

Lanthanide Metallocene Reactivity with Dialkyl Aluminum Chlorides: Modeling Reactions Used to Generate Isoprene Polymerization Catalysts

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The well-defined coordination environment of trivalent $[(C_5Me_5)_2Ln]^+$ complexes has been used to examine the reaction chemistry of the lanthanide carboxylate and R_2AlCl ($R = Me, Et, ^iBu$) components used in the preparation of lanthanide-based diene polymerization catalysts. Each of the R_2AlCl reagents can replace a carboxylate ligand with chloride in reactions with $[(C_5Me_5)_2Sm(O_2CC_6H_5)]_2$, but instead of forming a simple chloride complex like $[(C_5Me_5)_2SmCl]_3$, bimetallic lanthanide aluminum dichloro complexes $(C_5Me_5)_2Sm-(\mu-Cl)_2AlR_2$ are generated by ligand redistribution. These bis(chloride)-bridged complexes are also readily formed from the divalent precursor $(C_5Me_5)_2Sm(THF)_2$ and R_2AlCl . However, the analogous reaction between $(C_5Me_5)_2Sm(THF)_2$ and Et_3Al gives $(C_5Me_5)_2Sm(THF)-(\mu-\eta^2-Et)AlEt_3$, which contains the first $Ln(III)-(\eta^2-Et)$ linkage, a coordination mode that differentiates Et from Me . To determine if mixed mono-chloride/alkyl-bridged $(C_5Me_5)_2Ln-(\mu-Cl)(\mu-R)AlR_2$ complexes can be isolated, $(C_5Me_5)_2Y(\mu-Cl)Y(C_5Me_5)_2$ was reacted with R_3Al . These reactions form $[(C_5Me_5)_2Y(\mu-Cl)(\mu-R)AlR_2]_x$ complexes, but again there is a differentiation on the basis of R : the Me complex is a dimer and the others are monomers. $(C_5Me_5)_2Y(\mu-Cl)_2AlR_2$ complexes were similarly prepared for comparison with the mixed ligand species and for additional Me, Et , and iBu comparisons.

Introduction

Lanthanide-based polymerization of butadiene and isoprene to >98% *cis*-1,4-polybutadiene and polyisoprene is one of the best methods to make high *cis*-polydiene elastomers.^{1–26} This reaction is also one of the most effective catalytic reactions known for the lanthanide metals. Unfortunately, little is known about the mechanism of this catalysis. In fact, in the industrial

recipes for active catalysts, little is known about the catalyst precursor(s). In these cases, neodymium carboxylates are typically treated with an ethyl aluminum chloride and subsequently with an excess of an isobutyl aluminum hydride. A sequence involving conversion of carboxylate to chloride to alkyl (or hydride) is generally cited as the route to generate the initiating species for the catalytic polymerization, but in many cases neither the starting materials nor the intermediates are well defined.

To obtain more information on the specific steps of the catalyst preparation and the basis for specifically choosing an ethylaluminum reagent in the first step and an isobutylaluminum reagent in the second step, we have investigated dialkylaluminum chloride reactivity with a lanthanide carboxylate as a function of the alkyl

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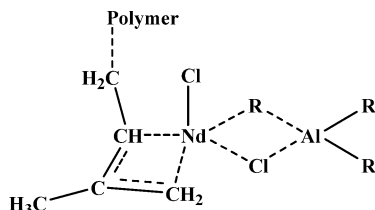


Figure 1. Literature schematic for an active center for Nd-based polymerizations.

group. We have used derivatives of the trivalent bis-(pentamethylcyclopentadienyl) unit, $[(C_5Me_5)_2Ln]^+$, to study this chemistry since the two C_5Me_5 rings fix and stabilize one large portion of the metal coordination sphere such that the reactive chemistry of the remainder can be more readily defined. Metallocene models can be used to determine the chemistry of the $(\mu-R)(\mu-Cl)-AlR_2$ portion of the structure shown in Figure 1, which has been described in the literature as a possible active center in Nd-based polymerizations.^{6,7,19}

Although Nd has traditionally been the lanthanide chosen for diene polymerizations, recent studies by an increasing number of groups studying this problem have shown that a wider variety of lanthanides can effect the high *cis*-1,4-polymerization.^{10,11,17,18,21–24} The two metals chosen for this study, Sm and Y, were selected for practical reasons. Due to the synthetic access provided by Sm(II),^{27,28} a much wider range of Sm complexes are available for these studies and much more background information is known than is available for Nd, the metal most often used in lanthanide-based diene polymerization.^{1–26} Since lanthanide reactivity is generally more sensitive to steric factors than to $4f^n$ configuration, due to the limited radial extension of the $4f$ orbitals, metals of similar size often have similar chemistry.^{27,29,30} In this regard, Sm is a reasonable model for Nd. Yttrium was chosen because the complex $(C_5Me_5)_2ClY(\mu-Cl)Y(C_5Me_5)_2$ has been shown to be an excellent diamagnetic platform to explore Lewis acid–base interactions with electropositive metals.³¹

Results

Reactivity of $[(C_5Me_5)_2Sm(O_2CC_6H_5)]_2$ with Et_2AlCl . The first step in the preparation of many lanthanide-based diene polymerization catalysts is the reaction of a neodymium carboxylate with Et_2AlCl . Ethyl-aluminum reagents are used specifically in the first step followed by *isobutyl*-aluminum reagents in the second. The Et_2AlCl reaction has been assumed to form $NdCl_3$ in analogy with Ziegler–Natta preparations of $TiCl_3$. However, recent studies with fully characterized lanthanide carboxylates show that the Et_2AlCl reaction product contains aluminum and ethyl groups.⁹

To examine this first step in the preparation of diene polymerization catalysts, the reaction of the bis-(pentamethylcyclopentadienyl) carboxylate, $[(C_5Me_5)_2-$

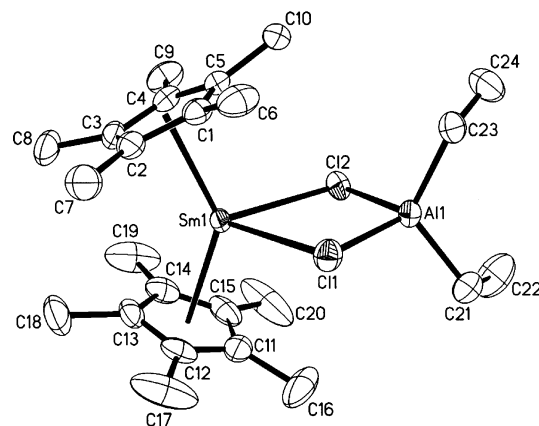
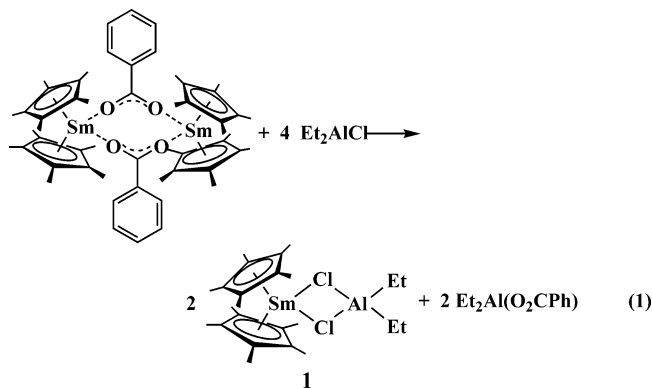


Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(\mu-Cl)_2AlEt_2$, **1**, with the probability ellipsoids drawn at the 50% level. Hydrogens atoms have been excluded for clarity.

$Sm(O_2CC_6H_5)]_2$,³² with Et_2AlCl was studied. A reaction occurs immediately upon mixing these reagents with a color change from yellow to red. A single organosamarium complex is observed by 1H NMR spectroscopy which was definitively identified by X-ray crystallography as a mixed metal complex containing aluminum, namely, the bridged species $(C_5Me_5)_2Sm(\mu-Cl)_2AlEt_2$, **1**, eq 1, Figure 2.



Hence, Et_2AlCl does not simply convert this lanthanide carboxylate to a chloride, which would give a product such as $[(C_5Me_5)_2Sm(\mu-Cl)]_3$ ³³ or $(C_5Me_5)_2SmCl(THF)$.³⁴ The formation of **1** via eq 1 is complicated and necessarily involves some ligand exchange chemistry to give the 2:1 Cl:Al ratio in the product.

