3614 *Inorg. Chem.* **1986**, *25*, 3614-3619

Contribution from the Departments of Chemistry, University of California,
Irvine, California 92717, and University of Alabama, University, Alabama 35486

Synthesis and X-ray Crystal Structure of Bis(pentamethylcyclopentadienyl) Lanthanide and Yttrium Halide Complexes

William J. Evans,*[1a,b] Jay W. Grate,[1b] Keith R. Levan,[1b] Ira Bloom,[1b] Timothy T. Peterson,[1b] Robert J. Doedens,[1b] Hongming Zhang,[1c] and Jerry L. Atwood[1c]

Received April 23, 1985

The synthesis and crystal and molecular structures of $(C_5Me_5)_2YCl(THF)$ (I), $(C_5Me_5)_2SmCl(THF)$ (II), and $(C_5Me_5)_2SmI(THF)$ (III) are described. $(C_5Me_5)_2YCl(THF)$ was isolated as a byproduct of the reaction of YCl_3 with KC_5Me_5. It crystallizes from THF/pentane at −20 °C in space group $P\bar{1}$ with unit cell dimensions a = 8.541 (2) Å, b = 17.216 (6) Å, c = 18.356 (6) Å, α = 63.04 (2)°, β = 88.83 (2)°, γ = 88.36 (2)°, V = 2404.7 Å^3, and D_{calcd} = 1.21 g cm^{-3} for Z = 4. $(C_5Me_5)_2SmCl(THF)$ was prepared by oxidation of $(C_5Me_5)_2Sm(THF)_2$ with $t\text{-}C_4H_9Cl$. It crystallizes from toluene at −30 °C in space group $P\bar{1}$ with unit cell dimensions a = 8.567 (5) Å, b = 17.331 (6) Å, c = 18.515 (6) Å, α = 62.71 (3)°, β = 88.46 (4)°, γ = 87.82 (4)°, V = 2441.3 Å^3, and D_{calcd} = 1.44 g cm^{-3} for Z = 4. $(C_5Me_5)_2SmI(THF)$ was prepared from $(C_5Me_5)_2Sm(THF)_2$ by oxidation with ICH_2CH_2I and from $[(C_5Me_5)_2SmH]_2$ by reaction with CH_3I. It crystallizes from toluene at 25 °C in space group $P\bar{1}$ with unit cell dimensions a = 8.812 (4) Å, b = 17.569 (7) Å, c = 18.464 (7) Å, α = 62.25 (4)°, β = 89.16 (4)°, γ = 87.68 (4)°, V = 2625 Å^3, and D_{calcd} = 1.63 g cm^{-3} for Z = 4. In each complex, the C_5Me_5 ring centroids, the THF oxygen atom, and the halide ligand describe a distorted tetrahedral geometry around the metal. The synthesis of $(C_5Me_5)_2SmCl_2Li(THF)_2$ and $(C_5Me_4Et)_2SmCl_2Li(THF)_2$ is also described.

Introduction

Bis(cyclopentadienyl) lanthanide and yttrium halide complexes are basic precursors in the organometallic chemistry of these elements.[2-6] Their synthesis is of fundamental importance to the field, and their structural parameters provide straightforward benchmarks upon which to evaluate more complex systems. Recent investigations of organoyttrium and organolanthanide chemistry in our laboratories have resulted in the preparation of X-ray-quality crystals of the three halide complexes $(C_5Me_5)_2YCl(THF)$ (I), $(C_5Me_5)_2SmCl(THF)$ (II), and $(C_5Me_5)_2SmI(THF)$ (III). The structures of each of these complexes have been determined and are reported herein. Since these are the first $(C_5Me_5)_2LnX(THF)$ complexes (X = halide) to be structurally characterized, they provide useful, basic structural data in the rapidly growing area[2-46] of bis(pentamethylcyclopentadienyl) lanthanide and yttrium chemistry. Taken together, these results allow detailed structural comparisons to be made on the basis of both the metal and the halide ligands present. The synthetic routes used to obtain these complexes are also informative with respect to $(C_5Me_5)_2LnX$ chemistry.

Experimental Section

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

Materials. Solvents were dried as previously described.[14] C_5Me_5H was either made by literature methods[47] or purchased (Aldrich).

---

(1) (a) Alfred P. Sloan Research Fellow. (b) University of California. (c) University of Alabama.

(2) Evans, W. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 12.

(3) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry*, 9th ed.; Moeller, T., Kruerke, U., Schleitzer-Rust, E., Eds.; Springer-Verlag: Berlin, 1983; Sc, Y, and La-Lu, Part D6, pp 137-282.

(4) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Chapter 21.

(5) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131-177.

(6) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474-493.

(7) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190-2191.

(8) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507-6508.

(9) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401-1403.

(10) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217-226.

(11) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270-4272.

(12) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405-409.

(13) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112-119.

(14) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941-946.

(15) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554-559.

(16) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671-1679.

(17) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728-3730.

(18) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191-195.

(19) Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620-4623.

(20) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999-3003.

(21) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267-3270.

(22) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985-986.

(23) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772-1774.

(24) Tilley, T. D.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1982**, *21*, 2644-2647.

(25) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647-2649.

(26) Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710-712.

(27) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432-437.

(28) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 856-859.

(29) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652-653.

(30) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271-3278.

(31) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337-339.

(32) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471-6473.

(33) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276-277.

(34) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493.

(35) Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *No. 212*, 459-479.

(36) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51-56 and references therein.

(37) Schumann, H.; Albrecht, I.; Reier, F.-W.; Hahn, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 522-523.

(38) Schumann, H.; Albrecht, I.; Pickardt, J.; Hahn, E. *J. Organomet. Chem.* **1984**, *276*, C5-C9.

(39) Albrecht, I.; Hahn, E.; Pickardt, J.; Schumann, H. *Inorg. Chim. Acta* **1985**, *110*, 145-147.

(40) Schumann, H.; Albrecht, I.; Hahn, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 985-986.

(41) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091-8103.

(42) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103-8110.

(43) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111-8118.

(44) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200-202.

(45) Haan, K. H. d.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 333-334.

(46) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1986**, *5*, 598-601.

