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A Convenient Route to Lanthanide Triiodide THF Solvates. Crystal Structures of $LnI_3(THF)_4$ [Ln = Pr] and $LnI_3(THF)_{3.5}$ [Ln = Nd, Gd, Y]

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The reaction between 1.5 equiv of elemental iodine and rare earth metals in powder form in THF at room temperature gives the rare earth triiodides $LnI_3(THF)_n$ in good yields. Purification by Soxhlet extraction of the crude solids with THF reliably gives the THF adducts $LnI_3(THF)_4$ [Ln = La, Pr] and $LnI_3(THF)_{3.5}$ [Ln = Nd, Sm, Gd, Dy, Er, Tm, Y] as microcrystalline solids. X-ray crystallography reveals that the early, larger lanthanide iodide $PrI_3(THF)_4$ crystallizes as discrete molecules having a pentagonal bipyramidal structure, whereas the later, smaller lanthanide iodides $LnI_3(THF)_{3.5}$ [Ln = Nd, Gd, Y] crystallize as solvent-separated ion pairs $[LnI_2(THF)_5][LnI_4(THF)_2]$ in which the cations adopt a pentagonal bipyramidal geometry and the anions adopt an octahedral geometry in the solid state.

Introduction

Anhydrous lanthanide trihalides (we include the group 3 elements Y and La in this definition due to the similar chemical properties of their +3 ions to those of the lanthanides) are among the most convenient and widely used starting materials for the synthesis of organometallic and metal-organic (e.g. amide, alkoxide, thiolate) complexes of these elements via metathesis reactions (eq 1). In addition, the lanthanide trihalides represent an important and versatile class of Lewis acid catalysts for a wide range of organic transformations.[1]

$$x\mathrm{ML} + \mathrm{LnX}_3 \rightarrow \mathrm{LnX}_{(3-x)}\mathrm{L}_x + x\mathrm{MX} \qquad (1)$$

The choice of lanthanide halide and alkali metal salt starting materials in metathesis reactions is often critical; in many cases the use of readily accessible lanthanide trichlorides and lithium salts results in either low yields or unwanted side-products such as "ate" complexes. For example, Lee and co-workers recently reported that $LnCl_3$ (Ln = La, Ce) does not react with the functionalized lithium amide Li[N($SiMe_2$-*t*-Bu)(2-C_5H_3N-6-Me)], even in boiling THF, whereas reactions with the corresponding potassium amide are complete within 2 days under the same conditions.[2] We have noted in our own studies on lanthanide phosphanides that attempted metathesis reactions between lanthanide trichlorides and alkali metal phosphanides (R_2P)M (M = Li or K) are always unsuccessful and that lanthanide triflates are also unreactive toward these reagents.[3] However, reactions between lanthanide di- or triiodides and the same potassium phosphanides are complete within 12 h at room temperature.[4−8] We attribute the lack of reactivity of the lanthanide trichlorides and triflates in these reactions to the difficulty in displacing a hard Cl^- or OTf^- anion with a softer phosphanide ligand from the hard lanthanide cations.

Lanthanide triiodides are, therefore, extremely useful starting materials and, given the prohibitively expensive nature of commercially available, unsolvated lanthanide triiodides, a convenient route to such compounds is highly desirable. Although attractive, the dehydration of hydrated lanthanide triiodides is often unsatisfactory and may lead to undesirable side-products; Bruno and co-workers have reported that attempts to thermally dehydrate $LaI_3{\cdot}9H_2O$ led to partial hydrolysis to polymeric $[LaIO]_n$.[9] Several routes to solvated lanthanide triiodides have been reported previ-