Complex **1** is a new example of a well-known class of organolanthanide complexes of general formula $(C_5Me_5)_2Ln(\mu-Z)_2Al(Z)_2$, where Z is a monoanionic ligand. Prior to this study only a few examples had been crystallographically characterized: $[(C_5Me_5)_2Sm(\mu-Me)_2AlMe_2]_2$,³⁵ $(C_5Me_5)_2Sm(\mu-Et)_2AlEt_2$,³⁶ $(C_5Me_5)_2Sm(\mu-^iBu)_2Al(^iBu)_2$,³⁷ $(C_5Me_5)_2Sm(\mu-Me)_2Al(C_5Me_5)(Me)$,³⁸ $(C_5Me_5)_2Yb(\mu-Cl)_2AlCl_2$,³⁹ and $(C_5Me_5)_2Y(\mu-Me)_2AlMe_2$.⁴⁰

Me_2AlCl and iBu_2AlCl Reactivity. Methyl and isobutyl aluminum chloride reactions with the carboxylate $[(C_5Me_5)_2Sm(O_2CC_6H_5)]_2$ were studied to eval-

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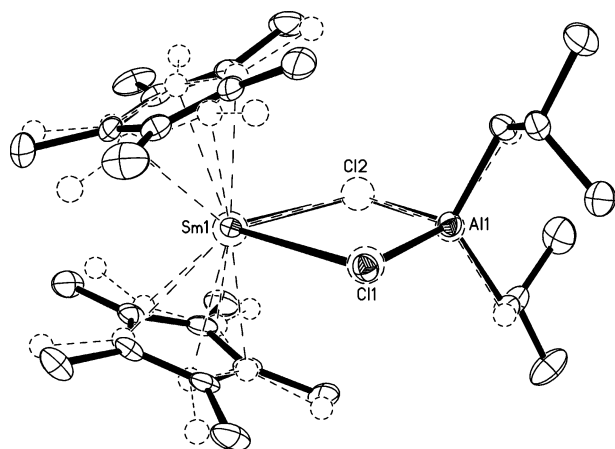
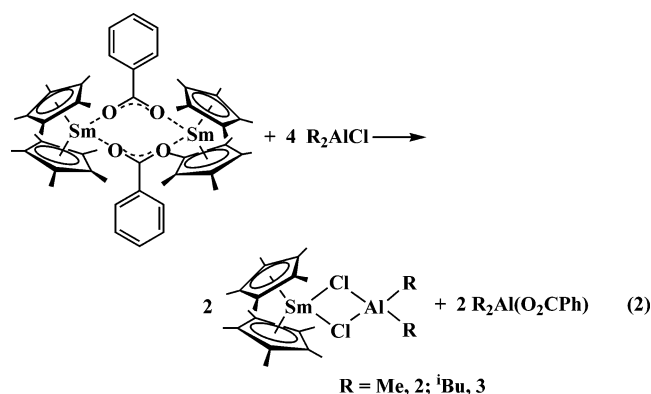


Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(\mu-Cl)_2AlMe_2$, **2** [dashed line], and $(C_5Me_5)_2Sm(\mu-Cl)_2Al(iBu)_2$, **3** [solid line], superimposed, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

uate differences from the ethyl analogue. As shown in eq 2, both Me_2AlCl and iBu_2AlCl react with $[(C_5Me_5)_2Sm(O_2CC_6H_5)]_2$ as does Et_2AlCl in eq 1. Like the ethyl analogue, both $(C_5Me_5)_2Sm(\mu-Cl)_2AlMe_2$, **2**, and $(C_5Me_5)_2Sm(\mu-Cl)_2Al(iBu)_2$, **3**, are red and display single 1H NMR C_5Me_5 resonances in C_6D_6 .



Both complexes were identified by X-ray crystallography, Figure 3. Hence, in eqs 1 and 2, no difference in reactivity is seen as a function of the alkyl group. The structural details of **1–3** are discussed later.

Direct Synthesis of $(C_5Me_5)_2Sm(\mu-Cl)_2AlEt_2$, **1.** Since $(C_5Me_5)_2Sm(THF)_2$ is the precursor to $[(C_5Me_5)_2Sm(O_2CC_6H_5)]_2$ ³² and since $(C_5Me_5)_2Sm(THF)_2$ is known to react with Me_3Al to make the related aluminum-bridged species $[(C_5Me_5)_2Sm(\mu-Me)_2AlMe_2]_2$ and Al metal,³⁵ eq 3, the reactions of $(C_5Me_5)_2Sm(THF)_2$ with Et_2AlCl and Me_2AlCl were examined as more efficient syntheses of complexes **1** and **2**. As shown in eq 4, this

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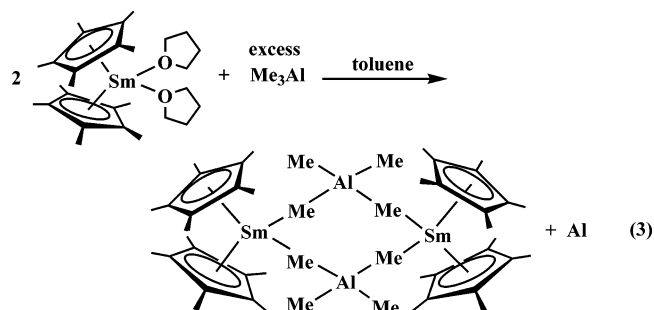
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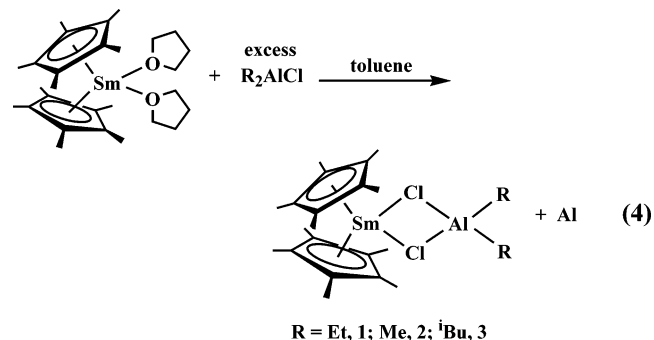
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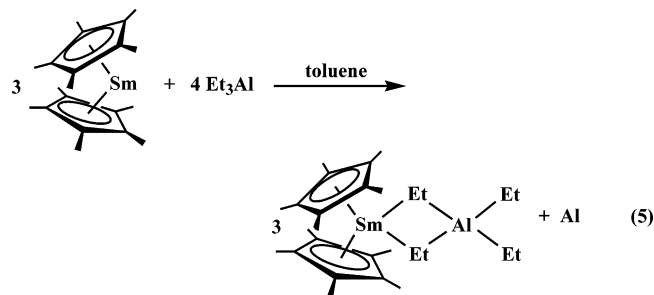
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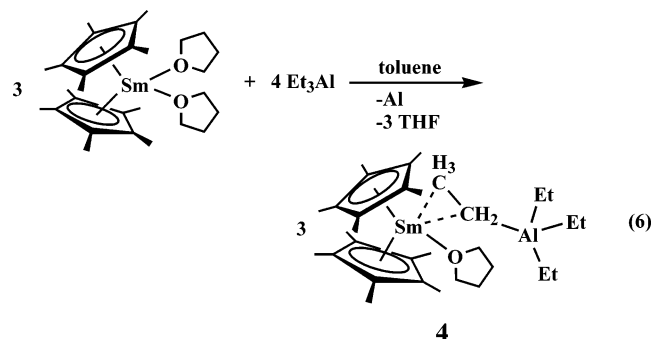
provides an even more direct route to these $(C_5Me_5)_2Sm(\mu-Cl)_2AlR_2$ complexes.



Variation in Ethyl versus Methyl Aluminum Chemistry. The reactions of $(C_5Me_5)_2Sm(THF)_2$ with Me_3Al , Et_2AlCl , and Me_2AlCl , eqs 3 and 4, were similar and also matched the reaction of Et_3Al with unsolvated $(C_5Me_5)_2Sm$, which forms another member of this class, $(C_5Me_5)_2Sm(\mu-Et)_2AlEt_2$,³⁶ eq 5. However, the reaction of $(C_5Me_5)_2Sm(THF)_2$ with Et_3Al gives a different product, **4**, which indicates a significant difference in methyl versus ethyl organoaluminum reactivity.



X-ray crystallography showed that although **4** was just a THF solvate of the known $(C_5Me_5)_2Sm(\mu-Et)_2AlEt_2$,³⁶ it had an unusual structure involving an η^2 -ethyl ligand: $(C_5Me_5)_2Sm(THF)(\mu-\eta^2-Et)AlEt_3$, **4**, eq 6, Figure 4.



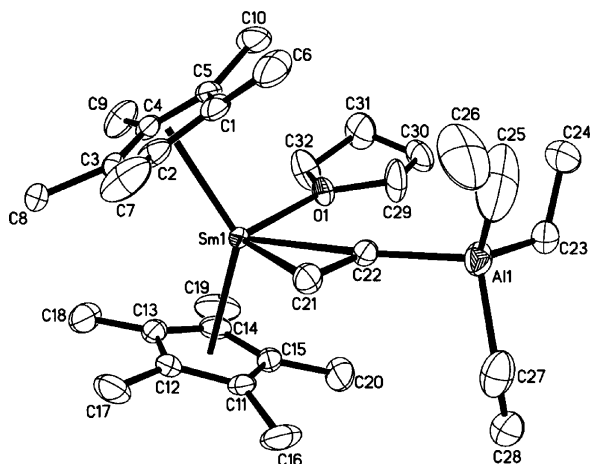
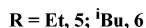
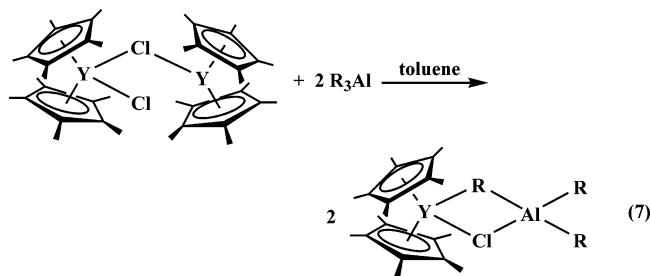


Figure 4. Thermal ellipsoid plot of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})-(\mu-\eta^2\text{-Et})\text{AlEt}_3$, **4**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

Complex **4** can also be synthesized by the addition of 1 equiv of THF to $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Et})_2\text{AlEt}_2$. In contrast, $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Me})_2\text{AlMe}_2]_2$ reacts with THF to form $(\text{C}_5\text{Me}_5)_2\text{SmMe}(\text{THF})$.³⁵ This is reasonable since the methyl group cannot form an η^2 -linkage like the ethyl group in **4**. To our knowledge, only one other η^2 -ethyl lanthanide complex is known, the divalent $(\text{C}_5\text{Me}_5)_2\text{-Yb}(\eta^2\text{-Et})\text{AlEt}_2(\text{THF})$.⁴¹

