# **ORGANOMETALLICS**

# Ln(II)/Pb(II)—Ln(III)/Pb(0) Redox Approach toward Rare-Earth-Metal Half-Sandwich Complexes

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**Supporting Information** 

**ABSTRACT:** The divalent bis(trimethylsilyl)amide complexes  $Ln[N(SiMe_3)_2]_2(THF)_2$  (Ln = Sm, Yb) react with 0.5 equiv of lead(II) pentamethylcyclopentadienide,  $Cp^*_2Pb$  ( $Cp^*$ =  $C_5Me_5$ ), in *n*-hexane to form the half-sandwich complexes  $Cp^*Ln[N(SiMe_3)_2]_2$  (Ln = Sm, Yb) in almost quantitative yield. The same reaction performed with Eu[N-



 $(SiMe_3)_2]_2(THF)_2$  resulted in the cocrystallization of the sandwich complex  $Cp^*_2Eu[N(SiMe_3)_2]$  and homoleptic  $Eu[N(SiMe_3)_2]_3$ . The divalent bis(dimethylsily)amide complexes  $Ln\{[\mu-N(SiHMe_2)_2]_2Ln[N(SiHMe_2)_2]_2(THF)\}_2$  (Ln = Sm, Yb) react with 1.5 equiv of  $Cp^*_2Pb$  in *n*-hexane/THF to form the half-sandwich complexes  $Cp^*Ln[N(SiHMe_2)_2]_2(THF)$  (Ln = Sm, Yb). The corresponding europium reaction did not provide any crystalline material. Treatment of divalent  $Eu[N(SiMe_3)_2]_2(THF)_2$  with 2 equiv of 3-*tert*-butyl-5-methylpyrazole (Hp2<sup>tBu,Me</sup>) in THF generates  $[(pz^{tBu,Me})Eu(\mu-pz^{tBu,Me})(THF)_2]_2$ . Oxidation of the europium(II) pyrazolate complex with 1 equiv of  $Cp^*_2Pb$  in THF afforded  $Cp^*Eu(\mu-pz^{tBu,Me})_2(THF)_2$ . The tetramethylaluminate compounds  $\{Ln(AlMe_4)_2\}_n$  (Ln = Sm, Yb) react with 0.5 equiv of PbCp\*<sub>2</sub> in *n*-hexane to produce mixtures of half-sandwich and metallocene complexes  $Cp^*Ln(AlMe_4)_2$  and  $[Cp^*_2Ln(\mu-AlMe_4)]_2$ , respectively. The attempted oxidation of  $\{Eu(AlMe_4)_2\}_n$  led to the formation of  $\{Cp^*Eu(AlMe_4)\}_3\}_n$  with 2 equiv of HCp\* performed in THF led to the isolation of the unexpected mixed chloride methylidene complex  $[Cp^*_3Sm_3(\mu_2-Cl)_3(\mu_3-Cl)(\mu_3-CH_2)(THF)_3]$ . Reacting  $\{Yb(AlEt_4)_2\}_n$  with 0.5 equiv of  $Cp^*_2Pb$  in *n*-hexane gave a mixture of products, from which  $Cp^*_2Yb(AlEt_4)$  was identified. Performing the same reaction in toluene in the presence of diethyl ether resulted in the formation of the divalent metathesis product  $Cp^*Yb(AlEt_4)(Et_2O)_2$ .

# INTRODUCTION

Trivalent rare-earth-metal half-sandwich complexes have gained considerable attention as catalysts or precatalysts for polymerization reactions.<sup>1</sup> Especially, half-sandwich dialkyl complexes have emerged as highly efficient and selective initiators for diene and styrene homo- and copolymerization reactions.<sup>2,3</sup> Such derivatives  $Cp^{X}Ln^{III}R_{2}$  (R = amido, hydrido, alkyl) are usually generated via protonolysis or salt metathesis reac-tions.<sup>2,3</sup> For example, dineosilyl and dibenzyl complexes  $Cp^{x}Ln^{III}(CH_{2}SiMe_{3})_{2}(THF)$  and  $Cp^{x}Ln^{III}(CH_{2}Ar)_{2}(THF)$ are readily obtained from  $Ln(CH_2SiMe_3)_3(THF)/Ln-(CH_2Ar)_3(THF)$  and cyclopentadiene  $HCp^{X,4,5}$  Similarly, homoleptic tetramethylaluminate complexes Ln(AlMe<sub>4</sub>)<sub>3</sub> give access to  $Cp^{X}Ln(AlMe_{4})_{2}$  by reaction with either  $HCp^{X}$  or  $M(I)Cp^{X}$  (M = alkali metal).<sup>6,7</sup> Such Ln(AlMe<sub>4</sub>)<sub>3</sub>-based protonolysis and salt metathesis protocols, however, are either inconvenient or nonapplicable for Yb(III) and Eu(III), respectively, which readily form the divalent derivatives  $\{Ln(AlMe_4)_2\}_n$ <sup>8</sup> In the present study, we assessed the feasibility of half-sandwich complexes  $Cp^{X}Ln^{III}R_{2}$  (R = amido, alkyl) by oxidizing well-defined divalent complexes  $Ln^{II}R_2(donor)_x$ . The redox potentials of the most common Ln(II) derivatives had been determined as follows: Sm(III)/ Sm(II), -1.55 V; Eu(III)/Eu(II), -0.35 V; Yb(III)/Yb(II),

-1.15 V.9 The bis(trimethylsilyl)amide complexes Ln[N- $(SiMe_3)_2]_2(THF)_2$  (Ln = Sm, Eu, Yb)<sup>10</sup> are attractive candidates for redox reactions due to their straightforward (ate complex free!) and high-yield synthesis. Alternatively, the complexes  $Ln{[\mu-N(SiHMe_2)_2]_2Ln[N(SiHMe_2)_2](THF)}_2$ (Ln = Sm, Eu, Yb), which can easily be prepared by a transsilylamination using Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub> and 2 equiv of  $HN(SiHMe_2)_{21}^{11}$  bear the sterically less demanding and more flexible ligand  $N(SiHMe_2)_2^{-}$ , which proved to be superior in various exchange reactions.<sup>12</sup> Moreover, such divalent silylamide complexes are easily converted into tetraalkylaluminates of the type  $\{Ln(AlMe_4)_2\}_n$  and  $\{Ln(AlEt_4)_2\}_n$  by treatment with an excess of trialkylaluminum reagents.<sup>8</sup> While tetramethylaluminate half-sandwich complexes Cp<sup>X</sup>Ln(AlMe<sub>4</sub>)<sub>2</sub> have been studied in detail,<sup>13</sup> all attempts to isolate the tetraethylaluminum analogues  $Cp^{X}Ln(AlEt_{4})_{2}$  have failed, presumably due to the thermal instability of homoleptic  $Ln(AlEt_4)_3^{14}$  undergoing  $\beta$ -H abstraction and/or the increased steric demand of the ethyl groups.

When they are combined with potentially reducing agents, organometallic lead(II) compounds can act similarly to  ${\rm Tl}(I)$ 

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compounds as oxidation/ligand transfer reagents,<sup>15</sup> as indicated by their redox potentials: TI(I)/Ti(0) at -0.34 V vs Pb(II)/ Pb(0) at -0.13 V ( $PbSO_4/Pb^0$ ,  $SO_4^{2-}$  at -0.36 V).<sup>16</sup> In organo rare-earth-metal chemistry, this method was first studied by Evans et al., who accessed homoleptic Cp\*<sub>3</sub>Sm from Cp\*<sub>2</sub>Sm-(Et<sub>2</sub>O) and Cp\*<sub>2</sub>Pb (Cp\* =  $C_5Me_5$ ).<sup>17</sup> Recently, the Lappert group used a similar approach to generate the likewise sterically encumbered  $[C_5H_3(SiMe_3)_2-1,3]_3Yb$  from divalent  $[C_{5}H_{3}(SiMe_{3})_{2}-1,3]_{2}Yb$  and  $[C_{5}H_{3}(SiMe_{3})_{2}-1,3]_{2}Pb$ .<sup>18</sup> Both studies examined the preparation of homoleptic, sterically crowded Ln(III) compounds. Surprisingly, the organolead(II)based redox route was not employed for the synthesis of trivalent heteroleptic organolanthanide compounds. Herein, we present the synthesis and X-ray crystallographic study of a series of rare-earth-metal half-sandwich complexes via oxidation/ligand transfer (redox transmetalation) accomplished by Cp\*<sub>2</sub>Pb.

#### RESULTS AND DISCUSSION

**Reactions Involving Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub>.** Cp\*<sub>2</sub>Pb performed excellently in the oxidation of the divalent samarium and ytterbium silylamide complexes, giving virtually quantitative conversions into the desired products  $Cp*Ln[N(SiMe_3)_2]_2$ (Ln = Sm (1a), Yb (1b); Scheme 1). The reactions were performed in the absence of (UV) light to protect Cp\*<sub>2</sub>Pb from decomposition. Even though both reactions proceeded fairly quickly, surprisingly the Sm reaction seemed to require a certain induction period. The Yb reaction, on the other hand, started immediately, forming a black suspension upon addition of the first drop of Cp\*<sub>2</sub>Pb solution. Given the larger size and higher reducing potential of Sm(II), this is very surprising, since the reaction conditions were the same. In our hands, the crude products of complexes 1, which were obtained as orange (1a) or purple (1b) crystalline solids, were of high purity, meaning that purification before further derivatization was unnecessary. Upon recrystallization from saturated *n*-hexane or toluene solutions single-crystal X-ray diffraction studies revealed the formation of the target compound  $Cp*Ln[N(SiMe_3)_2]_2$  (1; Figure 1 and Figure S1 in the Supporting Information) along with metallocene complexes  $Cp*_2Ln[N(SiMe_3)_2]$  (2) and homoleptic  $Ln[N(SiMe_3)_2]_3$  as a result of ligand redistribution.



