

# Reactivity of Trimethylaluminum with Lanthanide Aryloxides: Adduct and Tetramethylaluminate Formation

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The reaction of various highly substituted lanthanide(III) and -(II) aryloxide complexes with trimethylaluminum (TMA) was investigated. The solvent-free,  $\pi$ -arene-bridged dimers  $[\text{Ln}(\text{OAr}^{\text{Pr,H}})_3]_2$ , derived from the ortho- $i\text{Pr}_2$ -substituted aryloxide ligand  $\text{OC}_6\text{H}_3^{\text{Pr}_2-2,6}$ , form bis-TMA adduct complexes,  $\text{Ln}(\text{OAr}^{\text{Pr,H}})_3(\text{AlMe}_3)_2$ , for the metal centers yttrium, samarium, and lanthanum. Homoleptic monomeric  $\text{Ln}(\text{OAr})_3$ , featuring a large La center and sterically bulkier ortho- $t\text{Bu}_2$ -substituted aryloxide ligands, afford the mono-TMA adducts  $\text{La}(\text{OAr}^{\text{Bu,R}})_3(\text{AlMe}_3)$  ( $\text{R} = \text{H}, \text{Me}$ ). The hetero-bridged moieties “ $\text{Ln}(\mu\text{-OAr})(\mu\text{-Me})\text{Al}$ ” of these adduct complexes are rigid in solution, while at ambient temperature the exchange of bridging and terminal aluminum methyl groups is fast on the NMR time scale. Monomeric  $\text{Ln}(\text{OAr}^{\text{Bu,R}})_3$  ( $\text{R} = \text{H}, \text{Me}, t\text{Bu}$ ) of the smaller rare-earth-metal centers yttrium and lutetium react with TMA to give mono(tetramethylaluminate) complexes of the type  $(\text{Ar}^{\text{Bu,R}}\text{O})_2\text{Ln}[(\mu\text{-Me})_2\text{AlMe}_2]$ . The heteroleptic  $\text{Cp}^*$ -supported complex  $(\text{C}_5\text{Me}_5)\text{Y}(\text{OAr}^{\text{Bu,H}})_2$  also produced a tetramethylaluminate complex, namely  $(\text{C}_5\text{Me}_5)\text{Y}(\text{OAr}^{\text{Bu,H}})[(\mu\text{-Me})_2\text{AlMe}_2]$ , in the TMA reaction. The solvated aryloxide complexes  $\text{Ln}(\text{OAr})_2(\text{THF})_x$  ( $x = 1, 2$ ), featuring the divalent rare-earth-metal centers ytterbium and samarium, yield the bis-TMA adduct complexes  $\text{Ln}[(\mu\text{-OAr}^{\text{Bu,R}})(\mu\text{-Me})\text{AlMe}_2]_2$ . However, it was found that the generation of homoleptic hexane-insoluble  $[\text{Ln}(\text{AlMe}_4)_2]_n$  is an important reaction pathway governed by the size (oxophilicity) of the metal center ( $\text{Yb} \gg \text{Sm}$ ), the amount of TMA, the reaction period, and the substituents of the aryloxide ligand ( $\text{OAr}^{\text{Pr,H}} \gg \text{OAr}^{\text{Bu,H}} > \text{OAr}^{\text{Bu,Me}} \gg \text{OAr}^{\text{Bu,tBu}}$ ). For the Ln(III) aryloxide complexes, peralkylated complexes  $\text{Ln}(\text{AlMe}_4)_3$  were detected only in the presence of the least bulky ligand,  $\text{OAr}^{\text{Pr,H}}$ . Various mechanistic scenarios are depicted on the basis of the rare-earth-metal species identified, including byproducts such as  $[\text{Me}_2\text{Al}(\mu\text{-OAr})_2]$ , and of the interactivity of rare-earth alkoxide complexes with trialkylaluminum compounds known from the literature. The complexes  $\text{Y}(\text{OC}_6\text{H}_3^{\text{Pr}_2-2,6})[(\mu\text{-OC}_6\text{H}_3^{\text{Pr}_2-2,6})(\mu\text{-Me})\text{AlMe}_2]_2$  and  $\text{Ln}(\text{OC}_6\text{H}_3^{\text{Bu}_2-2,6})_2[(\mu\text{-Me})_2\text{AlMe}_2]$  ( $\text{Ln} = \text{Y}, \text{Lu}$ ) have been characterized by X-ray diffraction structure determinations.

## Introduction

Multicomponent Ziegler–Natta systems implicating rare-earth alkoxides and organoaluminum compounds display efficient polymerization catalysis: e.g., in diene and styrene polymerization.<sup>1</sup> As a consequence, there has been considerable interest in examining the interac-

tion of trialkylaluminum reagents with rare-earth-metal alkoxide and aryloxide complexes. In the course of these studies various Ln–Al heterobimetallic complexes have been isolated.<sup>2–10</sup> Table 1 summarizes structurally