Reactivity of $[(\text{C}_5\text{Me}_5)_2\text{YCl}]_2$ with R_3Al , $\text{R} = \text{Me}$, Et , $i\text{Bu}$. Given the propensity of the R_2AlCl reagents to make bis-chloride-bridged products in eqs 1, 2, and 4, rather than the stoichiometrically expected mono-chloride-bridged species, the reactivity of the diamagnetic $(\text{C}_5\text{Me}_5)_2\text{ClY}(\mu\text{-Cl})\text{Y}(\text{C}_5\text{Me}_5)_2$ ³¹ with R_3Al was examined to determine if mixed alkyl mono-chloride complexes, $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-R})\text{AlR}_2$, could be isolated and were stable to ligand redistribution. Before this study $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-alkyl})(\mu\text{-halide})\text{AlZ}_2$ complexes were unknown. However, $\text{Ln}(\mu\text{-alkyl})(\mu\text{-halide})\text{AlZ}_2$ units were considered to be candidates for polymerization catalysts, e.g., Figure 1.^{6,7,19}

Et_3Al and $i\text{Bu}_3\text{Al}$ react in minutes with $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})\text{YCl}(\text{C}_5\text{Me}_5)_2$ in toluene at room temperature to give $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-Et})\text{AlEt}_2$, **5**, and $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-}i\text{Bu})\text{Al}(i\text{Bu})_2$, **6**, eq 7, Figure 5, which were identified by X-ray crystallography. No evidence for ligand rearrangement to form $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{AlR}_2$ products (described below) was observed up to 55 °C.



In contrast to the ethyl and isobutyl reactions, Me_3Al reacts with $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})\text{YCl}(\text{C}_5\text{Me}_5)_2$ to generate the dimeric $[(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-Me})\text{AlMe}_2]_2$, **7**, eq 8,

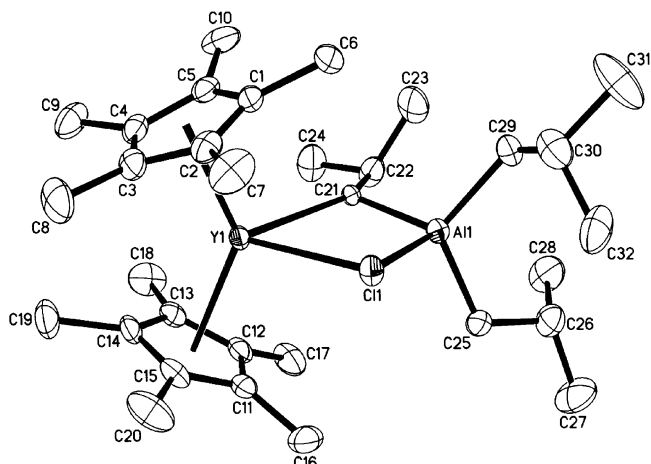


Figure 5. Thermal ellipsoid plot of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-}i\text{Bu})\text{-Al}(i\text{Bu})_2$, **6**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

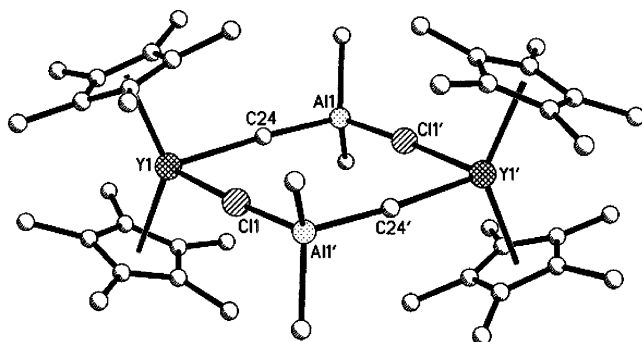
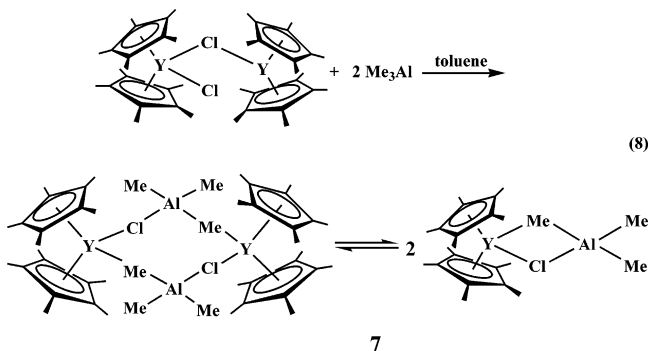


Figure 6. Ball and stick structure of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-Me})\text{AlMe}_2$, **7**.

Figure 6. The ^1H NMR spectrum of **7** differed from the ethyl and isobutyl analogues, **5** and **6**, in that it contained two C_5Me_5 resonances in C_6D_6 . The two C_5Me_5 resonances in the NMR spectrum are likely to arise from the monomer–dimer equilibrium shown in eq 8 in analogy with the equilibria found for $[(\text{C}_5\text{Me}_5)_2\text{-Ln}(\mu\text{-Me})_2\text{AlMe}_2]_2$ complexes, $\text{Ln} = \text{Sm}$,³⁵ Lu ,⁴⁰ and Y .⁴⁰ Variable-temperature NMR confirmation of a monomer–dimer equilibrium was thwarted by precipitation of **7** at -10 °C. However, upon heating to 55 °C, the two C_5Me_5 peaks at 1.89 and 1.88 ppm coalesce to one C_5Me_5 peak at 1.88 ppm.



Reactivity of $[(\text{C}_5\text{Me}_5)_2\text{LnCl}]_2$ with R_2AlCl ($\text{R} = \text{Me}$, Et , $i\text{Bu}$). To determine if the mixed alkyl halide-

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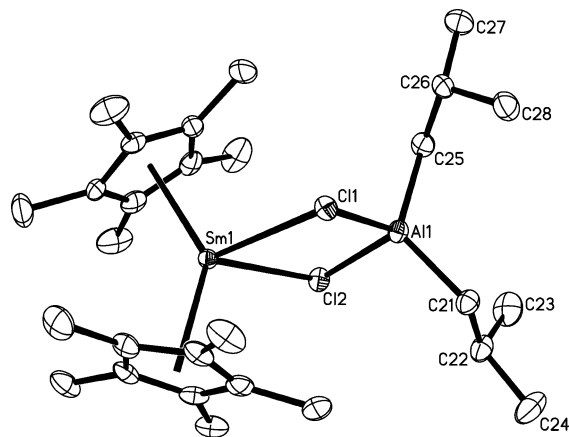
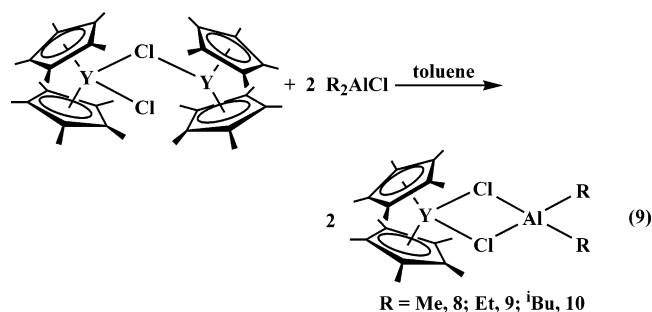
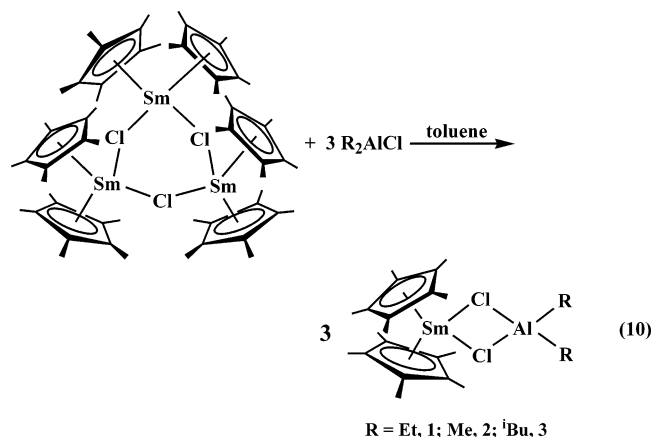


Figure 7. Thermal ellipsoid plot of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{Al}(\text{i-Bu})_2$, **10**, with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

bridged complexes would undergo ligand redistribution to bis(halide)-bridged species, it was advantageous to have the authentic $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{AlR}_2$ complexes for comparison. Accordingly, $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})\text{YCl}(\text{C}_5\text{Me}_5)$ was reacted with R_2AlCl reagents in analogy with the syntheses of **5–7** above to make the series of complexes $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{AlR}_2$ with $\text{R} = \text{Me}$, **8**; Et , **9**; i-Bu , **10**, according to eq 9. Complex **9** had previously been made from $(\text{C}_5\text{Me}_5)_2\text{YCl}(\text{THF})^{34}$ and Et_2AlCl .⁴² The structure of **10** is shown in Figure 7. No evidence of monomer–dimer equilibrium was observed for **8–10** from -10 to 55°C .



Given the results of eq 9 and for completeness, NMR studies of the reaction of $[(\text{C}_5\text{Me}_5)_2\text{SmCl}]_3$ with Me_2AlCl , Et_2AlCl , and $\text{i-Bu}_2\text{AlCl}$ were conducted. These reactions also model a possible reaction step described in the discussion section. As expected, these reactions cleanly form $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Cl})_2\text{AlR}_2$, **1–3**, eq 10.