Figure 1. Solid-state structure of  $Cp*Sm[N(SiMe_3)_2]_2$  (1a). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): 1a, Sm-N1 2.315(1), Sm-N2 2.303(1), N1-Si1 1.709(2), N1-Si2 1.716(2), N2-Si3 1.707(2), N2-Si4 1.716(2), Sm-C(Cp\*) 2.702(2)-2.731(2), Sm-Si1 3.2078(5), Sm…Si2 3.7055(7), Sm…Si3 3.1810(5), Sm…Si4 3.6971(7), Sm-N1-Si1 104.71(7), Sm-N1-Si2 133.05(8), Sm-N2-Si3 103.99(7), Sm-N2-Si4 133.28(8), Si1-N1-Si2 121.74(8), Si3-N2-Si4 122.53(8), N1-Sm-N2 115.29(5); 1b, Yb-N1 2.206(5), Yb-N2 2.215(8), N1-Si1 1.712(5), N1-Si2 1.732(4), N2-Si3 1.719(8), N2-Si4 1.702(6), Yb-C(Cp\*) 2.594(17)-2.623(6), Yb...Si1 3.121(1), Yb...Si2 3.640(1), Yb...Si3 3.639(1), Yb...Si4 3.093(1), Yb-N1-Si1 104.9(2), Yb-N1-Si2 134.8(2), Yb-N2-Si3 135.0(3), Yb-N2-Si4 103.5(4), Si1-N1-Si2 119.6(3), Si3-N2-Si4 121.3(5), N1- Yb-N2 115.0(2).

In THF, on the other hand, such disproportionation reactions did not occur, allowing the isolation of **1** in moderate to high yields.

The Nd analogue,  $Cp*Nd[N(SiMe_3)_2]_2$ , not accessible via redox transmetalation, has been obtained in high yields via a salt-metathesis protocol.<sup>19</sup> The isolation of the crystallographically authenticated cerium complex  $Cp*Ce[N(SiMe_3)_2]_2$ was achieved by a metathesis route in low yield.<sup>20</sup> Recently, the Sc analogue was synthesized in good yield by a protonolytic reaction at high temperatures (100 °C) over 48 h.<sup>21</sup> Complexes 1 exhibit a distorted-trigonal coordination geometry with asymmetrically arranged amido ligands, as observed for the cerium and scandium derivatives. The Ln–N distances (2.3154(14) and 2.3029(14) Å in 1a; 2.206(5), 2.215(8) Å in 1b) are consistent with the changes in the ion radii of the lanthanide atoms (Sc, 2.086(5) Å; Ce, 2.357(7) and 2.349(7) Å).

The europium(II) complex  $Eu[N(SiMe_3)_2]_2(THF)_2$  revealed a reactivity distinct from that of the ytterbium and samarium congeners. Instead of the putative  $Cp*Eu[N(SiMe_3)_2]_2$ , we could only isolate the sandwich complex  $Cp*_2Eu[N(SiMe_3)_2]_2$ (2; Figure 2) along with homoleptic  $Eu[N(SiMe_3)_2]_3^{22}$ 



Figure 2. Solid-state structure of  $Cp^*_2Eu[N(SiMe_3)_2]$  (2). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Eu–N 2.293(2), N–Si1 1.700(3), N–Si2 1.699(3), Eu–C(Cp\*) 2.724(3)-2.769(3), Eu-Si1 3.410(1), Eu-Si2 3.3777(9), Eu-C1 3.278(4), Eu-C4 3.204(4); Eu–N–Si1 116.55(13), Eu–N–Si2 114.76(13), Si1–N–Si2 128.62(15).

Although the exact mechanism for the formation of 2 is unclear, we assume that either the target compound Cp\*Eu- $[N(SiMe_3)_2]_2$  was initially formed as an intermediate, which then disproportionates, or the initial reaction might simply involve ligand exchange between two molecules of Eu[N- $(SiMe_3)_2]_2(THF)_2$  and one molecule of  $Cp^*_2Pb_1$ , giving the putative "Cp\*Eu[N(SiMe<sub>3</sub>)<sub>2</sub>](THF)<sub>x</sub>" and Pb[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, followed by a disproportionation into Cp\*2Eu(THF)2 and precursor  $Eu[N(SiMe_3)_2]_2(THF)_2$  and in a final step the oxidation/ligand transfer reaction. The second hypothesis is substantiated by the fact that compound 1a (Sm and Eu being of similar size) does not undergo such a ligand redistribution under the same reaction conditions with THF as a solvent. The most striking difference between Sm(II) and Eu(II) is the significantly lower redox potential of Eu, which will cause a slower reduction of Pb(II) to Pb(0), thus allowing enough time to perform a ligand transfer beforehand. A structural motif similar to that for 2 was observed previously for the Y(III)  $(P2_1/c, \text{ measured at } 98 \text{ K})$ <sup>23</sup> Sm(III)  $(R\overline{3}, 183 \text{ K})$ <sup>24</sup> and La(III) congeners ( $P\overline{3}$ , 155 K),<sup>25</sup> all of which have been prepared by applying salt metathesis protocols. Evans and coworkers pointed out that even though both the smaller-sized Y(III) and the large La(III) centers showed secondary "agostic" interactions of the type  $Ln^{III}\cdots CH_3$   $(Ln-N(SiMe_3)_2)$ , the midsized Sm(III) would not.<sup>25</sup> This finding is confirmed by the X-ray structure analysis of compound 2 ( $\tilde{R}\bar{3}$ , 122 K), with Eu being only marginally smaller than Sm. The Eu-N bond length (2.293(2) Å), as well as the Eu…C1 (3.278(4) Å) and Eu…C4 (3.204(4) Å) distances are comparable to the metric paramaters of Cp\*<sub>2</sub>Sm[N(SiMe<sub>3</sub>)<sub>2</sub>] (2.301(3) Å, 3.286 and 3.216

Å, respectively).<sup>24</sup> This distinct amido coordination might be due to opposing trends of Lewis acidity and steric unsaturation.

Reactions Involving  $Ln{[\mu-N(SiHMe_2)_2]_2Ln[N-$ (SiHMe<sub>2</sub>)<sub>2</sub>](THF)}<sub>2</sub>. The bis(dimethylsilyl)amide complexes  $Ln{[\mu-N(SiHMe_2)_2]_2Ln[N(SiHMe_2)_2](THF)}_2$  (Ln = Sm, Yb) reacted with Cp\*<sub>2</sub>Pb to afford the half-sandwich complexes  $Cp*Ln[N(SiHMe_2)_2]_2(THF)$  (Ln = Sm (3a), Yb (3b)) in high vields (Scheme 1). In contrast to the derivatization reactions of  $Ln[N(SiMe_3)_2]_2(THF)_2$ , the addition of THF during the synthesis was crucial for complete conversion. Several crystallization steps were necessary to obtain pure, crystalline compounds 3. However, ligand redistribution of 3 was by far not as pronounced as in the case of complexes 1 and occurred only to a negligible extent upon long-term storage of *n*-hexane solutions. Single crystals of 3 formed from concentrated nhexane solutions. The respective europium reaction only produced a green oily residue, which did not form any crystalline material even after several months at -40 °C. Due to the paramagnetic nature of europium, the NMR spectroscopic characterization of the reaction outcome was inconclusive.

Such half-sandwich complexes of composition Cp\*Ln[N- $(SiHMe_2)_2]_2(THF)_x$  seem to be rather scarce and have only been reported for diamagnetic rare-earth-metals (Ln = Sc, Lu, x= 0; Ln = Y, x = 1).<sup>21,26,27</sup> In all cases protonolytic amine elimination was used as the synthesis strategy, employing  $Ln[N(SiHMe_2)_2]_3(THF)_x$  and pentamethylcyclopentadiene. The crystal structures of 3a,b show the same distortedtetrahedral coordination geometry as the Y analogue (Figure 3). The Ln-N (2.3368(9) and 2.3368(9) Å in 3a; 2.244(1) and 2.224(1) Å in 3b) and Ln-O bonds (2.4649(8) Å in 3a, 2.331(1) Å in **3b**) are in the expected ranges. The solid-state structures of 3a,b feature distinct secondary interactions. In compound 3b only one amido ligand is strongly tilted toward the central atom, comparable to the case for the yttrium derivative, with a close Yb...Si3 contact of 3.0640(4) Å and a relatively acute Yb-N2-Si3 angle of 102.03(5)°. In compound 3a, both amido ligands are tilted toward the larger Sm<sup>III</sup> center, as opposed to the Y<sup>III</sup> and Yb<sup>III</sup> complexes, with Sm…Si1 and Sm. Si3 distances of only 3.2732(4) and 3.1404(3) Å, respectively. The corresponding Sm-N1(2)-Si1(3) angles are as acute as 107.45(4) and 101.89(4)°. These additional agostic interactions are also indicated in the DRIFT spectrum of 3a, which revealed a Si–H stretching vibration at 2065  $\text{cm}^{-1}$ , featured by two lower energy shoulders at 2046 and 1948 cm<sup>-1</sup>. Reaction Involving [ $(pz^{tBu,Me})Eu(\mu-pz^{tBu,Me})$  (THF)<sub>2</sub>]<sub>2</sub> (4).

**Reaction Involving [(pz<sup>rbu,Me</sup>)Eu(\mu-pz<sup>rbu,Me</sup>) (THF)<sub>2</sub>]<sub>2</sub> (4). To probe a more general applicability of this redox protocol for Ln(II) complexes bearing non silylamido nitrogen based ligands, we envisaged pyrazolates.<sup>28</sup> For the rare-earth-metals, this ligand class has been intensively explored by the Deacon group<sup>29</sup> and found to engage in Ln(II) \rightarrow Ln(III) redox chemistry.<sup>15,29,30</sup> The synthesis of the divalent europium pyrazolate precursor [(pz<sup>rbu,Me</sup>)Eu(\mu-pz<sup>rbu,Me</sup>) (THF)<sub>2</sub>]<sub>2</sub> (4) is accomplished via a straightforward protonolysis reaction involving Eu[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub> and 2 equiv of proligand 3***tert***-butyl-5-methylpyrazole (Hpz<sup>rbu,Me</sup>) in THF (Scheme 1 and Figure S2 in the Supporting Information). Oxidation of 4 with 1 equiv of Cp\*<sub>2</sub>Pb in THF yielded the trivalent target compound Cp\*Eu(\mu-pz<sup>rbu,Me</sup>)<sub>2</sub>(THF)<sub>2</sub> (5) in 66% crystallized yield.** 

The successful redox protocol provided evidence that (a)  $Cp*_2Pb$  is capable of oxidizing Eu(II) to Eu(III), also meaning that the formation of compound 2 is not an exception, and (b) the synthesis strategy is not limited to silylamide complexes.



