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Auto-ionization in Lutetium Iodide Complexes: Effect of the Ionic Radius on Lanthanide–Iodide Binding

Garth R. Giesbrecht,[1a] John C. Gordon,*,[1b] David L. Clark,[1c] and Brian L. Scott[1b]

Nuclear Materials Technology Division, Chemistry Division, and the Glenn T. Seaborg Institute for Transactinium Science, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Reaction of lutetium metal with 1.5 equiv of elemental iodine in 2-propanol leads to the isolation of $LuI_3(HO^iPr)_4$ (**1**). An X-ray crystal structure reveals an ionic structure with well-separated $[LuI_2(HO^iPr)_4]$ cations and [I] anions. Dissolution of **1** in pyridine generates the unusual alkoxide species $[LuI(O^iPr)(py)_5][I]$ (**2**) with the elimination of HI. An X-ray crystal structure of **2** confirmed the ionic nature of the compound, with the cationic portion of the complex exhibiting a seven-coordinated lutetium center with trans-disposed iodo and alkoxide ligands and five pyridine molecules equally displaced within the equatorial plane. Exposure of **2** to iodotrimethylsilane yields the expected triiodide species $[LuI_2(py)_5][I]$ (**3**), which may also be prepared by refluxing commercially available LuI_3 in THF, followed by crystallization from a THF/pyridine mixture. The solid-state structure of **3** is similar to that of **2**, with the alkoxide ligand having been replaced by an iodide. The formation of ionic structures **1**–**3** as opposed to the higher-coordinated neutral species may be traced to the small lutetium center and the presence of relatively strong Lewis bases within the coordination sphere of the metal.

Introduction

The synthesis of organometallic complexes of the lanthanides is often dependent on the availability of discrete, monomeric lanthanide trihalides as starting materials.[2] Although anhydrous lanthanide trichlorides, $(LnCl_3)_x$, have been accessible for many years,[3] their utility as synthons in organolanthanide chemistry is limited because of their polymeric nature and generally low solubility in common organic solvents. Although the solvated analogues are somewhat better behaved, the use of adducts such as $LnCl_3(THF)_x$ with lithium or sodium cyclopentadienide often leads to the incorporation of LiCl or NaCl in the coordination sphere of the resultant metal complex.[4−12] Additionally, control of the exact stoichiometry of the reaction product is often difficult because of the propensity of cyclopentadienyl lanthanide complexes to undergo redistribution chemistry.[11,13,14] In contrast, the solvated iodides, LnI_3L_x (L = Lewis base), are much more amenable to metathesis chemistry, allowing for the sequential addition of organic fragments of interest and the elimination of insoluble MI (M = Li, Na, K).[15−17] Early preparations of lanthanide iodides, such as drying of commercially available $LnI_3(H_2O)_9$, met with limited success, instead forming polymeric $(LnOI)_n$;[3] sub-

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* Author to whom correspondence should be addressed. Current address: U.S. Department of Energy, Office of Basic Energy Sciences, Catalysis and Chemical Transformations Program, SC-14, Germantown, 1000 Independence Avenue, SW, Washington, DC 20585-1290. E-mail: John.Gordon@science.doe.gov. Fax: 301-903-0271. Tel: 301-903-2153.

(1) (a) NMT-DO, Mail Stop J514. (b) C-SIC, Mail Stop J514. (c) G. T. Seaborg Institute for Transactinium Science, Mail Stop E500.

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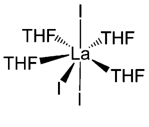
sequent syntheses employed the reaction of elemental metals with diiodo- or iodoethane in THF to form mixtures of $LnI_2(THF)_2$, $LnI_3(THF)_4$, and various metal alkyls, depending on the metal used and the reaction conditions.[18,19] More recently, we and others have reported the facile syntheses of $LnI_3(HO^iPr)_4$ (Ln = La,[20] Ce,[20] Nd[17,20]) by the reaction of lanthanide metal turnings with elemental iodine in 2-propanol; simple recrystallization of this material from THF produces THF- and toluene-soluble $LnI_3(THF)_4$. Alternatively, it has been revealed that the reaction of samarium diiodide with oxygen in THF leads to a triiodo species.[21] The type of complex formed depends on the size of the lanthanide being used; X-ray crystallography reveals three distinct structural types, with the larger lanthanum center forming the seven-coordinated $LaI_3(THF)_4$ (**I**),[22] while smaller lanthanide metals auto-ionize to form the ionic complexes $[LnI_2(THF)_5][LnI_4(THF)_2]$ (Ln = Sm,[21] Yb[23]) (**II**). Additionally, a related structure with an I_3 counterion has been reported (**III**).[24] Here, we detail our attempts to synthesize the analogous lutetium complexes, and the formation of some unusual ionic complexes of lutetium.



