M at 38 °C in C_6D_6, ppm): δ 149.5 ($\overline{CH_2CH_2CH_2CH_2O}$), 94.6 (q, J = 117 Hz, $C_5\mathit{Me}_5$), 33.4 (t, J = 125 Hz, $\overline{CH_2CH_2CH_2CH_2O}$), −73.7 (s, C_5Me_5). Near-IR–vis (19.6 mg/mL in toluene): charge transfer like absorption with no maximum in the visible region; ϵ 140 at 1100 nm.

$(C_5Me_5)_2Sm$. The green hexane soluble product separated as a filtrate in the Sm/C_5Me_5H reaction discussed above was isolated by removing the unreacted C_5Me_5H and hexane under dynamic vacuum on the vacuum line. The green residue was washed with pentane to remove a soluble orange-brown byproduct and a green solid, III, remained. Anal. Calcd for $Sm_3NC_{60}H_{90}$: Sm, 35.34; N, 1.10; C, 56.46; H, 7.10. Found: Sm, 35.30; N, 1.05; C, 56.30; H, 6.93. IR (KBr): 3100–2750 s, 1490 w, 1435 s, 1380 m, 1255 w br, 1155 w, 1020 s, 800 w cm^{-1}. When toluene was distilled onto the solid green product and the mixture was allowed to warm to room temperature, gas evolution was observed. Collection of the gas obtained from 247 mg of III (0.19 mmol) by Toepler pump gave 0.147 mmol of gas identified by GC as N_2 containing <0.5% H_2. Removal of the toluene left $(C_5Me_5)_2Sm$, IV, which has subsequently been identified by X-ray crystallography.[7] Complexometric Anal. Calcd for $SmC_{20}H_{30}$: Sm, 35.72. Found: Sm, 36.4. ^{1}H NMR (C_6D_6, ppm): δ 1.0–1.7 depending on concentration. Magnetic susceptibility: $\chi_M^{296K} = 5050 \times 10^{-6}$; $\mu_{eff} = 3.5\ \mu_B$. The yield of IV varied from 200 to 800 mg (2–7% based on starting Sm) depending on reaction conditions. The yield of IV can be enhanced by shortening the reaction time to 20–30 min and by maintaining a slow rate of vaporization.

$(C_5Me_4Et)_2Sm(THF)_2$. In a reaction analogous to the C_5Me_5H reaction described above, Sm metal (4.78 g, 31.8 mol) was vaporized over 40 min into a 0.246 M C_5Me_4EtH/hexane solution (6.21 g, 41.3 mmol in 168 mL) while the reaction flask was kept at −110 °C. The reactor was warmed to room temperature with a water bath and taken into a drybox. The reaction solution was filtered through a fine porosity frit to give a very small amount of precipitate (which was discarded) and an emerald green filtrate. After most of the hexane was removed by rotary evaporation, the excess C_5Me_4EtH was removed by dynamic pumping on the high vacuum line leaving a dark green, semicrystalline solid. Addition of THF to the green material produced an intense purple solution. The THF solution was concentrated by rotary evaporation, the concentrate was placed in a sealable tube equipped with a Teflon stopcock, and the sample was placed in a −78 °C bath overnight. The resulting purple crystals of $(C_5Me_4Et)_2Sm(THF)_2$, V, were separated from the mother liquor, redissolved in the minimum amount of THF, and recrystallized at −78 °C (1.93 g, 10%; the average yield was usually about 2 g, with a range of 0.7–3.5 g). Anal. Calcd for $SmC_{30}H_{50}O_2$: Sm, 25.3. Found: Sm, 25.6. ^{1}H NMR (C_6D_6, ppm): δ 11.29 (v br, THF), 10.10 ($C_5(CH_3)_4(\mathit{CH}_2CH_3)$), 4.54 ($C_5(\mathit{CH}_3)_4Et$), 3.39 (THF), 2.21 ($C_5(CH_3)_4(CH_2\mathit{CH}_3)$), 0.10 ($C_5(\mathit{CH}_3)_4Et$). Peak positions are concentration dependent.

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[17] The formal yield based on starting Sm is 12%. However, both unreacted Sm metal and C_5Me_5H can be recovered and recycled.

The tentative assignments were made from the intensities and by analogy to $(C_5Me_5)_2Sm(THF)_2$ with consideration of the spectra of $Fe(C_5Me_4Et)_2$,[14a] $Ti(C_5Me_4Et)_2Cl_2$,[14a] and $Th(C_5Me_4Et)Cl_3(MeCONMe_2)_2$.[14b] ^{13}C NMR (C_6D_6, ppm): 101.1, 96.8, 88.2, 56.5, 30.4, −62.6, −74.3, −77.1. The gated spectrum showed no change in the high-field signals, making them assignable to the ring carbons. The remaining signals displayed overlapping coupling patterns and therefore did not give easily discernible coupling constants. IR (Nujol): 1310 m, 1155 m, 1100 br w, 1060 sh, 1045 s, 970 w, 950 w, 910 w, 880 s, 660 m cm^{-1}. Magnetic susceptibility: $\chi_M^{298K} = 6150 \times 10^{-6}$; $\mu_{eff} = 3.8\ \mu_B$. Near-IR–vis (30.4 mg/mL in toluene): charge-transfer band 1600–915 nm; ϵ 80 at 1100 nm. D_2O decomposition: V (119 mg, 0.20 mmol) reacted with D_2O to produce a gas identified by GC as pure D_2 (0.075 mol, 75%).