Figure 3. Solid-state structures of  $Cp*Sm[N(SiHMe_2)_2]_2(THF)$  (3a, top) and Cp\*Yb[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(THF) (3b, bottom). Hydrogen atoms, except those attached to silicon atoms, are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): 3a, Sm-N1 2.3368(9), Sm-N2 2.3206(9), Sm-O 2.4649(8), N1-Si1 1.696(1), N1-Si2 1.708(1), N2-Si3 1.6911(9), N2-Si4 1.7045(9), Sm-C(Cp\*) 2.710(1)-2.727(1), Sm…Si1 3.2732(4), Sm…Si2 3.6654(4), Sm…Si3 3.1404(3), Sm…Si4 3.6863(5), Sm-N1-Si1 107.45(4), Sm-N1-Si2 129.33(5), Sm-N2-Si3 101.89(4), Sm-N2-Si4 132.05(5), Si1-N1-Si2 123.21(5), Si3-N2-Si4 126.05(5), N1-Sm-N2 119.31(3), N1-Sm-O 102.43(3), N2-Sm-O 83.81(3); 3b, Yb-N1 2.244(1), Yb-N2 2.224(1), Yb-O 2.331(1), N1-Si1 1.710(1), N1-Si2 1.716(1), N2-Si3 1.695(1), N2-Si4 1.705(1), Yb-C(Cp\*) 2.609(1)-2.621(1), Yb...Si1 3.3671(4), Yb... Si2 3.5150(4), Yb...Si3 3.0640(4), Yb...Si4 3.6087(4), Yb-N1-Si1 116.16(6), Yb-N1-Si2 124.64(6), Yb-N2-Si3 102.03(5), Yb-N2-Si4 132.99(6), Si1-N1-Si2 119.16(7), Si3-N2-Si4 124.96(7), N1-Yb-N2 121.01(4), N1-Yb-O 95.05(4), N2-Yb-O 84.94(4).

Interestingly, compound **5** is the first example of a structurally characterized half-sandwich rare-earth-metal bis(pyrazolate) complex. For comparison, the isolation of  $Cp_2^*Yb(pz_2^{Ph})$  has been accomplished by the redox reaction of  $Cp_2^*Yb(pz_2^{Ph})$  and  $Tl(pz_2^{Ph})$ .<sup>15</sup> The Eu(III) metal center in complex **5** adopts a pseudo-trigonal-bipyramidal geometry (Figure 4). The  $Cp^*$  centroid and O2(THF) represent the vertices, while the  $\sigma$ - $\eta^2$  binding pyrazolate ligands together with O1(THF) span the triangular plane. The central atom is positioned about 0.6 Å above that plane toward the Cp\* ligand. The Ct(Cp\*)–Eu–O2 angle is 175.27° and is slightly bent in the direction of O1. The pyrazolato ligands are coordinated asymmetrically in the sense that one is pointing its methyl group toward the in-plane THF molecule, while the other is pointing its *tert*-butyl group.



**Figure 4.** Solid-state structure of  $Cp^*Eu(pz^{fBu,Me})_2(THF)_2$  (5). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Eu–N1 2.420(2), Eu–N2 2.366(2), Eu–N3 2.372(2), Eu–N4 2.494(2), Eu–O1 2.470(2), Eu– O2 2.5758(18), Eu–C(Cp\*) 2.702(2)–2.741(2); O1–Eu–O2 73.26(7), N1–Eu–O1 88.78(7), O1–Eu–N4 94.18(7), N1–Eu–N2 33.52(7), N3–Eu–N2 96.86(7).

This finding is consistent with the N1–Eu–O1 and N4–Eu–O1 angles of 88.78(7) and  $94.18(7)^\circ$ , respectively.

**Reactions Involving {Ln(AIR<sub>4</sub>)<sub>2</sub>}.** Aiming at half-sandwich complexes  $Cp*Ln(AlR_4)_2$  (Ln = Sm, Yb; R = Me, Et), one might choose the oxidation protocols leading to bis(amide) complexes 1 and 3 and then proceed with the well-established alkylation employing an excess of AlR<sub>3</sub>, concomitantly forming aluminum amide. The drawback of this approach is the need for multiple crystallizations of the target compounds, since the byproducts,  $\{R_2Al[\mu-N(SiMe_3)_2]\}_2$  and  $\{R_2Al[\mu-N (SiHMe_2)$ , are highly soluble, nonvolatile solids. Alternatively, the Ln(II)/Pb(II)-Ln(III)/Pb(0) redox approach might be a viable strategy. Synthesis protocols for polymeric, nhexane-insoluble  $\{Ln(A|Me_4)_2\}_n$  from which  $\{Me_2A|[\mu-N (SiMe_3)_2]_2$  can easily be extracted with *n*-hexane, and polymeric, soluble  $\{Ln(A|Et_4)_2\}_n$ , which could be separated from  $\{Et_2Al[\mu-N(SiMe_3)_2]\}_2$  and other byproducts by several recrystallization steps, are well established.<sup>12</sup> Unfortunately, the oxidation of divalent tetramethylaluminate complexes of samarium and ytterbium,  $\{Ln(AlMe_4)_2\}_n$  with  $Cp_2^*Pb$  gave product mixtures consisting of the desired half-sandwich complexes  $Cp*Ln(AlMe_4)_2$  (Ln = Sm (6a), Yb (6b)) and the metallocene species  $[Cp*_2Ln(\mu-AlMe_4)]_2$  (Ln = Sm (7a), Yb (7b); Scheme 2). Complexes 6 and 7 could be cleanly separated by crystallization using n-hexane (6) and extraction with toluene (7), since the dimeric complexes 7 are insoluble in *n*-hexane. The isolated yields for  $Cp*Ln(AlMe_4)_2$  are 32% (6a) and 46% (6b) and for  $[Cp*_{2}Ln(\mu-AlMe_{4})]_{2}$  are 35% (7a) and 21% (7b). Thus, both reactions gave yields of 67% (based on Ln atoms); the overall yield with respect to Cp\*, on the other hand, is quantitative for the Sm reaction and 88% for Yb. It is noteworthy that homoleptic  $Yb(AlMe_4)_3$ , which is another potential precursor for half-sandwich complex **6b**, is obtainable in low yield only and engages in extensive  $Yb(AlMe_4)_3$ - ${Yb(AlMe_4)_2}_n$  "self-reductions" at ambient temperature.<sup>8</sup>

Complexes **6** are isomorphous with diamagnetic Cp\*Ln- $(AlMe_4)_2$  (Lu,<sup>26</sup> La,<sup>6</sup> and Y;<sup>31</sup> space group *Pbca*; Figure 5 and Figure S3 in the Supporting Information). The interatomic distances of **6** are in the expected range. In particular, the close distance between the lanthanide center and one terminal methyl group of the bent AlMe<sub>4</sub> moiety appears to increase



Scheme 2. Derivatization of Tetraalkylaluminate Complexes with Cp\*2Pb and HCp\*



Figure 5. Solid-state structure of Cp\*Yb(AlMe<sub>4</sub>)<sub>2</sub> (6b). Hydrogen atoms are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): 6b, Yb-C1 2.6179(15), Yb-C2 2.599(2), Yb-C5 2.519(2), Yb-C6 2.516(2), Yb-C(Cp\*) 2.577(1)-2.610(1), Yb...All 2.9007(5), Yb...Al2 3.0683(5), Yb...C4 3.354(2), Yb-C1-Al1 75.54(5), Yb-C2-Al1 76.02(5), Yb-C5-Al2 83.16(5), Yb-C6-Al2 83.13(5), torsion angles Yb-C1-Al1-C4 -73.90(7), Yb-C2-Al1-C4 74.52(7), Yb-C5-Al2-C8 123.02(7), Yb-C6-Al2-C8-122.81(6); 6a, Sm-C1 2.725(2), Sm-C2 2.729(2), Sm-C5 2.614(2), Sm-C6 2.603(2), Sm-C(Cp\*) 2.670(2)-2.714(2), Sm…Al1 2.9275(5), Sm…Al2 3.1695(6), Sm… C4 3.113(2), Sm-C1-Al1 74.02(6), Sm-C2-Al1 73.96(6), Sm-C5-Al2 84.13(6), Sm-C6-Al2 84.42(6), torsion angles Sm-C1-Al1-C4 -65.44(7), Sm-C2-Al1-C4 66.33(7), Sm-C5-Al2-C8 119.59(7), Sm-C6-Al2-C8 -119.81(8).

with decreasing size of the metal center (La…C4 3.140(3) Å, Y…C4 3.304(3)Å, Lu…C4(17) 3.447 (3) Å),<sup>6,26,31</sup> which is in accord with the Yb…C(CH<sub>3</sub>) distance of 3.354(2) Å in complex **6b**. The Sm analogue **6a**, however, revealed a distance slightly shorter (Sm1…C4 3.113(2) Å) than that of the significantly larger lanthanum center. The crystal structure of samarocene complex **7a** was determined earlier<sup>32</sup> (space group  $P2_1/n$ ) and found to be isostructural with the yttrocene  $[Cp*_2Y(AlMe_4)]_2$ .<sup>33</sup> The respective lanthanum complex produced crystals in two different space groups:  $P2_1/n$ (isomorphous with Y and Sm) and  $P\overline{1}$  (containing one molecule of lattice toluene).<sup>31</sup> Compounds **7a,b** crystallized

from toluene in the space group  $P\overline{1}$ , incorporating two solvent molecules into the lattice (Figure 6 and Figure S4 in the Supporting Information), being isostructural with the latter lanthanum derivative.