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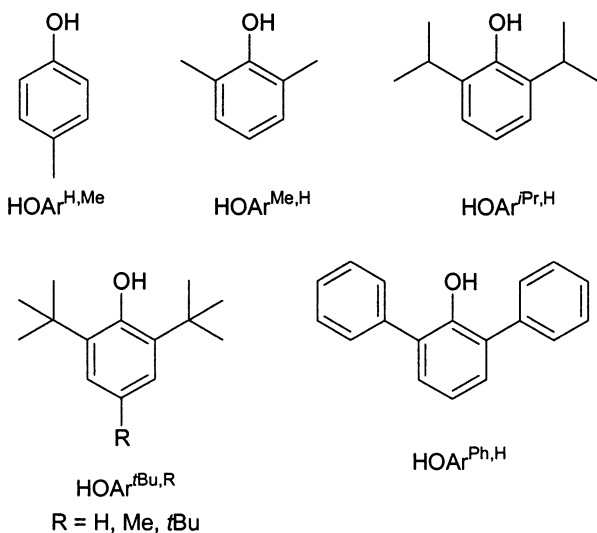
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**Table 1. Selected Bridging Bond Distances (Å) of Structurally Characterized Ln–Al Heterobimetallic Alkyl Complexes**

	$d(\text{Ln}-\text{O})$	$d(\text{Al}-\text{O})$	$d(\text{Ln}-\text{C})$	$d(\text{Al}-\text{C})$
$\text{Ln}(\mu\text{-OR})(\mu\text{-alkyl})\text{Al}(\text{alkyl})_2$				
$\text{Y}[(\mu\text{-O}t\text{Bu})(\mu\text{-Me})\text{AlMe}_2]_3$ <sup>2</sup>	2.21(1)	1.86(2)	2.69(3)	2.10(2)
$\text{Nd}[(\mu\text{-O}t\text{Bu})(\mu\text{-Me})\text{AlMe}_2]_3$ <sup>3</sup>	2.303(7)	1.871(7)	2.78(1)	2.05(2)
$(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Y}[(\mu\text{-O}t\text{Bu})(\mu\text{-Me})\text{AlMe}_2]_2$ <sup>4</sup>	2.280(4)	1.841(4)	2.562(6)	2.025(7)
$(t\text{BuO})(\text{THF})\text{Y}[(\mu\text{-O}t\text{Bu})(\mu\text{-Me})\text{AlMe}_2]_2$ <sup>2</sup>	2.254 <sup>a</sup>	1.841 <sup>a</sup>	2.702 <sup>a</sup>	2.052 <sup>a</sup>
$(\text{Ar}^{\text{Pr,H}}\text{O})\text{Sm}[(\mu\text{-OAr}^{\text{Pr,H}})(\mu\text{-Me})\text{AlMe}_2]_2$ <sup>5</sup>	2.292 <sup>a</sup>	1.870 <sup>a</sup>	2.626 <sup>a</sup>	2.047 <sup>a</sup>
$(\text{Ar}^{\text{Pr,H}}\text{O})\text{La}[(\mu\text{-OAr}^{\text{Pr,H}})(\mu\text{-Me})\text{AlMe}_2]_2$ <sup>6</sup>	2.377 <sup>a</sup>	1.856 <sup>a</sup>	2.780 <sup>a</sup>	2.047 <sup>a</sup>
$(\text{Ar}^{\text{Pr,H}}\text{O})\text{Sm}[(\mu\text{-OAr}^{\text{Pr,H}})(\mu\text{-Et})\text{AlEt}_2]_2$ <sup>6</sup>	2.294 <sup>a</sup>	1.876 <sup>a</sup>	2.638 <sup>a</sup>	2.061 <sup>a</sup>
$\text{Ln}(\mu\text{-OR})_2\text{Al}(\text{alkyl})_2$				
$(\text{Ar}^{\text{Me,H}}\text{O})_2(\text{THF})_2\text{Yb}[(\mu\text{-OAr}^{\text{Me,H}})_2\text{AlMe}_2]_2$ <sup>7</sup>	2.306(8)	1.85(1)		
$(\text{Ar}^{\text{Me,H}}\text{O})_2(\text{THF})_2\text{Nd}[(\mu\text{-OAr}^{\text{Me,H}})_2\text{AlEt}_2]_2$ <sup>7</sup>	2.447(7)	1.810(8)		
$\text{Nd}[(\mu\text{-OAr}^{\text{H,Me}})_2\text{AlMe}_2]_3$ <sup>8</sup>	2.356 <sup>a</sup>	1.843 <sup>a</sup>		
$\text{Ln}(\mu\text{-OR})\text{Al}(\text{alkyl})_3$				
$[\text{Me}_3\text{Al}(\mu\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OME})\text{Eu}$	2.420(8) <sup>b</sup>	1.811(5) <sup>b</sup>		
$(\mu\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OME})_2\text{AlMe}_2]_2$ <sup>9</sup>	2.548(7) <sup>c</sup>	1.771(4) <sup>c</sup>		

<sup>a</sup> Average value. <sup>b</sup>  $\text{AlMe}_3$  unit. <sup>c</sup>  $\text{AlMe}_2$  unit.