$(C_5Me_4Et)_2Sm$. In a typical reaction, Sm metal (3.8 g, 25.3 mol) was vaporized into 0.246 M C_5Me_4EtH/hexane solution (4.94 g, 32.9 mmol in 134 mL). The reaction was worked up as described above, except no THF was added to the initial green product. The green solid was crystallized two times from pentane at −116 °C (EtOH/N_2(l) slush bath) to give $(C_5Me_4Et)_2Sm$, VI, as green crystals (400 mg, 3.5%). X-ray quality crystals can be grown from benzene by slow evaporation at room temperature. Anal. Calcd for $SmC_{22}H_{34}$: Sm, 33.50; C, 58.87; H, 7.64; N, 0.00. Found: Sm, 34.41; C, 57.89; H, 7.34; N, 0.24. ^1H NMR (C_6D_6, ppm): δ 9.74, 3.22, −0.48, −1.16. IR (Nujol): 1310 m, 1140 m, 1065 sh, 1050 s, 1020 s, 970 m, 950 m, 790 w, 780 w, 760 w, 750 w, 730 s, 690 m, 670 w, 650 w cm^{-1}. Magnetic susceptibility: $\chi_M^{298K} = 4680 \times 10^{-6}$; $\mu_{eff} = 3.6\ \mu_B$. Near-IR (9.7 mg/mL in pentane) charge-transfer band 1600–340 nm with shoulder maxima at 815 (ϵ 70) and 525 nm (ϵ 40). Deuterolysis of VI (76.6 mg, 0.15 mmol) produced 0.05 mmol of gas at −196 °C. GC analysis (5A at 35 °C and 5A at −140 °C) showed it to be 100% D_2 (66% yield).

$(C_5Me_5)_2Sm(C_6H_5)(THF)$. In the glovebox, $(C_5Me_5)_2Sm(THF)_2$ (304 mg, 0.54 mmol) and $(C_6H_5)_2Hg$ (95.5 mg, 0.27 mmol) were dissolved in toluene (40 mL) and stirred overnight. The reaction mixture slowly changed from a dark purple to orange with the precipitation of a gray, metallic powder (Hg). Removal of solvent by rotary evaporation gave a gray-orange mass that was extracted with pentane and gravity filtered through a medium frit. Rotary evaporation of the filtrate gave orange crystals of the product VII (210.7 mg, 68%). Anal. Calcd for the desolvated complex $(C_5Me_5)_2SmC_6H_5$, i.e., $SmC_{26}H_{35}$: Sm, 30.20; C, 62.73; H, 7.08; Hg, 0.0. Found: Sm, 31.62; C, 60.80; H, 7.02; Hg, <0.05. ^1H NMR (C_6D_6, ppm): δ 1.44 (s, 9.6, C_5Me_5), −1.7 (br, 1, THF), −2.9 (v br, 1, THF). The tentative assignment of the latter two resonances to THF is by analogy to the resonances observed for THF in $(C_5Me_5)_2SmCl(THF)$[18] and $(C_5Me_5)_2SmI(THF)$.[18] The shifts of the THF resonances are variable depending upon the amount of THF present. Definitive assignment of resonances associated with the phenyl group have not been made. ^{13}C NMR (C_6D_6, ppm): 138.6, 119.8, 115.0, 62.2, 20.4, 16.7. IR (Nujol): 1410 w, 1340 w, 1300 w, 1100 s br, 1040 s, 980 m, 870 m, 800 s, 700 m, 675 m, 630 s, 600 s cm^{-1}. Magnetic susceptibility: $\chi_M^{299K} = 1150 \times 10^{-6}$; $\mu_{eff} = 1.6\ \mu_B$.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(C_6H_5)(THF)$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as described from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table II.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique as previously described.[19] A summary of data collection parameters is given in Table II. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[20]

Calculations were carried out with the SHELX system of computer programs.[21] Neutral atom scattering factors for Sm, O, and C were taken from Cromer and Waber,[22] and the scattering for samarium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[23] Scattering factors for hydrogen were from ref 24.

Table II. Crystal Data for $(C_5Me_5)_2Sm(C_6H_5)(THF)$

compd	$SmOC_{30}H_{43}$
mol wt	570.13
space group	$P2_1/c$
cell const	
a, Å	9.680 (5)
b, Å	17.291 (7)
c, Å	17.140 (7)
β, deg	103.78 (4)
cell vol, Å^3	2786.3
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.36
μ(calcd), cm^{-1}	21.6
radiatn	Mo Kα
max cryst dimens, mm	0.45 × 0.35 × 0.30
scan width, deg	0.8 + 0.2 tan θ
std reflctns	400, 080, 008
decay of std	<2%
reflctns measd	4012
2θ range	1–46
obsd reflctns	3308
no. of parameters varied	289
GOF	0.76
R	0.034
R_w	0.039

The space group was shown to be $P2_1/c$ by systematic absences. The position of the samarium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the metal atom revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.085$.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The final agreement factors are $R = 0.034$ and $R_w = 0.039$. A final difference Fourier showed no feature greater than 0.5 e$^-$/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table III.

$(C_5Me_4Et)_2Sm(C_6H_5)(THF)$. In the glovebox, $(C_5Me_4Et)_2Sm(THF)_2$ (400 mg, 0.67 mmol) and $(C_6H_5)_2Hg$ (119 mg, 0.34 mmol) were dissolved in toluene (50 mL) and the mixture stirred overnight with a Teflon-coated stir bar. The reaction mixture slowly turned from dark purple to orange. Removal of solvent by rotary evaporation gave a grayish solid which was extracted with pentane and gravity filtered through a medium porosity frit. Rotary evaporation of the filtrate left VIII as an orange semicrystalline solid (300 mg, 74%). Anal. Calcd for desolvated $(C_5Me_4Et)_2Sm(C_6H_5)$, i.e., $SmC_{28}H_{39}$: Sm, 28.59; C, 63.94; H, 7.47; Hg, 0.00. Found: Sm, 28.36; C, 63.70; H, 7.29; Hg, 0.0. ^1H NMR (C_6D_6, ppm): δ 1.73, 1.48, 1.35 (C_5Me_5), −1.7, −2.9 (THF). ^{13}C NMR (C_6D_6, ppm): 138.2, 121.6, 119.8, 115.3, 114.6, 62.8, 30.2, 24.7, 20.4, 16.7, 12.0. IR (Nujol) 1410 w, 1310 w, 1225 w, 1160 br, 1090 br, 1045 m, 1020 s, 990 w, 970 w, 955 w, 940 w, 915 m, 860 s, 800 m, 710 m, 700 s, 665 w, 600 s, cm^{-1}. Magnetic susceptibility: $\chi_M^{299K} = 1430 \times 10^{-6}$; $\mu_{eff} = 1.7\ \mu_B$. Near-IR (29.7 mg/mL in pentane) 1560 (ϵ 14), 1530 (4), 1470 (18), 1390 (7), 1370 (12), 1300 (5), 1290 (5), 1225 (21), 1200 (6), 1100 (10), 1080 (9), 950 (3) nm, and a charge-transfer band off scale. Decomposition with Me_3SiCl: Me_3SiCl (0.13 mL, 0.45 mol) was distilled onto $(C_5Me_4Et)_2Sm(C_6H_5)$ (THF) (80 mg, 0.15 mmol) dissolved in THF ($^1/_2$ mL) in a small round bottom flask. After the reaction mixture was stirred for 2 days, the volatile materials were removed by vacuum transfer in two portions. The most volatile fraction contained THF and Me_3SiCl by ^1H NMR spectroscopy. A low

