Synthesis and Characterization of the Samarium–Cobalt Complexes (C₅Me₅)₂(THF)SmCo(CO)₄ and [SmI₂(THF)₅][Co(CO)₄]: X-ray Crystal Structure of a Seven-Coordinate Samarium(III) Cation Complex

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Co₂(CO)₈ reacts with the divalent samarium complexes (C₅Me₅)₂Sm(THF)₂ and SmI₂(THF)$_x$ to form (C₅Me₅)₂(THF)SmCo(CO)₄ and [SmI₂(THF)₅][Co(CO)₄], respectively. Co₂(CO)₈ reacts with [(C₅Me₅)SmI(THF)₂]₂ to form a complex that disproportionates to (C₅Me₅)₂(THF)SmCo(CO)₄ and [SmI₂(THF)₅][Co(CO)₄]. The latter complex crystallizes from THF in the triclinic space group P1̄ with unit cell dimensions a = 8.829 (4) Å, b = 12.965 (4) Å, c = 14.740 (5) Å, α = 88.48 (3)°, β = 81.63 (3)°, γ = 87.51 (3)°, and Z = 2 for D_{calcd} = 1.86 g cm⁻³. Least-squares refinement on the basis of 1559 observed reflections led to a final R value of 0.041. The complex exists as discrete SmI₂(THF)₅⁺ cations and Co(CO)₄⁻ anions with no Sm–O–C–Co isocarbonyl linkage. The coordination geometry around the samarium atom is roughly pentagonal bipyramidal with the iodide atoms at the two apical positions (Sm–I distances 3.030 (2) and 3.009 (2) Å). The Sm–O(THF) distances vary from 2.44 (1) to 2.47 (1) Å. The Co(CO)₄⁻ anion has a tetrahedral geometry.

In the early 1970s, several reactions involving transition-metal carbonyl complexes and lanthanide reagents were reported.[2–9] Typical examples included (a) ionic metathesis reactions such as reaction of C₅H₅Mo(CO)₃⁻Na⁺ with LnCl₃ or (C₅H₅)₂LnCl-(THF),[5] (b) reactions of the elemental lanthanide with a transition-metal carbonyl halide such as Mn(CO)₅Br,[4] (c) reactions of lanthanide amalgams with mercury derivatives of transition-metal carbonyl anions such as Hg[Co(CO)₄]₂,[2] and (d) simple addition of tris(cyclopentadienyl)lanthanides to transition-metal carbonyls to form adducts.[3,7–9] Crystallographic characterization of the products of these reactions has proven difficult, and the precise structures remain unknown. NMR and IR spectroscopic evidence on lanthanide–transition-metal carbonyl reaction mixtures suggested that isocarbonyl linkages, Ln–O–C–M (Ln = lanthanide metal, M = transition metal), may exist in complexes of this type.[2–9] This is consistent with the highly oxophilic nature of the lanthanides in complexes.[10]

Divalent organolanthanide complexes react with transition-metal carbonyl complexes by reducing them to anionic species,[11–14] and recently, for the pentamethylcyclopentadienyl-substituted complex (C₅Me₅)₂Yb(OEt₂), X-ray crystallographic data on these mixed transition-metal–lanthanide systems have become available. Reaction of the ytterbium reagent with Co₂(CO)₈, Fe₃(CO)₁₂, and Mn₂(CO)₁₀ has given [(C₅Me₅)₂(THF)Yb][(μ-OC)Co-(CO)₄],[12] [(C₅Me₅)₂Yb]₂[(μ-OC)₄Fe₃(CO)₇],[13] and a mixture of [[(C₅Me₅)₂Yb][(μ-OC)₂Mn(CO)₃]]₂ and [[(C₅Me₅)₂Yb][(μ-OC)₃Mn(CO)₂]]$_n$,[14] respectively. In each product, the ytterbium exhibited the structural parameters of a trivalent species, the transition-metal carbonyl fragment was anionic, and the anions and cations were connected via Ln–O–C–M isocarbonyl linkages.

As part of our study of the chemistry of the most reactive divalent lanthanide, Sm(II),[15] we were interested in how the divalent organosamarium reagents (C₅Me₅)₂Sm(THF)₂[16,17] and [(C₅Me₅)SmI(THF)₂]₂,[17] as well as the inorganic Sm(II) reagent SmI₂(THF)$_x$,[18] reacted with transition-metal carbonyl complexes. Given the current interest in materials containing samarium and cobalt as in the SmCo₅ magnets,[19,20] we chose Co₂(CO)₈ as a reagent with which to make molecular samarium–transition-metal complexes. The synthesis and characterization of the products of these reactions, (C₅Me₅)₂(THF)SmCo(CO)₄ and [SmI₂(TH-F)₅][Co(CO)₄], are described below. The X-ray crystal structure of the latter complex is also presented and shows the first example of complexes of this type in which no isocarbonyl linkage is found.