**Chart 1. Phenols Used in the Literature and in This Work**

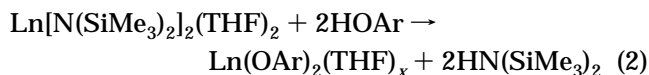
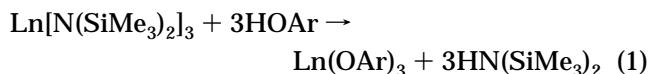
characterized derivatives according to the bonding mode of the organoaluminum moiety: that is, either  $\text{Ln}(\mu\text{-OR})(\mu\text{-alkyl})\text{Al}(\text{alkyl})_2$  or  $\text{Ln}(\mu\text{-OR})_x\text{Al}(\text{alkyl})_y$  ( $x = 1, 2$ ;  $y = 2, 3$ ;  $x + y = 4$ ). Interestingly, the formation of a “peralkylated”  $\text{Ln}(\mu\text{-alkyl})_x\text{Al}(\text{alkyl})_y$  fragment ( $x + y = 4$ ) has not yet been fully identified in such alkoxide-based *binary* systems. Note that the *ternary* system  $\text{Nd}(\text{O}i\text{Pr})_3/\text{AlEt}_3/\text{AlEt}_2\text{Cl}$  (1:10:1.5) formed crystals of molecular composition  $[\text{Al}_3\text{Nd}_6(\mu\text{-Cl})_6(\mu_3\text{-Cl})_6(\mu\text{-C}_2\text{H}_5)_9(\text{C}_2\text{H}_5)_5(\text{O}i\text{Pr})_2]$ , featuring a  $\text{Nd}(\mu\text{-Et})_3\text{AlEt}$  moiety, only after a period of several months.<sup>11</sup> Moreover, the formation of rare-earth alkyl species has been postulated for the binary systems  $\text{Nd}(\text{OR})_3/\text{Mg}n\text{Bu}_2$  and  $\text{Nd}(\text{OR})_3/\text{MgHex}_2$ .<sup>12</sup>

Recently, we started a systematic investigation of the alkylation capability of organoaluminum compounds toward rare-earth complexes with O-bonded ligands such as carboxylates, alkoxides, aryloxides, and silox-

ides, anticipating that steric factors and solubility behavior as well as the variation of the ligand  $\text{p}K_a$  value and the metal oxidation state might markedly affect the reaction protocol. Here we report on the reactivity of trimethylaluminum (TMA) toward variously substituted Ln(II) and Ln(III) aryloxide complexes.<sup>13</sup>

## Results and Discussion

**Synthesis of Lanthanide(III) and Lanthanide-(II) Aryloxides.** All of the lanthanide aryloxides were synthesized according to slightly modified literature procedures<sup>14,15</sup> using bis(trimethylsilyl)amide complexes  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  ( $\text{Ln} = \text{Y, La, Lu}$ )<sup>16</sup> and  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$  ( $\text{Ln} = \text{Sm, Yb}$ )<sup>17</sup> as starting materials (eqs 1 and 2). The silylamine elimination reactions were performed



in toluene at 110 °C (Ln(III)) or *n*-hexane at ambient temperature (Ln(II)), and the complexes were isolated by evaporating the solvent in vacuo. The analytical data are in agreement with those reported in the literature. For the divalent lanthanide aryloxides, the amount of coordinated tetrahydrofuran ( $x = 1, 2$ ) was determined by elemental analysis and, in the case of the ytterbium derivatives, by <sup>1</sup>H NMR spectroscopy.

**TMA Adduct Formation of Yttrium(III) and Lanthanum(III) Aryloxides.** Recently, Gordon et al. described the synthesis and structural characterization

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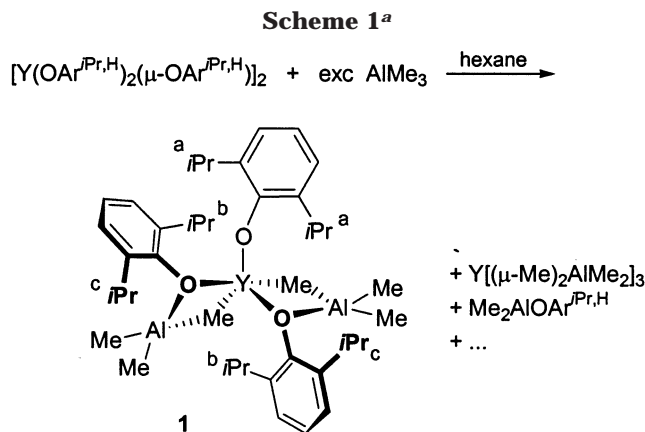
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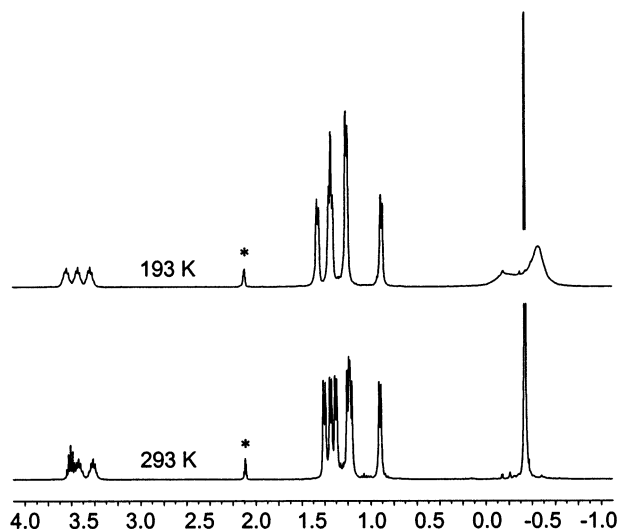


<sup>a</sup> The presence of different isopropyl groups in solution as shown by <sup>1</sup>H NMR spectroscopy is indicated by a, b, and c.

of bis(trialkylaluminum) adducts of lanthanide aryloxide complexes by employing 2,6-diisopropylphenoxide ligands and the *large* Ln(III) centers lanthanum and samarium.<sup>5,6</sup> The complexes Ln(OAr<sup>*i*Pr,H</sup>)<sub>3</sub>(AlR<sub>3</sub>)<sub>2</sub> (R = Me, Et) could be isolated from the reaction of the π-arene-bridged dimers [Ln(OAr<sup>*i*Pr,H</sup>)<sub>3</sub>] (Ln = La, Sm) with at least 4 equiv of AlR<sub>3</sub>. In the context of our Ziegler–Natta related work we have also been investigating the reactivity of TMA toward sterically crowded homoleptic yttrium and lanthanum aryloxides.