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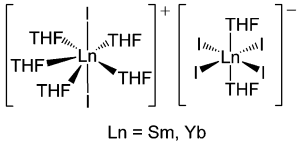

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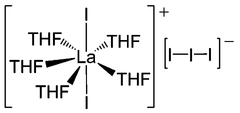

III

Results and Discussion

Lutetium turnings react with 1.5 equiv of iodine in 2-propanol at 0 °C to yield the tetrakis-2-propanol adduct of lutetium triiodide as a slightly yellow solid in moderate yield (eq 1). The presence of the coordinated 2-propanol

$$Lu + 1.5I_2 \xrightarrow[0\,°C]{HO^iPr} \underset{\mathbf{1}}{[LuI_2(HO^iPr)_4][I]} \qquad (1)$$

ligands is confirmed by strong absorptions in the infrared spectrum at ~3320 and 3180 cm^{-1} [17,20] and the observation of a broad −OH resonance at 4.97 ppm in the ^1H NMR spectrum. As found for the lanthanum, cerium, and neodymium derivatives, the metal turnings do not have to be vigorously cleaned prior to the reaction. This contrasts with the behavior of the uranium metal, where the turnings must be carefully cleaned in order to maximize the yield of the reaction.[15,25] The overall yield of the reaction is lower than that observed for the La, Ce, and Nd analogues. Although this may be a size effect, in reality the smaller lutetium complex is likely more soluble in 2-propanol than the La, Ce, and Nd derivatives, contributing to mechanical loss and difficulty of isolation.

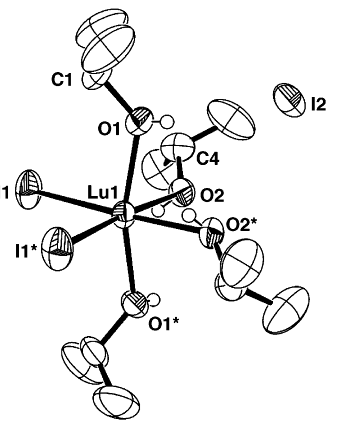

Figure 1. Thermal ellipsoid view of **1** drawn with 30% probability ellipsoids. Only the alcoholic protons of the 2-propanol groups are shown for clarity.

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

Lu1−I1	2.8947(10)	Lu1−I1*	2.8947(10)
Lu1−I2	4.746(2)	Lu1−O1	2.238(5)
Lu1−O1*	2.238(5)	Lu1−O2	2.271(4)
Lu1−O2*	2.271(4)		
I1−Lu1−I1*	97.38(4)	I1−Lu1−O1	94.10(12)
I1−Lu1−O1*	96.78(11)	I1−Lu1−O2	91.42(12)
I1−Lu1−O2*	171.18(12)	I1*−Lu1−O1	96.78(11)
I1*−Lu1−O1*	94.10(12)	I1*−Lu1−O2	171.18(12)
I1*−Lu1−O2*	91.42(12)	O1−Lu1−O1*	163.5(2)
O1−Lu1−O2	81.83(17)	O1−Lu1−O2*	85.52(17)
O1*−Lu1−O2	85.52(17)	O1*−Lu1−O2*	81.83(17)
O2−Lu1−O2*	79.8(2)	Lu1−O1−C1	130.1(5)
Lu1−O2−C4	129.5(4)		