0020-1669/86/1325-3614$01.50/0 © 1986 American Chemical Society

C_5Me_4EtH was made according to the literature.[48] Both types of cyclopentadienes were dried over activated 3A molecular sieves and degassed by dynamic vacuum transfer through a trap before use. LiC_5Me_5 and LiC_5Me_4Et were made by reacting the respective cyclopentadienes with $n\text{-}C_4H_9Li$ in pentane followed by filtration. Solutions of $SmI_2(THF)_x$ were prepared from excess Sm metal (Research Chemicals, Phoenix, AZ) and $1,2\text{-}C_2H_4I_2$ in THF solution.[49] $(C_5Me_5)_2Sm(THF)_2$ was prepared from $SmI_2(THF)_x$ and KC_5Me_5.[14] $[(C_5Me_5)_2SmH]_2$ was prepared according to the literature.[9] Anhydrous YCl_3 and $SmCl_3$ were prepared from the hydrates (Research Chemicals) by standard procedures.[50] $t\text{-}C_4H_9Cl$ and CH_3I were purified by drying over activated 5A molecular sieves and degassed by vacuum transfer.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer. Chemical shifts were assigned relative to C_6D_5H, 7.15 ppm, for spectra in benzene-d_6, or relative to C_4D_7HO, 1.72 ppm, for spectra in THF-d_8. Complete elemental analyses were obtained from the Analytische Laboratorien, Engelskirchen, West Germany. Complexometric analyses were performed as previously described.[51]

$(C_5Me_5)_2YCl(THF)$ (I). In the glovebox, solid KC_5Me_5 (4.61 g, 26.4 mmol) was added to a slurry of YCl_3 (2.58 g, 13.2 mmol) in 120 mL of THF in a 250-mL flask. The thick milky-gray suspension was stirred for 12 h at room temperature, during which time the gelatinous white solids appeared to become more granular. These solids were filtered from the solution. THF was removed from the filtrate by rotary evaporation, leaving a white powder, which was then extracted with two 50-mL portions of toluene. Solvent was removed from these toluene extracts to give a yellow solid (0.665 g). Examination of the ^1H NMR spectrum (C_6D_6) of the extracted solid showed a major peak at δ 2.02 as well as a complex pattern of at least nine less intense peaks in the C_5Me_5 region. Recrystallization of the yellow solid from THF/pentane at −20 °C gave crystals (0.43 g, 7%) of I, which displayed only the δ 2.02 resonance (plus resonances from THF). This spectrum was identical with that obtained by adding THF to the unsolvated $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$, which was fully characterized earlier.[15] The major product of the YCl_3/KC_5Me_5 reaction was $(C_5Me_5)_2YCl_2K(THF)_2$.[15]

$(C_5Me_5)_2SmCl(THF)$ (II). In the glovebox, $(C_5Me_5)_2Sm(THF)_2$ (3.934 g, 6.96 mmol) was dissolved in 100 mL of toluene in a 250-mL round-bottom flask containing a magnetic stirring bar. A stopcock adapter was attached to the flask, and the apparatus was attached to a vacuum line. $t\text{-}C_4H_9Cl$ (ca. 0.76 mL, ca. 7 mmol) was distilled into the flask cooled with a liquid-nitrogen bath. Upon warm-up, the reaction mixture changed from purple to orange-brown. The reaction was stirred for ca. 3 h and taken into the glovebox. Solvent was removed by rotary evaporation, and the solids were extracted with toluene. No toluene-insoluble products were observed upon filtration. Removal of toluene gave crude II (3.55 g, 6.72 mmol, 95%). ^1H NMR (C_6D_6): δ 1.20 (s, C_5Me_5, 30 H), −1.20 (s, br, $\omega_{1/2} = 60$ Hz, THF, 4 H), −2.20 (s, br, $\omega_{1/2} = 60$ Hz, THF, 4 H). ^{13}C NMR (C_6D_6): 116.8, 66.9, 22.0, 18.6 (q, $J = 116$ Hz). When the sample was cooled to −30 °C, orange crystals separated from the toluene solution. Complexometric anal. Calcd for $SmC_{24}H_{38}ClO$: Sm, 28.46. Found: Sm, 30.1.

$(C_5Me_5)_2SmI(THF)$ (III) from $[(C_5Me_5)_2SmH]_2$. In the glovebox, $[(C_5Me_5)_2SmH]_2$ (0.265 g, 0.628 mmol) in 10-mL hexane was placed in a round-bottom flask equipped with a stopcock adapter and a magnetic stir bar. The apparatus was attached to the Toepler pump manifold of a vacuum line and degassed via freeze–pump–thaw cycles. Excess CH_3I (0.4 mL, 6.42 mmol) was distilled in when the flask was cooled in a liquid-nitrogen bath. Gas evolution occurred upon warm-up. The gas was Toepler-pumped through a liquid-nitrogen trap (0.366 mmol, 58%) and identified as CH_4 by its mass spectrum. The original reaction flask was taken into the glovebox, and the solution was filtered. The resulting precipitate was extracted with THF, and the solvent was removed to give III (209 mg, 54%). Anal. Calcd for $SmC_{24}H_{38}IO$: Sm, 24.26; C, 46.51; H, 6.18; I, 20.47; O, 2.58. Found: Sm, 24.05; C, 46.30; H, 6.08; I, 20.55; O (by difference), 3.02. III is readily recrystallized as amber needles by diffusion of hexane into toluene solutions at −25 °C. ^1H NMR (C_6D_6): δ 1.16 (s, C_5Me_5, 30 H), −0.53 (s, br, $\omega_{1/2} = 60$ Hz, THF, 4 H), −0.99 (s, br, $\omega_{1/2} = 70$ Hz, THF, 4 H). ^{13}C NMR (C_6D_6): δ 117, 113, 22.6, 19.5. Magnetic susceptibility: $\chi_M^{297K} = 1230 \times 10^{-6}$; $\mu_{eff}^{297K} = 1.86\ \mu_B$. IR (Nujol on NaCl): 1340 m, 1170 w, 1095 s, br, 1040 sh, 1015 s, 950 w, 920 m, 870 s, 835 w, 725 m, 690 w, 670 w cm^{-1}.

$(C_5Me_5)_2SmI(THF)$ (III) from $(C_5Me_5)_2Sm(THF)_2$. In the glovebox, ICH_2CH_2I (178 mg, 0.632 mmol) was added to $(C_5Me_5)_2Sm(THF)_2$ (234 mg, 0.436 mmol) in 25 mL of toluene, and the mixture was stirred. The initially burgundy-colored solution immediately became amber. After the reaction was stirred for 1 h, the solvent was reduced to 10 mL by rotary evaporation and the solution was placed in a vial. Diffusion of hexane into this vial at −25 °C generated amber needles of III after 1 day (146 mg, 56%). The complex was identified by its ^1H NMR spectrum. No byproducts were definitively identified.