Structural Studies. Complexes **1–3** and **5–10** all contain trivalent bent metallocene $[(\text{C}_5\text{Me}_5)_2\text{Ln}]^+$ units coordinated to two bridging groups to form formally eight-coordinate samarium and yttrium centers. This is a very common ligand set, coordination number, and geometry for lanthanides. As shown in Tables 1 and 2, the bond distances and angles of the $[(\text{C}_5\text{Me}_5)_2\text{Ln}]^+$ moieties of **1–3**, **5**, **6**, and **8–10** fall in the range commonly observed for this class.⁴³ Detailed metric data will not be discussed for complex **7** since the diffraction data were weak. The side-on ethyl-bridged complex, **4**, will be discussed in a separate section below.

$(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})_2\text{AlR}_2$. Complexes **1–3** and **8–10** provided a basis to evaluate the structural effects, if any, of Et versus Me and i-Bu on a $[(\mu\text{-Cl})_2\text{AlR}_2]^-$ group bridged to a lanthanide. As shown in Table 1 and Figure 3, which is an overlay of the analogous Me and i-Bu complexes, **2** and **3**, the complexes are very similar; that is, bond distances and angles are not affected by the nature of the alkyl groups on the aluminum. For example, the $\text{Sm}-(\mu\text{-Cl})$ distances in **1–3** fall in a narrow range, $2.8126(8)$ – $2.8230(6)$ Å, as do the $\text{Sm}-\text{Cl}-\text{Al}$ angles, $94.61(3)$ – $95.98(3)^\circ$.

$(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})(\mu\text{-R})\text{AlR}_2$. Complexes **5** and **6** allow comparisons of bridging chloro, ethyl, and isobutyl groups in the same series, Table 2. The $2.698(1)$ and $2.699(1)$ Å $\text{Y}-(\mu\text{-Cl})$ distances are slightly shorter than those in the dichloro complexes **8–10**. The $2.721(5)$ Å $\text{Y}-\text{C}(\mu\text{-Et})$ distance in **5** is slightly longer than the $\text{Y}-(\mu\text{-Cl})$ length. This situation differs from the comparison of the symmetrically bridged complexes $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Cl})_2\text{AlEt}_2$, **1**, and $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Et})_2\text{AlEt}_2$, in which the $2.662(4)$ Å $\text{Sm}-\text{C}(\mu\text{-Et})$ bonds are shorter than the $2.821(1)$ Å $\text{Sm}-(\mu\text{-Cl})$ bonds. Hence these distances can be variable depending on the specific complex involved. The $2.790(2)$ Å $\text{Y}-\text{C}(\mu\text{-i-Bu})$ bond in **6** is even longer than the analogue in **5**, but longer alkyl distances are expected for the bulkier isobutyl group. A similar situation is observed between $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Et})_2\text{AlEt}_2$ ($\text{Sm}-\text{C}(\mu\text{-Et}) = 2.662(4)$ Å av)³⁶ and $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-i-Bu})_2\text{Al}(\text{i-Bu})_2$ ($\text{Sm}-\text{C}(\mu\text{-i-Bu}) = 2.745(1)$ Å).³⁷

$[(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-Me})\text{AlMe}_2]_2$, **7.** The fact that the mixed bridging ligand chloro methyl complex **7** crystallizes as a dimer vis-à-vis the monomeric ethyl and isobutyl complexes $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-Et})\text{AlEt}_2$, **5**, and $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-i-Bu})\text{Al}(\text{i-Bu})_2$, **6**, may reflect the facility with which a bridging methyl can form a nearly linear $\text{Ln}-[\mu\text{-C}(\text{alkyl})]-\text{Al}$ connection. This requires a nearly trigonal bipyramidal five-coordinate carbon, which may be easier to access with the three nonmetal substituents on the carbon being hydrogen. A similar case can be argued for the dimeric methyl complex $(\text{C}_5\text{Me}_5)_2\text{Sm}[(\mu\text{-Me})_2\text{AlMe}_2]_2\text{Sm}(\text{C}_5\text{Me}_5)_2$ ³⁵ versus monomeric ethyl $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Et})_2\text{AlEt}_2$ ³⁶ and isobutyl $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-i-Bu})_2\text{Al}(\text{i-Bu})_2$.³⁷

$(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})(\mu\text{-}\eta^2\text{-Et})\text{AlEt}_3$, **4.** The most unusual structural result of this study is the $\text{Sm}-(\mu\text{-}\eta^2\text{-C}_2\text{H}_5)-\text{Al}$ linkage in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})(\mu\text{-}\eta^2\text{-Et})\text{AlEt}_3$, **4**. The only other known ethyl lanthanide complex that binds in a η^2 -fashion involves the divalent ytterbium complex $(\text{C}_5\text{Me}_5)_2\text{Yb}(\mu\text{-}\eta^2\text{-C}_2\text{H}_5)\text{Al}(\text{THF})(\text{C}_2\text{H}_5)_2$.⁴¹

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Table 1. Bond Distances (Å) and Angles (deg) in (C₅Me₅)₂Sm(μ -Cl)₂AlEt₂, **1, (C₅Me₅)₂Sm(μ -Cl)₂AlMe₂, **2**, (C₅Me₅)₂Sm(μ -Cl)₂Al(^{*i*}Bu)₂, **3**, (C₅Me₅)₂Y(μ -Cl)₂AlMe₂, **8**, (C₅Me₅)₂Y(μ -Cl)₂AlEt₂, **9**, and (C₅Me₅)₂Y(μ -Cl)₂Al(^{*i*}Bu)₂, **10****

bond distances/angles	1	2	3	8	9	10
Ln(1)–Cnt	2.410/2.409	2.407/2.413	2.409/2.404	2.345/2.340	2.340/2.351	2.346/2.339
Ln(1)–C(C ₅ Me ₅) av	2.691(3)	2.695(2)	2.6919(3)	2.6354(19)	2.6376(13)	2.635(3)
Ln(1)–Cl(2)	2.8230(6)	2.8152(5)	2.8141(8)	2.7493(5)	2.7346(4)	2.7470(8)
Ln(1)–Cl(1)	2.8198(7)	2.8169(5)	2.8126(8)	2.7472(5)	2.7316(4)	2.7471(8)
Cl(1)–Al(1)	2.2638(11)	2.2627(9)	2.2763(12)	2.2588(8)	2.2762(6)	2.2791(11)
Cl(2)–Al(1)	2.2739(11)	2.2633(9)	2.2760(12)	2.2577(8)	2.2838(6)	2.2795(11)
Al(1)–C(21)	1.956(3)	1.946(3)	1.961(3)	1.9768(19)	1.9532(17)	1.971(3)
Al(1)–C(X) ^a	1.952(3)	1.946(3)	1.968(3)	1.9870(18)	1.9660(16)	1.964(3)
Cnt1–Ln(1)–Cnt2	136.9	136.8	137.1	137.4	137.4	137.1
Cnt–Ln(1)–Cl(1)	107.6/106.6	104.8/109.3	109.1/104.8	105.1/108.8	106.5/107.7	108.5/104.9
Cnt–Ln(1)–Cl(2)	107.5/106.6	109.9/105.0	106.6/107.5	108.1/105.3	105.0/107.3	106.7/107.1
Cl(1)–Al(1)–Cl(2)	96.58(4)	95.24(3)	95.85(5)	94.68(3)	94.87(2)	94.71(4)
Cl(2)–Ln(1)–Cl(1)	73.79(2)	72.83(2)	73.82(2)	74.351(16)	75.820(12)	75.23(2)
Al(1)–Cl(1)–Ln(1)	94.92(3)	95.95(3)	95.09(4)	95.50(2)	94.513(17)	94.92(3)
Al(1)–Cl(2)–Ln(1)	94.61(3)	95.98(3)	95.05(4)	95.47(2)	94.258(17)	94.92(3)

^a Compound number, Ln, X: **1**, Sm, 23; **2**, Sm, 22; **3**, Sm, 25; **8**, Y, 22; **9**, Y, 23; **10**, Y, 25.

Table 2. Bond Distances (Å) and Angles (deg) in (C₅Me₅)₂Y(μ -Cl)(μ -Et)AlEt₂, **5, and (C₅Me₅)₂Y(μ -Cl)(μ -^{*i*}Bu)Al(^{*i*}Bu)₂, **6****

bonds	5	6
Y(1)–Cnt	2.364/2.355	2.353/2.361
Y–C(C ₅ Me ₅) av	2.651(4)	2.647(3)
Y(1)–C(21)	2.721(5)	2.790(2)
Y(1)–Cl(1)	2.6986(13)	2.6981(7)
Cl(1)–Al(1)	2.345(2)	2.3528(11)
Al(1)–C(X) ^a	1.984(6)	1.977(3)
Al(1)–C(25)	1.992(6)	1.985(3)
Al(1)–C(21)	2.001(6)	2.048(3)
Cnt1–Y(1)–Cnt2	136.6	135.6
Cnt–Y(1)–Cl(1)	107.4/106.1	104.9/108.2
Cnt–Y(1)–C(21)	107.6/106.7	109.0/107.9
Cl(1)–Y(1)–C(21)	75.80(12)	74.43(6)
Al(1)–C(21)–Y(1)	95.3(2)	95.94(10)
Al(1)–Cl(1)–Y(1)	88.37(6)	91.56(3)

^a **5**, X = 23; **6**, X = 29.