Experimental Section

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

Materials. Solvents were purified and (C₅Me₅)₂Sm(THF)₂, [(C₅Me₅)₂SmI(THF)₂]₂, and SmI₂(THF)$_x$ were prepared as previously described.[17] Co₂(CO)₈ was obtained from Alfa and sublimed immediately prior to use.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. ¹H NMR spectra were obtained on a Bruker 250-MHz spectrometer. Chemical shifts were assigned relative to C₆D₅H, 7.15 ppm, for spectra in benzene-d_6 or relative to THF, 1.72 ppm, for spectra in THF-d_8. Magnetic moments were obtained on the Bruker 250-MHz NMR spectrometer by the Evans method.[21] Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany.

(C₅Me₅)₂(THF)SmCo(CO)₄. Reaction of (C₅Me₅)₂Sm(THF)₂ with Co₂(CO)₈. In the glovebox, (C₅Me₅)₂Sm(THF)₂ (0.519 g, 0.92 mmol) and Co₂(CO)₈ (0.158 g, 0.46 mmol, freshly sublimed) were dissolved in pentane in a 125-mL flask containing a magnetic stirring bar. The solution immediately became dark orange-brown, and a precipitate formed. The reaction mixture was stirred for 12 h, and then the solvent was removed by using a rotary evaporator. The solid was washed with hexane and then toluene on a glass frit. Extraction of the frit with THF produced a bright orange solution, which yielded a pale orange solid upon solvent removal (0.469 g, 86% yield based on (C₅Me₅)₂Sm(THF)₂). The product was recrystallized from THF/hexane at glovebox temperature

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over several days, yielding single crystals suitable for X-ray crystallography. Anal. Calcd. for SmCoC$_{28}$H$_{38}$O$_5$: Sm, 22.65; Co, 8.88; C, 50.66; H, 5.77; O, 12.05. Found: Sm, 22.50; Co, 8.80; C, 50.38; H, 5.66; O, 12.66 (by difference). ^{1}H NMR (C$_4$D$_8$O): δ 0.70, 1.75 (THF), 3.57 (THF). Magnetic susceptibility: χ_g = 1.94 × 10^{-6} at 299 K in THF (μ = 1.76 μ_B). IR (Nujol mull on NaCl): 3630 w, 2025 s, 1950 s, 1920 w, 1860 br, 1785 br, 1170 w, 1100 w, 1020 m, 975, 870, 565, 550 cm^{-1}. Solution IR (THF): 2010, 1910 br, 1855 s, 1775 br, 1740 cm^{-1}. Near-IR (47 mg/mL in THF): 1560 nm (ϵ = 8.0), 1515 (9.0), 1475 (11.0), 1360 (10.0), 1280 (spike), 1245 (44.0), 1220 (sh), 1115 (sh), 1095 (17.9), 1075 (17.9). (C$_5$Me$_5$)$_2$Sm(THF)Co(CO)$_4$ crystallizes from THF/hexane in space group $P2_1/m$ with unit cell constants a = 18.767 (1) Å, b = 9.245 (5) Å, c = 35.41 (1) Å and β = 95.06 (5)°. A refinable solution for the structure has not yet been obtained.