$(C_5Me_5)_2SmCl_2Li(THF)_2$. In the glovebox, $SmCl_3$ (2.741 g, 10.7 mmol) and LiC_5Me_5 (3.037 g, 21.4 mmol) were stirred together in an Erlenmeyer flask in 100 mL of THF overnight. The solvent was removed by rotary evaporation, and the residue was extracted with pentane through a fine-porosity frit to give an orange filtrate. The solvent was removed from the filtrate to give the product as an orange powder (5.0 g, 73%). Anal. Calcd for $SmC_{28}H_{46}Cl_2LiO_2$: Sm, 23.39. Found: Sm, 22.6. ^1H NMR (C_6D_6): δ 3.98 (s, THF, 8 H), 1.67 (s, THF, 8 H), 1.37 (s, C_5Me_5, 30 H). ^{13}C NMR (C_6D_6): δ 116.3 (s, C_5Me_5), 68.6 (t, $J =$ 166 Hz, $\overline{\mathrm{O}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}}\mathrm{H_2}$), 25.7 (q, $J = 167$ Hz, $C_5(\mathit{C}H_3)_5$), 18.2 (t, $J = 133$ Hz, $\overline{\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2}}$). IR (Nujol): 1160 m, 1045 s, 910 s, 890 s, 670 m cm^{-1}. Magnetic susceptibility: $\chi_M^{299K} = 1320 \times 10^{-6}$; $\mu_{eff}^{299K} = 1.8\ \mu_B$.

$(C_5Me_4Et)_2SmCl_2Li(THF)_2$. $SmCl_3$ (161 mg, 0.67 mmol) and LiC_5Me_4Et (200 mg, 1.34 mmol) were stirred together in 30 mL of THF overnight. Rotary evaporation of the solvent and extraction through a fine-porosity frit produced an orange filtrate. Solvent removal gave the product as orange crystals (186 mg, 40%). Anal. Calcd for $SmC_{29}H_{49}Cl_3LiO_2$: Sm, 22.41. Found: Sm, 23.2. ^1H NMR (C_6D_6): δ 4.0 (s, 3, THF), 2.0 (s, 2, $C_5Me_4(C\mathit{H}_2CH_3)$), 1.7 (s, 6, THF plus $C_5Me_4(CH_2C\mathit{H}_3)$), 1.4 (s, 11, $C_5(C\mathit{H}_3)_4Et$). These tentative assignments are based on assignments for $Fe(C_5Me_4Et)_2$,[48] $Ti(C_5Me_4Et)_2Cl_2$,[48] and $Th(C_5Me_4Et)Cl_3(MeCONMe_2)_2$.[52] ^{13}C NMR (C_6D_6): δ 116.7, 115.6, 68.7 (t, $J = 150$ Hz), 26.1, 25.6 (t, $J = 133$ Hz), 18.1, 17.8, 11.3. The remaining coupling constants could not be determined due to overlap of the multiplets. IR (Nujol): 1420 w, 1360 s, 1310 s, 1290 w, 1160 w, br, 1045 s, 910 m, 890 s, 760 w, 720 m, 670 m cm^{-1}. Magnetic susceptibility: $\chi_M^{292K} = 1460 \times 10^{-6}$; $\mu_{eff}^{292K} = 1.9\ \mu_B$.

X-ray Data Collection and Structure Determination and Refinement for $(C_5Me_5)_2YCl(THF)$ (I). The procedure for data collection and processing has been described.[53] All computations were carried out with a local version of the UCLA Crystallographic Computing Package.[54] Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled capillaries. Lattice parameters were determined by least-squares refinement against 15 accurately centered reflections ($2\theta > 30°$). A summary of data collection parameters is given in Table I.

Reflections were measured by using a Syntex $P2_1$ diffractometer. The diffracted intensities were collected by the θ–2θ scan technique in bisecting geometry. The scan rate varied from 2.5 to 12°/min depending on the intensity of the peak. The intensities were corrected for Lorentz and polarization effects, absorption (by Gaussian integration), and standard decay. The p factor in the expression[55] for the standard deviations of the observed intensities was assigned a value of 0.05.

Triclinic symmetry was suggested by interaxial angles and confirmed by a Delaunay reduction. Intensity statistics were consistent with a centrosymmetric structure. The positions of the yttrium atoms were determined by inspection of a Patterson map, and the remaining nonhydrogen atoms were located by difference Fourier methods. The final refinement model employed anisotropic thermal parameters for all nonhydrogen atoms. On a final difference Fourier map, evidence was found for the positions of only about one-third of the hydrogen atoms; these atoms were therefore not included in the electron density model. Final fractional coordinates are given in Table II.

X-ray Data Collection and Structure Determination and Refinement for $(C_5Me)_2SmCl(THF)$ (II) and $(C_5Me_5)_2SmI(THF)$ (III). Single crystals of the air-sensitive compounds were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($2\theta > 20°$) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ

---

(47) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5. Manriquez, J. M.; Fagan, P. J.; Schertz, L. D.; Marks, T. J. *Inorg. Synth.* **1982**, *21*, 181–185. Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119–121.

(48) Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466–469.

(49) Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chim.* **1981**, *5*, 479–484.

(50) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–391.

(51) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119.

(52) Bagnall, K. W.; Behesht, A.; Heatley, F.; Tempest, A. C. *J. Less-Common Met.* **1979**, *64*, 267–275.

(53) Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153–156.

(54) Strouse, C. E., personal communication to R.J.D.

(55) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1969**, *6*, 197–204.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $(C_5Me_5)_2LnX(THF)$ (Ln = Y, Sm; X = Cl, I)

	I	II	III
compd	$YOClC_{24}H_{38}$	$SmOClC_{24}H_{38}$	$SmOIC_{24}H_{38}$
mol wt	466.93	528.5	469.47
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cell constants			
a, Å	8.541 (2)	8.567 (5)	8.812 (4)
b, Å	17.216 (6)	17.331 (6)	17.569 (7)
c, Å	18.356 (6)	18.515 (6)	18.464 (7)
α, deg	63.04 (2)	62.71 (3)	62.25 (4)
β, deg	88.83 (2)	88.46 (4)	87.68 (4)
γ, deg	88.36 (2)	87.82 (4)	86.67 (4)
cell vol, $Å^3$	2404.7	2441.3	2525
Z	4	4	4
ρ(calcd), g cm^{-3}	1.211	1.44	1.63
μ(calcd), cm^{-1}	25.74	25.31	36.13
radiation	Mo $K\bar{\alpha}$	Mo $K\bar{\alpha}$	Mo $K\bar{\alpha}$
transmssn factor range	0.61–0.87	0.65–0.74	0.32–0.49
max cryst dimens, mm	0.75 × 0.43 × 0.12	0.40 × 0.12 × 0.12	0.20 × 0.25 × 0.35
scan width (in 2θ), deg	-1.0 from $2\theta(K\alpha_1)$ to $+1.0$ from $2\theta(K\alpha_2)$	$0.8 + 0.2 \tan\theta$	$0.8 + 0.2 \tan\theta$
std reflcns	$2\bar{1}\bar{2}$, $\bar{3}20$, 240	400, 020, 002	200, 060, 004
variation of stds	5%	±5%	<2%
no. of reflcns measd	6328 ($h,\pm k,\pm l$)	5478	5908
2θ range, deg	0–55	2–40	2–42
no. of obsd reflcns, $I > 3\sigma(I)$	4031	2515	3814
no. of params varied	487	247	447
max Δ/σ in final cycle	0.015	0.01	0.02
GOF	2.47	3.46	1.17
R^a	0.068	0.079	0.062
$R_w{}^a$	0.087	0.082	0.063