Table 3. Bond Distances (Å) and Angles (deg) in (C₅Me₅)₂Sm(THF)(η^2 -Et)AlEt₃, **4**

Sm(1)–Cnt1	2.446
Sm(1)–Cnt2	2.434
Sm(1)–C(21)	2.938(4)
Sm(1)–C(22)	2.757(3)
Sm(1)–O(1)	2.483(2)
Sm(1)–C(C ₅ Me ₅) av	2.717(3)
Al(1)–C(22)	2.086(3)
Al(1)–C(23)	1.995(5)
Al(1)–C(25)	1.959(6)
Al(1)–C(27)	2.051(5)
C(21)–C(22)	1.531(5)
Cnt1–Sm(1)–Cnt2	135.0
Cnt1–Sm(1)–C(21)	98.8/101.8
Cnt1–Sm(1)–C(22)	110.0/108.1
Cnt1–Sm(1)–O(1)	103.9/103.9
Al(1)–C(22)–Sm(1)	168.73(17)
C(21)–C(22)–Al(1)	110.2(2)
C(21)–C(22)–Sm(1)	81.04(19)
O(1)–Sm(1)–C(22)	82.45(9)
C(22)–Sm(1)–C(21)	30.98(10)

The [(C₅Me₅)₂Sm]⁺ part of **4** has metrical parameters that are similar to those in **1–3** with slightly larger Sm–(ring centroid) and average Sm–C(C₅Me₅) bond distances, Table 3. The 2.483(2) Å Sm–O(THF) distance matches that in other (C₅Me₅)₂SmR(THF) complexes: 2.473(9) Å, R = Me;³⁵ 2.499 Å, R = CH₂Ph;⁴⁵ 2.511(4) Å, R = Ph;⁴⁶ 2.49(1) Å, R = CPh.⁴⁷

However, the (Et₄Al)[–] component of **4** is not bound as it is in its unsolvated analogue (C₅Me₅)₂Sm(μ -Et)₂-AlEt₂. In that complex, the ethyl groups bridge via the methylene carbon with an average 2.622(4) Å Sm–C(CH₂) distance. In **4**, both carbon ethyl groups are oriented toward samarium, but both are at longer distances. The methylene carbon is the closest, with a Sm–C(CH₂) of 2.757(4) Å; the Sm–C(CH₃) distance is 2.938(4) Å.

Comparisons of the analogous distances in divalent (C₅Me₅)₂Yb(μ -Et)AlEt₂(THF),⁴¹ 2.85(2) Å for the methylene carbon and 2.94(2) Å for the methyl carbon, are problematic since the error limits are so large that 3 σ is comparable to the 0.061 Å difference in the eight-coordinate radii of Sm(III) (1.079 Å) and Yb(II) (1.14 Å). The Et₃Al fragment in the Yb complex appears to be weakly bonded since addition of 1 or 2 equiv of ether, THF, or pyridine readily induces cleavage of the Yb–Et bond. In contrast, the Sm–(μ - η^2 -Et) interaction in **4** is not destroyed by addition of Et₂O or THF since **4** can be recrystallized from both solvents. This greater stability in **4** could arise since the (μ - η^2 -Et) ligand is part of an anionic (Et₄Al)[–] ligand versus a neutral Et₃Al and is coordinated to a more electropositive trivalent versus divalent metal center. These two complexes also differ in that the Lewis base present, THF, attaches to Sm(III) in **4** and to Al(III) rather than Yb(II) in (C₅Me₅)₂Yb(μ -Et)AlEt₂(THF). This is consistent with the charge-to-radius ratios of the metals in the latter compound. In addition, THF ligation to samarium in **4** probably occurs since the aluminum center is already four-coordinate.

Discussion

Formation of Bridging Dichloride Products. The reaction between [(C₅Me₅)₂Sm(O₂CC₆H₅)]₂ and Et₂AlCl, eq 1, shows that in this bis(cyclopentadienyl) ligand environment the carboxylate ligand is not simply converted to an analogous chloride by Et₂AlCl. This contrasts with the earlier assumption that the neodymium carboxylates used as diene polymerization catalyst precursors react with Et₂AlCl to replace the carboxy-

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Table 4. X-ray Data Collection Parameters for (C₅Me₅)₂Sm(μ-Cl)₂AlEt₂, **1**, (C₅Me₅)₂Sm(μ-Cl)₂AlMe₂, **2**, (C₅Me₅)₂Sm(μ-Cl)₂Al(ⁱBu)₂, **3**, (C₅Me₅)₂Sm(THF)(η²-Et)AlEt₃, **4**, (C₅Me₅)₂Y(μ-Cl)(μ-Et)AlEt₂, **5**, (C₅Me₅)₂Y(μ-Cl)(μ-ⁱBu)Al(ⁱBu)₂, **6**, (C₅Me₅)₂Y(μ-Cl)₂AlMe₂, **8**, (C₅Me₅)₂Y(μ-Cl)₂AlEt₂, **9**, and (C₅Me₅)₂Y(μ-Cl)₂Al(ⁱBu)₂, **10**

	1	2	3	4
empirical formula	C ₂₄ H ₄₀ AlCl ₂ Sm	C ₂₂ H ₃₆ AlCl ₂ Sm	C ₂₈ H ₄₈ AlCl ₂ Sm	C ₃₂ H ₅₈ AlOSm
fw	576.79	548.74	632.89	636.11
temp (K)	188(2)	189(2)	163(2)	188(2)
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	11.3012(8)	10.5377(3)	12.5407(14)	12.4653(4)
<i>b</i> (Å)	11.6036(8)	12.8976(4)	13.0117(15)	15.0338(5)
<i>c</i> (Å)	11.8415(8)	18.4332(6)	20.340(2)	17.6839(6)
α (deg)	114.7230(10)	90	71.891(2)	92.4550(10)
β (deg)	91.5790(10)	103.8850(10)	79.783(2)	96.4750(10)
γ (deg)	107.0620(10)	90	79.527(2)	93.7510(10)
volume (Å ³)	1328.08(16)	2432.07(13)	3076.0(6)	3281.57(19)
<i>Z</i>	2	4	4	4
ρ _{calcd} (Mg/m ³)	1.442	1.499	1.367	1.288
μ (mm ⁻¹)	2.453	2.674	2.124	1.836
R1 ^a (<i>I</i> > 2.0σ(<i>I</i>))	0.0248	0.0199	0.0306	0.0313
wR2 ^b (all data)	0.0659	0.0461	0.0840	0.0783
	5	6	8	
empirical formula	C ₂₆ H ₄₅ AlClY	C ₃₂ H ₅₇ AlClY	C ₂₂ H ₃₆ AlCl ₂ Y	
fw	508.96	593.12	487.30	
temp (K)	188(2)	183(2)	163(2)	
cryst syst	triclinic	monoclinic	monoclinic	
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	
<i>a</i> (Å)	8.6649(7)	17.5839(7)	10.4245(12)	
<i>b</i> (Å)	10.6166(9)	8.8091(3)	12.8985(15)	
<i>c</i> (Å)	15.1444(13)	22.9626(9)	18.323(2)	
α (deg)	91.701(2)	90	90	
β (deg)	91.785(2)	108.3530(10)	103.951(2)	
γ (deg)	98.111(2)	90	90	
volume (Å ³)	1377.7(2)	3375.9(2)	2391.0(5)	
<i>Z</i>	2	4	4	
ρ _{calcd} (Mg/m ³)	1.227	1.167	1.354	
μ (mm ⁻¹)	2.255	1.850	2.704	
R1 (<i>I</i> > 2.0σ(<i>I</i>))	0.0572	0.0380	0.0268	
wR2 (all data)	0.1451	0.1026	0.0730	
	9	10		
empirical formula	C ₂₄ H ₄₀ AlCl ₂ Y	C ₂₈ H ₄₈ AlCl ₂ Y		
fw	515.35	593.12		
temp (K)	163(2)	163(2)		
cryst syst	triclinic	triclinic		
space group	<i>P</i> 1	<i>P</i> 1		
<i>a</i> (Å)	8.8505(10)	12.481(2)		
<i>b</i> (Å)	9.5965(11)	12.996(2)		
<i>c</i> (Å)	16.7001(19)	20.233(4)		
α (deg)	85.234(2)	71.826(3)		
β (deg)	77.644(2)	79.651(3)		
γ (deg)	69.362(2)	79.978(3)		
volume (Å ³)	1296.6(3)	3042.8(9)		
<i>Z</i>	2	4		
ρ _{calcd} (Mg/m ³)	1.320	1.247		
μ (mm ⁻¹)	2.497	2.134		
R1 (<i>I</i> > 2.0σ(<i>I</i>))	0.0206	0.0405		
wR2 (all data)	0.0530	0.1151		

^a R1 = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^b wR2 = [Σ[w(*F*_o² - *F*_c²)/Σ[w(*F*_o²)]]^{1/2}.

lates with chlorides and generate NdCl₃.^{20,26} Instead of forming a single chloride analogue of the carboxylate, e.g., [(C₅Me₅)₂Sm(μ-Cl)]₃,³³ a mixed metal Sm/Al product is obtained via eq 1: (C₅Me₅)₂Sm(μ-Cl)₂AlEt₂. Chloride ligands are delivered to the lanthanide in this reaction and carboxylate is lost, but in this case, a heterometallic complex results.

Interestingly, this result matches a recent study of the reaction of Et₂AlCl with the well-defined lanthanide carboxylates, {Ln[O₂CC(Me)₂Et]₃}_x, which showed that this initial product is more complicated than LnCl₃.⁹ Those Ln(O₂CR)₃/Et₂AlCl reactions formed mixed

metal species containing Ln, Al, and Cl in a 2:1:5 ratio as well as carboxylate and ethyl ligands.