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Table III. Final Fractional Coordinates for $(C_5Me_5)_2Sm(C_6H_5)(THF)$

atom	*x/a*	*y/b*	*z/c*	*U*(eqv), Å^2	atom	*x/a*	*y/b*	*z/c*	*U*(eqv), Å^2
Sm	0.15404 (3)	0.04539 (2)	0.27051 (2)	0.041	H(7)B	0.4633	−0.0544	0.4029	0.080
C(1)	0.338 (1)	0.1457 (6)	0.3275 (5)	0.086	H(8)A	0.5533	−0.1695	0.4028	0.080
C(2)	0.293 (1)	0.2230 (8)	0.3235 (6)	0.103	H(8)B	0.5658	−0.1601	0.3099	0.080
C(3)	0.375 (1)	0.2822 (6)	0.3628 (6)	0.098	H(9)A	0.3604	−0.2291	0.3675	0.080
C(4)	0.504 (1)	0.2663 (6)	0.4073 (6)	0.102	H(9)B	0.3953	−0.2379	0.2792	0.080
C(5)	0.553 (1)	0.1937 (6)	0.4127 (6)	0.092	H(10)A	0.2374	−0.1598	0.2290	0.080
C(6)	0.466 (1)	0.1362 (5)	0.3738 (6)	0.097	H(10)B	0.1859	−0.1633	0.3130	0.080
O(1)	0.3076 (5)	−0.0727 (3)	0.3046 (3)	0.063	H(16)A	0.1876	0.1531	0.4737	0.080
C(7)	0.4539 (8)	−0.0730 (5)	0.3467 (6)	0.084	H(16)B	0.3116	0.0870	0.4888	0.080
C(8)	0.502 (1)	−0.1540 (5)	0.3473 (8)	0.117	H(16)C	0.1948	0.0879	0.5436	0.080
C(9)	0.380 (1)	−0.2002 (5)	0.3208 (8)	0.112	H(17)A	0.0981	−0.1167	0.4200	0.080
C(10)	0.2672 (9)	−0.1512 (5)	0.2883 (7)	0.098	H(17)B	0.1331	−0.0762	0.5086	0.080
C(11)	0.0971 (9)	0.0684 (6)	0.4179 (4)	0.077	H(17)C	0.2537	−0.0775	0.4563	0.080
C(12)	0.0708 (9)	−0.0100 (5)	0.4011 (5)	0.073	H(18)A	−0.0602	−0.1316	0.3299	0.080
C(13)	−0.0486 (8)	−0.0155 (5)	0.3375 (5)	0.064	H(18)B	−0.1367	−0.0930	0.2435	0.080
C(14)	−0.0979 (8)	0.0574 (5)	0.3151 (4)	0.064	H(18)C	−0.2185	−0.0934	0.3165	0.080
C(15)	−0.009 (1)	0.1103 (4)	0.3643 (5)	0.077	H(19)A	−0.2545	0.0263	0.2388	0.080
C(16)	0.210 (1)	0.0978 (9)	0.4888 (5)	0.175	H(19)B	−0.2419	0.1183	0.2200	0.080
C(17)	0.150 (1)	−0.0733 (7)	0.4533 (7)	0.167	H(19)C	−0.3186	0.0906	0.2905	0.080
C(18)	−0.124 (1)	−0.0890 (6)	0.3030 (7)	0.127	H(20)A	0.0524	0.2191	0.4002	0.080
C(19)	−0.2405 (9)	0.0791 (8)	0.2631 (6)	0.129	H(20)B	−0.1180	0.2090	0.3926	0.080
C(20)	−0.037 (1)	0.1957 (5)	0.3677 (8)	0.170	H(20)C	−0.0576	0.2165	0.3117	0.080
C(21)	0.195 (1)	0.1069 (5)	0.1301 (4)	0.078	H(26)A	0.2302	0.2116	0.1386	0.080
C(22)	0.050 (1)	0.1123 (5)	0.1241 (4)	0.075	H(26)B	0.3128	0.1805	0.0720	0.080
C(23)	−0.0069 (8)	0.0373 (6)	0.1155 (4)	0.070	H(26)C	0.3897	0.1749	0.1676	0.080
C(24)	0.104 (1)	−0.0139 (4)	0.1172 (4)	0.068	H(27)A	0.0502	0.2134	0.1304	0.080
C(25)	0.2293 (9)	0.0284 (5)	0.1265 (4)	0.071	H(27)B	−0.0981	0.1979	0.1576	0.080
C(26)	0.297 (1)	0.1715 (7)	0.1268 (6)	0.174	H(27)C	−0.0969	0.1977	0.0625	0.080
C(27)	−0.042 (2)	0.1841 (6)	0.1178 (6)	0.161	H(28)A	−0.2032	0.0675	0.0958	0.080
C(28)	−0.162 (1)	0.0151 (8)	0.0913 (5)	0.141	H(28)B	−0.2026	−0.0226	0.1242	0.080
C(29)	0.075 (1)	−0.0987 (5)	0.0972 (5)	0.127	H(28)C	−0.1869	−0.0017	0.0338	0.080
C(30)	0.373 (1)	0.0004 (8)	0.1259 (6)	0.151	H(29)A	0.1760	−0.1171	0.1077	0.080
H(2)	0.1960	0.2353	0.2902	0.080	H(29)B	0.0267	−0.1086	0.0398	0.080
H(3)	0.3383	0.3366	0.3580	0.080	H(29)C	0.0246	−0.1273	0.1329	0.080
H(4)	0.5659	0.3089	0.4360	0.080	H(30)A	0.3661	−0.0573	0.1230	0.080
H(5)	0.6499	0.1813	0.4458	0.080	H(30)B	0.4396	0.0159	0.1776	0.080
H(6)	0.5033	0.0821	0.3815	0.080	H(30)C	0.4101	0.0201	0.0799	0.080
H(7)A	0.5111	−0.0390	0.3191	0.080					