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ously: (i) the reduction of mercuric iodide by elemental lanthanides to give $LnI_3(THF)_{3.5}$ [Ln = Sm, Yb],[10] (ii) the reaction between an alkyl iodide (CH_2I_2 or EtI) and an elemental lanthanide to give $LnI_3(THF)_n$ [Ln = La, Ce, $n = 4$; Nd, $n = 3.5$],[9,11] (iii) the direct reaction of iodine and an elemental lanthanide in 2-propanol to give $LnI_3(HO\text{-}i\text{-}Pr)_4$ [Ln = La, Ce, Nd],[12] and (iv) oxidation of samarium(II) diiodide by O_2 to give $SmI_3(THF)_{3.5}$.[13] The compound $YbI_3(THF)_{3.5}$ has also been isolated in low yield from the reaction between an organoytterbium(II) complex and neopentyl iodide.[14] [In addition, the preparation of various adducts $LnI_3(L)_n$ from anhydrous LnI_3 has been reported, where $(L)_n$ is a neutral O-, N-, or S-donor ligand.][15] Many of these routes suffer from significant drawbacks, including the separation and disposal of elemental mercury, the potential formation of organolanthanide side-products, low yields, and the incorporation of protic ligands in the product which may interfere with further metathesis reactions.

Somewhat surprisingly, the straightforward reaction between elemental iodine and lanthanide metals in nonprotic solvents has not previously been described. We report herein the synthesis of a series of lanthanide triiodides by this route as their THF adducts and the crystallographic characterization of four of these compounds.

Results and Discussion

Our initial attempts to prepare lanthanide triiodides via the reaction of lanthanide metals with 1,2-diiodoethane in THF were unsuccessful: although the triiodides $LnI_3(THF)_n$ are formed under these conditions they are heavily contaminated with a dark red-brown material which could not be removed, even after multiple recrystallizations (attempts to remove this impurity by heating under vacuum were unsuccessful, precluding iodine as the contaminant). It has been noted previously that reactions between iodoethane and either lanthanum or cerium may give mixtures of metal alkyls and halides and it is possible that these involatile red-brown impurities may be derived from organolanthanide side products.[16]

The direct reaction of uranium turnings with elemental iodine has previously been employed for the synthesis of the solvated uranium(III) iodide, $UI_3(THF)_4$.[17] Similarly, we find that treatment of lanthanide metal powders with 1.5 equiv of iodine in THF at room temperature results in complete consumption of the metals and precipitation of the triiodides $LnI_3(THF)_n$ as crude powders after approximately 3 days. Addition of light petroleum to the reaction mixtures yields further solids, and these crude products may be purified, after careful removal of excess iodine by sublimation, by Soxhlet extraction with THF over a period of several hours to give synthetically useful quantities of the triiodides $LnI_3(THF)_n$ [Ln = La, Pr (**1**), $n = 4$; Ln = Nd (**2**), Sm, Gd (**3**), Dy, Er, Tm, Y (**4**), $n = 3.5$] as analytically pure, microcrystalline solids.

Crystallographically characterized THF adducts of the lanthanide trichlorides adopt a variety of structures in the solid state, including polymeric $[LnCl_3(THF)_2]_n$ (Ln = Y, La, Ce, Pr, Nd),[18−21] monomeric $LnCl_3(THF)_n$ (Ln = Yb, Lu, $n = 3$; Nd, Sm, Eu, Gd, $n = 4$),[19,21−25] dimeric $[YbCl_3(THF)_2]_2$,[21] and the ion pair compounds $[LnCl_2(THF)_5][LnCl_4(THF)_2]$ (Ln = Y, Gd, Dy, Er, Tb, Tm, Yb).[18,20,26−30] The exact stoichiometry of the trichloride isolated appears to be dependent upon the ionic radius of the metal, the synthetic route employed, and the precise workup conditions. In contrast, only two structural types have been observed for THF adducts of the lanthanide triiodides: the seven-coordinate monomer $LaI_3(THF)_4$[31] and the ion pairs $[LnI_2(THF)_5][LnI_4(THF)_2]$ (Ln = Sm, Yb).[13,14] In order to investigate the influence of cation size on structure we set out to study the solid state structures of the triiodides obtained by the direct reaction of iodine with the metals described above.