Et₂AlCl, Me₂AlCl, and ⁱBu₂AlCl all react similarly with [(C₅Me₅)₂Sm(O₂CC₆H₅)]₂, eqs 1 and 4, such that there is no difference between these reagents in what they deliver to the lanthanide coordination sphere. Hence, in this model for replacing carboxylate with chloride, the nature of the R group in the R₂AlCl reagent is not critical except as the substituent on aluminum. In addition, the structural data on **1–3** and **8–10** show that there are no structural effects of Me versus Et versus ⁱBu as substituents on Al in the (C₅Me₅)₂Ln-

(μ -Cl) $_2$ AlR $_2$ products. The only variation in properties as a function of R in this series is that the isobutyl derivatives are distinctly more soluble in nonpolar solvents.

Reactions 1 and 4 do not simply involve chloride for carboxylate substitution reactions since a dichloride product is obtained. The initial stages of the reaction could involve breakup of the [(C $_5$ Me $_5$) $_2$ Sm(O $_2$ CC $_6$ H $_5$)] $_2$ dimer by R $_2$ AlCl to form a (C $_5$ Me $_5$) $_2$ Sm(μ -O $_2$ CC $_6$ H $_5$)(μ -Cl)AlR $_2$ intermediate. Ligand redistribution could subsequently occur to generate the dichloride samarium and diethyl aluminum carboxylate products that are observed. It is also possible that the aluminum moiety could dissociate from (C $_5$ Me $_5$) $_2$ Sm(μ -O $_2$ CC $_6$ H $_5$)(μ -Cl)AlR $_2$ taking carboxylate instead of chloride. This would leave a (C $_5$ Me $_5$) $_2$ SmCl unit which could complex with another equivalent of R $_2$ AlCl to form the observed (C $_5$ Me $_5$) $_2$ Sm(μ -Cl) $_2$ AlR $_2$. The latter reaction has been independently confirmed via eq 10. In either scenario, 2 equiv of R $_2$ AlCl are needed to form the observed dichloride product.

In contrast to the [(C $_5$ Me $_5$) $_2$ Sm(O $_2$ CC $_6$ H $_5$)] $_2$ carboxylate reactions with R $_2$ AlCl, eqs 1 and 2, the reactions of the chlorides, (C $_5$ Me $_5$) $_2$ ClY(μ -Cl)Y(C $_5$ Me $_5$) $_2$ and [(C $_5$ Me $_5$) $_2$ Sm(μ -Cl)] $_3$, with R $_2$ AlCl, eq 7–10, are more straightforward. In these reactions, no ligand redistribution occurs and the expected (C $_5$ Me $_5$) $_2$ Ln(μ -Cl) $_2$ AlR $_2$ products are observed.

Formation of Mixed Alkyl Chloride-Bridged Complexes. The formation of the (C $_5$ Me $_5$) $_2$ Y(μ -R)(μ -Cl)-AlR $_2$ products, 5–7, from (C $_5$ Me $_5$) $_2$ ClY(μ -Cl)Y(C $_5$ Me $_5$) $_2$ and R $_3$ Al via eqs 7 and 8 is also straightforward. In this case, the bimetallic precursor already is half opened and complexation by R $_3$ Al can make the products directly. These complexes demonstrate that mixed alkyl chloride complexes can exist and do not simply ligand redistribute to make (C $_5$ Me $_5$) $_2$ Ln(μ -Cl) $_2$ AlR $_2$ species that so readily form in eqs 1, 2, and 4. Prior to this study no mixed halide alkyl lanthanide metallocenes had been isolated as far as we know.

Improved Syntheses Based on Divalent Precursors. In connection with the carboxylate reactivity studies, an improved route to the (C $_5$ Me $_5$) $_2$ Sm(μ -Cl) $_2$ AlR $_2$ complexes was found starting with the divalent precursor (C $_5$ Me $_5$) $_2$ Sm(THF) $_2$, according to eq 4. This reaction has direct precedent in the reactions of Sm(II) metallocenes with R $_3$ Al, which form [(C $_5$ Me $_5$) $_2$ Sm(R $_2$ AlR $_2$)] $_x$ complexes and Al.^{35–37} Ligand redistribution again is observed in eq 4 as it was in eqs 1 and 2. These reactions also show the preference of samarium and aluminum to be bridged by two chloride ligands rather than by an alkyl group and a chloride. The (C $_5$ Me $_5$) $_2$ Sm(THF) $_2$ /Et $_3$ Al reaction, eq 6, differs from the Me $_3$ Al analogue in that THF is retained and an unusual η^2 -ethyl-bridged complex is isolated.

Methyl versus Ethyl versus Isobutyl Differentiation. Variations in organolanthanide/organoaluminum reactivity as a function of the R group may provide the reasons that ethyl aluminum reagents are routinely preferred in the first step of making diene polymerization catalysts, and methyl aluminum complexes are generally not thought to be active as activators in the last step. Isobutyl aluminum and ethyl aluminum complexes are preferred for the last step, possibly

because they can β -hydrogen eliminate to make hydrides. Prior to this study, the reasons for the preference for Et in the first step were not as easily postulated.

The formation of (C $_5$ Me $_5$) $_2$ Sm(THF)(μ - η^2 -Et)AlEt $_3$, 4, from (C $_5$ Me $_5$) $_2$ Sm(THF) $_2$ and Et $_3$ Al versus formation of (C $_5$ Me $_5$) $_2$ SmMe(THF) in the methanol analogue³⁵ is a clear differentiation in the organolanthanide chemistry of Et $_3$ Al and Me $_3$ Al. This reaction and the isolation of 4 show another way in which Et could be unique over Me: the structure of 4 (as well as that of the divalent ytterbium analogue⁴¹) shows that an ethyl aluminum moiety can bind η^2 to a metal. This could provide a method to protect an additional coordination site of the metal while more monomer is coming into the metal center to coordinate before insertion. The importance of agostic metal alkyl interactions is well discussed in olefin polymerization chemistry as a means to stabilize reactive intermediates.^{48,49} The larger alkyl aluminum complexes could be preferred over methyl complexes for similar reasons since they could provide stabilization via η^2 -interactions.

Another difference between methyl and ethyl that was identified in this study is the fact that the methyl complex [(C $_5$ Me $_5$) $_2$ Y(μ -Cl)(μ -Me)AlMe $_2$] $_2$, 5, prefers to exist in the solid state as a methyl-bridged dimer, in contrast to monomeric (C $_5$ Me $_5$) $_2$ Y(μ -Cl)(μ -Et)AlEt $_2$, 6. The isobutyl complex (C $_5$ Me $_5$) $_2$ Y(μ -Cl)(μ - i -Bu)Al(i -Bu) $_2$, 7, also exists in the solid state as a monomer. This is likely due to the facility by which methyl groups form linear M–R–M' bridges compared to ethyl or isobutyl. This may also be a factor in determining why methyl aluminum reagents are not as favored for lanthanide-based isoprene polymerization. If formation of oligomeric complexes via methyl bridges is detrimental, then the ethyl and isobutyl aluminum reagents would be preferred.

Conclusions

These studies show that in at least the well-defined coordination environment provided by two pentamethylcyclopentadienyl ligands, R $_2$ AlCl reagents react with a lanthanide carboxylate ligand to deliver chloride. The product is not a simple chloride for carboxylate exchange product, however, but a mixed metal complex containing aluminum bridged by two chloride ligands, [(C $_5$ Me $_5$) $_2$ Ln(μ -Cl) $_2$ AlR $_2$]. The [(C $_5$ Me $_5$) $_2$ LnCl] $_2$ /AlR $_3$ reactions show that mono-chloro mono-alkyl mixed bridged complexes {(C $_5$ Me $_5$) $_2$ Ln[(μ -Cl)(μ -R)AlR $_2$]} $_x$ can form and are stable. However, in the R $_2$ AlCl/[(C $_5$ Me $_5$) $_2$ Ln(carboxylate)] $_2$ as well as the (C $_5$ Me $_5$) $_2$ Sm(THF) $_2$ /Et $_2$ AlCl reaction, dichlorides are apparently favored.

Although the alkyl aluminum carboxylate chemistry in the R $_2$ AlCl reactions is similar for Et, Me, and i Bu, this study shows that ethyl aluminum complexes can form η^2 -ethyl complexes with trivalent lanthanides, a coordination linkage not possible for methyl. Methyl- and ethyl-bridged complexes can also differ in that methyl tends to form linear Ln–Me–Al bridged dimers more readily than ethyl. Hence, ethyl aluminum reagents may be preferred because they can lead to enhanced ligation of intermediates and may keep bridging to a minimum in reactions with lanthanides.

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Experimental Section

The chemistry described below was performed under argon or nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Solvents were saturated with UHP grade argon and dried by passage through drying columns by GlassContour (Irvine, CA). $[(C_5Me_5)_2YCl]_2$,³¹ $(C_5Me_5)_2Sm(THF)_2$,⁵⁰ and $(C_5Me_5)_2Sm(AlEt_4)_3$ ³⁶ were prepared as described in the literature. Me_3Al , Et_3Al , iBu_3Al , Me_2AlCl , Et_2AlCl , and iBu_2AlCl were purchased from Aldrich and used as specified. 1H , ^{13}C , and ^{27}Al NMR spectra were obtained using an Omega 500 MHz and a GN 500 MHz NMR spectrometer. ^{27}Al NMR shifts are referenced to 1 M $AlCl_3$ in H_2O . Infrared spectra were recorded as thin films on an ASI ReactIR 1000 spectrometer.⁵¹ Complexometric analyses were performed as previously described.⁵² Complexometric titration of yttrium in mixed yttrium–aluminum complexes was done in the presence of triethanolamine.⁵³ Elemental analyses were performed by Desert Analytics (Tucson, AZ) and Analytische Laboratorien (Lindlar, Germany).