volatility fraction showed, among others, ^1H NMR resonances at δ 7.38, 7.21, and 0.13 attributable to $(C_6H_5)SiMe_3$. Integration against an internal standard (ethylene carbonate) indicated a yield of 35%. GC analysis against authentic material confirmed the identity of $(C_6H_5)SiMe_3$.

Results

Metal Vapor Synthesis. Choice of System. We chose to explore the reaction of samarium metal vapor with C_5Me_5H and C_5Me_4EtH both as a possible route[25] to soluble, halide-free organosamarium(II) complexes as well as an opportunity to study the oxidative addition of C–H bonds to lanthanide metals. Of the readily accessible divalent lanthanides Eu^{2+}, Yb^{2+}, and Sm^{2+}, samarium was the most interesting because it is the most reactive. The superior reactivity arises because samarium is the most strongly reducing ($E = -1.5$ V vs. NHE for $Sm^{3+} + e \rightarrow Sm^{2+}$)[26] and the largest metal of the three. The latter property confers reactivity because organolanthanides traditionally can be stabilized by sterically saturating the coordination environment of the metal. In general, the larger the metal, the more coordinatively unsaturated and reactive are its complexes.[27] Unfortunately, this high potential reactivity never was previously utilized with organosamarium(II) complexes since the only organometallic species known at the time $[(C_5H_5)_2Sm]_n$[28,29] and $[(CH_3C_5H_4)_2Sm]_n$[30] were insoluble. The more highly substituted ring systems offered the possibility of solubility.

Oxidative addition of C–H to lanthanide metals was of interest because previous lanthanide metal vapor studies led to organometallic hydride products presumably formed by this route.[3f,g] The best characterized systems involved the reactions of the metals with terminal alkynes, $RC{\equiv}CH$, which generated products of the type $[HYb_2(C{\equiv}CR)_3]_n$ and $[HLn(C{\equiv}CR)_2]_n$ (Ln = Er, Sm).[3f] These studies did not yield crystallizable products, however. Given the success of the C_5Me_5 ligand in providing crystalline products for experimentally difficult systems with Ti and Zr[31] and with Th and U,[32] this ligand seemed like an excellent candidate with which to trap a crystalline C–H oxidative addition product.

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The Sm/C_5Me_5H Reaction. Vaporization of samarium metal into an approximately 0.25 M solution of C_5Me_5H in hexane kept at −117 to −123 °C in a rotary metal vapor reaction generated a yellow, then green, and finally black solution. After 40 min of vaporization, the reaction was stopped, the system was brought to room temperature, and the entire reactor assembly was taken into an inert-atmosphere glovebox. Filtration of the reaction mixture gave the main product of this reaction as a dark precipitate and minor product as a green filtrate.

$(C_5Me_5)_2Sm(THF)_2$. The black precipitate was washed with toluene and extracted with THF to give a purple-brown filtrate from which a purple brown solid, I, could be isolated. Complete elemental analysis of I was consistent with the formula $(C_5Me_5)SmH(THF)_2$, and deuterolysis produced HD and D_2 in a 1.9:1 ratio, which is close to the expected ratio for a divalent hydride. The yield of the gas was only 57% of that expected, however, and the magnetic susceptibility was less than that expected for a pure Sm(II) complex. Subsequent recrystallization of I gave a purple solid containing a smaller percentage of Sm and less hydride (by deuterolysis). A second recrystallization gave $(C_5Me_5)_2Sm(THF)_2$, II, a product characterized by analytical, spectroscopic, and X-ray crystallographic[5,33] methods.

The ^1H NMR spectrum of II in C_6D_6 exhibited relatively sharp singlets at δ 2.45 ($\Delta w_{1/2}$ = 8 Hz) and 4.43 ($\Delta w_{1/2}$ = 33 Hz) and a broad absorption at δ 17.99 ($\Delta w_{1/2}$ = 92 Hz). Exchange of the solvated THF in II with THF-d_8 gave a complex which displayed only the δ 2.45 absorption. Hence, this absorption was assigned to C_5Me_5, the δ 4.4 absorption to the β-CH_2 group most distant from the paramagnetic Sm(II) center and the broad resonance to the α-CH_2 group. The ^{13}C NMR spectrum of II in C_6D_6 exhibited a pattern of absorptions just the opposite of that found in other (pentamethylcyclopentadienyl)lanthanide complexes, namely, the ring carbon atoms resonated at high field, δ − 73.7, while the methyl carbons resonated at low field, δ 94.6.