In accordance with the reactivity of the ortho-*i*Pr<sub>2</sub>-substituted aryloxide complexes of the heavier metal centers lanthanum and samarium, the reaction of the corresponding yttrium compound [Y(OAr<sup>*i*Pr,H</sup>)<sub>2</sub>(μ-OAr<sup>*i*Pr,H</sup>)<sub>2</sub>] with 6 equiv of TMA in *n*-hexane yielded the bis-TMA adduct Y(OAr<sup>*i*Pr,H</sup>)<sub>3</sub>(AlMe<sub>3</sub>)<sub>2</sub> (**1**) in 46% yield after 16 h at ambient temperature. Complex **1** could be separated from the reaction mixture by crystallization at –45 °C. A detailed investigation of the crude reaction mixture of the above reaction revealed the formation of three other products (Scheme 1). The homoleptic (peralkylated) yttrium tetramethylaluminate Y[(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>3</sub><sup>18</sup> and the corresponding aryloxide monoxide exchange product [Me<sub>2</sub>Al(μ-OAr<sup>*i*Pr,H</sup>)<sub>2</sub>] were unequivocally identified by <sup>1</sup>H NMR spectroscopy. The third compound also contains an aryloxide ligand; however, its full composition is still unclear.

In contrast to the lanthanum congener (two septets in a 2:1 ratio)<sup>5,6</sup> the ambient-temperature <sup>1</sup>H NMR spectrum of complex **1** shows three different septets at 3.44, 3.57, and 3.64 ppm for the isopropyl methine protons (integral ratio 2:2:2) and six doublets for the diastereotopic isopropyl methyl groups (integral ratio 6:6:6:6:6:6; Figure 1). On the other hand, the coordinated TMA molecules show only a single proton resonance at –0.29 ppm. This NMR scenario can be ascribed to a rather rigid structure of **1** in solution. First, the separate signal for the terminal aryloxide ligand excludes any TMA migration. Second, the two separate signals for the bridging aryloxide ligands indicate enhanced steric crowding at the yttrium center, which counteracts rotation about the O–C<sub>ipso</sub> axis. Finally and not surprisingly, the smaller bridging methyl groups rapidly exchange with the terminal ones at ambient



**Figure 1.** Region of the <sup>1</sup>H NMR spectrum (*d*<sub>8</sub>-toluene, 400 MHz) of complex **1** at various temperatures. The solvent signal is indicated by an asterisk.

temperature. However, the last fluxional process is suppressed at lowered temperature. Figure 1 shows that at –80 °C decoalescence of the TMA methyl resonance occurred into two separate signals (integral ratio: 2:1) representing the terminal and bridging methyl groups. Note that this decoalescence was not observed for the larger metal centers La and Sm.<sup>5,6</sup> The presence of Ln···H–C α-agostic interactions in solution, which have been discussed for the La and Sm derivatives, is not suggested by the relevant spectroscopic features of compound **1**. Both the <sup>1</sup>J<sub>C–H</sub> coupling constant of 108–109 Hz and ν<sub>CH</sub> stretching vibrations of >2900 cm<sup>–1</sup> are not indicative of any significant agostic bonding in complex **1**.

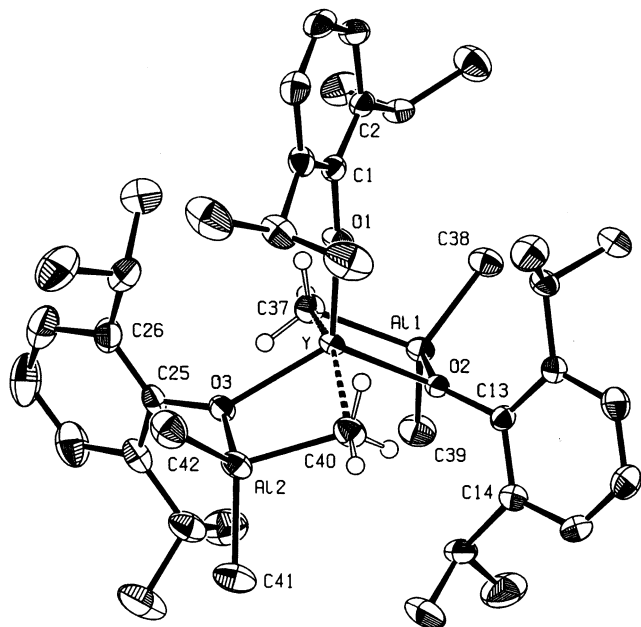
Recrystallization of TMA adduct **1** from saturated *n*-hexane solutions yielded single crystals suitable for an X-ray structure analysis. Its solid-state structure, which is structurally related to those previously reported for the samarium and lanthanum derivatives, is shown in Figure 2. Selected intramolecular bond distances and angles are presented in Table 2.