[SmI$_2$(THF)$_5$][Co(CO)$_4$]. Reaction of SmI$_2$ with Co$_2$(CO)$_8$. In the glovebox, SmI$_2$(THF)$_2$ (1.05 g, 1.92 mmol) was dissolved in 60 mL of THF in a 125-mL flask equipped with a stir bar. Co$_2$(CO)$_8$ (0.331 g, 0.97 mmol) was dissolved in ca. 5 mL of THF and immediately added to the blue SmI$_2$ solution. Within 1 min the mixture lightened, yielding an off-white precipitate and a light brown solution. The solvent volume was slowly reduced to ca. 15 mL on the rotary evaporator, and the solid product was isolated by filtration. The colorless solid was rinsed twice with 10 mL of hexane and weighed (1.68 g, 1.80 mmol, 94% (for SmI$_2$Co(CO)$_4$(THF)$_5$)). Rotary evaporation of the mother liquor leaves almost no residue, confirming the quantitative nature of this reaction. The product is conveniently recrystallized by preparing a saturated solution in THF and cooling to −25 °C overnight. This yields single crystals suitable for X-ray crystallography. Anal. Calcd for SmI$_2$CoC$_{20}$H$_{32}$O$_8$ (i.e., the tetrasolvate SmI$_2$Co(CO)$_4$(THF)$_4$): Sm, 17.42; I, 29.39; Co, 6.82; C, 27.82; H, 3.75; O, 14.82. Found: Sm, 17.65; I, 29.14; Co, 6.93; C, 27.75; H, 3.85; O, 14.68 (by difference). Powdered or crystalline samples discolor on long storage (weeks) at glovebox temperature. ^{1}H NMR (THF-d_8): δ 1.72 (THF), 3.57 (THF). IR (KBr): 2989 s, 2903 s, 1930–1840 s, br, 1783 s, 1486 w, 1451 m, 1344 w, 1297 vw, 1245 w, 1233 w, 1179 w, 1138 w, 1034 m, 1013 s, 953 vw, 919 m, and 822 s cm^{-1}.

Reaction of [(C$_5$Me$_5$)$_2$SmI(μ-I)(THF)$_2$]$_2$ with Co$_2$(CO)$_8$. [(C$_5$Me$_5$)$_2$SmI(THF)$_2$]$_2$ (0.563 g, 0.506 mmol) was dissolved in 50 mL of THF, and solid Co$_2$(CO)$_8$ (0.175 g, 0.512 mmol) was added with stirring. The solution immediately changed from dark green to orange-red. After 30 min the solvent was removed and the solid residue dried. A sample had very little solubility in toluene. The solid was dissolved in 8 mL of THF and centrifuged, leaving a small amount of off-white solid and an orange supernatant. The off-white solid was suspended in 8 mL of THF and centrifuged. (The off-white solid had very little solubility in THF). The supernatants were combined in a 50 mL Erlenmeyer flask, hexane was layered above it, and the flask was kept at −25 °C overnight. This recrystallization experiment yielded an orange mother liquor and an orange crystalline product, which was rinsed twice with hexane and dried on the rotary evaporator (0.513 g, 0.706 mmol, 70% based on (C$_5$Me$_5$)SmICo(CO)$_4$(THF)$_2$, 63% based on (C$_5$Me$_5$)SmICo(CO)$_4$(THF)$_3$). Anal. Calcd for SmICoC$_{22}$H$_{31}$O$_6$ (i.e., the disolvate (C$_5$Me$_5$)SmICo(CO)$_4$(THF)$_2$): Sm, 20.67; Co, 8.10; I, 17.44; C, 36.31; H, 4.30; O, 13.19. Found: Sm, 22.50; Co, 8.70; I, 19.03; C, 39.95; H, 4.52; O, 5.30 (by difference). The Sm:Co:I ratio is 1.00:1.00:0.99. ^{1}H NMR (THF-d_8): δ 0.81 (s, C$_5$(CH$_3$)$_5$, 15 H), 1.72 (m, THF, 12 H), 3.56 (m, THF, 12 H). IR (KBr): 2960 s, 2900 s, 2330 w, 2020 s, 1950–1750 vs, br, 1450, 1370 w, 1260 w, 1170 vw, 1080 w, 1010 s, 915 w, 850 s, 800 w cm^{-1}. The orange crystalline product, when dissolved in THF, left a small amount of off-white solid. All efforts to recrystallize the product slowly to isolate single crystals resulted in the deposition of more off-white powder. This powder, which is sparingly soluble in THF, has only THF in the ^{1}H NMR, and has an IR spectrum identical with that of the product of the reaction of SmI$_2$ with Co$_2$(CO)$_8$. Single crystals of this material grown from cold THF were in color and appearance identical with those of the SmI$_2$/Co$_2$(CO)$_8$ product. The original orange mother liquor, on standing for several days, deposited off-white solids and also left orange crystals at the solvent line. These orange crystals had a ^{1}H NMR signal at δ 0.70 (C$_5$Me$_5$) identical with that of (C$_5$Me$_5$)$_2$SmCo(CO)$_4$(THF)$_2$.