$(C_5Me_5)_2Sm$. The green byproduct of the Sm/C_5Me_5H reaction, which was originally isolated from the reaction mixture by filtration, was separated from unreacted C_5Me_5H and hexane by trap to trap distillation of the latter organics under dynamic vacuum. The green residue could be washed with pentane to give a green solid, III, which upon dissolution in toluene appeared to liberate nitrogen. Complete elemental analysis of III before treatment with toluene was also consistent with the presence of nitrogen but definitive identification of this complex was not made. However, the product formed when III was dissolved in toluene has been fully characterized by analytical, spectroscopic, and crystallographic[7] methods as $(C_5Me_5)_2Sm$, IV. IV readily and quantitatively converts to II in the presence of THF.

The Sm/C_5Me_4EtH Reaction. The reaction of samarium metal vapor with C_5Me_4EtH in hexane paralleled the Sm/C_5Me_5H reaction in the colors observed during the reaction and in the main products obtained. The main difference in the two systems is that the C_5Me_4Et complexes are more soluble in nonpolar solvents.

$(C_5Me_4Et)_2Sm(THF)_2$. Filtration of the initially formed reaction mixture gave a green filtrate and very little precipitate, in contrast to the C_5Me_5 reaction, in which the precipitate was the source of the main product $(C_5Me_5)_2Sm(THF)_2$. To isolate $(C_5Me_4Et)_2Sm(THF)_2$, V, excess C_5Me_4EtH and hexane were removed from the filtrate under dynamic vacuum, THF was added to the residue, and two recrystallizations from THF at −78 °C were carried out. Given the enhanced solubility of all of the products in the C_5Me_4Et system, no attempt was made to isolate intermediate hydride or nitrogen-containing byproducts. Complex V was characterized by elemental analysis, deuterolysis, ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, magnetic susceptibility measurement, and NIR spectroscopy and was found to be similar to II. Deuterolysis of twice recrystallized V produced pure D_2. The NMR spectra of V are more complicated than those of II due to the lower symmetry of the C_5Me_4Et ring vs. C_5Me_5, but assignments could be made on the basis of intensities and the known spectra of II, $(C_5Me_4Et)_2Fe$,[14a] $(C_5Me_4Et)_2TiCl_2$,[14a] and $(C_5Me_4Et)ThCl_3(MeCONMe_2)_2$.[14b] The ^{13}C NMR spectrum of V like that of II had a resonance pattern opposite that of organosamarium(III) complexes; i.e., the ring carbons were observed at high field and the alkyl carbons were found at low field.

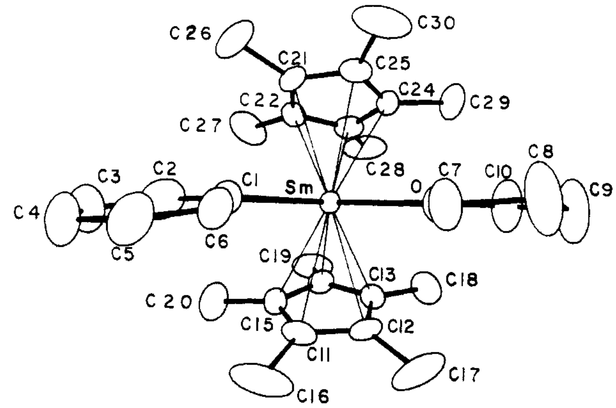

Figure 1. ORTEP plot of the molecular structure of $(C_5Me_5)Sm(C_6H_5)(THF)$.

$(C_5Me_4Et)_2Sm$. To isolate a THF-free C_5Me_4Et samarium(II) complex, the residue obtained by removing C_5Me_4EtH and hexane from the original reaction filtrate was recrystallized from pentane at −116 °C. Analytically pure $(C_5Me_4Et)_2Sm$, VI, was isolated in this way and characterized by the usual spectroscopic and analytical methods.

Synthesis of $(C_5Me_5)_2Sm(C_6H_5)(THF)$, VII, and $(C_5Me_4Et)_2Sm(C_6H_5)(THF)$, VIII. The reaction of $(C_5Me_5)_2Sm(THF)_2$, II, and $(C_5Me_4Et)_2Sm(THF)_2$, V, with organomercury reagents was investigated to see if these divalent complexes would be viable precursors for a halide-free synthesis of organosamarium(III) complexes involving Sm–C bonds. Both II and V react with $Hg(C_6H_5)_2$[34] to form the phenyl complexes $(C_5Me_5)_2Sm(C_6H_5)(THF)$ and $(C_5Me_4Et)_2Sm(C_6H_5)(THF)$ as shown in eq 1 for II.

$$2(C_5Me_5)_2Sm(THF)_2 + Hg(C_6H_5)_2 \rightarrow 2(C_5Me_5)_2Sm(C_6H_5)(THF) + Hg \quad (1)$$

In each case, the purple color of the divalent starting material gradually changed into an orange color characteristic of Sm(III) while metallic mercury deposited in the flask. Rotary evaporation of solvent, pentane extraction of the residue, and filtration gave the phenyl products. The new complexes were characterized by complete elemental analysis, IR, ^1H NMR, and ^{13}C NMR spectroscopy, magnetic moment measurement, and, in the case of VII, X-ray crystallography.