Figure 6. Solid-state structure of  $[Cp_{2}^{*}Yb(\mu-AlMe_{4})]_{2}$  (7b). Hydrogen atoms and lattice solvent (two molecules of toluene) are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): 7b, Yb–C1 2.625(2), Yb–C4' 2.643(2), Yb–C5–9(Cp\*) 2.598(2)–2.622(2), Yb–C15–19(Cp\*) 2.598(2)–2.640(2), Yb-C1–Al 173.15(10), C1–Yb–C4' 87.12(6); 7a, Sm–C1 2.743(4), Sm–C4' 2.755(4), Sm–C5–9(Cp\*) 2.686(4)–2.708(5), Sm–C15–19(Cp\*) 2.686(5)–2.728(5), Sm-C4 174.0(2), C1–Sm–C4' 87.69(13).

The exact mechanism for the formation of dimeric metallocenes  $[Cp_{2}Ln(\mu-AlMe_{4})]_{2}$  (7) is not entirely clear. It is very unlikely that the monomeric half-sandwich complexes  $Cp^{*}Ln(AlMe_{4})_{2}$  disproportionate into  $[Cp_{2}Ln(\mu-AlMe_{4})]_{2}$  and  $Ln(AlMe_{4})_{3}$ , since formation of the latter homoleptic tetramethylaluminates has not been observed for the half-sandwich complexes  $Cp^{*}Ln(AlMe_{4})_{2}$ . The reaction proceeds presumably via a ligand exchange reaction between the divalent precursor  $\{Ln(AlMe_{4})_{2}\}_{n}$  and  $Cp^{*}_{2}Pb$  to afford an intermediate species such as " $Cp^{*}Ln(AlMe_{4})$ ". This divalent intermediate could get oxidized by another  $Cp^{*}_{2}Pb$  molecule to form  $[Cp^{*}_{2}Ln(\mu-AlMe_{4})]_{2}$  (7). Preliminary experiments, in which

 $Pb[N(SiMe_3)_2]_2^{34}$  was treated with 4 equiv of AlR<sub>3</sub> in *n*-hexane, established that putative " $Pb(AIR_4)_2$ " rapidly decomposed with formation of Pb(0). The degradation is presumably following a radical mechanism similar to that for Tl(I) organyls.<sup>35</sup> Since Pb(II) alkyl species are known to be unstable,<sup>36</sup> any transient "Pb(AlMe<sub>4</sub>)<sub>2</sub>" would decompose into Pb(0), Al<sub>2</sub>Me<sub>6</sub>, and methyl-radical coupling products, predominantly ethane; to some degree it might act again as an oxidation/ligand transfer agent. Three facts support this hypothesis: (i) there has been no evidence for the formation of homoleptic  $Ln(AlMe_4)_{3}$ , (ii) the yield based on Cp\* is almost quantitative, whereas the yield of trivalent lanthanide complexes is 66%, meaning that all the Cp\*<sub>2</sub>Pb was consumed without oxidizing all available Ln(II) metal centers, and (iii) the results from the attempted oxidation of the europium complex  $\{Eu(AlMe_4)_2\}_n$ . In the case of europium, we could not detect any Ln-containing product, in either the n-hexane mother liquor or the toluene extract. Extraction of the solid reaction residue with THF, on the other hand, led to the isolation of polymeric  $\{Cp^*Eu(\mu-AlMe_4)\}$  $(THF)_{3}_{n}$  (8, Figure 7) and elemental lead.



**Figure 7.** Connectivity of  $\{Cp*Eu(\mu-AlMe_4)(THF)_3\}_n$  (8) in the solid state. Hydrogen atoms are omitted, and all atoms are represented by spheres of arbitrary radii (green, Eu; orange, Al; red, O; gray, C). Crystal data: monoclinic unit cell, a = 18.387(4) Å, b = 8.989(2) Å, c = 19.826(4) Å,  $\beta = 101.445(3)^\circ$  at 103 K, solved and refined in space group *Cm*. Due to the poor quality of the data, a ball and stick representation visualizes the connectivity. A detailed discussion of interatomic distances and angles has to be ruled out.

Compound 8 is the THF adduct of the aforementioned putative intermediate "Cp\*Ln(AlMe<sub>4</sub>)". The polymeric nature of 8, with tetramethylaluminate ligands bridging between the rare-earth-metal centers,<sup>37</sup> seems to be unique and rather unexpected, especially since a related Yb compound was obtained as the separated ion pair  $[Cp*Yb-(THF)_4]^+[AlMe_4]^{-.8b}$  In order to investigate whether the formation of polymeric 8 is size-related or an intrinsic europium effect, the analogous reaction that led to  $[Cp*Yb-(THF)_4]^+[AlMe_4]^{-.8b}$  was performed with  $\{Sm(AlMe_4)_2\}_n$ . Accordingly,  $\{Sm(AlMe_4)_2\}_n$  was reacted with 2 equiv of HCp\*. Crystallization of the crude product from THF afforded few orange single crystals, which to our surprise were determined as the methylidene complex Cp\*<sub>3</sub>Sm<sub>3</sub>( $\mu_2$ -Cl)<sub>3</sub>( $\mu_3$ -Cl)( $\mu_3$ -CH<sub>2</sub>)(THF)<sub>3</sub> (9; Figure 8).

Complex 9 is isostructural with  $Cp_{3}Ln_{3}(\mu_{2}-Cl)_{3}(\mu_{3}-Cl)(\mu_{3}-CH_{2})(THF)_{3}$  (Ln = Y, La;  $P2_{1}/n$ ), which were synthesized by adding Me<sub>2</sub>AlCl to the half-sandwich complexes  $Cp^{*}Ln$ -(AlMe<sub>4</sub>)<sub>2</sub> and subsequently treating the isolable multinuclear complexes  $[Cp^{*}Ln(AlMe_{4})_{x}Cl_{y}]_{z}$  with THF.<sup>38</sup> Since the Sm(II) amide precursor Sm[N(SiMe\_{3})\_{2}]\_{2}(THF)\_{2} was obtained from SmI<sub>2</sub>(THF)<sub>x</sub>, we assume that the chlorido ligands stem from an Me<sub>2</sub>AlCl impurity in AlMe<sub>3</sub> used for the synthesis of



Figure 8. Solid-state structure of  $[Cp_{3}^{*}Sm_{3}(\mu_{2}\text{-}Cl)_{3}(\mu_{3}\text{-}Cl)(\mu_{3}\text{-}CH_{2})$ -(THF)<sub>3</sub>] (9). Hydrogen atoms, except those attached to the methylidene group, are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Sm1-Cl1 2.7990(6), Sm1-Cl2 2.9056(5), Sm1-Cl4 2.8038(6), Sm1-C25 2.464(2), Sm1-O3 2.533(2), Sm2-Cl2 2.9407(5), Sm2-Cl3 2.8079(6), Sm2-Cl4 2.8038(6), Sm2-C25 2.486(2), Sm2-O2 2.485(2), Sm3-Cl1 2.7834(6), Sm3-Cl2 2.9069(5), Sm3-Cl3 2.7824(6), Sm3-C25 2.534(2), Sm3-O1 2.530(2), Sm1-C(Cp\*) 2.697(2)-2.750(2), Sm2-C(Cp\*) 2.699(2)-2.738(2), Sm3-C(Cp\*) 2.696(2)-2.720(2), Sm1···Sm2 3.6869(2), Sm1···Sm3 3.7359(2), Sm2…Sm3 3.7711(2); Sm1-Cl1-Sm3 84.01(2), Sm3-Cl3-Sm2 84.84(2), Sm2-Cl4-Sm1 82.22(2), Sm1-Cl2-Sm2 78.19(1), Sm1-Cl2-Sm3 79.99(1), Sm2-Cl2-Sm3 80.31(1), Sm1-C25-Sm2 96.28(7), Sm1-C25-Sm3 96.74(8), Sm2-C25-Sm3 97.40(8), Cl2-Sm1-O3 71.22(4), Cl2-Sm2-O2 73.15(4), Cl2-Sm3-O1 72.87(4).

the precursor  $\{Sm(AlMe_4)_2\}_n$ . This impurity might form a mixed, divalent  $AlMe_4/chloride$  species  $\{Sm(Cl)_x(AlMe_4)_y\}$  (x + y = 2), which is only soluble in donating solvents, such as THF, and therefore inseparable from the main product  $\{Sm(AlMe_4)_2\}_n$ .

While heteroleptic tetramethylaluminates have been investigated in detail, the respective tetraethylaluminates have attracted much less attention. The substitution of the alkyl groups seem to be a marginal variation, but for example halfsandwich derivatives Cp\*Ln(AlEt<sub>4</sub>)<sub>2</sub> have not yet been reported. The increased steric demand of the AlEt<sub>4</sub> ligand and its enhanced sensitivity to alkyl degradation via  $\beta$ -H abstraction presumably cause this dearth of data. When  $\{Yb(AlEt_4)_2\}_n$  was reacted with 0.5 equiv of  $Cp^*_2Pb$  in nhexane, instant precipitation of Pb(0) was observed. Upon workup of the reaction mixture, two products could be isolated. Attempts to obtain crystals from the yellow, toluene-soluble component produced only glasslike solids.<sup>39</sup> From the nhexane-soluble component, however, blue single crystals suitable for X-ray crystallography were obtained, revealing the formation of the metallocene complex  $Cp_2^*Yb(AlEt_4)$  (10; Figure 9).