X-ray Data Collection, Structure Determination, and Refinement for [SmI$_2$(THF)$_5$][Co(CO)$_4$]. Single crystals of the air-sensitive compound were sealed under N$_2$ in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of ((sin θ)/λ)^2 values for 15 reflections (θ > 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 scan technique as previously described.[22] A summary of data collection parameters is given in Table

Table I. Crystal Data for [SmI$_2$(THF)$_5$][Co(CO)$_4$]

compd	SmCoI$_2$C$_{24}$H$_{40}$O$_9$
mol wt	935.69
space group	$P\bar{1}$
cell const	
a, Å	8.829 (4)
b, Å	12.965 (4)
c, Å	14.740 (5)
α, deg	88.48 (3)
β, deg	81.63 (3)
γ, deg	87.51 (3)
cell vol, Å^3	1667.4
molecules/unit cell	2
ρ(calcd), g cm^{-3}	1.86
μ(calcd), cm^{-1}	42.06
radiatn	Mo Kα
max cryst dimens, mm	0.20 × 0.25 × 0.30
scan width, deg	0.8 + 0.2 tan θ
std reflcns	200, 020, 002
decay of std	<3%
no. of reflcns measd	2350
2θ range	2–40
no. of obsd reflcns	1559
no. of params varied	234
R	0.041
R_w	0.045

I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[23] Calculations were carried out with the SHELX system of computer programs.[24] Neutral-atom scattering factors for Sm, Co, I, O, and C were taken from Cromer and Waber,[25] and the scattering for Sm, Co, and I was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[26] Scattering factors for hydrogen were from ref 27.

The space group was shown to be $P\bar{1}$ by the successful solution and refinement of the structure. The positions of the samarium and iodide atoms were revealed by the inspection of a Patterson map. A difference Fourier map phased on these atoms revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.090$.

All non-hydrogen atoms with the exception of the ring carbon atoms in the THF rings were refined with anisotropic thermal parameters. The final agreement factors are $R = 0.041$ and $R_w = 0.045$. A final difference Fourier showed no feature greater than 1.5 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 θ)/λ was noted. The final values of the positional parameters are given in Table II.

Results and Discussion

(C$_5$Me$_5$)$_2$Sm(THF)$_2$ Reaction. Purple-black (C$_5$Me$_5$)$_2$Sm(THF)$_2$ (I) reacts rapidly with Co$_2$(CO)$_8$ in pentane to form an orange product characterized as (C$_5$Me$_5$)$_2$(THF)SmCo(CO)$_4$ (II) by complete elemental analysis. The color, near-infrared and ^{1}H NMR spectra, and magnetic moment of II were characteristic of a Sm^{3+} organometallic complex. The carbonyl region of the infrared spectra contained several strong broad bands with absorptions at energies as low as 1740 cm^{-1}.

These data were consistent with the reduction of Co$_2$(CO)$_8$ by the Sm^{2+} center in I to form a (C$_5$Me$_5$)$_2$Sm(THF)$^+$ complex of the Co(CO)$_4^-$ anion. The reduction of Co$_2$(CO)$_8$ to Co(CO)$_4^-$ is well established,[28,29] and Sm^{2+} is a strong enough reducing agent to accomplish this transformation.[15] A similar reaction has been reported in which the weaker reducing agent (C$_5$Me$_5$)$_2$Yb(OEt$_2$) converts Co$_2$(CO)$_8$ to (C$_5$Me$_5$)$_2$(THF)YbCo(CO)$_4$.[12]

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Table II. Positional Parameters for [SmI₂(THF)₅][Co(CO)₄]