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum[w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2}$.

scan technique as previously described.[56] Summaries of data collection parameters are given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the last, an empirical method similar to that of Churchill was employed.[57]

The diffraction pattern of $(C_5Me_5)_2SmCl(THF)$ showed only triclinic symmetry, and the structure was solved and refined successfully in the centrosymmetric space group $P\bar{1}$. The two samarium atoms were located by direct methods with the MULTAN 80 program system.[58] Subsequent difference Fourier maps served to locate all other non-hydrogen atoms. Neutral-atom scattering factors of Sm, Cl, C, and O were taken from Cromer and Waber.[59] Structure refinement was carried out by use of the SHELX program system[60] with anisotropic thermal parameters for Sm and Cl atoms. Because of poor crystal quality, only about 50% of the measured reflections were considered observed. Owing to the small number of observed data, carbon and oxygen atoms were refined only with isotropic thermal parameters. The function minimized in the least-squares calculation was $\sum w|\Delta F^2|$ with unit weights, a choice made on the basis of the manner in which the data were collected.[56] No unaccountable electron density was shown by the final difference Fourier. 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.

For $(C_5Me_5)_2SmI(THF)$, data collection and structure determination and refinement proceeded as for the chloride complex, II, except as noted. A much better crystal was obtained, and a larger data set allowed refinement with anisotropic thermal parameters for all non-hydrogen atoms except the carbon atoms on the THF. Positional parameters are given in Table IV.

Results and Discussion

Synthesis. On the basis of traditional principles of organolanthanide synthesis, the complexes $(C_5Me_5)_2YCl(THF)$ (I), $(C_5Me_5)_2SmCl(THF)$ (II), and $(C_5Me_5)_2SmI(THF)$ (III) should be obtainable by a variety of synthetic methods.[2] The most common method for the synthesis of bis(cyclopentadienyl) lanthanide and yttrium halides is simply the stoichiometric reaction of 2 equiv of the cyclopentadienyl anion with the metal halide (eq 1; Ln = lanthanide or yttrium; X = halide; R = H or CH_3; M = alkali metal). When this method was used for the synthesis

$$LnX_3 + 2C_5R_5M \rightarrow (C_5R_5)_2LnX + 2MX \qquad (1)$$

of I, however, this complex was in fact a minor byproduct in a reaction that generated an alkali-metal halide adduct as the major product (eq 2). Similarly, reaction of 2 equiv of LiC_5Me_5 or

$$2YCl_3 + 4KC_5Me_5 \rightarrow (C_5Me_5)_2YCl_2K(THF)_2 + (C_5Me_5)_2YCl(THF) + 3KCl \qquad (2)$$

LiC_5Me_4Et with $SmCl_3$ gives LiCl adducts (eq 3; $C_5R_5 = C_5Me_5$, C_5Me_4Et). The formation of alkali-metal halide adducts is a

$$2LiC_5R_5 + SmCl_3 \xrightarrow{THF} (C_5R_5)_2SmCl_2Li(THF)_2 + LiCl \qquad (3)$$

common feature of organolanthanide chemistry involving the C_5Me_5 ligand, and numerous examples of complexes of the type $(C_5R_5)_2LnX_2M(solvate)_2$ (where R = alkyl, X = halide; and M = alkali metal) are known.[7,21,30,61,62] Analogues of $(C_5Me_5)_2SmCl_2Li(THF)_2$ with tetramethylethylenediamine (TMEDA) replacing the two THF molecules and with Na(TMEDA) or $Na(Et_2O)_2$ replacing $Li(THF)_2$ are known.[21]

An alternative synthesis of $(C_5Me_5)_2YCl(THF)$ is to add THF to the unsolvated complex $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$.[15] I is obtained in quantitative yield, but the unsolvated precursor is not easily prepared.

Complexes II and III were prepared by a route that avoided the possible formation of alkali-metal halide adducts, namely, the oxidation of $(C_5Me_5)_2Sm(THF)_2$ with alkyl halides (eq 4).

$$(C_5Me_5)_2Sm(THF)_2 \xrightarrow{RX} (C_5Me_5)_2SmX(THF) \qquad (4)$$

Oxidation of divalent lanthanide complexes with alkyl halides is a general reaction for $LnI_2(THF)_x$ and $(CH_3C_5H_4)_2Ln(THF)$ complexes (Ln = Sm, Yb)[63] and has also been reported for

---

(56) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53.

(57) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962.

(58) Main, P.; et al. "MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", 1980.

(59) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109.

(60) Sheldrick, G. M. "SHELX, a System of Computer Programs for X-Ray Structure Determination", 1976.

(61) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140–142.

(62) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1191–1193.

Table II. Final Fractional Coordinates for $(C_5Me_5)_2YCl(THF)$ (I)