$(C_5Me_5)_2Sm(\mu-Cl)_2AlEt_2$, 1. $(C_5Me_5)_2Sm(THF)_2$ (0.076 g, 0.13 mmol) was dissolved in 5 mL of toluene and cooled to $-35^\circ C$. Et_2AlCl (0.67 mL of a 1 M solution, 0.65 mmol) was added dropwise via syringe to the toluene solution and stirred overnight to give a red solution. Removal of solvent under vacuum yielded a red solid. X-ray quality crystals of **1** were grown from a concentrated toluene solution at $-35^\circ C$ (0.046 g, 59%). Anal. Calcd for $C_{24}H_{40}AlCl_2Sm$: Sm, 26.07; Al, 4.67; Cl, 12.29; C, 49.97; H, 6.99. Found: Sm, 26.08; Al, 5.00; Cl, 12.74; C, 48.70; H, 6.98. 1H NMR (C_6D_6 , $25^\circ C$): δ 0.28 (s, 30H, C_5Me_5), 0.48 (q, 2H, $MeCH_2$), 0.86 (t, 3H, $MeCH_2$). ^{13}C NMR (C_6D_6): δ 120.0 (C_5Me_5), 20.6 (C_5Me_5), 9.7 ($Al-CH_2Me$), 5.6 ($Al-CH_2Me$). IR (thin film): 3092 w, 3038 w, 2895 s, 2856 s, 2791 w, 2729 w, 2532 w, 1961 w, 1814 w, 1579 w, 1478 m, 1451 m, 1382 w, 1347 w, 1262 m, 1227 w, 1181 m, 1096 w, 1015 m, 984 w, 946 w, 857 w, 838 w, 803 w, 780 w, 680 m, 548 w, 529 cm^{-1} .

$(C_5Me_5)_2Sm(\mu-Cl)_2AlEt_2$, 1, from $[(C_5Me_5)_2Sm(O_2CPh)]_2$. Et_2AlCl (0.11 mL of a 1 M solution, 0.11 mmol) was added by syringe to a yellow solution of $[(C_5Me_5)_2Sm(O_2CPh)]_2$ (0.028 g, 0.026 mmol) in 5 mL of toluene. The solution turned red after 4 h and was stirred overnight. Removal of solvent under vacuum left a red oil, from which **1** could be isolated by recrystallization from a concentrated toluene solution (23 mg, 76%).

$(C_5Me_5)_2Sm(\mu-Cl)_2AlMe_2$, 2. In a fashion similar to **1**, $(C_5Me_5)_2Sm(THF)_2$ (0.41 g, 0.73 mmol) was dissolved in 5 mL of toluene and cooled to $-35^\circ C$. Me_2AlCl (1.9 mL, 5.0 mmol) was added dropwise via syringe to the cooled toluene solution and stirred overnight to give a red solution. The solution was centrifuged to remove insoluble aluminum metal. Removal of solvent under vacuum yielded a red solid (0.26 g, 66%). X-ray quality crystals of **2** were grown from a concentrated toluene solution at $-35^\circ C$. Anal. Calcd for $C_{22}H_{36}AlCl_2Sm$: Sm, 27.40; Al, 4.92; C, 48.15; H, 6.61. Found: Sm, 27.70; Al, 5.06; C, 47.99; H, 6.70. 1H NMR (C_6D_6 , $25^\circ C$): δ 1.13 (s, 6, Me), 0.28 (s, 30H, C_5Me_5). ^{13}C NMR (C_6D_6): δ -4.4 ($Al-Me$), 20.4 (C_5Me_5), 120.5 (C_5Me_5). IR (thin film): 3092 w, 3038 w, 2895 s, 2856 s, 2791 w, 2729 w, 2532 w, 1961 w, 1814 w, 1579 w, 1478 m, 1451 m, 1382 w, 1347 w, 1262 m, 1227 w, 1181 m, 1096 w, 1015 m, 984 w, 946 w, 857 w, 838 w, 803 w, 780 w, 680 m, 548 w, 529 cm^{-1} .

$(C_5Me_5)_2Sm(\mu-Cl)_2AlMe_2$, 2, from $[(C_5Me_5)_2Sm(O_2CPh)]_2$. Me_2AlCl (0.15 mL of a 1 M solution, 0.15 mmol) was added by

syringe to $[(C_5Me_5)_2Sm(O_2CPh)]_2$ (41 mg, 0.038 mmol) in toluene (5 mL). The solution turned red after 4 h and was stirred overnight. Removal of solvent under vacuum left a red oil, from which **2** was isolated by recrystallization from a concentrated toluene solution (29 mg, 71%).

$(C_5Me_5)_2Sm(\mu-Cl)_2Al(iBu)_2$, 3. iBu_2AlCl (135 μL , 0.69 mmol) was added via syringe to $(C_5Me_5)_2Sm(THF)_2$ (79 mg, 0.14 mmol) in benzene (10 mL). After the mixture was heated to reflux overnight, the solution was deep red. Removal of solvent under vacuum yielded **3** as a red solid (64 mg, 72%). X-ray quality crystals were grown from a concentrated solution in toluene layered with $(Me_3Si)_2O$. Anal. Calcd for $C_{28}H_{48}AlCl_2Sm$: Sm, 23.64. Found: Sm, 24.54. 1H NMR (C_6D_6 , $25^\circ C$): δ 0.30 (s, 30H, C_5Me_5), 0.65 (d, 2H, Me_2CHCH_2), 1.24 (d, 6H, Me_2CHCH_2), 2.2 (m, 1H, Me_2CHCH_2). ^{13}C NMR (C_6D_6): δ 20.4 (C_5Me_5), 120.6 (C_5Me_5), 24.8 (Me_2CHCH_2), 26.4 (Me_2CHCH_2), 28.2 (Me_2CHCH_2). ^{27}Al NMR (C_6D_6): δ 50.8. IR (thin film): 2949 s, 2922 m, 2891 s, 2861 m, 1463 m, 1401 w, 1378 m, 1328 m, 1262 w, 1181 m, 1162 w, 1065 m, 1007 m, 919 w, 857 m, 780 m, 730 w, 688 cm^{-1} .

$(C_5Me_5)_2Sm(\mu-Cl)_2Al(iBu)_2$, 3, from $[(C_5Me_5)_2Sm(O_2CPh)]_2$. iBu_2AlCl (135 μL , 0.69 mmol) was added by syringe to $[(C_5Me_5)_2Sm(O_2CPh)]_2$ (0.150 g, 0.14 mmol) in toluene (10 mL). The solution turned from yellow to red after stirring overnight. Removal of solvent under vacuum left a red oil, from which **3** was isolated by recrystallization from a concentrated toluene solution (121 mg, 69%).

$(C_5Me_5)_2Sm(THF)(\mu-\eta^2-Et)AlEt_3$, 4, from $(C_5Me_5)_2Sm(THF)_2$. Et_3Al (4.8 mL of a 1 M solution, 4.8 mmol) was added dropwise via syringe to a solution of $(C_5Me_5)_2Sm(THF)_2$ (0.68 g, 1.2 mmol) in 5 mL of toluene and stirred overnight to give a red-orange solution. The solution was centrifuged to remove any insoluble materials. Removal of solvent under vacuum yielded a red solid (0.50 g, 65%). X-ray quality crystals of **3** were grown from a concentrated diethyl ether solution at $-35^\circ C$. Anal. Calcd for $C_{32}H_{58}AlOSm$: Sm, 23.64; Al, 4.24; C, 60.42; H, 9.19. Found: Sm, 23.74; Al, 4.41; C, 59.90; H, 9.30. 1H NMR (C_7D_8 , $25^\circ C$): δ 3.42 (m, 4H, THF), 1.88 (b, CH_2Me), 1.35 (b, CH_2Me), 0.99 (m, 4H, THF), 0.28 (s, 30H, C_5Me_5). 1H NMR (C_6D_6): δ 3.32 (m, 4H, THF), 1.44 (t, $^3J_{HH} = 8.1$ Hz, 12H, CH_2Me), 0.93 (m, 4H, THF), 0.54 (s, 30H, C_5Me_5), 0.23 (q, $^3J_{HH} = 8.1$ Hz, 8H, CH_2Me). ^{13}C NMR (C_6D_6): δ 118.4 (C_5Me_5), 71.0 (THF), 25.2 (THF), 20.0 (C_5Me_5), 10.6 (CH_2Me), 0.26 (CH_2Me). IR (thin film): 2895 s, 2856 s, 2795 w, 2729 w, 1444 m, 1382 m, 1293 w, 1262 m, 1231 w, 1185 m, 1150 w, 1119 m, 1027, 984 m, 950 m, 838 m, 780 w, 703 w, 656 m, 533 cm^{-1} .

$(C_5Me_5)_2Sm(THF)(\mu-\eta^2-Et)AlEt_3$, 4, from $(C_5Me_5)_2Sm(\mu-Et)_2AlEt_2$. THF (8 μL , 0.09 mmol) was added via a syringe to $(C_5Me_5)_2Sm(\mu-Et)_2AlEt_2$ (0.051 g, 0.09 mmol) in 7 mL of toluene and stirred overnight. The toluene solution was concentrated under vacuum, and X-ray quality crystals of **3** were grown at $-35^\circ C$ (0.054 g, 94%).