This finding is consistent with the corresponding reaction of  $\{Yb(AlMe_4)_2\}_n$  and plumbocene, resulting in the isolation of  $[Cp^*_2Yb(\mu-AlMe_4)]_2$  (7b). For structural comparison, the samarocene complex  $Cp^*_2Sm(AlEt_4)$  features a motif similar to that of 10,<sup>40</sup> while the larger size of lanthanum led to a dimerization and therewith to the formation of  $[Cp^*_2La(\mu-AlEt_4)]_2$ .<sup>16</sup> In order to investigate the influence of donor molecules on the  $\{Yb(AlEt_4)_2\}_n/Cp^*_2Pb$  reaction, diethyl ether (Et<sub>2</sub>O), as a softer donor than THF, was admitted. Addition of Et<sub>2</sub>O to a bright orange solution of  $\{Yb(AlEt_4)_2\}_n$  in toluene



Figure 9. Solid-state structure of molecule A of  $Cp^*_2Yb(AlEt_4)$  (10). Hydrogen atoms and lattice solvent (two molecules of toluene) are omitted for clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): molecule A, Yb1–C1 2.64(2), Yb1–C3 2.60(2), Yb1–C9–13(Cp\*) 2.60(2)-2.63(2), Yb1–C19–23(Cp\*) 2.62(2)-2.65(2), Yb1···Al1 3.094(6), Al1···C2 2.88(2), Al1···C4 2.78(3), Yb1–C1–Al1 80.5(5), Yb1–C3–Al1 82.2(6), C1–Yb1–C3 83.7(5), C1–Al1–C3 113.2(7), Al1–C1–C2 103.3(13), Al1–C3–C4 99.3(13); molecule B, Yb2–C29 2.65(2), Yb2–C31 2.58(2), Yb2– C37–41(Cp\*) 2.58(8)-2.64(2), Yb2–C47–51(Cp\*) 2.62(2)-2.64(2), Yb2···Al2 3.084(6), Al2···C30 2.90(3), Al2···C32 2.80(3), Yb2–C29– Al2 79.9(6), Yb2–C31–Al2 82.4(6), C29–Yb2–C31 83.8(5), C29– Al2–C31 113.4(8), Al2–C29–C30 104.0(14), Al2–C31–C32 100.3(13).

caused a color change, clearly indicating Yb(II)···donor interactions, presumably forming the diethyl ether analogue of  $Ln(AlEt_4)_2(THF)_2$  (Ln = Sm, Yb).<sup>41</sup> A black suspension formed upon addition of 0.5 equiv of Cp\*<sub>2</sub>Pb indicated a redox reaction with Pb(0) as the byproduct. Single-crystal X-ray diffraction studies, however, revealed the formation of divalent Cp\*Yb(AlEt\_4)(Et\_2O)\_2 (11; Figure 10) in 69% crystallized



Figure 10. Solid-state structure of  $Cp*Yb(AlEt_4)$  ( $Et_2O_2$  (11). Hydrogen atoms are omitted for the sake of clarity. Atoms are represented by atomic displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Yb-C9 2.687(2), Yb-C16 2.923(2) Yb-O1 2.396(1), Yb-O2 2.411(1), Yb-C(Cp\*) 2.645(2)-2.694(2), Al-C9 2.053(2), Al-··C16 3.004(2); Yb-C9-Al 163.66(9), Al-C9-C16 112.8(1), C9-Yb-O1 93.00(5), C9-Yb-O2 105.25(6), O1-Yb-O2 100.94(5).

yield, suggesting the absence of any pronounced Yb(II)  $\rightarrow$  Yb(III) redox chemistry. Interestingly, the coordination mode of the AlEt<sub>4</sub> moiety resembles that of Cp\*<sub>2</sub>Yb(AlEt<sub>3</sub>·THF),<sup>42</sup> which was generated by the addition of 1 equiv of AlEt<sub>3</sub> to Cp\*<sub>2</sub>Yb(THF) in toluene. The Yb-C distances involving the side-on coordinated ethyl group are 2.687(2) and 2.923(2) Å in **11** and 2.85(2) and 2.94(2) Å in Cp\*<sub>2</sub>Yb(AlEt<sub>3</sub>·THF).

Apparently, the softer donor  $Et_2O$  did not cleave the  $AlEt_4$  ligand or lead to the formation of an ion pair as observed for  $[Cp^*Yb(THF)_4]^+[AlMe_4]^{-.8b}$ 

# CONCLUSIONS

The Cp\*2Pb-based oxidative route toward Ln(III) halfsandwich complexes, employing 0.5 equiv of oxidant per divalent rare-earth-metal atom, proved to be highly effective for samarium and vtterbium (dimethylsilyl)amide and (trimethylsilyl)amide complexes.  $Cp*Ln[N(SiMe_3)_2]_2$  and  $Cp*Ln[N(SiHMe_2)_2]_2$ (THF) (Ln = Sm, Yb) could be isolated in moderate to excellent yields. When the reactions were performed with  $Eu[N(SiMe_3)_2]_2(THF)_2$ , an inevitable disproportionation into the sandwich complex Cp\*2Eu[N- $(SiMe_3)_2$ ] and homoleptic  $Eu[N(SiMe_3)_2]_3$  was observed. The complementary reaction employing the (dimethylsilyl)amido ligand did not deliver crystalline material. Using the plumbocene-based oxidation routine on divalent [(pz<sup>tBu,Me</sup>)Eu- $(\mu$ -pz<sup>fBu,Me</sup>)(THF)<sub>2</sub>]<sub>2</sub> resulted in the formation of Cp\*Eu-(pz<sup>fBu,Me</sup>)<sub>2</sub>(THF)<sub>2</sub> proving that Pb(II) compounds are able to oxidize Eu(II) in complexes with nitrogen-based ligands. The reactions performed on the divalent tetramethylaluminates  ${Ln(AlMe_4)_2}_n$  (Ln = Sm, Yb) gave a product mixture, from which half-sandwich complexes Cp\*Ln(AlMe<sub>4</sub>)<sub>2</sub> and sandwich complexes  $[Cp*_2Ln(\mu-AlMe_4)]_2$  (Ln = Sm, Yb) were isolated, indicating two competing reaction mechanisms: (i) the envisaged oxidation/ligand transfer (redox transmetalation) and (ii) the undesired, redox-inactive ligand exchange (metathesis) followed by decomposition via radicals originating from Pb(II) alkyl species. In the case of europium, polymeric  $\{Cp*Eu(\mu-AlMe_4)(THF)_3\}_n$  could be isolated, clearly showing that for Eu(II) the second redox-inactive mechanism prevails. The reaction of  $\{Sm(AlMe_4)_2\}_n$  with 2 equiv of HCp\* led to the formation of the mixed methylidene/chloride complex  $Cp*_3Sm_3(\mu_2-Cl)_3(\mu_3-Cl)(\mu_3-CH_2)(THF)_3$  in minor yields, suggesting dimethylaluminum chloride as a contaminant in commercially available trimethylaluminum. In a switch from tetramethyl- to tetraethylaluminates, the reaction of {Yb- $(AlEt_4)_2$ , with plumbocene afforded only the sandwich complex Cp\*<sub>2</sub>Yb(AlEt<sub>4</sub>) as crystalline material, suggesting that the intermediate  $Cp*Yb(AlEt_4)_2$  is destabilized by either intra- or intermolecular decomposition pathways of the tetraethylaluminato ligands. A solvent switch from *n*-hexane to toluene-diethyl ether led to the isolation of divalent  $Cp*Yb(AlEt_4)(Et_2O)_2$  via redox-inactive ligand transfer of Cp\*2Pb. Overall, the feasibility of such redox protocols is crucially affected by the redox potentials of the rare-earth-metal centers (Sm versus Eu versus Yb), the counter ligands (alkyl versus amido), and the reaction conditions (reaction time and solvent).

#### EXPERIMENTAL SECTION

**General Considerations.** All manipulations were performed under rigorous exclusion of air and moisture, using glovebox techniques (MB Braun MB200B; <1 ppm of  $O_2$ , <1 ppm of  $H_2O$ , argon atmosphere). The solvents *n*-hexane, toluene, diethyl ether (Et<sub>2</sub>O), and tetrahydrofuran (THF) were purified using Grubbs columns (MBraun SPS, solvent purification system).  $C_6D_6$  (99.6%, Sigma-Aldrich) was dried over Na/K alloy. All solvents were stored inside a glovebox. 1,1,1,3,3,3-Hexamethyldisilazane (95%, Sigma-Aldrich) was used as received, 1,2-Diiodoethane (99%, Sigma-Aldrich) was recrystallized from diethyl ether prior to use, ytterbium metal (99.9%, Sigma-Aldrich), samarium metal (99.9%, ABCR), and europium metal (99.9%, ABCR) were used as received, *n*-butyllithium

(1.6 M in hexanes, Sigma-Aldrich) was used as received, and sodium bis(trimethylsilyl)amide was synthesized by reacting sodium amide (95%, Sigma-Aldrich) with 1.1 equiv of 1,1,1,3,3,3-hexamethyldisilazane in *n*-hexane.  $LnI_2(THF)_2$  (Ln = Sm, Eu, Yb) were synthesized according to the original procedure described by Kagan et al.43 Accordingly, excess metal was reacted with 1,2-diiodoethane in THF for 18 h followed by centrifugation, filtration, and crystallization from saturated THF solutions at -40 °C.  $Ln[N(SiMe_3)_2]_2(THF)_2$  (Ln = Sm, Eu, Yb),<sup>10</sup> Ln{ $[\mu$ -N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Ln[N(SiHMe<sub>2</sub>)<sub>2</sub>](THF)}<sub>2</sub> (Ln = Sm, Eu, Yb),<sup>11</sup> and {Ln(AlR<sub>4</sub>)<sub>2</sub>} (Ln = Sm, Eu, Yb; R = Me, Et)<sup>8</sup> were synthesized according to slightly modified literature procedures. Cp\*2Pb was obtained from the reaction of PbCl2 with 1.9 equiv of Cp\*Li in THF and its solid-state structure reinvestigated (Figure S5 in the Supporting Information).<sup>44</sup> <sup>1</sup>H NMR and <sup>13</sup>C spectra were recorded on a Bruker Biospin DPX 400 or on a Bruker Biospin AV500. Due to the paramagnetic nature of Eu(II), Eu(III), Sm(III), and Yb(III), some of the NMR spectroscopic characterizations were inconclusive, but <sup>1</sup>H chemical shifts (without integrals) were included in cases of the correct number of signals. IR spectra were recorded on a Nicolet protégé 460 instrument using DRIFT (diffuse reflectance infrared Fourier transform) or on a Thermo Scientific Nicolet 6700 FT-IR spectrometer using CsI plates and Nujol. For all the DRIFT measurements, the ratio of potassium bromide to metal complex was kept constant at 20:1. Elemental analyses were performed on an Elementar Vario EL III instrument.