atom	*x*	*y*	*z*
Y(1)	0.3793 (1)	−0.2444 (1)	−0.4889 (1)
Y(2)	0.1165 (1)	−0.2498 (1)	0.0167 (1)
Cl(1)	0.6079 (4)	−0.1392 (2)	−0.5528 (2)
Cl(2)	−0.1187 (4)	−0.1421 (2)	−0.0340 (2)
O(1)	0.2035 (8)	−0.1377 (5)	−0.5865 (5)
O(2)	0.2871 (9)	−0.1402 (5)	−0.0786 (5)
C(1)	0.5514 (14)	−0.3507 (10)	−0.5264 (8)
C(2)	0.4671 (20)	−0.3014 (9)	−0.5960 (9)
C(3)	0.3111 (18)	−0.3242 (10)	−0.5801 (8)
C(4)	0.2935 (14)	−0.3856 (8)	−0.5009 (8)
C(5)	0.4401 (17)	−0.4061 (7)	−0.4668 (7)
C(6)	0.2647 (16)	−0.1704 (8)	−0.3982 (7)
C(7)	0.4198 (15)	−0.1921 (9)	−0.3741 (8)
C(8)	0.4369 (15)	−0.2797 (8)	−0.3365 (8)
C(9)	0.2986 (17)	−0.3168 (7)	−0.3331 (7)
C(10)	0.1791 (13)	−0.2477 (9)	−0.3743 (8)
C(11)	0.7272 (18)	−0.3577 (14)	0.6347 (12)
C(12)	0.5281 (29)	−0.2411 (13)	−0.6795 (12)
C(13)	0.1723 (24)	−0.2936 (14)	−0.6446 (11)
C(14)	0.1421 (19)	−0.4317 (12)	−0.4657 (11)
C(15)	0.4932 (25)	−0.4865 (10)	−0.3837 (11)
C(16)	0.1939 (21)	−0.0757 (9)	−0.4372 (10)
C(17)	0.5451 (18)	−0.1270 (10)	−0.3798 (9)
C(18)	0.5885 (17)	−0.3313 (12)	−0.2915 (11)
C(19)	0.2419 (23)	−0.4126 (10)	−0.2773 (11)
C(20)	0.0047 (15)	−0.2556 (11)	−0.3763 (11)
C(21)	0.1266 (22)	−0.4073 (8)	0.0241 (9)
C(22)	0.2180 (15)	−0.3552 (11)	−0.0449 (8)
C(23)	0.1187 (20)	−0.2964 (8)	−0.1027 (8)
C(24)	−0.0332 (16)	−0.3116 (9)	−0.0711 (8)
C(25)	−0.0261 (18)	−0.3765 (10)	0.0054 (9)
C(26)	0.1284 (31)	−0.1903 (12)	0.1278 (10)
C(27)	0.0510 (15)	−0.2686 (14)	0.1647 (11)
C(28)	0.1532 (18)	−0.3322 (9)	0.1778 (9)
C(29)	0.3007 (16)	−0.2921 (13)	0.1436 (10)
C(30)	0.2828 (29)	−0.2104 (12)	0.1160 (13)
C(31)	0.1913 (32)	−0.4928 (11)	0.0923 (12)
C(32)	0.3947 (18)	−0.3704 (13)	−0.0610 (12)
C(33)	0.1492 (25)	−0.2555 (12)	−0.1960 (12)
C(34)	−0.1851 (20)	−0.2687 (13)	−0.1161 (11)
C(35)	−0.1716 (24)	−0.4169 (15)	0.0605 (12)
C(36)	0.0761 (45)	−0.0989 (15)	0.1060 (12)
C(37)	−0.1144 (20)	−0.2725 (21)	0.1926 (16)
C(38)	0.1264 (30)	−0.4321 (11)	0.2360 (14)
C(39)	0.4587 (21)	−0.3481 (19)	0.1546 (15)
C(40)	0.4350 (31)	−0.1555 (17)	0.0880 (17)
C(41)	0.2572 (16)	−0.0648 (10)	−0.6561 (12)
C(42)	0.1162 (19)	−0.0150 (12)	−0.6999 (14)
C(43)	−0.0121 (16)	−0.0740 (11)	−0.6716 (12)
C(44)	0.0356 (15)	−0.1380 (10)	−0.5883 (10)
C(45)	0.2337 (18)	−0.0513 (9)	−0.1269 (14)
C(46)	0.3668 (22)	−0.0077 (13)	−0.1768 (18)
C(47)	0.4985 (22)	−0.0672 (14)	−0.1558 (17)
C(48)	0.4508 (16)	−0.1486 (10)	−0.0970 (12)

Table III. Final Fractional Coordinates for $(C_5Me_5)_2SmCl(THF)$ (II)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eqv), Å^2
Sm(1)	0.3776 (2)	0.2452 (1)	0.48742 (9)	0.031
Cl(1)	0.619 (1)	0.1382 (6)	0.5562 (6)	0.057
O(1)	0.194 (2)	0.134 (1)	0.585 (1)	0.039
C(10)	0.301 (5)	0.390 (3)	0.499 (2)	0.067
C(11)	0.440 (4)	0.411 (2)	0.465 (2)	0.050
C(12)	0.545 (5)	0.357 (2)	0.525 (2)	0.073
C(13)	0.468 (5)	0.308 (3)	0.592 (2)	0.058
C(14)	0.306 (5)	0.331 (2)	0.575 (2)	0.056
C(15)	0.136 (5)	0.434 (3)	0.461 (2)	0.094
C(16)	0.482 (6)	0.484 (3)	0.382 (3)	0.112
C(17)	0.720 (8)	0.354 (4)	0.520 (4)	0.165
C(18)	0.533 (7)	0.246 (4)	0.682 (3)	0.127
C(19)	0.158 (7)	0.297 (3)	0.638 (3)	0.105
C(20)	0.421 (4)	0.190 (2)	0.374 (2)	0.057
C(21)	0.259 (4)	0.168 (2)	0.396 (2)	0.049
C(22)	0.183 (4)	0.241 (2)	0.373 (2)	0.051
C(23)	0.281 (4)	0.315 (2)	0.331 (2)	0.058
C(24)	0.437 (4)	0.276 (2)	0.335 (2)	0.044
C(25)	0.539 (6)	0.127 (3)	0.380 (3)	0.107
C(26)	0.189 (6)	0.078 (3)	0.436 (3)	0.108
C(27)	0.001 (5)	0.262 (3)	0.369 (2)	0.088
C(28)	0.242 (5)	0.409 (3)	0.274 (2)	0.090
C(29)	0.584 (5)	0.327 (3)	0.290 (3)	0.089
C(51)	0.021 (5)	0.134 (3)	0.584 (2)	0.086
C(52)	−0.018 (5)	0.068 (3)	0.673 (2)	0.089
C(53)	0.121 (6)	0.007 (3)	0.700 (3)	0.094
C(54)	0.261 (7)	0.064 (4)	0.656 (3)	0.113
Sm(2)	0.1145 (2)	0.2512 (1)	−0.01898 (9)	0.030
Cl(2)	−0.143 (1)	0.1385 (6)	0.0272 (5)	0.052
O(2)	0.281 (2)	0.140 (1)	0.080 (1)	0.047
C(30)	−0.033 (4)	0.316 (2)	0.070 (2)	0.041
C(31)	−0.020 (4)	0.380 (2)	−0.005 (2)	0.053
C(32)	0.131 (4)	0.408 (2)	−0.021 (2)	0.061
C(33)	0.216 (5)	0.357 (3)	0.050 (3)	0.074
C(34)	0.116 (3)	0.294 (2)	0.103 (2)	0.039
C(35)	−0.184 (5)	0.268 (3)	0.116 (2)	0.091
C(36)	−0.154 (5)	0.424 (3)	−0.064 (3)	0.108
C(37)	0.196 (6)	0.497 (3)	−0.093 (3)	0.116
C(38)	0.401 (6)	0.362 (3)	0.065 (3)	0.124
C(39)	0.151 (5)	0.224 (3)	0.196 (2)	0.082
C(40)	0.310 (4)	0.303 (2)	−0.151 (2)	0.046
C(41)	0.291 (4)	0.218 (2)	−0.121 (2)	0.055
C(42)	0.139 (4)	0.195 (2)	−0.133 (2)	0.059
C(43)	0.058 (5)	0.271 (3)	−0.171 (2)	0.070
C(44)	0.153 (4)	0.338 (2)	−0.183 (2)	0.052
C(45)	0.447 (6)	0.356 (3)	−0.160 (3)	0.117
C(46)	0.414 (6)	0.155 (3)	−0.090 (3)	0.122
C(47)	0.089 (7)	0.102 (4)	−0.110 (3)	0.155
C(48)	−0.116 (7)	0.268 (4)	−0.198 (3)	0.138
C(49)	0.124 (5)	0.436 (3)	−0.237 (2)	0.095
C(61)	0.436 (5)	0.147 (3)	0.102 (3)	0.089
C(62)	0.490 (8)	0.057 (5)	0.154 (4)	0.166
C(63)	0.366 (9)	−0.011 (5)	0.166 (4)	0.163
C(64)	0.227 (7)	0.047 (4)	0.118 (3)	0.106