The five-coordinate yttrium center adopts a distorted-trigonal-bipyramidal geometry, the two bridging methyl groups occupying the apical position C37–Y–C40 angle (156.58(6)°). The terminal and bridging Y–O bond lengths of 2.023(1) and 2.230 Å (average), respectively, lie in the range of yttrium alkoxide complexes such as Cp\*Y(OAr<sup>*t*Bu,H</sup>)<sub>2</sub> (average 2.078 Å),<sup>19</sup> (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)Y[(μ-O*t*Bu)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub>, and Y[(μ-O*t*Bu)(μ-Me)AlMe<sub>2</sub>]<sub>3</sub> (Table 1). Another interesting aspect of the molecular structure is the coordination chemistry of the bridging five-coordinate carbon atoms, which display a distorted-trigonal-bipyramidal geometry with one hydrogen atom and the yttrium metal in the apical positions (∠Y–C–H = 175(1), 179(2)°). The hydrogen atoms of the bridging methyl groups were located and refined. The Y–C(μ) distance of 2.542 Å (average) is similar to the 2.562(6) Å in formally seven-coordinate (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)Y[(μ-O*t*Bu)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (Table 1).

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**Figure 2.** PLATON<sup>50</sup> drawing of the complex  $\text{Y}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Pr}_2\text{-}2,6)[(\mu\text{-OC}_6\text{H}_3\text{-}2,6\text{-Pr}_2\text{-}2,6)(\mu\text{-Me})\text{AlMe}_2]_2$  (**1**). Atoms are represented by atomic displacement ellipsoids at the 50% level.

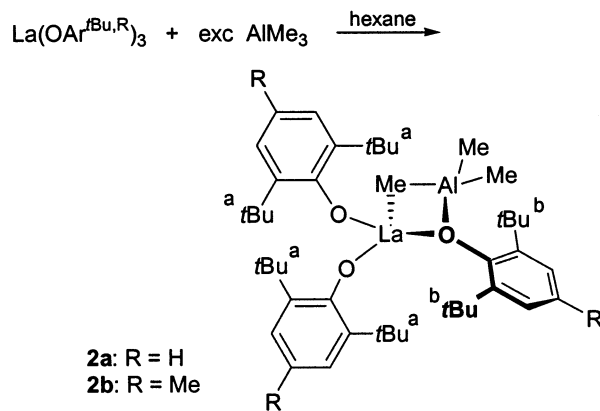
**Table 2. Selected Bond Lengths (Å) and Angles (deg) for  $(\text{ArO})\text{Y}[(\mu\text{-OAr})(\mu\text{-Me})\text{AlMe}_2]_2$  (**1**)**

Y–Al1	3.1924(5)	O1–C1	1.368(2)
Y–Al2	3.1871(6)	O2–Al1	1.861(1)
Y–O1	2.023(1)	O3–Al2	1.873(1)
Y–O2	2.231(1)	Al1–C37	2.069(2)
Y–O3	2.229(1)	Al1–C38	1.954(2)
Y–C37	2.544(2)	Al1–C39	1.962(2)
Y–C40	2.541(2)	Al2–C40	2.070(2)
O2–C13	1.409(2)	Al2–C41	1.962(2)
O3–C25	1.406(2)	Al2–C42	1.955(2)
O1–Y–O2	117.68(4)	O3–Y–C40	75.40(6)
O1–Y–O3	118.51(4)	C37–Y–C40	156.58(6)
O2–Y–O3	123.80(4)	Y–O1–C1	174.3(1)
O1–Y–C37	102.07(6)	Y–O2–C13	125.33(9)
O1–Y–C40	101.34(6)	Y–O3–C25	129.0(1)
O2–Y–C37	74.85(5)	Y–O2–Al1	102.17(5)
O2–Y–C40	94.90(6)	Y–O3–Al2	101.64(5)
O3–Y–C37	92.63(5)	Y–C37–H371	175(1)
		Y–C40–H402	179(2)

A similar reactivity was observed for the bulkier 2,6-di-*tert*-butylphenoxide ligand  $\text{OAr}^{\text{tBu,H}}$  and its 4-methyl-substituted derivative  $\text{OAr}^{\text{tBu,Me}}$ . However, use of an excess of TMA (> 4 equiv) in *n*-hexane yielded the mono-TMA adducts  $\text{La}(\text{OAr}^{\text{tBu,R}})_3(\text{AlMe}_3)$  (**2**) exclusively (Scheme 2). It appears plausible that the enhanced steric bulk of the *t*Bu vs the *i*Pr groups ensures the coordination of only one TMA molecule.

Complexes **2** were isolated via crystallization from saturated *n*-hexane solutions as colorless amorphous solids in good yields (**2a**, 83%; **2b**, 87%), which can be redissolved in aliphatic and aromatic solvents. Elemental analysis and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy confirmed the overall composition shown in Scheme 2. Two separated sets of  $\text{Ar}^{\text{tBu,R}}\text{O}$  resonances with an integral ratio of 2:1 were observed, although the mobility of the coordinated TMA at ambient temperature causes a distinct broadening of the signals. This observation is in good agreement with the integrity of the aluminum–oxygen bonds reported by Gordon and co-

**Scheme 2<sup>a</sup>**



<sup>a</sup> The presence of different *tert*-butyl groups in solution as shown by <sup>1</sup>H NMR spectroscopy is indicated by a and b.