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Table IV. Bond Lengths (Å) and Angles (deg) for $(C_5Me_5)_2Sm(C_6H_5)(THF)$

Bond Distances

Sm-O(1)	2.511 (4)	Sm-C(1)	2.511 (8)
Sm-C(11)	2.739 (7)	Sm-C(12)	2.726 (7)
Sm-C(13)	2.711 (7)	Sm-C(14)	2.732 (7)
Sm-C(15)	2.744 (8)	Sm-C(21)	2.745 (7)
Sm-C(22)	2.728 (7)	Sm-C(23)	2.744 (7)
Sm-C(24)	2.755 (7)	Sm-C(25)	2.751 (7)
Sm-Cnt(1)	2.461	Sm-Cnt(2)	2.475
Sm-Ave(1)	2.73 (1)	Sm-Ave(2)	2.745 (9)
O(1)-C(7)	1.428 (9)	O(1)-C(10)	1.422 (9)
C(1)-C(2)	1.40 (1)	C(1)-C(6)	1.31 (1)
C(2)-C(3)	1.37 (1)	C(3)-C(4)	1.33 (1)
C(4)-C(5)	1.33 (1)	C(5)-C(6)	1.37 (1)
C(7)-C(8)	1.47 (1)	C(8)-C(9)	1.40 (1)
C(9)-C(10)	1.39 (1)	C(11)-C(12)	1.40 (1)
C(11)-C(15)	1.40 (1)	C(11)-C(16)	1.52 (1)
C(12)-C(13)	1.39 (1)	C(12)-C(17)	1.50 (1)
C(13)-C(14)	1.37 (1)	C(13)-C(18)	1.51 (1)
C(14)-C(15)	1.39 (1)	C(14)-C(19)	1.50 (1)
C(15)-C(20)	1.51 (1)	C(21)-C(22)	1.39 (1)
C(21)-C(25)	1.40 (1)	C(21)-C(26)	1.50 (1)
C(22)-C(23)	1.40 (1)	C(22)-C(27)	1.51 (1)
C(23)-C(24)	1.39 (1)	C(23)-C(28)	1.51 (1)
C(24)-C(25)	1.39 (1)	C(24)-C(29)	1.52 (1)
C(25)-C(30)	1.48 (1)		

Bond Angles

O(1)-Sm-C(1)	98.3 (3)	C(1)-Sm-Cnt(1)	103.636
O(1)-Sm-C(1)	103.862	C(1)-Sm-Cnt(2)	106.149
O(1)-Sm-Cnt(1)	103.111	Cnt(1)-Sm-Cnt(2)	135.934
Sm-O(1)-C(7)	125.5 (4)	Sm-O(1)-C(10)	127.6 (4)
C(7)-O(1)-C(10)	106.8 (6)	Sm-C(1)-C(2)	117.1 (8)
Sm-C(1)-C(6)	129.0 (8)	C(2)-C(1)-C(6)	112.6 (8)
C(1)-C(2)-C(3)	123.6 (9)	C(2)-C(3)-C(4)	119 (1)
C(3)-C(4)-C(5)	119.9 (9)	C(4)-C(5)-C(6)	119.2 (9)
C(1)-C(6)-C(5)	126 (1)	O(1)-C(7)-C(8)	106.2 (7)
C(7)-C(8)-C(9)	107.7 (8)	C(8)-C(9)-C(10)	107.4 (8)
O(1)-C(10)-C(9)	110.4 (7)	C(12)-C(11)-C(15)	107.3 (7)
C(12)-C(11)-C(16)	123 (1)	C(15)-C(11)-C(16)	129 (1)
C(11)-C(12)-C(13)	107.7 (7)	C(11)-C(12)-C(17)	122.9 (9)
C(13)-C(12)-C(17)	129 (1)	C(12)-C(13)-C(14)	109.0 (7)
C(12)-C(13)-C(18)	126.6 (9)	C(14)-C(13)-C(18)	124.1 (8)
C(13)-C(14)-C(15)	108.1 (7)	C(13)-C(14)-C(19)	127.3 (9)
C(15)-C(14)-C(19)	122.9 (8)	C(11)-C(15)-C(14)	107.9 (7)
C(11)-C(15)-C(20)	126 (1)	C(14)-C(15)-C(20)	125.0 (9)
C(22)-C(21)-C(25)	108.0 (7)	C(22)-C(21)-C(26)	128 (1)
C(25)-C(21)-C(26)	124 (1)	C(21)-C(22)-C(23)	108.1 (7)
C(21)-C(22)-C(27)	129 (1)	C(23)-C(22)-C(27)	123 (1)
C(22)-C(23)-C(24)	107.6 (7)	C(22)-C(23)-C(28)	127 (1)
C(24)-C(23)-C(28)	124 (1)	C(23)-C(24)-C(25)	108.4 (7)
C(23)-C(24)-C(29)	120.6 (9)	C(25)-C(24)-C(29)	130 (1)
C(21)-C(25)-C(24)	107.8 (8)	C(21)-C(25)-C(30)	123 (1)
C(24)-C(25)-C(30)	129 (1)		

Structure of $(C_5Me_5)_2Sm(C_6H_5)(THF)$, VII. As shown in Figure 1, complex VII has the bent metallocene structure typical of bis(cyclopentadienyl)metal complexes which contain two other ligands.[35] Bond distances and angles are given in Table IV.

The ring centroid–Sm–ring centroid angle of 136.9° is in the range commonly observed for bis(pentamethylcyclopentadienyl)lanthanide and -actinide complexes.[33,36] The angle between the THF oxygen atom, the metal, and the phenyl carbon, 98.3 (3)°, is somewhat wider than the normal 85–95° angles found for $(C_5Me_5)_2M(X)Y$ systems. For example, the THF oxygen–metal–halogen angles in the crystal structure of $(C_5Me_5)_2SmCl(THF)$, IX,[18] are 90.4 (5)° and 91.6 (5)°, and in the crystal structure of $(C_5Me_5)_2SmI(THF)$, X,[18] they are 88.8 (3)° and 90.5 (3)°.