Single crystals of compounds **1**−**4** were obtained by concentrating and cooling the THF mother liquor obtained after Soxhlet extraction of the crude solids to 6 °C for 12 h. Compound **1** crystallizes as a discrete molecular species which is isostructural with the previously reported lanthanum and uranium analogues.[17,31] The molecular structure of **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The Pr atom is coordinated by the three iodides and four THF molecules in a distorted pentagonal bipyramidal geometry such that two of the iodide ligands are mutually *trans*. The Pr−I(axial) and Pr−I(equatorial)

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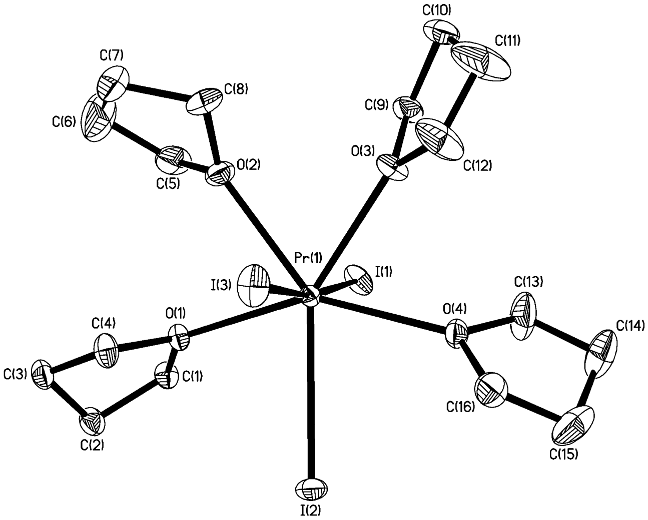

Figure 1. Molecular structure of **1** with 50% probability ellipsoids and with H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pr(1)−O(1)	2.455(2)	Pr(1)−O(4)	2.487(2)	Pr(1)−O(3)	2.500(2)
Pr(1)−O(2)	2.528(2)	Pr(1)−I(1)	3.0896(3)	Pr(1)−I(3)	3.1091(3)
Pr(1)−I(2)	3.1578(3)				

O(4)−Pr(1)−O(3)	69.99(8)	O(1)−Pr(1)−O(2)	70.12(8)
O(3)−Pr(1)−O(2)	70.66(8)	O(1)−Pr(1)−I(1)	87.21(5)
O(4)−Pr(1)−I(1)	90.35(6)	O(3)−Pr(1)−I(1)	87.84(6)
O(2)−Pr(1)−I(1)	88.79(6)	O(1)−Pr(1)−I(3)	96.07(5)
O(4)−Pr(1)−I(3)	90.66(6)	O(3)−Pr(1)−I(3)	84.85(6)
O(2)−Pr(1)−I(3)	85.26(6)	I(1)−Pr(1)−I(3)	171.781(9)
O(1)−Pr(1)−I(2)	73.57(6)	O(4)−Pr(1)−I(2)	75.94(6)
I(1)−Pr(1)−I(2)	94.400(9)	I(3)−Pr(1)−I(2)	93.758(9)

distances are 3.0896(3)/3.1091(3) Å and 3.1578(3) Å, respectively, and the Pr−O distances range from 2.455(2) to 2.528(2) Å; the I(1)−Pr−I(3) angle is 171.781(9)°.

Compounds **2**−**4** are isostructural and isomorphous; the crystal structure of **3** is shown in Figure 2, and selected bond lengths and angles for **2**−**4** are given in Table 2. Compounds **2**−**4** crystallize as ion pairs with the same structural motif as the previously reported compounds $[LnI_2(THF)_5][LnI_4(THF)_2]$ (Ln = Sm, Yb), with which they are isostructural.[13,14] The lanthanide centers in the cations adopt slightly distorted pentagonal bipyramidal geometries, coordinated by two, mutually *trans*, iodides and five equatorial THF molecules; the anions adopt an octahedral geometry, coordinated by two, mutually *trans*, molecules of THF and four iodides. The anions possess exact crystallographic inversion symmetry while a crystallographic C_2-axis passes through O(4), the lanthanide center, and the midpoint of the C(14)−C(14′) bond of the cation. As expected, the Ln−I distances in the cations [3.0428(6) Å (**2**), 2.9952(4) Å (**3**), and 2.9685(6) Å (**4**)] are somewhat shorter than the Ln−I distances in the corresponding anions [3.0843(6)/3.0718(7) Å (**2**), 3.0264(5)/3.0435(4) Å (**3**), 3.0181(6)/2.9984(7) Å (**4**)].