atom	x/a	y/b	z/c	U(equiv), Å²
Sm(1)	0.4288 (1)	0.25449 (9)	0.74832 (8)	0.040
I(1)	0.2194 (2)	0.2682 (1)	0.6025 (1)	0.066
I(2)	0.6180 (2)	0.2327 (1)	0.9024 (1)	0.072
O(1)	0.385 (2)	0.439 (1)	0.7845 (9)	0.058
C(1)	0.396 (3)	0.488 (2)	0.873 (2)	0.078
C(2)	0.363 (3)	0.596 (2)	0.856 (2)	0.110
C(3)	0.280 (3)	0.608 (2)	0.782 (2)	0.110
C(4)	0.345 (3)	0.520 (2)	0.721 (2)	0.101
O(2)	0.200 (1)	0.269 (1)	0.8650 (9)	0.049
C(5)	0.068 (2)	0.333 (2)	0.851 (1)	0.069
C(6)	-0.012 (3)	0.355 (2)	0.949 (2)	0.081
C(7)	0.022 (2)	0.254 (2)	0.997 (2)	0.065
C(8)	0.185 (3)	0.225 (2)	0.955 (2)	0.076
O(3)	0.343 (2)	0.079 (1)	0.782 (1)	0.069
C(9)	0.193 (3)	0.043 (2)	0.770 (2)	0.098
C(10)	0.200 (5)	-0.060 (3)	0.813 (3)	0.207
C(11)	0.326 (3)	-0.091 (2)	0.844 (2)	0.109
C(12)	0.430 (3)	-0.001 (2)	0.824 (2)	0.091
O(4)	0.614 (1)	0.135 (1)	0.6610 (9)	0.061
C(13)	0.780 (3)	0.125 (2)	0.666 (2)	0.074
C(14)	0.843 (3)	0.050 (2)	0.597 (2)	0.086
C(15)	0.729 (3)	0.033 (2)	0.541 (2)	0.102
C(16)	0.580 (3)	0.069 (2)	0.588 (2)	0.115
O(5)	0.620 (2)	0.356 (1)	0.6518 (9)	0.063
C(17)	0.735 (3)	0.418 (2)	0.683 (2)	0.087
C(18)	0.821 (3)	0.464 (2)	0.603 (2)	0.100
C(19)	0.758 (4)	0.436 (3)	0.528 (2)	0.128
C(20)	0.648 (3)	0.358 (2)	0.550 (2)	0.098
Co(1)	0.2002 (4)	0.2473 (3)	0.2567 (2)	0.073
C(21)	0.218 (3)	0.144 (2)	0.179 (2)	0.091
O(6)	0.233 (3)	0.075 (2)	0.131 (2)	0.120
C(22)	0.194 (3)	0.359 (2)	0.187 (2)	0.096
O(7)	0.190 (3)	0.433 (2)	0.143 (2)	0.152
C(23)	0.041 (3)	0.237 (3)	0.331 (2)	0.107
O(8)	-0.065 (3)	0.233 (2)	0.384 (2)	0.156
C(24)	0.351 (3)	0.246 (2)	0.314 (2)	0.094
O(9)	0.454 (2)	0.243 (2)	0.356 (1)	0.119

Single crystals of **II** were not isostructural with those of (C₅Me₅)₂(THF)YbCo(CO)₄. Given the difference in radii of Yb³⁺ and Sm³⁺, 0.106 Å,[30] this is perhaps not surprising. A refinable solution to the X-ray diffraction data on **II** did not readily become apparent, however. This compound may have a complex polymeric structure as was found with the (C₅Me₅)₂Yb(OEt₂)/Mn₂(CO)₁₀ system.[14]

SmI₂(THF)ₓ Reaction. Dark blue SmI₂(THF)ₓ (**III**) reacts quickly with Co₂(CO)₈ in THF to form an off-white precipitate, which analyzed as the tetrasolvate I₂(THF)₄SmCo(CO)₄. The ¹H NMR spectrum of this material contained resonances attributable only to THF, and the infrared spectrum exhibited strong broad absorptions in the 1750–1950 cm⁻¹ range. Single crystals of this product were studied by X-ray diffraction techniques and shown to be the pentasolvate [SmI₂(THF)₅][Co(CO)₄] (**IV**), whose structure is described below.

Structure of [SmI₂(THF)₅][Co(CO)₄]. Complex **IV** crystallizes from THF with a structure containing discrete SmI₂(THF)₅⁺ cations and Co(CO)₄⁻ anions. This is the first structure of a transition-metal carbonyl complex reduced by a divalent lanthanide in which isocarbonyl linkages are not found.

The Co(CO)₄⁻ anion has a structure that is close to tetrahedral. The bond lengths and angles in the anion (Table III) are within the range of metrical parameters reported for structures of other Co(CO)₄⁻ complexes.[12,31–35] The Co(CO)₄⁻ is well separated from