**Cp\*Sm[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1a).** Cp\*<sub>2</sub>Pb (0.098 g, 0.20 mmol) was dissolved in n-hexane (5 mL) and added dropwise to Sm[N- $(SiMe_3)_2]_2(THF)_2$  (0.251 g, 0.41 mmol) dissolved in *n*-hexane (5 mL). The reaction mixture was stirred for another 18 h at ambient temperature, during which a black suspension had formed; this was centrifuged to remove elemental lead, which appeared as a gray-black solid residue, and the resulting orange solution was filtered. The solution was dried under reduced pressure, leaving an orange crystalline solid (0.243 g, 0.40 mmol, 98%). The solid was recrystallized from THF at -40 °C to give the product as orange plates. Crystallized yield: 0.150 g, 0.25 mmol, 61%. Single crystals for X-ray structure determination were grown from a saturated toluene solution. <sup>1</sup>H NMR (400 MHz, THF-D<sub>8</sub>, 26 °C): δ 1.45 (s, 15H, C<sub>5</sub>Me<sub>5</sub> CH<sub>3</sub>), -4.28 (s, 36H, SiMe<sub>3</sub>) ppm. <sup>13</sup>C NMR (400 MHz, THF-D<sub>8</sub>, 26 °C):  $\delta$  121.6 (C<sub>5</sub>Me<sub>5</sub>), 20.8 (C<sub>5</sub>Me<sub>5</sub> CH<sub>3</sub>), -0.5 (br, SiMe<sub>3</sub>) ppm. DRIFT (*ṽ*): 2951 (s), 2912 (m), 2879 (m), 2735 (vw), 2652 (vw), 2480 (vw), 1919 (vw), 1858 (vw), 1495 (vw), 1443 (w), 1389 (w), 1350 (vw), 1246 (s), 989 (vs), 879 (s), 835 (vs), 769 (s), 754 (m), 727 (w), 673 (m), 600 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>51</sub>N<sub>2</sub>Si<sub>4</sub>Sm (606.36 g/mol): C, 43.58; H, 8.48; N, 4.62. Found: C, 43.71; H, 9.09; N, 4.62. Although these results are outside the range viewed as establishing analytical purity (H, +0.21%), they are provided to illustrate the best values obtained to date.

Cp\*Yb[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1b). Cp\*<sub>2</sub>Pb (0.104 g, 0.22 mmol) was dissolved in n-hexane (5 mL) and added dropwise to Yb[N-(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub> (0.277 g, 0.43 mmol) dissolved in *n*-hexane (5 mL). After addition was complete, a dark suspension had formed. The reaction mixture was stirred for another 18 h at ambient temperature and centrifuged to remove elemental lead, which appeared as a grayblack solid residue, and the resulting purple solution was filtered. The solution was dried under reduced pressure, leaving a purple crystalline solid (0.269 g, 0.43 mmol, 99%). The solid was recrystallized from THF at -40 °C to give the product as purple plates. Crystallized yield: 0.213 g, 0.34 mmol, 79%. <sup>1</sup>H NMR (400 MHz, THF-D<sub>8</sub>, 26 °C):  $\delta$ 82.90 (vbr), 0.68 (br) ppm. DRIFT ( $\tilde{\nu}$ ): 2951 (s), 2897 (m), 2862 (m), 2730 (vw), 2480 (vw), 1910 (vw), 1856 (vw), 1487 (vw), 1437 (w), 1383 (w), 1332 (vw), 1250 (s), 1025 (w), 975 (vs), 882 (s), 843 (vs), 769 (m), 750 (m), 726 (w), 672 (m), 610 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>51</sub>N<sub>2</sub>Si<sub>4</sub>Yb (629.04 g/mol): C, 42.01; H, 8.17; N, 4.45. Found: C, 42.40; H, 8.12; N, 4.53.

**Cp\*<sub>2</sub>Eu[N(SiMe<sub>3</sub>)<sub>2</sub>] (2).** Cp\*<sub>2</sub>Pb (0.057 g, 0.12 mmol) was dissolved in *n*-hexane (4 mL) and added dropwise to Eu[N- $(SiMe_3)_2]_2(THF)_2$  (0.147 g, 0.24 mmol) dissolved in *n*-hexane (5 mL). After addition was complete, formation of gray and yellow precipitates in an orange solution was observed. Ten minutes later, a

dark suspension had formed; after another 20 min the solution had turned dark green and a gray-black metallic precipitate had formed. The reaction mixture was stirred for another 18 h at ambient temperature and centrifuged, the resulting dark green solution was filtered, and the gray-black solid residue was extracted with n-hexane (2 mL). The solution was dried under vacuum, leaving a mixture of green and orange solids (0.142 g). The solid was recrystallized from nhexane at -40 °C, yielding  $Cp_{2}^{*}Eu[N(SiMe_{3})_{2}]$  as dark green hexagonal plates and  ${\rm Eu}[{\rm N} \bar{(}Si\bar{M}e_3)_2]_3$  as bright orange needles. Determination of the yield was not possible, due to cocrystallization of  $Eu[N(SiMe_3)_2]_3$ . Anal. Calcd for  $C_{26}H_{48}EuNSi_2$  (582.81 g/mol): C, 53.58; H, 8.30; N, 2.40. Found: C, 51.39; H, 6.93; N, 2.77. Although these results are outside the range viewed as establishing analytical purity (C, -1.79%; H, -0.97%), they are provided to illustrate the best values obtained to date. Since the crystals needed to be manually separated under a light microscope, the sufficiently pure material received was just enough for an elemental analysis but not for DRIFT. Deviation from the calculated values for carbon and nitrogen might be explained by contamination of minimal amounts of cocrystallized needles of  $Eu[N(SiMe_3)_2]_3$ , which were mechanically inseparable from the plates of  $Cp*_2Eu[N(SiMe_3)_2]$ 

**Cp\*Sm[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(THF)** (3a). Cp\*<sub>2</sub>Pb (0.098 g, 0.21 mmol) was dissolved in *n*-hexane (4 mL) and added dropwise to Sm{[ $\mu$ - $N(SiHMe_2)_2]_2Sm[N(SiHMe_2)_2](THF)\}_2$  (0.194 g, 0.14 mmol) dissolved in n-hexane (4 mL). After addition was complete, a dark suspension had formed. The reaction mixture was stirred for another 3 h at ambient temperature and centrifuged, the resulting dark yellow to orange solution was filtered, and the gray-black solid residue was extracted with n-hexane (2 mL). The solution was dried under reduced pressure, leaving a slightly oily orange-red solid (0.247 g). The solid was recrystallized from n-hexane at -40 °C. Crystallized yield: 0.088 g (0.14 mmol, 33%). After X-ray structure determination, the entire sample was dried under vacuum, dissolved in THF to provide each metal center with coordinating THF molecules, dried again (0.246 g, 0.40 mmol, 97%), and recrystallized from *n*-hexane. Two crops with a combined yield of 0.133 g (0.21 mmol, 50%) were collected. DRIFT  $(\tilde{\nu})$ : 2962 (m), 2904 (m), 2862 (w), 2729 (vw), 2119 (w, sh), 2065 (m), 2046 (w, shoulder), 1948 (w, br sh), 1865 (vw), 1446 (w), 1379 (vw), 1348 (vw), 1244 (s), 1178 (vw), 1153 (vw), 1026 (s), 953 (s, sh), 893 (vs), 837 (vs), 787 (s), 764 (s), 694 (w), 690 (w), 633 (vw), 602 (w) cm  $^{-1}$  Anal. Calcd for  $C_{22}H_{51}N_2OSi_4Sm$  (622.36 g/mol): C, 42.46; H, 8.26; N, 4.50. Found: C, 43.04; H, 8.24; N, 4.35. Although these results are outside the range viewed as establishing analytical purity (C, +0.18%), they are provided to illustrate the best values obtained to date.

**Cp\*Yb[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(THF) (3b).** Cp\*<sub>2</sub>Pb (0.114 g, 0.24 mmol) was dissolved in THF (5 mL) and added dropwise to Yb{[ $\mu$ -N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Yb[N(SiHMe<sub>2</sub>)<sub>2</sub>](THF)}<sub>2</sub> (0.235 g, 0.16 mmol) dissolved in THF (3 mL). After addition was complete, a cloudy red solution and a metal (Pb) ball had formed. The reaction mixture was stirred for another 18 h at ambient temperature before the solution was filtered and dried under reduced pressure, leaving an oily red-purple solid (0.316 g). The solid was recrystallized from *n*-hexane at -40 °C. Crystallized yield: purple crystals, 0.228 g (0.35 mmol, 73%). DRIFT ( $\tilde{\nu}$ ): 2964 (m), 2910 (m), 2868 (w), 2742 (vw), 2129 (w, shoulder), 2075 (m), 1849 (w), 1450 (w), 1379 (vw), 1350 (vw), 1250 (s), 1180 (vw), 1157 (vw), 1066 (m, shoulder), 1036 (m, broad), 895 (vs), 839 (s), 793 (m), 764 (s), 704 (w), 683 (w), 631 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>51</sub>N<sub>2</sub>OSi<sub>4</sub>Yb (645.04 g/mol): C, 40.96; H, 7.97<sub>2</sub> N, 4.34. Found: C, 40.61; H, 8.11; N, 4.29.