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**, **3**, and **4**[a]

2

Nd(1)−I(1)	3.0843(6)	Nd(1)−I(2)	3.0718(7)	Nd(2)−I(3)	3.0428(6)
Nd(1)−O(1)	2.397(6)	Nd(2)−O(2)	2.458(7)	Nd(2)−O(3)	2.470(6)
Nd(2)−O(4)	2.467(9)				

I(1)−Nd(1)−I(2)	88.171(19)	I(1)−Nd(1)−I(2A)	91.829(19)
I(1)−Nd(1)−O(1)	86.75(17)	I(1)−Nd(1)−O(1A)	93.25(17)
I(2)−Nd(1)−O(1)	88.52(17)	I(2)−Nd(1)−O(1A)	91.48(17)
I(3)−Nd(2)−O(2)	90.73(15)	I(3)−Nd(2)−O(2B)	88.50(15)
I(3)−Nd(2)−O(3)	90.52(17)	I(3)−Nd(2)−O(3B)	89.78(17)
I(3)−Nd(2)−O(4)	90.481(18)	O(2)−Nd(2)−O(2B)	72.2(3)
O(2)−Nd(2)−O(3B)	72.1(2)	O(3)−Nd(2)−O(4)	71.77(16)
I(3)−Nd(2)−I(3B)	179.04(4)		

3

Gd(1)−I(1)	3.0264(5)	Gd(1)−I(2)	3.0435(4)	Gd(1)−O(1)	2.347(4)
Gd(2)−I(3)	2.9952(4)	Gd(2)−O(2)	2.416(4)	Gd(2)−O(3)	2.425(4)
Gd(2)−O(4)	2.421(6)				

I(1)−Gd(1)−I(2)	91.561(13)	I(1)−Gd(1)−I(2A)	88.439(13)
I(1)−Gd(1)−O(1)	88.89(12)	I(1)−Gd(1)−O(1A)	91.11(12)
I(2)−Gd(1)−O(1)	93.16(11)	I(2)−Gd(1)−O(1A)	86.84(11)
I(3)−Gd(2)−O(2)	90.65(10)	I(3)−Gd(2)−O(2B)	88.75(10)
I(3)−Gd(2)−O(3)	89.63(10)	I(3)−Gd(2)−O(3B)	90.60(10)
I(3)−Gd(2)−O(4)	90.372(12)	O(2)−Gd(2)−O(2B)	72.4(2)
O(2)−Gd(2)−O(3)	72.16(15)	O(3)−Gd(2)−O(4)	71.66(10)
I(3)−Gd(2)−I(3B)	179.26(2)		

4

Y(1)−I(1)	3.0181(6)	Y(1)−I(2)	2.9984(7)	Y(1)−O(1)	2.299(6)
Y(2)−I(3)	2.9685(6)	Y(2)−O(2)	2.387(5)	Y(2)−O(3)	2.391(5)
Y(2)−O(4)	2.395(7)				

I(1)−Y(1)−I(2)	91.359(18)	I(1)−Y(1)−I(2A)	88.641(18)
I(1)−Y(1)−O(1)	92.63(14)	I(1)−Y(1)−O(1A)	87.37(14)
I(2)−Y(1)−O(1)	88.83(15)	I(2)−Y(1)−O(1A)	91.17(15)
I(3)−Y(2)−O(2)	90.40(14)	I(3)−Y(2)−O(2B)	89.15(14)
I(3)−Y(2)−O(3)	89.61(15)	I(3)−Y(2)−O(3B)	90.56(15)
I(3)−Y(2)−O(4)	90.28(2)	O(2)−Y(2)−O(2B)	72.2(3)
O(2)−Y(2)−O(3)	72.00(19)	O(3)−Y(2)−O(4)	71.89(13)
I(3)−Y(2)−I(3B)	179.44(5)		

[a] The suffix A or B denotes an atom generated by an inversion center or 2-fold rotation axis, respectively.