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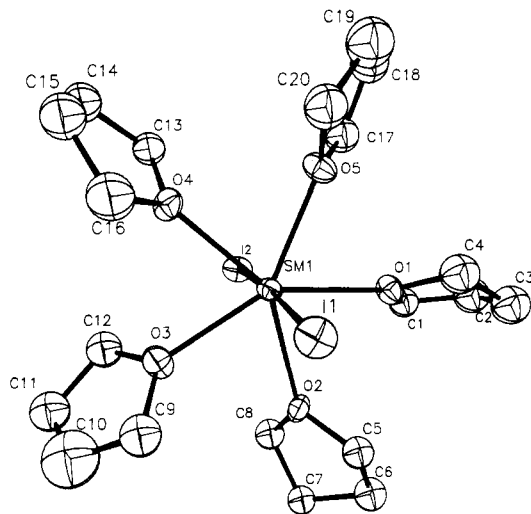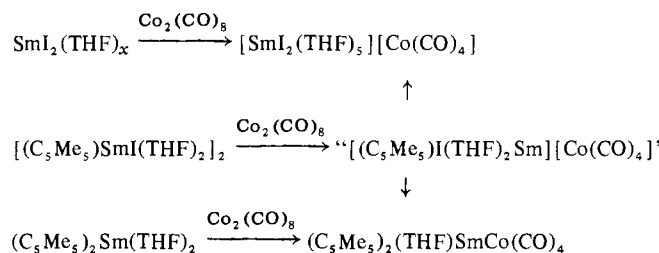
Table III. Bond Distances (Å) and Angles (deg) for the Anion in [SmI₂(THF)₅][Co(CO)₄]

Distances			
Co(1)–C(21)	1.77 (3)	Co(1)–C(22)	1.76 (3)
Co(1)–C(23)	1.66 (3)	Co(1)–C(24)	1.68 (3)
C(21)–O(6)	1.15 (3)	C(22)–C(7)	1.14 (3)
C(23)–O(8)	1.14 (3)	C(24)–O(9)	1.16 (3)

Angles			
C(21)–Co(1)–C(22)	105 (1)	C(21)–Co(1)–C(23)	110 (1)
C(22)–Co(1)–C(23)	112 (2)	C(21)–Co(1)–C(24)	111 (1)
C(22)–Co(1)–C(24)	111 (1)	C(23)–Co(1)–C(24)	109 (2)
Co(1)–C(21)–O(6)	177 (3)	Co(1)–C(22)–O(7)	178 (3)
Co(1)–C(23)–O(8)	177 (3)	Co(1)–C(24)–O(9)	178 (3)

Table IV. Bond Distances (Å) and Angles (deg) for the Cation in [SmI₂(THF)₅][Co(CO)₄]

Distances			
Sm(1)–I(1)	3.030 (2)	Sm(1)–I(2)	3.009 (2)
Sm(1)–O(1)	2.47 (1)	Sm(1)–O(2)	2.46 (1)
Sm(1)–O(3)	2.45 (1)	Sm(1)–O(4)	2.45 (1)
Sm(1)–O(5)	2.45 (1)	C(1)–C(2)	1.44 (3)
C(1)–O(1)	1.48 (3)	C(2)–C(3)	1.40 (3)
C(3)–C(4)	1.51 (3)	C(4)–O(1)	1.45 (3)
C(5)–C(6)	1.54 (3)	C(5)–O(2)	1.44 (2)
C(6)–C(7)	1.52 (3)	C(7)–C(8)	1.52 (3)
C(8)–O(2)	1.43 (2)	C(9)–C(10)	1.46 (4)
C(9)–O(3)	1.46 (3)	C(10)–C(11)	1.31 (4)
C(11)–C(12)	1.52 (3)	C(12)–O(3)	1.43 (3)
C(13)–C(14)	1.47 (3)	C(13)–O(4)	1.48 (2)
C(14)–C(15)	1.41 (3)	C(15)–C(16)	1.46 (3)
C(16)–O(4)	1.47 (3)	C(17)–O(5)	1.45 (3)
C(17)–C(18)	1.44 (3)	C(18)–C(19)	1.37 (3)
C(19)–C(20)	1.43 (3)	C(20)–O(5)	1.49 (3)