Single crystals of $LuI_3(HO^iPr)_4$ (**1**) were grown by the evaporation of a concentrated toluene solution. The molecular structure of compound **1** is presented in Figure 1. A list of relevant bond lengths and angles is available in Table 1. The complete details of the structural analyses of compounds **1**−**3** are listed in Table 3. In contrast to $LaI_3(HO^iPr)_4$ and $CeI_3(HO^iPr)_4$, which crystallize as neutral coordination compounds,[20] the smaller ionic radius of lutetium in compound **1** results in an ionic complex in which the metal center is coordinated in an octahedral fashion by two cis iodide atoms and four 2-propanol ligands. The charge is then balanced by a single negative iodide atom, which resides at a distance from the lutetium atom that is too far to be considered a bonding interaction (Lu1−I2 = 4.75 Å). The molecule lies on a mirror plane; thus, the two lutetium−iodide distances are equal at 2.8947(10) Å. This distance compares favorably with those determined in (η^5-$C_5H_3(SiMe_3)_2$-1,3)$_2$LuI(THF) (2.896(1) Å) and (η^5-$C_5H_3(SiMe_3)_2$-1,3)(η^5-$C_5H_4(SiMe_3)$)LuI(THF) (2.914(2) Å), the only other struc-

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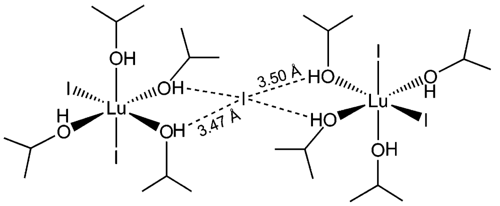
turally characterized compounds containing Lu−I bonds.[26] The protons residing on the oxygen atoms were located and refined, unequivocally establishing these groups as neutral 2-propanol adducts as opposed to isopropoxide groups. The Lu−O distances (2.238(5) and 2.271(4) Å) are slightly shorter than those found in the neutral coordination compounds of $LaI_3(HO^iPr)_4$ and $CeI_3(HO^iPr)_4$,[20] as expected for the higher coordination number in these complexes and the larger size of the metal centers (La−O = 2.492(7)−2.525(6) Å; Ce−O = 2.479(5)−2.495(5) Å). The Lu−O−C bond angles of 130.1(5) and 129.5(4)° are also consistent with 2-propanol as opposed to the isopropoxide groups. Overall, the octahedral coordination geometry about the lutetium atom is slightly distorted; this is due to the steric bulk of the two cis-disposed iodide ligands (I1−Lu1−I1* = 97.38(4)°), which causes the 2-propanol groups to form angles that are smaller than expected. It also appears that weak intermolecular forces hold the complex together in an extended array. The iodide anion (I2) is loosely bound to four 2-propanol hydrogen atoms from two separate $[LuI_2(HO^iPr)_4]^+$ units at a distance of ~3.50 Å.



Dissolution of **1** in pyridine generates the unexpected mixed iodo−alkoxide species, $[LuI(O^iPr)(py)_5][I]$ (**2**), as a yellow solid in good yield (eq 2). This reaction likely

$$[LuI_2(HO^iPr)_4][I] \xrightarrow[-3HO^iPr \atop -HI]{py} \underset{\mathbf{2}}{[LuI(O^iPr)(py)_5][I]} \qquad (2)$$

involves the elimination of HI, which has been observed in the alcoholysis of a number of transition-metal halides.[27,28] It has also been suggested that the synthesis of $UI_2(O^iPr)_2(HO^iPr)_2$ from uranium metal, iodine, and 2-propanol involves the production of an intermediate such as $UI_4(HO^iPr)_x$, which then eliminates HI to form the final uranium iodo−alkoxide product.[25] The coordinated pyridine ligands are somewhat labile upon exposure to vacuum; elemental analysis is consistent with approximately four molecules of pyridine per lutetium. The ^1H NMR spectrum of **2** reveals the presence of a single isopropoxide ligand; additionally, the broad −OH resonance found for compound **1** was not observed. The −OH stretch is also absent in the infrared spectrum of **2**, further suggesting that one of the 2-propanol ligands in **1** has been converted to an isopropoxide group in **2**.