Although only a selection of the triiodides $LnI_3(THF)_n$ have been crystallographically characterized, it appears that just two structural motifs are favored by these compounds, and that there is a sharp distinction between the structures of the triiodides of the earlier, larger rare earths La and Pr, which crystallize as discrete molecular species, and the rest of the series Nd−Tm and Y, which crystallize as solvent-separated ion pairs [according to Shannon, Y^{3+} and Ho^{3+} have essentially identical ionic radii].[32]

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. THF and light petroleum (bp 40−60 °C) were distilled under nitrogen from potassium or sodium/potassium alloy. THF was stored over activated 4 Å molecular sieves, and light petroleum was stored over a potassium film. Rare earth metal powders were purchased from the Aldrich Chemical Co. and, where necessary, were freed from mineral oil by washing with dry light petroleum.

Infrared spectra were recorded as Nujol mulls on a BioRad FTS3000 spectrometer. Iodide content was analyzed gravimetrically as AgI;[33] lanthanide content was analyzed by complexometric titration with the disodium salt of ethylenediaminetetraacetic acid using hexamethylenetetramine as buffer and xylenol orange as indicator.[34]

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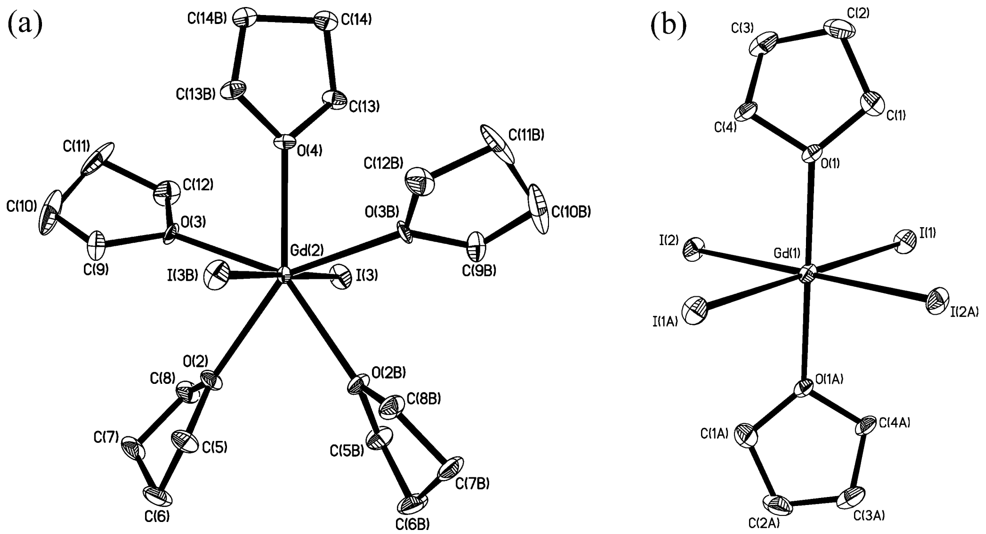

Figure 2. Structure of (a) the cation and (b) the anion of **3** with 50% probability ellipsoids and with H atoms omitted for clarity.

Table 3. Crystallographic Data for **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{16}H_{32}I_3O_4Pr$	$C_{28}H_{56}I_6Nd_2O_7$	$C_{28}H_{56}Gd_2I_6O_7$	$C_{28}H_{56}I_6O_7Y_2$
fw	810.0	1554.6	1580.6	1444.0
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$
a, Å	8.6820(4)	12.8595(10)	12.8046(9)	12.7749(14)
b, Å	17.3291(7)	12.1213(9)	12.1093(8)	12.0737(14)
c, Å	16.5834(7)	28.828(2)	28.717(2)	28.626(3)
β, deg	92.883(2)	98.392(2)	98.299(2)	98.204(2)
V, Å^3	2491.84(19)	4445.4(6)	4406.1(5)	4370.1(9)
Z	4	4	4	4
ρ_{calcd}, g cm^{-3}	2.159	2.323	2.383	2.195
μ, mm^{-1}	5.69	6.51	7.22	6.92
reflns collected	21557	16015	18924	18385
indep reflns (R_{int})	5995 (0.0264)	5275 (0.0351)	5319 (0.0467)	5240 (0.0761)
reflns with $F^2 > 2\sigma$	5277	4851	4001	3458
min, max transm	0.156, 0.463	0.081, 0.246	0.326, 0.869	0.288, 0.545
R, R_w [$F^2 > 2\sigma$]^a	0.0252, 0.0521	0.0616, 0.1550	0.0376, 0.0725	0.0505, 0.1156
R, R_w (all data)^a	0.0312, 0.0538	0.0673, 0.1577	0.0601, 0.0790	0.0969, 0.1351
largest diff. peak and hole, e Å^{-3}	1.05, −1.12	2.21, −3.42	1.05, −2.06	2.18, −1.21