Angles			
I(1)–Sm(1)–I(2)	175.70 (7)	I(1)–Sm(1)–O(1)	92.7 (3)
I(2)–Sm(1)–O(1)	88.4 (3)	I(1)–Sm(1)–O(2)	88.3 (3)
I(2)–Sm(1)–O(2)	88.0 (3)	O(1)–Sm(1)–O(2)	72.9 (4)
I(1)–Sm(1)–O(3)	87.5 (3)	I(2)–Sm(1)–O(3)	89.2 (3)
O(1)–Sm(1)–O(3)	146.2 (5)	O(2)–Sm(1)–O(3)	73.3 (5)
I(1)–Sm(1)–O(4)	93.7 (3)	I(2)–Sm(1)–O(4)	88.0 (3)
O(1)–Sm(1)–O(4)	141.5 (4)	O(2)–Sm(1)–O(4)	145.2 (4)
O(3)–Sm(1)–O(4)	72.1 (5)	I(1)–Sm(1)–O(5)	91.2 (3)
I(2)–Sm(1)–O(5)	93.1 (3)	O(1)–Sm(1)–O(5)	70.4 (5)
O(2)–Sm(1)–O(5)	143.2 (4)	O(3)–Sm(1)–O(5)	143.4 (5)
O(4)–Sm(1)–O(5)	71.5 (5)	C(2)–C(1)–O(1)	104 (2)
C(1)–C(2)–C(3)	110 (3)	C(2)–C(3)–C(4)	102 (2)
C(3)–C(4)–O(1)	104 (2)	C(6)–C(5)–O(2)	104 (2)
C(5)–C(6)–C(7)	100 (2)	C(6)–C(7)–C(8)	104 (2)
C(7)–C(8)–O(2)	104 (2)	C(10)–C(9)–O(3)	100 (3)
C(9)–C(10)–C(11)	119 (4)	C(10)–C(11)–C(12)	104 (3)
C(11)–C(12)–O(3)	107 (2)	C(14)–C(13)–O(4)	106 (2)
C(13)–C(14)–C(15)	108 (2)	C(14)–C(15)–C(16)	109 (3)
C(15)–C(16)–O(4)	105 (2)	C(18)–C(17)–O(5)	107 (2)
C(17)–C(18)–C(19)	108 (3)	C(18)–C(19)–C(20)	113 (3)
C(19)–C(20)–O(5)	103 (2)	Sm(1)–O(1)–C(1)	127 (1)
Sm(1)–O(1)–C(4)	126 (1)	C(1)–O(1)–C(4)	107 (2)
Sm(1)–O(2)–C(5)	122 (1)	Sm(1)–O(2)–C(8)	126 (1)
C(5)–O(2)–C(8)	112 (1)	Sm(1)–O(3)–C(9)	125 (1)
Sm(1)–O(3)–C(12)	124 (1)	C(9)–O(3)–C(12)	111 (2)
Sm(1)–O(4)–C(13)	126 (1)	Sm(1)–O(4)–C(16)	125 (1)
C(13)–O(4)–C(16)	108 (2)	Sm(1)–O(5)–C(17)	127 (1)
Sm(1)–O(5)–C(20)	126 (1)	C(17)–O(5)–C(20)	107 (2)

the SmI₂(THF)₅⁺ cation. The closest approach of any atom in the anion to an atom in the cation is between the Co(CO)₄⁻ carbonyl oxygen atom O(6) and the C(8) carbon atom of a THF in SmI₂(THF)₅⁺. The O(6)–C(8) distance is 3.25 Å. The shortest anion to samarium distance is the O(6)–Sm length, which is 5.56 Å.

The SmI₂(THF)₅⁺ cation adopts a pentagonal-bipyramidal structure as shown in Figure 1. The iodide ligands are in the axial positions, and the oxygen atoms of the five THF molecules lie in the equatorial pentagonal plane. This arrangement places the larger iodide ligands in the sterically less crowded axial positions. As shown in Table IV, the I–Sm–I angle approaches

Figure 1. Molecular structure of $[SmI_2(THF)_5]^+$.

linearity at 175.70 (7)°, and the ten I–Sm–O angles fall in a narrow range, 87.5 (3)–93.7 (3)°, around 90°. The O–Sm–O angles for adjacent THF molecules are in the range 70.4 (5)–73.3 (5)°, spanning the 72° angle for a regular pentagon. The five oxygen atoms are planar to within 0.09 Å, and the Sm atom is only 0.03 Å out of the best average plane of these oxygen atoms. If one considers the "average plane" of the five atoms of each THF ring, one can calculate "dihedral angles" between each THF and the plane of the five oxygen atoms. These "dihedral angles" describe the relative orientation of the THF rings and have values of 65.5, 58.9, 61.5, 62.2, and 62.3° for the rings with O(1)–O(5), respectively. These data show that the THF rings are canted with respect to the equatorial plane of the pentagonal bipyramid rather than perpendicular. All rings tip in the same direction like the blades of a propeller.

The Sm–I distances of 3.009 (2) and 3.030 (2) Å in IV are slightly smaller than the Sm–I distances in $(C_5Me_5)_2SmI(THF)$, 3.043 (2) and 3.053 (2) Å.[36] This trend is consistent with the fact that the latter molecule is formally eight-coordinate compared to the seven-coordinate structure of IV. Shannon's compilation of metallic radii adjusted for coordination number has eight-coordinate Sm^{3+} 0.059 Å larger than seven-coordinate Sm^{3+}.[37] The Sm–O(THF) distances in IV range from 2.45 (1) to 2.47 (1) Å with an average of 2.456 Å compared to the following values in eight-coordinate Sm^{3+} structures: $(C_5Me_5)_2SmI(THF)$,[36] 2.45 (1) Å; $(C_5Me_5)_2SmCl(THF)$,[36] 2.44 (2) and 2.48 (2) Å; $(C_5Me_5)_2Sm(C_6H_5)(THF)$,[38] 2.511 (4) Å.