The larger angle found in VII may occur to accommodate the orientation adopted by the phenyl ring. As can be seen from Figure 1, the phenyl ring lies roughly in the plane (hereafter called the bisector plane) which bisects the ring centroid–metal–ring centroid angle and is normal to the plane defined by the ring centroids and the metal.[37] The THF molecule although not planar also lies roughly in the bisector plane as is also found in IX and X. Although this observed orientation is the most sterically crowded arrangement of the phenyl and THF substituents with respect to each other, it does provide the least steric interaction between these ligands and the C_5Me_5 rings. The problem of steric crowding of C_5Me_5 rings with X and Y

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[37] Cf. $(C_5H_5)_2Ti(C_6H_5)_2$ (Kocman, V.; Rucklidge, J. C.; O'Brien, R. J.; Santo, W. *J. Chem. Soc., Chem. Commun.* **1971**, 340) and $(C_5H_5)_2Zr(C_6H_5)[CH(SiMe_3)_2]$ (Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081–1083) which do not have the phenyl ligands in the plane. In $(C_5H_5)_2Ti(C_6H_3Me_2)$, the metal is 0.087 Å out of the plane of the aryl ring (Olthof, G. J.; Bolhuis, F. V. *J. Organomet. Chem.* **1976**, *122*, 47–52.

substituents in $(C_5Me_5)_2M(X)Y$ systems has been discussed for a series of $(C_5Me_5)_2Yb(\mu\text{-halide})M(\text{solvent})_2$ molecules.[38] Apparently, this is the predominant factor influencing the structure of VII.

The average Sm–C(ring) distances in VII, 2.73 (1) and 2.745 (9) Å, are comparable to the analogous distances in IX, 2.72 Å, and X, 2.72 and 2.73 Å. The Sm–O(THF) distance in VII, 2.511 (4) Å, is somewhat longer than the Sm–O(THF) distances in IX, 2.44 (2) and 2.48 (2) Å, and in X, 2.45 (1) Å.

The Sm–C(phenyl) bond length in VII, 2.511 (8) Å, is only the second non-cyclopentadienyl C–Sm distance reported in the literature to our knowledge. Comparison of this distance with the Sm–C(alkynide) bond lengths of 2.55 (1) Å in $[(CH_3C_5H_4)_2Sm(\mu\text{-}C{\equiv}CCMe_3)]_2$, XI,[39] is complicated by the conflicting trends that alkynide bonds are normally shorter than aryl bonds and bridging bonds are normally longer than terminal bonds in complexes of this type. For example, the V–C(alkynide) bond in $(C_5H_5)_2VC{\equiv}CCMe_3$,[40] 2.075 (5) Å, is 0.05–0.08 Å shorter than the V–C(aryl) bonds in $[(CH_3C_5H_4)_2V]_2(C_6H_4)$,[41] 2.125 (11) and 2.154 (10) Å, and the Yb–C(methyl bridge) bonds in $[(C_5H_5)_2Yb(\mu\text{-}CH_3)]_2$,[42] 2.486 (17) and 2.536 (17) Å, are 0.12–0.17 Å longer than the Yb–C(terminal CH_3) bond in $(C_5H_5)_2Yb(CH_3)(THF)$, XII,[43] 2.361 (10) Å. If the considerable extrapolations necessary to compare Sm–C bond lengths in VII and XI are used, one might conclude that the Sm–C distance in VII is normal.

Comparison of the 2.511 (8) Å Sm–C distance can also be made with other lanthanide aryl complexes if metal size and coordinative saturation are considered. Two other aryl lanthanide complexes have been crystallographically studied, although neither has a simple unsubstituted phenyl ligand. $[Li(THF)]_4[Lu(2,6\text{-}Me_2C_6H_3)_4]$, XIII,[44] has Lu–C(aryl) distances of 2.425 (15), 2.439 (16), 2.442 (15), and 2.501 (17) Å. $Lu(o\text{-}C_6H_4CH_2NMe_2)_3$, XIV,[45] in which the amino groups also complex the metal, has Lu–C(aryl) distances of 2.425 (7), 2.426 (7), and 2.455 (7) Å. Since Lu^{3+} is approximately 0.12 Å smaller than Sm^{3+},[46] the Lu–C distances in XIII and XIV are somewhat long compared to the Sm–C distance in VII. This may be due to increased steric congestion in the lutetium species.

Discussion

The original strategy to use C_5Me_5 as a solubilizing ligand for Sm(II) and to use the metal vapor technique as a clean synthetic route to soluble divalent samarium complexes was successful in the C_5Me_4RH/Sm system (R = Me, Et). The major divalent samarium products $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_4Et)_2Sm(THF)_2$ are soluble in alkanes and display the high reactivity anticipated for this strongly reducing oxidation state.[5,6] Both complexes can be prepared in good yield in preparative scale quantities by metal vapor methods, and this route has been used to provide the material for preliminary reactivity studies.[5,6] Since that time a solution synthesis based on $SmI_2(THF)_x$ has been developed that provides access to even larger quantities of these complexes without a metal vapor reactor system.[33,47]

The characterization of intermediates in the C_5Me_5H/Sm reaction which contains hydridic ligands along with Sm(II) strongly suggests that oxidative addition of C–H is an important component of this reaction. As shown in eq 2, Sm could insert into the acidic C–H linkage of

$$C_5Me_5H + Sm \rightarrow [C_5Me_5SmH] \xrightarrow{THF} (C_5Me_5)_2Sm(THF)_2 \quad (2)$$

C_5Me_5H to form a divalent hydride, possibly with an initial (η^1-C_5Me_5) ligand which rearranges to the η^5-C_5Me_5 form. The coordinatively unsaturated "$(C_5Me_5)SmH$" would be expected to be highly reactive and could react with additional C_5Me_5H in solution to form $(C_5Me_5)_2Sm$, IV, and H_2. Alternatively, the "C_5Me_5SmH" moiety could undergo a ligand redistribution reaction to form IV. Other routes to IV also are possible. In light of the limited stability of the initially formed divalent hydridic product, the specific mechanism(s) for the formation of IV is likely to remain unknown. Clearly oxidation of the metal via metal hydride moieties occurs in this system. The rapid conversion of $(C_5Me_5)_2Sm$ to the solvated product $(C_5Me_5)_2Sm(THF)_2$ upon THF addition is readily accounted for on the basis of the coordinatively unsaturated environment found in IV.