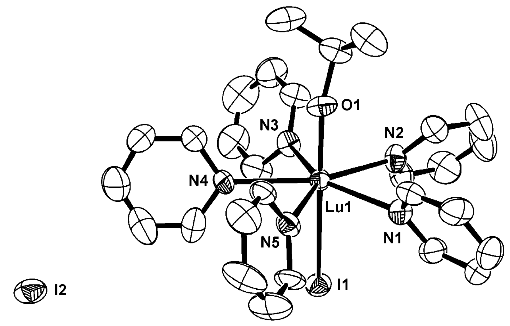


Figure 2. Thermal ellipsoid view of **2** drawn with 30% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

Lu1−I1	3.0738(13)	Lu1−I2	6.400(4)
Lu1−O1	2.001(5)	Lu1−N1	2.464(8)
Lu1−N2	2.480(7)	Lu1−N3	2.443(6)
Lu1−N4	2.509(6)	Lu1−N5	2.468(7)
O1−Lu1−I1	176.82(14)	O1−Lu1−N1	89.4(3)
O1−Lu1−N2	89.6(3)	O1−Lu1−N3	91.9(3)
O1−Lu1−N4	93.4(2)	O1−Lu1−N5	93.9(3)
I1−Lu1−N1	88.18(19)	I1−Lu1−N2	87.8(2)
I1−Lu1−N3	88.87(18)	I1−Lu1−N4	89.80(15)
I1−Lu1−N5	87.35(18)	N1−Lu1−N2	73.4(2)
N1−Lu1−N3	145.7(2)	N1−Lu1−N4	143.9(2)
N1−Lu1−N5	72.6(2)	N2−Lu1−N3	72.3(2)
N2−Lu1−N4	142.6(2)	N2−Lu1−N5	145.8(2)
N3−Lu1−N4	70.3(2)	N3−Lu1−N5	141.3(2)
N4−Lu1−N5	71.2(2)		

Crystals of **2** were obtained by cooling a pyridine/THF mixture to −30 °C. The molecular structure of compound **2** is available in Figure 2 with relevant bond lengths and angles presented in Table 2. Compound **2** exhibits an ionic structure similar to that of **1** with a $[LuI(O^iPr)(py)_5]$ cation and a naked iodine anion. The geometry of the seven-coordinated cation is best described as pentagonal bipyramidal, with the alkoxide and iodide groups occupying the axial sites (O1−Lu1−I1 = 176.82(14)°). The equatorial sites are taken up by the five pyridine ligands with an average N−Lu−N angle between adjacent pyridine molecules of 72.0°. The Lu1−I1 distance of 3.0738(13) Å is slightly longer than that reported for compound **1**, which may be a result of the more crowded coordination sphere in **2**. The outer sphere iodide ligand is located 6.40 Å from the lutetium center, which is significantly farther away than that observed in the 2-propanol adduct. The Lu1−O1 bond length is consistent with an isopropoxide ligand as opposed to a coordinated 2-propanol group (2.001(5) Å) and thus is shorter than the Lu−O distances reported for **1**. This bond length compares favorably with the terminal cerium−isopropoxide bond lengths determined for $[Ce_2(O^iPr)_8(HO^iPr)_2]$ (2.037(9) and 2.046(9) Å)[29] as well as those found in the pentanuclear oxoalkoxide cluster $[Yb_5(\mu_5\text{-}O)(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4(O^iPr)_5]$ (1.981(29)−2.026(29) Å).[30] It is interesting to note that the lutetium center in **2** is seven coordinated, although still maintaining an ionic structure. In contrast, even though heptacoordination is obviously feasible for lutetium complexes, the 2-propanol adduct **1** prefers to only bind to two of the three iodide ligands while remaining six coordinated. This difference in

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Table 3. Crystallographic Data[a]

compound	**1**	**2**	**3**
formula	$C_{12}H_{32}I_3LuO_4$	$C_{28}H_{32}I_2LuN_5O$	$C_{25}H_{25}I_3LuN_5$
molecular weight	796.05	883.36	951.17
temperature (K)	203(2)	203(2)	203(2)
crystal system	tetragonal	orthorhombic	monoclinic
space group	$I\bar{4}2d$	$P2_12_12_1$	$P2_1/c$
crystal size (mm)	0.36 × 0.28 × 0.18	0.36 × 0.08 × 0.08	0.24 × 0.20 × 0.18
a (Å)	12.565(4)	16.993(9)	26.185(15)
b (Å)	12.565(4)	13.044(7)	15.912(10)
c (Å)	32.192(15)	14.664(11)	16.144(9)
β (deg)	90	90	106.192(11)
V (Å^3)	5082(3)	3251(3)	6460(7)
Z	8	4	8
D_{calcd} (g/mL)	2.081	1.805	1.956
absorption coefficient (mm^{-1})	7.536	4.963	5.944
F(000)	2928	1680	3520
θ range (deg)	1.74−23.29	1.83−25.37	1.51−22.46
total reflections	12 445	20 572	30 154
independent reflections	1839	5600	8058
GOF	1.567	1.876	7.534
R1	0.0251	0.0373	0.2192
wR2	0.0570	0.0901	0.4475