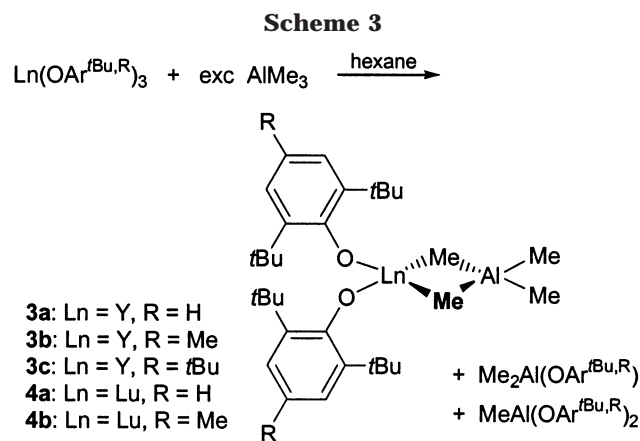
workers.<sup>5,6</sup> For complex **2a**, lowering of the temperature to  $-90$  °C gave a better separation of the aryloxy signals, while an additional decoalescence of the coordinated TMA into bridging and terminal methyl groups did not occur. Proton-coupled <sup>13</sup>C NMR spectra of complexes **2** showed at all temperatures (+20 to  $-90$  °C) quadruplet signals for the aluminum-bound methyl groups with <sup>1</sup>J<sub>C–H</sub> coupling constants of about 110 Hz, which are similar to those reported for  $(\text{Ar}^{\text{tPr,H}}\text{O})\text{La}[(\mu\text{-OAr}^{\text{tPr,H}})(\mu\text{-Me})\text{AlMe}_2]_2$ .<sup>6</sup> Such marginally decreased coupling constants have been associated with the presence of  $\text{La}\cdots\text{H}-\text{C}$   $\alpha$ -agostic interactions.<sup>6</sup> However, for complexes **2**, their infrared spectra recorded as Nujol mulls did not show any definite evidence for the presence of such agostic interactions in the solid state.

**Aryloxy–Tetramethylaluminate Interchange in Yttrium(III) and Lutetium(III) Aryloxides.** Surprisingly, the corresponding yttrium and lutetium aryloxy complexes displayed quite a different reaction behavior with TMA. Under identical reaction conditions—6 equiv of TMA, 16 h, ambient temperature—mono(tetramethylaluminate) complexes of the type  $(\text{Ar}^{\text{tBu,R}}\text{O})_2\text{Y}[(\mu\text{-Me})_2\text{AlMe}_2]$  (**3a**, R = H; **3b**, R = Me; **3c**, R = *t*Bu) and  $(\text{Ar}^{\text{tBu,R}}\text{O})_2\text{Lu}[(\mu\text{-Me})_2\text{AlMe}_2]$  (**4a**, R = H; **4b**, R = Me) formed along with  $[\text{Me}_2\text{Al}(\mu\text{-OAr}^{\text{tBu,R}})]_2$  and  $\text{MeAl}(\text{OAr}^{\text{tBu,R}})_2$  (Scheme 3).<sup>20,21</sup> It is worth noting that addition of 1 equiv of TMA did not produce a mono-TMA adduct, in analogy to the formation of  $\text{La}(\text{OAr}^{\text{tBu,R}})_3(\text{AlMe}_3)$  (**2**); instead, unreacted starting materials and complexes **3** and **4** were identified. In the >2 equiv reactions higher alkylated byproducts such as  $(\text{Ar}^{\text{tBu,R}}\text{O})\text{-Ln}[(\mu\text{-Me})_2\text{AlMe}_2]_2$  and even homoleptic “peralkylated” tetramethylaluminates  $\text{Ln}(\text{AlMe}_4)_3$  (**5**)<sup>18</sup> could not be detected independent of the amount of TMA (e.g., 12 equiv) and the reaction period (<4 days).

The aluminate complexes **3a,b** and **4** were isolated in moderate to good yields (55–70%) by repeated crystallization from *n*-hexane solutions at  $-45$  °C. Due to its high solubility in aliphatic solvents, it was only compound **3c** which could not be separated from the byproducts (characterization by NMR only). Microanalytical and NMR spectroscopic data are in agreement

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with the molecular composition of complexes **3** and **4** given in Scheme 3. The proton NMR spectra of the yttrium complexes showed characteristic doublets ( $^2J_{Y-H} = 3.7$  Hz) for the AlMe<sub>4</sub> moieties at 0.02 (**3a**), 0.04 (**3b**), and 0.03 ppm (**3c**), respectively. A variable-temperature NMR study revealed that a further separation of these signals into bridging and terminal methyl groups did not occur for complex **3a**, even at  $-90$  °C. However, for the lutetium complex **4a**, the sharp singlet of the AlMe<sub>4</sub> moiety at 0.30 ppm broadens into the baseline at  $-90$  °C, indicating reduced exchange of the bridging and terminal methyl groups at the smaller metal center (enhanced steric crowding!). The low-temperature NMR experiments also exclude the presence of the monomer–dimer equilibrium  $2(\text{ArO})_2\text{Ln}[(\mu\text{-Me})_2\text{AlMe}_2] \rightleftharpoons (\text{ArO})_2\text{-Ln}[(\mu\text{-Me})\text{AlMe}_2(\mu\text{-Me})_2\text{Ln}(\text{OAr})_2]$ . Such dimerization reactions are a common feature of structurally related lanthanidocene aluminate complexes of the type Cp\*<sub>2</sub>Ln(AlMe<sub>4</sub>).<sup>22–24</sup> The formation of a Ln-bonded tetramethylaluminate moiety in the solid state could be unequivocally proven by the X-ray structure analyses of complexes **3a** and **4a**. Single crystals were obtained by slowly cooling warm *n*-hexane solutions. The solid-state structure of **4a** is shown in Figure 3, and relevant intramolecular bond lengths and angles are presented in Table 3. Both tetramethylaluminates are isotypes and crystallize in the orthorhombic space group *Pbca*. The metal center is four-coordinated by two aryloxy oxygen atoms and one  $\eta^2$ -coordinating tetramethylaluminate ligand, resulting in a distorted-tetrahedral geometry. The molecular structure of the approximate C<sub>2</sub>-symmetric complexes **3a** and **4a** resembles those of structurally characterized lanthanidocene complexes of the type Cp<sub>2</sub>Ln( $\mu\text{-Me}$ )<sub>2</sub>AlMe<sub>2</sub>, featuring a different ancillary ligand set.<sup>25</sup>