There are relatively few structurally characterized inorganic seven-coordinate lanthanide complexes available for comparison with $SmI_2(THF)_5^+$. Although high coordination numbers are common for the lanthanides due to the large size of the metals,[39] eight- to ten-coordinate structures are generally preferred to seven-coordinate systems.[40] Most of the known seven-coordinate lanthanide structures involve either polymeric systems or monomers with three chelating bidentate ligands and one monodentate species. These complexes generally adopt capped octahedral or capped trigonal-prismatic structures.[40] To our knowledge, the only structurally characterized seven-coordinate monomeric lan-

Scheme I

$$SmI_2(THF)_x \xrightarrow{Co_2(CO)_8} [SmI_2(THF)_5][Co(CO)_4]$$

$$\uparrow$$

$$[(C_5Me_5)SmI(THF)_2]_2 \xrightarrow{Co_2(CO)_8} \text{"}[(C_5Me_5)I(THF)_2Sm][Co(CO)_4]\text{"}$$

$$\downarrow$$

$$(C_5Me_5)_2Sm(THF)_2 \xrightarrow{Co_2(CO)_8} (C_5Me_5)_2(THF)SmCo(CO)_4$$

thanide complex containing only monodentate ligands is [Er-$(DMP)_7][ClO_4]_3$ where DMP is 3,6-dimethyl-4-pyrone.[41] This complex displays a distorted pentagonal-bipyramidal structure with an axial-O–Er–axial-O angle of 171.1 (2)° and equatorial O–Er–O angles of 69–75°. The complex has axial Er–O distances of 2.209 (6) and 2.256 (6) Å and equatorial Er–O distances ranging from 2.256 to 2.327 Å. In this complex, the consistently shorter metal–oxygen distances observed are consistent with the smaller size of Er^{3+} and the difference in hybridization of the oxygen donor atom in the pyrone vs THF.

$[(C_5Me_5)SmI(THF)_2]_2$ Reaction. Like the other Sm^{2+} reagents, dark green $[(C_5Me_5)SmI(THF)_2]_2$ (V) loses its color rapidly upon treatment with $Co_2(CO)_8$. The product had the orange-red color characteristic of organometallic Sm^{3+} complexes, a ^1H NMR spectrum containing a C_5Me_5 resonance distinct from that of II, and an IR spectrum with several strong absorptions suggesting that $Co_2(CO)_8$ had been reduced. Elemental analysis on this product indicated a Sm:Co:I ratio of 1.00:1.00:0.99, consistent with a formula such as $(C_5Me_5)(THF)_2ISmCo(CO)_4$, but the analysis was not exact for this formula. Related to this, the complex was not particularly stable, and when it was dissolved in THF, it deposited an off-white precipitate. IR and NMR analysis of the off-white powder generated over several days from a THF solution indicated it was $[SmI_2(THF)_5][Co(CO)_4]$. The remaining orange solution deposited orange crystals identical with $(C_5Me_5)_2(THF)SmCo(CO)_4$. Hence, it appears that the initial product of the reaction of V with $Co_2(CO)_8$ (possibly (C_5Me_5)-$I(THF)_2SmCo(CO)_4$) undergoes ligand redistribution to form II and IV (Scheme I).

Summary

$Co_2(CO)_8$ is readily reduced by the three divalent samarium complexes $(C_5Me_5)_2Sm(THF)_2$, $[(C_5Me_5)_2SmI(THF)_2]_2$, and $SmI_2(THF)_x$ to form products that contain $Co(CO)_4^-$ species. The $[(C_5Me_5)SmI(THF)_2]_2$ reagent gives the least stable product, which ultimately converts to a mixture of the products of the $(C_5Me_5)_2Sm(THF)_2$ and $SmI_2(THF)_x$ reactions. Structural characterization of the product of the $SmI_2(THF)_x$ reaction, $[SmI_2(THF)_5][Co(CO)_4]$, indicates that even with the very oxophilic trivalent lanthanide metals in complexes containing only two anionic ligands, isocarbonyl formation does not always occur.

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