pentamethylcyclopentadienyl derivatives of ytterbium(II)[29,46] and uranium(III).[64–66]

Complex III was also prepared from the hydride $[(C_5Me_5)_2SmH]_2$[9] by reaction with CH_3I (eq 5).

$$[(C_5Me_5)_2SmH]_2 + 2CH_3I \rightarrow 2CH_4 + 2(C_5Me_5)_2SmI(THF) \quad (5)$$

Methyl halide decomposition reactions are commonly used to chemically verify the presence of hydridic metal hydride ligands.[67] Frequently, only the gaseous CH_4 product is examined. Hence, this result represents an organolanthanide case in which full characterization of this reaction is carried out.

Complex III has also been synthesized from the divalent $[(C_5Me_5)SmI(THF)_2]_2$.[14] III is obtained in 24% yield as a byproduct in the reaction of $[(C_5Me_5)SmI(THF)_2]_2$ with $C_6H_5C{\equiv}CC_6H_5$.[68] Although the mechanism of this reaction is obscure, it does demonstrate that $[(C_5Me_5)SmI(THF)_2]_2$ can readily oxidize and ligand redistribute.

Structure. As is evident from the unit cell parameters and atomic coordinates, complexes I–III are isomorphous and isostructural.[69] Each crystallizes in space group $P\bar{1}$ with $Z = 4$; close examination of the atomic coordinates confirms the lack of

---

(63) Evans, W. J.; Zinnen, H. A., unpublished results.

(64) Finke, R. G.; Schiraldi, D., A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875–1876.

(65) Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.* **1981**, 232–234.

(66) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. M. *Organometallics* **1982**, *1*, 170–180.

(67) Muetterties, E. L. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971.

(68) Compare the $(C_5Me_5)_2Sm(THF)_2$ reaction of ref 8.

(69) These three crystal structures were solved at different times, in different laboratories, and initially in different triclinic cells. All published parameters are referred to the transformed cells defined by the parameters in Table I. Certain of the supplementary material is referred to the unit cells originally employed. In these cases transformation matrices are given. We are grateful to a reviewer for helping to work out some of the necessary transformations.

Table IV. Final Fractional Coordinates for $(C_5Me_5)_2SmI(THF)$ (III)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eqv), Å^2
Sm(1)A	0.3753 (1)	−0.25141 (6)	−0.48394 (5)	0.040 (2)
I(1)A	0.6635 (2)	−0.1529 (1)	−0.5529 (1)	0.083 (23)
O(1)A	0.231 (1)	−0.1311 (8)	−0.5912 (7)	0.053 (3)
C(1)A	0.066 (3)	−0.124 (2)	−0.601 (2)	0.092 (7)
C(2)A	0.027 (3)	−0.045 (2)	−0.681 (2)	0.100 (8)
C(3)A	0.165 (4)	0.001 (2)	−0.708 (2)	0.114 (9)
C(4)A	0.294 (4)	−0.059 (2)	−0.662 (2)	0.122 (10)
C(5)A	0.277 (3)	−0.392 (2)	−0.487 (2)	0.078 (13)
C(6)A	0.419 (4)	−0.420 (1)	−0.455 (1)	0.090 (58)
C(7)A	0.519 (2)	−0.371 (2)	−0.519 (2)	0.093 (38)
C(8)A	0.430 (3)	−0.320 (1)	−0.590 (1)	0.055 (35)
C(9)A	0.289 (3)	−0.334 (2)	−0.569 (2)	0.083 (12)
C(10)A	0.289 (3)	−0.316 (1)	−0.325 (1)	0.069 (31)
C(11)A	0.399 (3)	−0.189 (1)	−0.374 (1)	0.065 (42)
C(12)A	0.257 (3)	−0.168 (2)	−0.397 (1)	0.072 (3)
C(13)A	0.179 (2)	−0.247 (2)	−0.369 (1)	0.080 (44)
C(14)A	0.426 (2)	−0.279 (2)	−0.330 (1)	0.081 (47)
C(15)A	0.122 (4)	−0.431 (3)	−0.445 (3)	0.184 (40)
C(16)A	0.450 (4)	−0.490 (2)	−0.369 (2)	0.121 (57)
C(17)A	0.700 (4)	−0.385 (3)	−0.512 (3)	0.202 (71)
C(18)A	0.517 (5)	−0.264 (2)	−0.674 (2)	0.157 (51)
C(19)A	0.165 (4)	−0.297 (2)	−0.634 (2)	0.159 (15)
C(20)A	0.241 (4)	−0.408 (2)	−0.266 (2)	0.119 (65)
C(21)A	0.527 (3)	−0.127 (2)	−0.379 (2)	0.132 (10)
C(22)A	0.194 (4)	−0.077 (2)	−0.441 (2)	0.137 (63)
C(23)A	0.009 (3)	−0.257 (3)	−0.371 (2)	0.151 (86)
C(24)A	0.577 (3)	−0.325 (2)	−0.289 (2)	0.124 (34)
Sm(1)B	0.1136 (1)	−0.25373 (6)	0.02316 (5)	0.037 (1)
I(1)B	−0.1748 (2)	−0.1373 (1)	−0.1986 (9)	0.070 (18)
O(1)B	0.262 (1)	−0.1331 (8)	−0.0741 (7)	0.049 (7)
C(1)B	0.197 (3)	−0.043 (2)	−0.107 (2)	0.099 (8)
C(2)B	0.329 (4)	0.010 (2)	−0.160 (2)	0.122 (10)
C(3)B	0.449 (4)	−0.044 (2)	−0.165 (2)	0.144 (12)
C(4)B	0.418 (3)	−0.139 (2)	−0.102 (2)	0.098 (8)
C(5)B	0.123 (2)	−0.204 (1)	0.142 (1)	0.053 (20)
C(6)B	0.276 (2)	−0.221 (1)	0.127 (1)	0.052 (10)
C(7)B	0.301 (2)	−0.306 (1)	0.152 (1)	0.056 (13)
C(8)B	0.162 (3)	−0.348 (1)	0.188 (1)	0.060 (16)
C(9)B	0.054 (2)	−0.288 (2)	0.179 (1)	0.059 (31)
C(10)B	0.118 (3)	−0.290 (1)	−0.105 (1)	0.083 (4)
C(11)B	−0.026 (2)	−0.312 (1)	−0.070 (1)	0.065 (11)
C(12)B	−0.007 (3)	−0.383 (2)	0.006 (1)	0.078 (17)
C(13)B	0.156 (3)	−0.401 (1)	0.011 (1)	0.080 (47)
C(14)B	0.232 (3)	−0.342 (2)	−0.057 (2)	0.093 (19)
C(15)B	0.048 (3)	−0.129 (2)	0.143 (2)	0.110 (25)
C(16)B	0.397 (3)	−0.150 (2)	0.098 (2)	0.099 (22)
C(17)B	0.459 (2)	0.353 (2)	0.150 (1)	0.086 (27)
C(18)B	0.153 (3)	−0.447 (1)	0.236 (1)	0.085 (33)
C(19)B	−0.108 (3)	−0.302 (2)	0.217 (2)	0.101 (25)
C(20)B	0.146 (4)	−0.216 (2)	−0.196 (1)	0.099 (61)
C(21)B	−0.178 (3)	−0.275 (2)	−0.115 (2)	0.128 (35)
C(22)B	−0.133 (4)	−0.433 (2)	0.065 (2)	0.141 (55)
C(23)B	0.230 (5)	−0.489 (2)	0.082 (2)	0.156 (94)
C(24)B	0.398 (3)	−0.350 (2)	−0.075 (2)	0.137 (45)