The Ln–O bond distances of 2.023(2) and 2.032(2) Å (**3a**) and 1.999(3) and 2.006(3) Å (**4a**) are slightly longer than those reported for the homoleptic aryloxy Y(OAr<sup>tBu,H</sup>)<sub>3</sub> (average 2.00 Å),<sup>26</sup> which is in accord with their formally higher coordination number. For comparison,

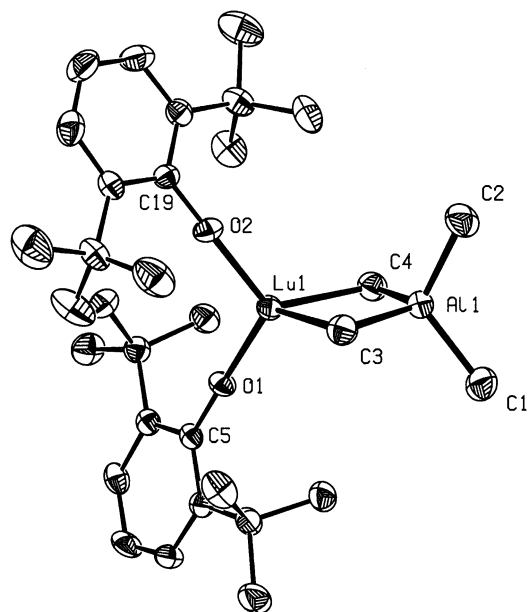
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**Figure 3.** PLATON<sup>50</sup> drawing of the complex Lu(OC<sub>6</sub>H<sub>3</sub>-tBu-2,6)<sub>2</sub>[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (**4a**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level.

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for (Ar<sup>tBu,H</sup>O)<sub>2</sub>Y[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (**3a**) and (Ar<sup>tBu,H</sup>O)<sub>2</sub>Lu[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (**4a**)**

	<b>3a</b> (Ln = Y)	<b>4a</b> (Ln = Lu)
Ln–Al	3.067(1)	3.000(1)
Ln–O1	2.023(2)	2.006(3)
Ln–O2	2.032(2)	1.999(3)
Ln–C3	2.500(4)	2.435(4)
Ln–C4	2.494(3)	2.425(4)
Al–C3	2.101(3)	2.105(4)
Al–C4	2.086(4)	2.101(4)
Al–C1	1.964(4)	1.966(6)
Al–C2	1.964(4)	1.965(5)
Ln–O1–C5	176.1(2)	178.6(2)
Ln–O2–C19	178.2(2)	177.4(2)
O1–Ln–O2	114.55(8)	114.4(1)
C3–Ln–C4	85.3(1)	88.03(1)
C3–Al–C4	107.8(1)	106.8(2)
C1–Al–C2	117.0(2)	116.9(2)