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2]$, where a = 0.0283, 0.0347, and 0.0338.

binding may be traced to the relative donor strengths of pyridine versus 2-propanol.

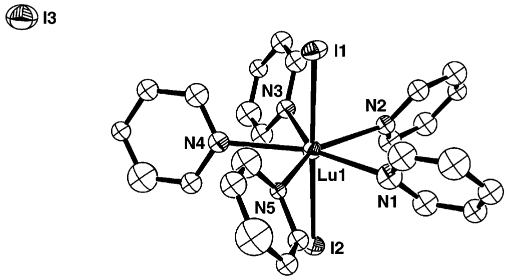

Figure 3. Thermal ellipsoid view of **3** drawn with 30% probability ellipsoids.

Reaction of **2** with iodotrimethylsilane results in the replacement of the isopropoxide group with an iodide with the elimination of isopropyltrimethylsilyl ether (eq 3). The

$$[\mathrm{LuI(O^iPr)(py)_5}][\mathrm{I}] + \mathrm{(TMS)I} \xrightarrow[-\mathrm{(TMS)O^iPr}]{\mathrm{py}} \underset{\mathbf{3}}{[\mathrm{LuI_2(py)_5}][\mathrm{I}]} \quad (3)$$

triiodide **3** is isolated as a light yellow solid in good yield. The ^{1}H NMR spectrum of **3** reveals resonances for free pyridine only; no peaks arising from an isopropoxide group were visible. The elemental analysis of **3** was consistent with approximately 3.4 molecules of pyridine per LuI_3 unit, which suggests some degree of solvent loss (see later). Alternatively, compound **3** may be prepared starting with commercially available LuI_3. Heating gray, insoluble LuI_3 to reflux in THF overnight yields a white insoluble material, which we suppose to be $LuI_3(THF)_x$. This material is insoluble in aromatic solvents such as toluene and benzene, as well as THF, although it is readily soluble in pyridine. Dissolution in pyridine displaces the THF ligands to form the pyridine adduct **3** as a yellow solid (eq 4).

$$\mathrm{LuI_3} \xrightarrow[\text{(2) py/THF}]{\text{(1) THF, }\Delta} \underset{\mathbf{3}}{[\mathrm{LuI_2(py)_5}][\mathrm{I}]} \quad (4)$$

Crystals of $[LuI_2(py)_5][I]$ (**3**) that were suitable for X-ray diffraction were obtained by slow evaporation of a saturated THF/pyridine mixture. The molecular structure of compound **3** is shown in Figure 3. Because of the twinning and disorder within the crystal chosen, a high-resolution structure was not obtained. Although this precludes a detailed discussion of bond lengths and angles within the compound, the structure was of high enough quality to clearly establish the identity of the complex as the ionic triiodide complex $[LuI_2(py)_5][I]$. The structure of **3** is similar to that of **2** with the exception that the isopropoxide group in **2** has been replaced by an iodide atom. The two iodides occupy the axial sites within the lutetium coordination sphere, with five-coordinated pyridine molecules in the equatorial plane. As for compounds **1** and **2**, a single iodide atom resides at a significant distance from the lutetium center. The cationic portion of the complex exhibits a structure similar to that observed for the related samarium and ytterbium complexes $[LnI_2(THF)_5][LnI_4(THF)_2]$ (Ln = Sm,[21] Yb[23]) and the lanthanum species $[LaI_2(THF)_5][I_3]$,[24] in which the linear LnI_2 units of the positively charged component of the compounds are equatorially coordinated by five THF molecules. However, in the case of these larger lanthanides, the charge is balanced by a $[LnI_4(THF)_2]$ or $[I_3]$ anion, instead of the single iodide atom observed here. A comparison with the octahedral species $[LnI_2(HMPA)_4][I]$ (Ln = Tm,[31] Sm;[32] HMPA = hexamethylphosphoramide) and $[SmI_2(OPMePh_2)_4][I]$[33] is also worth noting; in these cases, the lanthanide metal is at the center of an octahedron, although the anion in all of the three complexes is a single iodide atom. Although the

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coordination of the third I^- ion to the Ln(III) cation to yield the seven-coordinated complexes would not have been unreasonable, the formation of ionic structures instead can be traced to steric crowding around the Ln(III) centers.