$(C_5Me_5)_2Y(\mu-Cl)(\mu-Et)AlEt_2$, 5. Et_3Al (0.17 mL of a 1 M solution, 0.18 mmol) was added dropwise via syringe to a solution of $[(C_5Me_5)_2YCl]_2$ (69 mg, 0.09 mmol) in 5 mL of toluene and stirred overnight. Removal of solvent under vacuum yielded a white solid (0.81 g, 92%). Colorless cubes were grown from a concentrated toluene solution at $-35^\circ C$. Anal. Calcd for $C_{26}H_{45}AlClY$: Y, 17.47; Al, 5.30; C, 61.36; H, 8.91. Found: Y, 17.81; Al, 5.51; C, 60.56; H, 8.33. 1H NMR (C_6D_6 , $25^\circ C$): δ 1.88 (s, 30H, C_5Me_5), 1.46 (t, $^3J_{HH} = 7.8$ Hz, 9H, CH_2Me), 0.12 (q, $^3J_{HH} = 7.8$ Hz, 6H, CH_2Me). ^{13}C NMR (C_6D_6): δ 120.7 (C_5Me_5), 11.4 (C_5Me_5), 9.68 (CH_2Me), 3.49 (CH_2Me). IR (thin film): 3092 w, 3073 w, 3038 w, 2903 s, 2860 s, 2798 w, 2729 w, 1957 m, 1814 m, 1478 m, 1440 m, 1382 m, 1262 m, 1227 w, 1193 w, 1096 w, 1061 w, 1023 m, 988 w, 950 w, 838 w, 803 w, 764 w, 676 m, 544 cm^{-1} .

$(C_5Me_5)_2Y(\mu-Cl)(\mu-iBu)Al(iBu)_2$, 6. iBu_3Al (0.12 mL of a 1 M solution, 0.12 mmol) was added dropwise via syringe to a solution of $[(C_5Me_5)_2YCl]_2$ (49 mg, 0.062 mmol) in 5 mL of toluene and stirred overnight. Removal of solvent under

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vacuum yielded a white solid (0.035 g, 95%). Colorless cubes were grown from a concentrated toluene solution at -35°C . Anal. Calcd for $\text{YAlClC}_{32}\text{H}_{57}$: Y, 14.99; Al, 4.55; Cl, 5.98; C, 64.80; H, 9.69. Found: Y, 16.06; Al, 5.25; Cl, 5.88; C, 62.38; H, 9.83. ^1H NMR (C_6D_6): δ 1.89 (s, 30H, C_5Me_5), 2.9 (m, $^3J_{\text{HH}} = 6.6$ Hz, 1H, Me_2CHCH_2), 1.24 (d, $^3J_{\text{HH}} = 6.5$ Hz, 18H, CH_2CHMe_2), 0.27 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, CH_2CHMe_2). ^{13}C NMR (C_6D_6): δ 121.7 (C_5Me_5), 29.1 (C_5Me_5), 27.5 (CH_2CHMe_2), 25.9 (CH_2CHMe_2), 12.0 (CH_2CHMe_2). IR (thin film): 2949 s, 2914 s, 2860 s, 2729 w, 1459 m, 1401 m, 1378 m, 1363 w, 1320 m, 1262 w, 1177 m, 1061 m, 1015 m, 946 w, 834 w, 811 w, 679 m, 548 w, 529 cm^{-1} .

$[(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-Me})\text{AlMe}_2]_2$, 7. Me_3Al (19 μL , 0.19 mmol) was added dropwise via syringe to a solution of $[(\text{C}_5\text{Me}_5)_2\text{YCl}]_2$ (75 mg, 0.09 mmol) in 5 mL of benzene and stirred overnight. Removal of solvent under vacuum yielded a white solid (0.085 g, 96%). Colorless cubes were grown from a concentrated benzene solution at room temperature. Anal. Calcd for $\text{C}_{23}\text{H}_{39}\text{AlCl}_2\text{Y}$: Y, 19.06; Cl, 7.61. Found: Y, 19.25; Cl, 7.00. ^1H NMR (C_6D_6): δ 1.92, 1.89 (s, 60H, C_5Me_5), 1.82 (s, 9H), -0.07 (s), -0.29 (s), -0.49 (d). ^1H NMR (C_7D_8): δ 1.89 (s, 60H, C_5Me_5), 1.79 (s), -0.12 (s), -0.36 (s), -0.53 (d). ^{13}C NMR (C_6D_6): δ 120.8 (C_5Me_5), 120.7 (C_5Me_5), 119.6 (C_5Me_5), 11.9 (C_5Me_5), 11.7 (C_5Me_5), -3.6 (Al-Me). IR (thin film): 2964 m, 2907 m, 2860 m, 1610 m, 1440 m, 1378 w, 1262 s, 1208 m, 1089 m, 1019 s, 799 m, 703 m, 521 cm^{-1} .

$(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{AlMe}_2$, 8. Me_2AlCl (38.5 μL , 0.41 mmol) was added dropwise via syringe to a stirred suspension of $[(\text{C}_5\text{Me}_5)_2\text{YCl}]_2$ (162 mg, 0.21 mmol) in 5 mL of toluene. A clear solution immediately formed, and the reaction was stirred for 2 h. Removal of solvent under vacuum yielded a white solid (192 mg, 94%). X-ray quality crystals were grown from a concentrated solution in toluene. Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{Al}_2\text{Y}$: Y, 18.2. Found: Y, 18.3. ^1H NMR (C_6D_6): δ 1.88 (s, 30H, C_5Me_5), -0.066 (s, 6H, Al-Me). ^{13}C NMR (C_6D_6): δ -5.1 (Al-Me), 11.4 (C_5Me_5), 120.5 (C_5Me_5). ^{27}Al NMR (C_6D_6): δ 52.9. IR (thin film): 2922 m, 2864 m, 1606 m, 1494 s, 1459 m, 1382 m, 1212 w, 1158 w, 1104 w, 1081 m, 1031 m, 965 w, 930 w, 895 w, 803 m, 784 m, 721 m, 691 cm^{-1} .

$(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{AlEt}_2$, 9. Following the above procedure Et_2AlCl (55 μL , 0.44 mmol) was added to $[(\text{C}_5\text{Me}_5)_2\text{YCl}]_2$ (166 mg, 0.21 mmol) to give **9** as a white solid (199 mg, 92%). X-ray quality crystals were grown from a concentrated solution in hexane. Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{Cl}_2\text{Al}_2\text{Y}$: Y, 17.3. Found: Y, 17.3. ^1H NMR (C_6D_6): δ 1.88 (s, 30H, C_5Me_5), 0.55 (q, $^3J_{\text{HH}} = 8.1$ Hz, 2H, MeCH_2), 1.39 (t, $^3J_{\text{HH}} = 8.2$ Hz, 3H, MeCH_2). ^{13}C NMR (C_6D_6): δ 3.3 (Al- CH_2Me), 8.7 (Al- CH_2Me), 11.3 (C_5Me_5), 120.5 (C_5Me_5). ^{27}Al NMR (C_6D_6): δ 53.2. IR (thin film): 2957 s, 2918 s, 2864 s, 1382 m, 1262 w, 1227 w, 1189 w, 1166 w, 1096 w, 1061 w, 1023 m, 984 m, 949 w, 922 w, 803 m, 703 m, 652 cm^{-1} .

$(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{Al}(\text{iBu})_2$, 10. Following the above procedure iBu_2AlCl (85 μL , 0.44 mmol) was added to $[(\text{C}_5\text{Me}_5)_2\text{YCl}]_2$ (174 mg, 0.22 mmol) in 10 mL of toluene to yield **10** as a white solid (229 mg, 91%). X-ray quality crystals were grown from a

concentrated solution in hexane layered with $(\text{Me}_3\text{Si})_2\text{O}$. Anal. Calcd for $\text{C}_{28}\text{H}_{48}\text{Cl}_2\text{Al}_2\text{Y}$: Y, 15.0. Found: Y, 15.1. ^1H NMR (C_6D_6): δ 1.90 (s, 30H, C_5Me_5), 2.9 (m, $^3J_{\text{HH}} = 6.5$ Hz, 1H, Me_2CHCH_2), 1.24 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, Me_2CHCH_2), 0.65 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H, Me_2CHCH_2). ^{13}C NMR (C_6D_6): δ 11.4 (C_5Me_5), 120.5 (C_5Me_5), 25.5 (Me_2CHCH_2), 26.5 (Me_2CHCH_2), 28.2 (Me_2CHCH_2). ^{27}Al NMR (C_6D_6): δ 50.5. IR (thin film): 2953 s, 2922 s, 2864 s, 1401 m, 1378 m, 1324 w, 1181 w, 1162 w, 1065 m, 1019 m, 946 w, 811 m, 687 cm^{-1} .

X-ray Data Collection, Structure Determination, and Refinement. **$(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Cl})_2\text{AlMe}_2$, 2.** A red crystal of approximate dimensions $0.14 \times 0.16 \times 0.24$ mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART⁵⁴ program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT⁵⁵ and SADABS⁵⁶ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁷ program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later determined to be correct. The structure was solved by direct methods and refined on F_2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁸ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference Fourier map and refined (x , y , z and U_{iso}). At convergence, $wR_2 = 0.0461$ and $\text{GOF} = 0.0199$ for 379 variables refined against 5888 unique data. As a comparison for refinement on F , $R_1 = 0.0199$ for those 5189 data with $I > 2.0\sigma(I)$. The structures of complexes **1**, **3–6**, and **8–10** were determined similarly. Experimental parameters for data collection and structure refinement are given in Table 2.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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