I( $pz^{H_{u,M_e}}$ )Eu( $\mu$ - $pz^{H_{u,M_e}}$ )(THF)<sub>2</sub>]<sub>2</sub> (4). A colorless solution of Hpz<sup>H\_{u,M\_e}</sup> (0.112 g, 0.81 mmol) in THF (8 mL) was added dropwise to Eu[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub> (0.250 g, 0.40 mmol) dissolved in THF (2 mL). After addition was complete, the solution had changed from dark to light yellow. The reaction mixture was stirred for another 18 h at ambient temperature before the solution was dried under vacuum, leaving a yellow solid residue (0.208 g). The residue was redissolved in THF, filtered, and concentrated under reduced pressure. At -40 °C the concentrated solution afforded bright yellow single crystals of compound 4 (0.164 g, 0.14 mmol, 72% on Eu). DRIFT ( $\tilde{\nu}$ ): 3343

(vw), 3103 (vw), 3083 (vw), 2957 (vs), 2923 (s), 2902 (s), 2875 (s), 2714 (vw), 2691 (vw), 1564 (vw), 1508 (m), 1461 (m), 1413 (m), 1359 (m), 1307 (w), 1233 (m), 1207 (w), 1044 (m), 1028 (m), 999 (w), 965 (w), 919 (w), 886 (w), 785 (m), 766 (w), 725 (vw), 689 (w), 668 (vw), 566 (vw), 497 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>48</sub>H<sub>84</sub>Eu<sub>2</sub>N<sub>8</sub>O<sub>4</sub> (1141.15 g/mol): C, 50.52; H, 7.42; N, 9.82. Found: C, 48.94; H, 7.19; N, 10.47. Although these results are outside the range viewed as establishing analytical purity (C, -1.16%), they are provided to illustrate the best values obtained to date. We assume that about half of the coordinated THF molecules are removed by vacuum drying, leaving [(pz<sup>tBu,Me</sup>)Eu( $\mu$ -pz<sup>tBu,Me</sup>)(thf)]<sub>2</sub>; corrected yield of 0.16 mmol, 82% on Eu. Anal. Calcd for C<sub>40</sub>H<sub>68</sub>Eu<sub>2</sub>N<sub>8</sub>O<sub>2</sub> (996.97 g/mol): C, 48.19; H, 6.88; N, 11.24. Found: C, 48.94; H, 7.19; N, 10.47.

**Cp\*Eu(pz<sup>tBu,Me</sup>)<sub>2</sub>(THF)<sub>2</sub> (5).** Compound 4 (0.169 g 0.18 mmol) was obtained from the reaction of Eu[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub> (0.214 g, 0.35 mmol) with 2 equiv of Hpz<sup>rBu,Me</sup> (0.096 g, 0.69 mmol) in THF (8 mL) as described above. The yellow solid was dissolved in THF (4 mL), and a solution of Cp\*2Pb (0.084 g, 0.18 mmol) in THF (4 mL) was added dropwise. During the addition, a dark red suspension formed. The reaction mixture was stirred for another 18 h at ambient temperature, during which a suspension of a dark blue solution and gray Pb powder had formed. The suspension was centrifuged, the blue THF solution was filtered, and the gray residue was extracted with THF. The solution was dried under vacuum, leaving a blue oily solid (0.257 g). The weight of the Pb powder (0.038 g, 0.18 mmol, >99%) indicated full conversion. The reaction product was dissolved in THF, filtered, and crystallized at -40 °C, forming blue rhombohedra. Yield (two crops combined): 0.162 g, 0.23 mmol, 66% (Eu). <sup>1</sup>H NMR (400 MHz,  $C_6D_{6'}$  21 °C):  $\delta$  8.80 (vbr), 1.76 (s), - 2.15 (s), - 10.58 (s) ppm. DRIFT ( $\tilde{\nu}$ ): 3107 (vw), 2958 (vs), 2920 (s), 2897 (vs), 2856 (s), 2717 (vw), 1558 (vw), 1516 (s), 1502 (m), 1458 (s), 1444 (m), 1419 (s), 1385 (w), 1358 (m), 1315 (w), 1232 (m), 1205 (w), 1034 (vs), 1001 (m), 962 (w), 922 (w), 883 (s), 777 (s), 723 (w), 687 (w), 665 (vw), 567 (vw), 505 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>34</sub>H<sub>57</sub>EuN<sub>4</sub>O<sub>2</sub> (705.82 g/mol): C, 57.86; H, 8.14; N, 7.94. Found: C, 57.71; H, 8.17; N, 7.99.

 $Cp*Sm(AIMe_4)_2$  (6a) and  $[Cp*_2Sm(\mu-AIMe_4)]_2$  (7a).  $Cp*_2Pb$ (0.131 g, 0.28 mmol) was dissolved in n-hexane (5 mL) and added dropwise to  $\{Sm(AlMe_4)_2\}$  (0.179 g, 0.55 mmol) suspended in nhexane (7 mL). After addition was complete, the suspension had changed from light violet to black. The reaction mixture was stirred for another 18 h at ambient temperature and centrifuged, the resulting red solution was filtered, and the black solid residue was extracted with nhexane  $(2 \times 6 \text{ mL})$ . The solid residue was collected and dried under vacuum. The weight (0.196 g) indicated that the Sm-containing compound remained undissolved. Extracting with toluene  $(3 \times 4 \text{ mL})$ gave an orange solution. The n-hexane solution was dried under reduced pressure, leaving red crystalline  $Cp*Sm(AlMe_4)_2$  (6a; 0.080 g, 0.17 mmol, 32% Sm). Recrystallization from n-hexane (two crops) gave 0.032 g (0.07 mmol, 13%) of the product. The toluene extract contained 0.097 g of [Cp\*2Sm(µ-AlMe4)]2 (7a) (0.10 mmol, 35% Sm) of which 0.090~g~(0.09 mmol, 32% Sm) could be crystallized from a very concentrated toluene solution at -40 °C, in the form of  $[Cp*_2Sm(\mu-AlMe_4)]_2 \cdot 2C_6H_5Me.$ 

Complex **6a**. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 21 °C):  $\delta$  0.84 (s,  $C_5Me_5$ ), -3.24 (s, AlMe4) ppm. DRIFT ( $\tilde{\nu}$ ): 3016 (w), 2970 (m, sh), 2914 (s), 2902 (s), 2875 (s, sh), 2796 (m), 2737 (w), 2449 (vw), 2278 (vw), 1795 (vw), 1768 (vw), 1489 (w), 1441 (m), 1381 (m), 1228 (m), 1201 (s), 1192 (s), 1163 (vw), 1024 (w), 935 (w), 800 (w), 694 (vs), 650 (m), 584 (s), 555 (s), 513 (m), 478 (m), 451 (w), 417 (w) cm<sup>-1</sup>. Anal. Calcd for  $C_{18}H_{39}Al_2Sm$  (459.83 g/mol): C, 47.02; H, 8.55. Found: C, 47.37; H, 8.47.

Complex **7a.** <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 21 °C):  $\delta$  1.73 (s, monomer), 0.85 (s, dimer), 0.68 (s, monomer), -2.14 (s, dimer), -14.30 (s, dimer), -17.51 (s, monomer) ppm. The two sets of signals are attributed to the monomer–dimer equilibrium 2 Cp\*<sub>2</sub>Sm(AlMe<sub>4</sub>) = [Cp\*<sub>2</sub>Sm( $\mu$ -AlMe<sub>4</sub>)]<sub>2</sub>; for a detailed discussion, see ref 32. DRIFT ( $\tilde{\nu}$ ): 3017 (w), 2958 (m, sh), 2914 (vs), 2880 (s), 2863 (s), 2824 (w), 2732 (vw), 2309 (vw), 1490 (w), 1438 (m), 1420 (w), 1381 (m), 1177 (m), 1094 (vw, sh), 1065 (vw), 1021 (w), 936 (vs), 817 (m),

801 (m), 777 (m), 742 (s), 677 (m), 622 (s), 566 (s), 546 (s), 525 (vw) cm $^{-1}$ . Anal. Calcd for  $C_{48}H_{84}Al_2Sm_2$  (1015.86 g/mol): C, 56.75; H, 8.33. Found: C, 56.71; H, 8.20.

 $Cp*Yb(AIMe_4)_2$  (6b) and  $[Cp*_2Yb(\mu-AIMe_4)]_2$  (7b).  $Cp*_2Pb$ (0.118 g, 0.25 mmol) was dissolved in n-hexane (5 mL) and added dropwise to  $\{Yb(AlMe_4)_2\}$  (0.171 g, 0.49 mmol) suspended in nhexane (3 mL). After addition was complete, a dark blue suspension had formed. The reaction mixture was stirred for another 18 h at ambient temperature and centrifuged, the resulting blue solution was filtered, and the black solid residue was extracted with n-hexane (4 mL). The solid residue was collected and dried under vacuum. The weight (0.092 g) indicated that Yb-containing species were still undissolved. Repeated extraction with *n*-hexane only dissolved another 2 mg, whereas use of toluene allowed the isolation of 0.043 g of a dark blue substance. The solutions were dried under reduced pressure, leaving both blue crystalline solids with a combined weight of 0.175 g (0.132 g n-hexane fraction, 0.043 g toluene fraction). The combined solids were dissolved in toluene and crystallized at -40 °C to give dark blue crystals of  $[Cp*_2Yb(\mu-AlMe_4)]_2 \cdot 2C_6H_5Me$  (7b). Yield: 0.055 g (0.05 mmol, 21% Yb). The mother liquor was dried under reduced pressure, dissolved in *n*-hexane, filtered, and crystallized at -40 °C to give blue platelike crystals of Cp\*Yb(AlMe<sub>4</sub>)<sub>2</sub> (6b) (0.052 g, 0.11 mmol, 22%).

Complex **6b**. DRIFT ( $\tilde{\nu}$ ): 2923 (m), 2890 (m), 2839 (w), 2743 (vw), 1494 (vw), 1443 (w), 1434 (w), 1411 (vw), 1382 (w), 1238 (w), 1214 (m), 1194 (m), 1187 (m), 1066 (vw), 1027 (w), 695 (vs), 638 (w), 582 (m), 508 (w), 471 (w), 469 (w), 413 (vw) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>39</sub>Al<sub>2</sub>Yb (482.53 g/mol): C, 44.81; H, 8.15. Found: C, 45.18; H, 7.95.