Conclusions

As reported earlier for the larger lanthanides, direct oxidation of lutetium with iodine in 2-propanol provides a convenient route to a tetrakis-2-propanol adduct of lutetium triiodide. Although the cerium and lanthanum analogues crystallize as neutral coordination compounds, the smaller size of lutetium results in an ionic complex with a $[LuI_2(HO^iPr)_4]$ cation stabilized by an iodide anion. Although the coordination of a neutral 2-propanol molecule instead of an anionic halide group may be counterintuitive, it is also evidence of the "soft" nature of the iodide atom and the ease with which the iodo group can be removed. The labile property of the Ln−I bond is well documented[26] and has been exploited to generate organolanthanide cations via the reaction of the organolanthanide iodide complexes with silver tetraphenylborate[34] or silver hexabromocarborane;[35] analogous reactions with chloride derivatives are more problematic.[36] Less surprising is the reaction of LuI_3 with pyridine to form the ionic pyridine solvate $[LuI_2(py)_5][I]$, for which similar THF adducts are known. In the related $[LnI_2(THF)_5][LnI_4(THF)_2]$ species,[21,23] the counterion consists of the six-coordinated anionic metal centers. The difference in structure between these compounds and the lutetium iodides reported here is likely the result of the smaller, more electropositive lutetium center and the higher degree of steric crowding in these derivatives.

Experimental Section

General Considerations. All of the manipulations were carried out under an inert atmosphere of oxygen-free ultra-high-purity-grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox. Lutetium metal was purchased from Strem and used as received. Iodine, iodotrimethylsilane, and LuI_3 were purchased from Aldrich and used as received. 2-Propanol was purchased from Aldrich and distilled over sodium prior to use. Pyridine was purchased from Aldrich and distilled over sodium benzophenone prior to use. Toluene and tetrahydrofuran were deoxygenated by passage through a column of supported copper redox catalyst (Cu-0226 S) and dried by passing through a second column of activated alumina.[37] Toluene-d_8 and pyridine-d_5 were distilled over sodium benzophenone and degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AMX 300 spectrometer at ambient temperature unless otherwise noted. ^1H NMR chemical shifts are given relative to residual C_7D_7H ($\delta = 2.09$ ppm) or C_5D_4HN ($\delta = 8.74$ ppm). ^{13}C NMR chemical shifts are given relative to C_7D_8 ($\delta = 20.4$ ppm) or C_5D_5N ($\delta = 150.35$ ppm). Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as Nujol mulls between KBr plates. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley, Berkeley, CA.

$[LuI_2(HO^iPr)_4][I]$ (1). Lutetium turnings (1.00 g, 5.71 mmol) were placed in a large Schlenk tube along with 100 mL of dry 2-propanol and a stir bar. Elemental iodine (2.17 g, 8.57 mmol) was added to the flask under an argon purge, while the temperature of the reaction mixture was kept at 0 °C with an ice-water bath. The brown slurry was stirred overnight or until all of the metal turnings were consumed. The flask was then taken into the glovebox, and the reaction mixture was filtered through Celite to give a dark red/brown solution. The solvent was then removed under vacuum, and the oily residue was extracted with a small amount of toluene to give a dark brown solution. Slow evaporation yielded large colorless crystals of **1** (1.51 g, 34% yield). ^1H NMR (toluene-d_8) δ: 4.97 (br s, 1H, O*H*), 4.59 (sept, $^3J_{H-H} = 6.0$ Hz, 1H, C*H*Me$_2$), 1.23 (d, $^3J_{H-H} = 6.0$ Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8) δ: 32.03 (*C*HMe$_2$), 24.23 (CH*Me*$_2$). IR (Nujol, cm^{-1}): 3320 (br), 3180 (sh), 1290 (m), 1158 (w), 1275 (m), 1143 (m), 1086 (s), 922 (s), 910 (m), 808 (m), 792 (m), 777 (w), 724 (m). Anal. Calcd for $LuI_3(C_3H_8O)_{3.4}$: C, 16.12; H, 3.61. Found: C, 16.16; H, 3.76.