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data.

Since the preparations of the triiodides are essentially identical, only that of $LaI_3(THF)_4$ is given in detail.

$LaI_3(THF)_4$. Iodine (7.97 g, 31.42 mmol) was added to a slurry of lanthanum powder (2.91 g, 20.95 mmol) in THF (30 mL) with stirring in an ice bath (0 °C). After complete addition, the mixture was allowed to warm to room temperature and was stirred for 3 days until consumption of the metal powder was complete. Light petroleum (80 mL) was added to the reaction mixture in order to precipitate dissolved lanthanum iodide and the mother liquor was decanted, leaving a light brown powder which was washed with light petroleum (2 × 30 mL). The crude solid was heated under vacuum (140 °C, 10^{-2} mmHg) for 3 h to remove residual iodine, affording an off-white powder. Soxhlet extraction of this solid with THF (150 mL) afforded $LaI_3(THF)_4$ as a colorless crystalline solid. Yield: 14.95 g, 88.3%. Found: I, 46.67; La, 17.05%. $C_{16}H_{32}O_4I_3$-La requires: I, 47.11; La, 17.19%. IR: ν (cm^{-1}) 1348 m, 1297 w, 1249 w, 1176 m, 1077 m, 1037 w, 1009 w, 976 w, 924 w, 858 m, 844 m, 796 w, 587 w, and 556 w.

$PrI_3(THF)_4$ (1). Iodine (8.94 g, 35.22 mmol) and praeseodymium turnings (3.31 g, 23.49 mmol) gave **1** as a pale green-yellow microcrystalline solid. Yield: 15.03 g, 79.2%. Found: I, 46.85; Pr, 17.22%. $C_{16}H_{32}O_4I_3Pr$ requires: I, 47.00; Pr, 17.40%. IR: ν (cm^{-1}) 1353 m, 1287 w, 1238 w, 1173 m, 1077 m, 1057 w, 1006 w, 982 w, 958 w, 853 m, 849 m, 785 w, 572 w and 532 w.

$NdI_3(THF)_{3.5}$ (2). Iodine (5.15 g, 20.29 mmol) and neodymium powder (1.95 g, 13.52 mmol) gave **2** as a pale blue microcrystalline solid. Yield: 8.65 g, 82.3%. Found: I, 48.24; Nd, 18.62%. $C_{14}H_{28}O_{3.5}I_3Nd$ requires: I, 48.98; Nd, 18.56%. IR: ν (cm^{-1}) 1354 m, 1315 w, 1260 w, 1238 w, 1176 m, 1076 m, 1067 m, 1004 s, 973 w, 922 m, 906 w, 851 s, 849 s, 796 w, 630 w, 598 w, and 538 w.

$SmI_3(THF)_{3.5}$. Iodine (7.72 g, 30.42 mmol) and samarium powder (3.05 g, 20.28 mmol) gave $SmI_3(THF)_{3.5}$ as a yellow microcrystalline solid. Yield: 12.43 g, 78.2%. Found: I, 47.96; Sm, 19.11%. $C_{14}H_{28}O_{3.5}I_3Sm$ requires: I, 48.59; Sm, 19.19%. IR: ν (cm^{-1}) 1356 m, 1314 w, 1256 w, 1232 w, 1173 m, 1077 m, 1038 m, 1003 s, 974 w, 922 m, 850 s, 849 s, 793 w, 669 w, 597 w, and 538 w.