Complex **7b**. DRIFT ( $\tilde{\nu}$ ): 2958 (m, sh), 2913 (vs), 2891 (m), 2866 (m), 2827 (w), 2734 (vw), 1490 (w), 1439 (m), 1428 (w), 1382 (w), 1179 (m), 1065 (vw), 1023 (w), 878 (s), 805 (m), 782 (m), 744 (m), 675 (m), 622 (s), 593 (w), 568 (m), 544 (m), 521 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>48</sub>H<sub>84</sub>Al<sub>2</sub>Yb<sub>2</sub> (1061.27 g/mol): C, 54.32; H, 7.98. Found: C, 54.33; H, 7.79.

 $[Cp*Eu(\mu-AIMe_4)(THF)_3]_n$  (8).  $Cp*_2Pb$  (0.119 g, 0.25 mmol) was dissolved in *n*-hexane (5 mL) and added dropwise to  $\{Eu(AIMe_4)_2\}$ (0.165 g, 0.50 mmol) suspended in n-hexane (7 mL). After addition was complete, a red-orange suspension had formed. The reaction mixture was stirred for 18 h at ambient temperature in the dark and centrifuged, and the resulting colorless solution was filtered and dried under vacuum and found to contain only an insignificant amount of solid product (0.014 g). In addition, extraction of the dark colored solid residue with 4 mL of toluene led to minor isolated yields (0.002 g). Therefore, the solid residue was extracted with THF  $(2 \times 4 \text{ mL})$ and the resulting yellow solution was filtered and concentrated under reduced pressure. Storage of that solution at -40 °C led to the formation of yellow-green crystals (0.272 g, 0.46 mmol, 92%). DRIFT (*ṽ*): 3080 (vw), 3017 (w), 2981 (s), 2958 (s), 2903 (vs), 2854 (vs), 2809 (m), 2724 (vw), 2120 (vw), 1602 (vw), 1492 (w), 1461 (m), 1448 (m), 1374 (w), 1341 (w), 1293 (vw), 1244 (vw), 1160 (m), 1081 (s), 1037 (vs), 920 (m), 876 (s), 852 (w), 741-673 multiple signals (s), 565 (s), 467 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>26</sub>H<sub>51</sub>AlEuO<sub>3</sub> (590.63 g/mol): C, 52.87; H, 8.70. Found: C, 54.07; H, 8.21. Although these results are outside the range viewed as establishing analytical purity (C, +0.80%; H, -0.09%), they are provided to illustrate the best values obtained to date.

[Cp\*<sub>3</sub>Sm<sub>3</sub>( $\mu_2$ -Cl)<sub>3</sub>( $\mu_3$ -Cl)( $\mu_3$ -CH<sub>2</sub>)(THF)<sub>3</sub>] (9). {Sm(AlMe<sub>4</sub>)<sub>2</sub>]<sub>n</sub> (0.112 g, 0.34 mmol) was dissolved in THF (5 mL), and HCp\* (0.094 g, 0.69 mmol) diluted with THF (5 mL) was added slowly. The reaction mixture was stirred for 18 h before all volatiles were removed under vacuum, leaving an almost black oily solid (0.266 g). The residue was dissolved in a few drops of THF and crystallized at -40 °C, yielding a few orange single crystals which were identified as 9 by X-ray diffraction. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 21 °C): δ 3.09 (s), 1.77 (d, 22 Hz), 0.21 (s), -0.38 (s) ppm.

**Cp\*<sub>2</sub>Yb(AlEt<sub>4</sub>) (10).**  $Cp*_2Pb$  (0.073 g, 0.15 mmol) was dissolved in *n*-hexane (6 mL) and added dropwise to {Yb(AlEt<sub>4</sub>)<sub>2</sub>} (0.140 g, 0.31 mmol) dissolved in *n*-hexane (8 mL). The dark yellow solution turned instantly greenish before a gray suspension formed. The

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reaction mixture was stirred for 18 h at ambient temperature in the dark and centrifuged, and the resulting blue-purple solution was filtered and dried under vacuum, leaving 0.084 g of a blue solid. The gray-green solid residue was extracted with toluene, and the resulting gold-yellow solution was dried under vacuum, leaving 0.101 g of a greenish yellow solid. The blue compound was dissolved in a small amount of *n*-hexane and filtered, where 0.007 g of a yellow toluenesoluble solid residue was recovered. The blue n-hexane solution was dried under vacuum to yield 0.069 g of blue solid. Recrystallization of the blue solid from an *n*-hexane solution at -40 °C led to the formation of a small amount of sticky blue rhombohedra, which were identified as compound 10 by X-ray crystallography (0.069 g, 0.12 mmol, 39% Yb). DRIFT (v): 2933 (vs), 2902 (vs), 2860 (vs), 2792 (m), 2729 (w), 1649 (vw), 1452 (m), 1409 (m), 1381 (m), 1240 (w), 1186 (w), 1147 (w), 1101 (vw), 1059 (m), 1018 (m), 985 (m), 955 (m), 920 (w), 897 (w), 864 (w), 841 (vw), 804 (vw), 712 (vw), 650 (s), 594 (m, sh), 544 (m), 455 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>50</sub>AlYb (586.74 g/mol): C, 57.32; H, 8.59. Found: C, 54.94; H, 8.51. Although these results are outside the range viewed as establishing analytical purity (C, -1.98%), they are provided to illustrate the best values obtained to date.

 $Cp*Yb(AlEt_4)(Et_2O)_2$  (11). { $Yb(AlEt_4)_2$ } (0.201 g, 0.44 mmol) was dissolved in toluene (4 mL) and diethyl ether (Et<sub>2</sub>O, 1 mL) was added with stirring. During the addition the solution changed from orange to brown-green. Cp\*2Pb (0.105 g, 0.22 mmol) was dissolved in toluene (4 mL) and added dropwise. Instantly, a black suspension formed. The reaction mixture was stirred for 18 h at ambient temperature in the dark and centrifuged, and the solid residue was extracted with toluene (3 mL). The resulting red-brown solution was filtered and dried under vacuum, leaving 0.311 g of a green oil. Metallic lead was collected, and its weight was determined as 0.035 g (0.17 mmol, 77%). Since the green oil was only sparingly soluble in n-hexane, 0.5 mL of Et<sub>2</sub>O was added to dissolve the oil completely. The solution was concentrated under reduced pressure and left to crystallize at -40 °C. Compound 11 crystallized as shapeless orange chunks (0.182 g, 0.30 mmol, 69%), which seemed to lose one of the coordinated Et<sub>2</sub>O molecules and thereby turn oily.  $^1\mathrm{H}$  NMR (500 MHz, C7D8, 26 °C):  $\delta$  3.05 (q,  $^3J_{\mathrm{HH}}$ 6.9 Hz, 3H, Et<sub>2</sub>O CH<sub>2</sub>), 2.02 (s, 15H, C<sub>5</sub>Me<sub>5</sub> CH<sub>3</sub>), 1.37 (t, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, 12H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.82 (t,  ${}^{3}J_{HH}$  7.1 Hz, 5H, Et<sub>2</sub>O CH<sub>3</sub>), -0.04 (q,  ${}^{3}J_{HH}$  7.9 Hz, 8H, AlCH<sub>2</sub>CH<sub>3</sub>) ppm.  ${}^{13}$ C NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>, 26 °C): δ 115.1 (C<sub>5</sub>Me<sub>5</sub>), 66.6 (Et<sub>2</sub>O CH<sub>2</sub>), 14.5 (Et<sub>2</sub>O CH<sub>3</sub>), 12.0 (AlCH<sub>2</sub>CH<sub>3</sub>), 11.6 (C<sub>5</sub>Me<sub>5</sub> CH<sub>3</sub>), 5.7 (br, AlCH<sub>2</sub>CH<sub>3</sub>) ppm. IR (Nujol;  $\tilde{\nu}$ ): 2924 (vs), 2725 (m), 2670 (m), 1460 (s, Nujol), 1377 (s, Nujol), 1304 (m), 1169 (w), 1153 (w), 1123 (vw), 1089 (vw), 1077 (vw), 1059 (vw), 1042 (vw), 966 (w), 919 (vw), 892 (w), 846 (w), 771 (w), 722 (m, Nujol), 646 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>26</sub>H<sub>55</sub>AlO<sub>2</sub>Yb (599.72 g/mol): C, 52.07; H, 9.24. Found: C, 50.25; H, 9.52. Although these results are outside the range viewed as establishing analytical purity (C, -1.42%), they are provided to illustrate the best values obtained to date. Loss of one molecule of Et<sub>2</sub>O would result in Cp\*Yb(AlEt<sub>4</sub>) (Et<sub>2</sub>O). Anal. Calcd for C222H45AlOYb (525.64 g/mol): C, 50.27; H, 8.63. Found: C, 50.25; H, 9.52.

X-ray Crystallography and Crystal Structure Determination of Complexes 1-11. Crystals of compounds 1-11 were grown by standard techniques from saturated solutions at -40 °C. Suitable crystals for diffraction experiments were selected in a glovebox and mounted in Paratone-N (Hampton Research) on a nylon loop. Data collection was done on a Bruker AXS TXS rotating anode APEXII  $Pt^{135}$  CCD detector using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data collection and data processing were done using APEX2,<sup>45</sup> SAINT,<sup>46</sup> and SADABS<sup>47</sup> version 2008/1 or TWINABS,<sup>48</sup> whereas structure solution and final model refinement were done using SHELXS<sup>49</sup> version 2013/1 or SHELXT<sup>50</sup> version 2014/4 and SHELXL<sup>51</sup> version 2014/7. All molecular plots were generated using the program ORTEP-3.52 Further details of the refinement and crystallographic data are given in Table S1 and in the CIF files in the Supporting Information. CCDC 1424143-1424157 also contain supplementary crystallographic data for this paper.

# ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00837.

NMR spectroscopic and crystallographic data (PDF) Crystallographic data (CIF)

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All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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