Both $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_4Et)_2Sm(THF)_2$ react cleanly with $Hg(C_6H_5)_2$ to form trivalent samarium phenyl complexes. The redox reaction provides a convenient, halide-free route to Sm(III) species and avoids any possibility of forming alkali-metal halide adducts as could occur in ionic metathesis reactions. As demonstrated by the syntheses of $(C_5Me_5)_2Ln(\mu\text{-halide})M(\text{solvent})_2$ complexes,[38,48–52] alkali-metal halide adduct formation is facile in syntheses of complexes of this type. Syntheses that avoid alkali-metal halide byproducts are therefore desirable, particularly when a new complex is prepared and characterized for the first time. Reactions of mercury reagents with divalent lanthanides provide such routes and may prove to be generally useful.

The X-ray crystallographic study of $(C_5Me_5)_2Sm(C_6H_5)(THF)$ provides the first structural information on an organolanthanide complex containing an unsubstituted phenyl ligand. The isolation of this molecule as a THF adduct contrasts with unsolvated lutetium derivative $(C_5Me_5)_2LuC_6H_5$,[53] which may be too sterically crowded for adduct formation. Since the THF can be removed from the samarium derivatives, access to a coordinatively unsaturated and hence reactive[26c] phenyl species is possible with this combination of metal and ligands.

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Registry No. I, 93473-71-3; II, 79372-14-8; IV, 90866-66-3; V, 93473-72-4; VI, 93473-73-5; VII, 93473-74-6; VIII, 93473-75-7; $(C_6H_5)SiMe_3$, 768-32-1; $(C_6H_5)_2Hg$, 587-85-9; Sm, 7440-19-9; C_5Me_5H, 4045-44-7; C_5Me_4EtH, 93473-76-8.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

A Study of Ionic and Radical Reactivities of Bridging Sulfido Ligands in Dimeric Cyclopentadienyl Complexes of Molybdenum†

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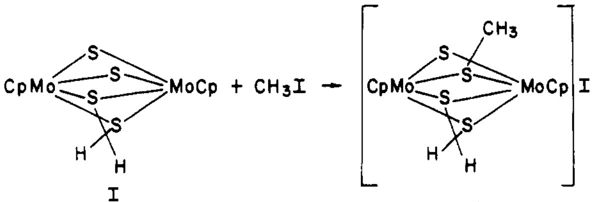
Reaction of $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ (I, Cp = $C_5H_4CH_3$) with methyl iodide or methyl fluorosulfate leads to the formation of the cationic dimer $[(CpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2]^+$ (II). The bisulfate salt of II has been characterized by an X-ray diffraction study which confirms that a bridging sulfido ligand in I is the site of electrophilic attack. The salt crystallizes in space group $P2_1/n$ with $a = 10.155$ (2) Å, $b = 17.478$ (9) Å, $c = 22.201$ (7) Å, $\beta = 97.89$ (2)°, and $V = 3903$ (2) Å^3. The electrochemical characteristics of II are compared to those of related molybdenum dimers. II undergoes two reversible one-electron reductions in acetonitrile at −0.34 and −1.24 V vs. SCE to form a neutral mixed valence Mo(III)/Mo(IV) dimer, V, and an anionic Mo(III)/Mo(III) derivative, VII, respectively. The reactivity of each member of this redox series has been characterized. The bridging sulfido ligand in II reacts readily with carbanions and alkyl-substituted borohydride reagents. In contrast, the sulfido ligand in VII is strongly nucleophilic. For example, VII reacts with acetylene to form, upon protonation, the ethenyl thiolate bridged derivative $(CpMo)_2(\mu\text{-}SC_2H_3)(\mu\text{-}SCH_3)S_2CH_2$ (IV). The reactivity of the unsaturated ligand in IV toward further reduction has been investigated.

Introduction

We have recently reported that the molybdenum(IV) dimer $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ (I) promotes the hydrogenation of alkynes to cis alkenes, allenes to alkenes, and ketenes to aldehydes[2] and the hydrogenolysis of carbon disulfide to hydrogen sulfide and thioformaldehyde.[3] The bridging cis sulfido ligands in the molybdenum complex are proposed to be the reactive site that reacts with hydrogen and substrate. However, mechanistic details of these reactions have not been established. In order to obtain information on both the ionic and radical reactivity of bridging sulfur ligands in molybdenum dimers of this type, we have undertaken a study of the sulfur-alkylated derivative of I $[(CpMo)_2(\mu\text{-}S)(\mu\text{-}SR)S_2CH_2]^+$ (II). The redox-active nature of this cationic Mo(IV) dimer has enabled us to vary the formal oxidation states of the metal ions in order to induce potential electrophilic, nucleophilic, or radical characteristics at one bridging sulfido ligand. The alkylation of the other sulfido bridge has served the purpose of preventing the facile side reaction of adduct formation that is known to occur between unsaturated substrates and a pair of cis sulfido ligands.[2] The investigations have helped to define the range of reactivity to be expected for sulfur ligands in these dimers. For example, the sulfido bridge in a neutral mixed-valence dimer does not show the reactivity characteristic of a sulfur-based radical; but the ligand in an anionic molybdenum(III) dimer has been shown to be strongly nucleophilic. Its reaction with acetylene to form, upon protonation, a dimer with an alkenyl thiolate bridge demonstrates one pathway in which alkyne reduction may be mediated by sulfur sites in metal sulfur catalysts. The possible relationship of these derivatives to hydrogenation intermediates is discussed.

Results and Discussion

Reactivity of Sulfido Ligands in $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$. Previous work in this laboratory has shown that the nature of the thiolate ligands in quadruply bridged molybdenum dimers significantly alters the reactivity of sulfido bridges in the complex.[2] An additional example of this type of effect on reactivity has been observed in this study. While $[CpMo(\mu\text{-}S)SCH_3]_2$[5] does not react with methyl iodide, the related Mo(IV) dimer I reacts readily to form the air-stable cation II (reaction 1). Other electrophilic alkylating agents



(1)

I

II

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† This paper is dedicated to the memory of Professor Earl L. Muetterties, whose catholicity of interests inspired new growth in organometallic chemistry.

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