any symmetry relationship between the two crystallographically independent molecules.

Each complex has an atomic arrangement typical of a bent metallocene complex[70] with two extra ligands. As shown in Figure 1, the two ring centroids plus the halide and oxygen atom of THF describe a distorted tetrahedral geometry. The similarity of the structures can be best seen by examining the compilation of values of the four angles (ring centroid)–metal–(ring centroid), (ring centroid)–metal–halide, (ring centroid)–metal–oxygen, and halide–metal–oxygen given in Table V. The (ring centroid)–metal–(ring centroid) angles and the halide–metal–oxygen angles are in the range normally observed for bis(pentamethylcyclopentadienyl) lanthanide and actinide diligand complexes.[14,66] Complete bond distance and angular data for I–III are given in the supplementary material.

Important bond distance data for I–III are given in Table V. The average metal–C(ring) distances in I–III are 2.655, 2.72, and 2.725 Å, respectively. Comparing I and II, we find a change of yttrium for samarium makes the metal–carbon distances 0.06–0.07 Å shorter, which is consistent with the 0.06[71]–0.084 Å[72] difference in the radial sizes of yttrium and samarium.[73] Comparing II and III, we find the iodide for chloride change causes no significant change in Sm–C distances.

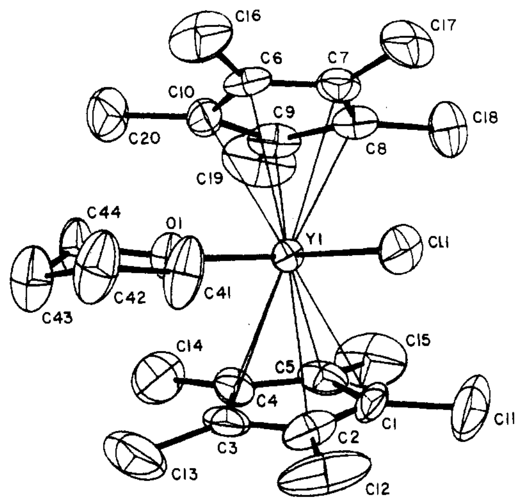

Figure 1. ORTEP plot of $(C_5Me_5)_2YCl(THF)$ (I)

Table V. Summary of Bond Distances and Angles for $(C_5Me_5)_2YCl(THF)$ (I), $(C_5Me_5)_2SmCl(THF)$ (II), and $(C_5Me_5)_2SmI(THF)$ (III)

	I	II	III
Ln–X, Å	2.579 (3)	2.709 (8)	3.043 (2)
	2.577 (3)	2.765 (8)	3.053 (2)
Ln–O, Å	2.410 (7)	2.48 (2)	2.45 (1)
	2.410 (7)	2.44 (2)	2.45 (1)
Ln–cntrd, Å	2.382 (1)	2.47 (4)	2.47 (2)
	2.379 (1)	2.43 (3)	2.46 (2)
	2.373 (1)	2.45 (4)	2.44 (2)
	2.388 (1)	2.45 (4)	2.45 (2)
cntrd–Ln–cntrd, deg	136.2 (4)	133 (1)	136 (1)
	136.6 (4)	136 (1)	137 (1)
cntrd–Ln–X, deg	106.0 (3)	105.2 (3)	106.2 (2)
	106.0 (3)	106.6 (3)	106.1 (2)
	105.4 (3)	105.9 (3)	104.7 (2)
	105.5 (3)	105.3 (3)	106.4 (2)
cntrd–Ln–O, deg	104.6 (4)	106.5 (6)	105.7 (4)
	104.7 (4)	103.6 (7)	104.2 (4)
	103.9 (4)	102.4 (6)	104.4 (4)
	105.6 (4)	105.2 (6)	104.6 (4)
X–Ln–O, deg	89.6 (2)	90.4 (5)	88.8 (3)
	90.5 (2)	91.6 (5)	90.5 (3)

The variations in the metal–halide distances are not as predictable as the variations in the metal–ring carbon distances. The average of the Y–Cl distances in I differs from the average Sm–Cl distance in II by 0.16 Å. Using the extreme values for M–Cl distances in each molecule, one finds that the difference varies from 0.13 to 0.19 Å. These differences are substantially larger than the 0.06–0.08 Å difference in ionic radii of the metals. Comparing the Sm–Cl distances in II with the Sm–I distances in III, one finds that the difference of the averages is 0.31 Å with a difference of 0.34 Å between the extremes. These differences can be compared to a 0.397[71]–0.42 Å[72] difference normally assumed between the size of chloride and iodide ions. Another pair of structurally characterized organolanthanide molecules differing by iodide for chloride substitution is $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (IV) and $(C_5Me_5)_2Yb(\mu\text{-}I)_2Li(OEt_2)_2$ (V).[30] Complex IV has Yb–(μ-Cl) distances of 2.596 (1) and 2.594 (1) Å; complex V has

---

(70) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(71) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(72) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

(73) Cf.: Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276–283.

an Yb–(μ-I) distance of 3.027 (1) Å. In this case, the difference, 0.432 Å, is close to that expected on the basis of the different size of the halide ligand. In both comparisons, I vs. II and II vs. III, the Sm–Cl distance in II is longer by 0.05–0.10 Å than the sum of ionic radii would predict.