$[LuI(O^iPr)(py)_5][I]$ (2). 1 (500 mg, 0.630 mmol) was dissolved in 5 mL of pyridine, forming a pale yellow solution. An equal volume of THF was added, and the solution cooled to −30 °C, resulting in yellow needles of **2** (480 mg, 85% yield). ^1H NMR (pyridine-d_5) δ: 8.74 (s, 10H, *o*-py−H), 7.59 (s, 5H, *p*-py−H), 7.22 (s, 10H, *m*-py−H), 4.76 (sept, $^3J_{H-H} = 6.0$ Hz, 1H, C*H*Me$_2$), 1.49 (d, $^3J_{H-H} = 6.0$ Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ: 136.59, 124.60, 70.06 (*C*HMe$_2$), 26.31 (CH*Me*$_2$). One pyridine peak was obscured by the solvent resonance. IR (Nujol, cm^{-1}): 1630 (w), 1599 (m), 1525 (w), 1365 (sh), 1215 (w), 1168 (w), 1148 (m), 1063 (m), 1038 (m), 1006 (m), 758 (m), 744 (m), 704 (m), 676 (m), 626 (m). Anal. Calcd for $LuI_2(OCHMe_2)(C_5H_5N)_{3.9}$: C, 33.93; H, 3.35; N, 6.86. Found: C, 33.54; H, 3.45; N, 6.53.

$[LuI_2(py)_5][I]$ (3). Method A. 2 (500 mg, 0.566 mmol) was dissolved in 10 mL of pyridine, forming a pale yellow solution. Iodotrimethylsilane (115 mg, 0.566 mmol) was dissolved in 5 mL pyridine, forming a yellow solution and a white precipitate. The solid/solution was added to the pyridine solution of **2**, forming a yellow solution. This was then stirred at room temperature overnight. The solvent was removed under vacuum, yielding a waxy yellow solid. The solid was washed with small portions of hexanes and dried under vacuum to give **3** as a yellow solid (490 mg, 91% yield). **Method B.** LuI_3 (1.00 g, 1.80 mmol) was slurried in THF, and the mixture was heated to reflux overnight. The insoluble white solid was collected on a frit and then slurried again in a small amount of THF. Pyridine was added dropwise to the rapidly stirred solution until the solid dissolved, forming a yellow solution. Slow evaporation of the THF/pyridine mixture yielded **3** as small yellow plates (1.20 g, 72% yield). ^1H NMR (pyridine-d_5) δ: only resonances for free pyridine were observed. $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ: 150.74, 136.52, 124.52. IR (Nujol, cm^{-1}): 1366 (sh), 1344 (m), 1294 (w), 1246 (w), 1171 (m), 1040 (m), 992 (s), 950 (w), 914 (m), 830 (s), 722 (m), 669 (m). Anal. Calcd for $LuI_3(C_5H_5N)_{3.4}$: C, 24.76; H, 2.08; N, 5.78. Found: C, 24.76; H, 1.90; N, 5.56.

Crystallographic Studies. A crystal was mounted onto a glass fiber using a spot of silicone grease. Because of the air sensitivity, the crystal was mounted from a pool of mineral oil under argon gas flow. The crystal was placed on a Bruker P4/CCD diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The instrument was equipped with a sealed, graphite-monochromatized Mo Kα X-ray source ($\lambda = 0.71073$ Å). A

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hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using the SMART[38] software. Frame integration, including Lorentz polarization corrections, and final cell parameter calculations were carried out using the SAINT[39] software. The data were corrected for absorption using the SADABS[40] program. Decay of reflection intensity was monitored via analysis of the redundant frames. The structure was solved using direct methods and difference Fourier techniques. All of the hydrogen atom positions were idealized and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all of the nonhydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.[41] Additional details of data collection and structure refinement are listed in Table 3.

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Supporting Information Available: Crystallographic information files for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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