$GdI_3(THF)_{3.5}$ (3). Iodine (8.71 g, 34.32 mmol) and gadolinium turnings (3.60 g, 22.89 mmol) gave **3** as an off-white microcrystalline solid. Yield: 16.03 g, 88.6%. Found: I, 47.21; Gd, 19.95%. $C_{14}H_{28}O_{3.5}I_3Gd$ requires: I, 48.17; Gd, 19.90%. IR: ν (cm^{-1}) 1354 m, 1312 w, 1254 w, 1229 w, 1174 m, 1077 m, 1040 m, 1006 s, 975 w, 923 m, 850 s, 849 s, 793 w, 663 w, 594 w, and 549 w.

$DyI_3(THF)_{3.5}$. Iodine (9.69 g, 38.18 mmol) and dysprosium powder (4.14 g, 25.48 mmol) gave $DyI_3(THF)_{3.5}$ as an off-white microcrystalline solid. Yield: 16.99 g, 83.8%. Found: I, 47.47; Dy, 20.50%. $C_{14}H_{28}O_{3.5}I_3Dy$ requires: I, 47.85; Dy, 20.43%. IR: ν (cm^{-1}) 1351 m, 1312 w, 1268 w, 1238 w, 1174 m, 1077 m, 1043 m, 1006 s, 973 w, 955 w, 927 w, 911 w, 852 m, 796 w, 635 w, 593 w, and 546 w.

$ErI_3(THF)_{3.5}$. Iodine (4.71 g, 18.57 mmol) and erbium powder (2.07 g, 12.38 mmol) gave $ErI_3(THF)_{3.5}$ as an off-white microcrystalline solid. Yield: 8.79 g, 88.7%. Found: I, 47.27; Er, 20.90%. $C_{14}H_{28}O_{3.5}I_3Er$ requires: I, 47.57; Er, 20.90%. IR: ν (cm^{-1}) 1355 m, 1310 w, 1242 w, 1232 w, 1173 m, 1078 m, 1055 m, 1010 s, 976 w, 961 w, 938 w, 914 w, 866 m, 784 w, 625 w, 595 w, and 549 w.

$TmI_3(THF)_{3.5}$. Iodine (2.25 g, 8.89 mmol) and thulium powder (1.00 g, 5.92 mmol) gave $TmI_3(THF)_{3.5}$ as an off-white microcrystalline solid. Yield: 3.99 g, 83.9%. Found: I, 46.94; Tm, 20.87%. $C_{14}H_{28}O_{3.5}I_3Tm$ requires: I, 47.47; Tm, 21.06%. IR: ν (cm^{-1}) 1356 m, 1317 w, 1259 w, 1235 w, 1176 m, 1077 m, 1040 m, 998 s, 975 w, 920 m, 835 s, 793 sh, 678 w, 589 w, and 532 w.

$YI_3(THF)_{3.5}$ (4). Iodine (5.78 g, 22.77 mmol) and yttrium powder (1.35 g, 15.18 mmol) gave **4** as an off-white microcrystalline solid. Yield: 8.65 g, 78.9%. Found: I, 52.35; Y, 12.38%. $C_{14}H_{28}O_{3.5}I_3Y$ requires: I, 52.73; Y, 12.31%. IR: ν (cm^{-1}) 1359 m, 1314 w, 1264 w, 1175 m, 1077 m, 1038 m, 1002 s, 975 w, 915 m, 850 s, 788 sh, 668 m, 597 w, and 539 w.

Crystal Structure Determinations of 1−4. For **1**−**4**, measurements were made at 150 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and narrow (0.3° in ω) frame exposures. For all compounds, cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods or Patterson synthesis and were refined on F^2 values for all unique data. Table 3 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; U(H) was set at 1.2 times U_{eq} for the parent atom. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.[35]

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Supporting Information Available: For **1**, **2**, **3**, and **4** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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(35) (a) *SMART and SAINT software for CCD diffractometers*; Bruker AXS Inc.: Madison, WI, 1997. (b) Sheldrick, G. M. *SHELXTL user manual*, version 6; Bruker AXS Inc.: Madison, WI, 2001.