In contrast to the large variation observed in metal–halide distances in I–III when metal and halide sizes are accounted for, the distances of the metal to the THF oxygen atom do not vary substantially from those expected. The Sm–O distances in II are similar to those in III. The difference between these distances and the Y–O distance in I is commensurate with the 0.06–0.08 Å difference in the radial sizes of these metals.

In summary, the overall structures of the complexes in this series of formally 8-coordinate $(C_5Me_5)_2LnX(THF)$ complexes are very similar as are the metal–carbon and metal–oxygen bond distances. However, the metal–halide distances vary substantially even when the sizes of the metal and halides are considered.

Conclusion

The structural analysis of complexes I–III provides another example of the similarity of organoyttrium(III) and organolanthanide(III) complexes.[74] This study also shows how metrical data can vary in a series of closely related molecules. In addition to providing these structural data, the synthesis of these complexes generates useful precursors for further studies in organolanthanide chemistry.

Acknowledgment. For support of this research, we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E.) and the National Science Foundation (J.L.A.). We also thank the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.) and Dr. Henry W. Choi for experimental assistance.

Supplementary Material Available: Figure showing numbering schemes for II and III and tables of bond distances and angles and thermal parameters (12 pages); tables of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

---

(74) For a discussion with leading references, see: Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291–1300.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University,
College Station, Texas 77843, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Reactivity of the Dirhenium(III) Carboxylate Complexes $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl or Br) toward Monodentate Phosphines. A Novel Disproportionation Reaction Leading to Dirhenium(IV,II) Alkoxide Complexes of the Type $(RO)_2X_2ReReX_2(PPh_3)_2$ (X = Cl or Br; R = Me, Et, or Pr)

Akhil R. Chakravarty,[1a] F. Albert Cotton,*[1a] Ann R. Cutler,[1b] and Richard A. Walton*[1b]

Received April 9, 1986

The reactions of quadruply bonded dirhenium(III) carboxylate complexes of the type $Re_2(O_2CR)_2X_4L_2$ (X = Cl or Br; R = CH_3 or C_2H_5; L = H_2O, py, DMF, or Me_2SO) with monodentate tertiary phosphines in alcohol solvents have been examined. Whereas $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = H_2O or py) reacts with PMe_3, PMe_2Ph, and $PMePh_2$ in ethanol to give the dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$, the reactions between $Re_2(O_2CR)_2X_4L_2$ (X = Cl or Br; R = CH_3 or C_2H_5; L = H_2O, DMF, or Me_2SO) and PPh_3 in refluxing alcohol solvents ROH (R = Me, Et, *n*-Pr, or *i*-Pr) afford red crystalline, diamagnetic complexes of stoichiometry $Re_2(OR)_2X_4(PPh_3)_2$. The ethoxide derivative has been characterized by X-ray crystallography and shown to possess the novel structure $(EtO)_2Cl_2ReReCl_2(PPh_3)_2$. This is best described formally as a Re(IV)–Re(II) complex that has been derived from the Re(III)–Re(III) core by an intramolecular disproportionation. A comparison is made between the properties of these new mixed halide–alkoxide complexes and those of their symmetrical Re(III)–Re(III) halide analogues $Re_2X_6(PR_3)_2$. Crystal and structural data for $Re_2Cl_4(OEt)_2(PPh_3)_2$: space group $P2_1/c$ with a = 10.782 (3) Å, b = 14.330 (3) Å, c = 26.924 (7) Å, β = 96.98 (2)°, V = 4129 (3) Å^3, Z = 4. The Re–Re distance is 2.231 (1) Å.

Introduction

The reaction of the octahalodirhenate dianions with simple carboxylic acids and/or their anhydrides yields one of three classes of compounds, viz., $Re_2(O_2CR)_4X_2$, $Re_2(O_2CR)_3X_3$, or $Re_2(O_2CR)_2X_4$.[2,3] These materials are related by a qualitatively similar electronic structure: each of them contains a quadruply bonded Re_2^{6+} core. To date, only the reactivity of the tetracarboxylate species has been examined to any significant extent.[2,3]

While the preparation and structural details of the anhydrous dirhenium(III) carboxylates $Re_2(O_2CR)_2X_4$ (X = Cl or Br) and certain of their 1:2 adducts $Re_2(O_2CR)_2X_4L_2$ (e.g., L = H_2O, py, DMF, Me_2SO, and Ph_3PO) have been thoroughly documented,[2-5] few aspects of the reaction chemistry of these species have been explored. This may of course have reflected the expectation that little of note would be uncovered, but as we shall see, these compounds display some unusual and surprising reaction chemistry.

The present manuscript addresses two points: (1) the redox chemistry of the complexes $Re_2(O_2CCH_3)_2X_4L_2$ and (2) a study

---

(1) (a) Texas A&M University. (b) Purdue University.

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(3) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 1.

(4) Koz'min, P. A.; Surazhskaya, M. D. *Sov. J. Coord. Chem. (Engl. Transl.)* **1980**, *6*, 309.

(5) (a) Shtemenko, A. V.; Golovaneva, I. F.; Kotel'nikova, A. S.; Misailova, T. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 704. (b) Shtemenko, A. V.; Kotel'nikova, A. S.; Koz'min, P. A.; Surazhskaya, M. D.; Larina, T. B.; Lebedev, V. G. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1275. (c) Kotel'nikova, A. S.; Moskovkin, A. S.; Misailova, T. V.; Miroshnichenko, I. V.; Bagirov, Sh. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1656. (d) Koz'min, P. A.; Surazhskaya, M. D.; Larina, T. B. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1981**, *26*, 57. (e) Shtemenko, A. V.; Bagirov, Sh. A.; Kotel'nikova, A. S.; Lebedev, V. G.; Kazymov, O. I.; Alieva, A. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1981**, *26*, 58. (f) Misailova, T. V.; Kotel'nikova, A. S.; Golovaneva, I. F.; Evstaf'eva, O. N.; Lebedev, V. G. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1981**, *26*, 343.

0020-1669/86/1325-3619$01.50/0 © 1986 American Chemical Society