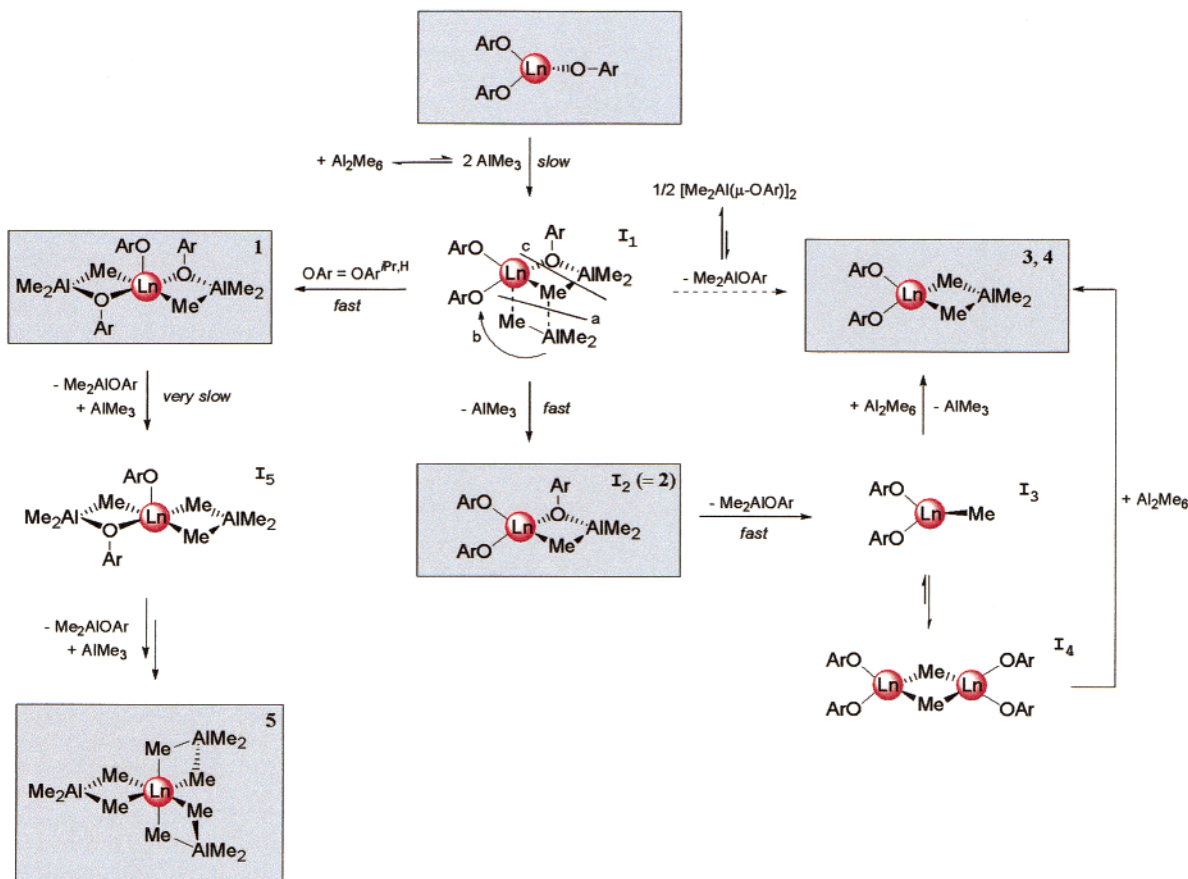
the five-coordinate complexes Lu(OAr<sup>tPr,H</sup>)<sub>3</sub>(THF)<sub>2</sub> and Lu[calix[4]arene(OBenz)<sub>2</sub>][N(SiHMe<sub>2</sub>)<sub>2</sub>] feature Lu–O(aryloxy) bond lengths of 2.043 and 2.011 Å (average), respectively.<sup>27,28</sup> The bond distances of the symmetric ( $\mu\text{-Me}$ )<sub>2</sub>AlMe<sub>2</sub> unit in **3a** are comparable to those of other hetero- and homoleptic tetramethylaluminates. The Y–C( $\mu$ ) distance of 2.497 Å (average) is similar to those in eight-coordinate Cp<sub>2</sub>Y( $\mu\text{-Me}$ )<sub>2</sub>AlMe<sub>2</sub> (2.58(4) Å)<sup>29</sup> and six-coordinate Y[( $\mu\text{-Me}$ )<sub>2</sub>AlMe<sub>2</sub>]<sub>3</sub> (2.505(7)–2.514(8) Å).<sup>18</sup> For comparison, the Lu–C( $\mu$ ) bond lengths in homometallic asymmetrically bridged Cp\*<sub>2</sub>Lu( $\mu\text{-Me}$ )LuCp\*<sub>2</sub>Me featuring seven- or eight-coordinate lutetium centers are 2.440(9) and 2.756(9) Å, respectively.<sup>30</sup> The slightly longer Y–Al distance of 3.067(1) Å (**3a**) in comparison to the 3.000(1) Å in **4a** reflects the larger size of the yttrium center. As reported earlier for the homoleptic

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**Scheme 4. Formation of TMA Adducts (1 and 2) and Tetramethylaluminates (3–5) from Lanthanide(III) Aryloxides<sup>a</sup>**


<sup>a</sup> Fully characterized complexes are shown in boxes ( $I_1$ : a–c indicate different reaction pathways).

aryloxides,<sup>26</sup> the Ln–O–C<sub>ipso</sub> angles of 176.1(2)/178.2(2)<sup>o</sup> (**3a**) and 177.4(2)/178.6(2)<sup>o</sup> (**4a**) are almost linear.

The formation of tetramethylaluminate units using homoleptic lanthanide aryloxides as starting materials has not been observed so far. In the case of the even less bulky 2,6-dimethylphenoxides Ln(OAr<sup>Me,H</sup>)<sub>3</sub>(THF)<sub>x</sub> (Ln = Y, Yb), Evans et al. have been able to isolate bis-(aryloxy)-bridged systems of the type (Ar<sup>Me,H</sup>O)<sub>2</sub>(THF)<sub>2</sub>-Ln[(μ-OAr<sup>Me,H</sup>)<sub>2</sub>AlR<sub>2</sub>].<sup>7</sup> Although the formation of further alkylated products was theorized, none could be isolated or characterized by spectroscopic methods. Labile alkylation products were also discussed by Gordon et al., resulting from the system Ln(OAr<sup>Pr,H</sup>)<sub>3</sub>(AlR<sub>3</sub>)<sub>2</sub> (R = Me, Et) via elimination of [R<sub>2</sub>Al(μ-OAr<sup>Pr,H</sup>)<sub>2</sub>].<sup>6</sup>

From the several products obtained from these TMA addition reactions, it appears that once the sterically crowded lanthanide(III) aryloxides start to react, several pathways are possible. Factors such as the size of the metal center, the steric bulk of the aryloxy ligand, and, hence, complex agglomeration govern the mechanistic scenario proposed in Scheme 4. Initial attack of TMA, which is a dimer in hexane solution, onto the tris-(aryloxy) complexes Ln(OAr)<sub>3</sub> appears to be the rate-determining step. Although coordination of additional donor molecules to formally three-coordinated homoleptic aryloxy complexes carrying the bulkiest aryloxy ligands has been structurally evidenced in, e.g., Sm(OAr<sup>tBu,Me</sup>)<sub>3</sub>(THF),<sup>31</sup> Yb(OAr<sup>tBu,tBu</sup>)<sub>3</sub>(THF),<sup>32</sup> and Ce-

(OAr<sup>tBu,H</sup>)<sub>3</sub>(CN<sup>tBu</sup>)<sub>2</sub>,<sup>33</sup> formation of intermediate  $I_1$  should be impeded for steric reasons. For ortho-*t*Bu<sub>2</sub>-substituted aryloxy ligands and large Ln metal centers such as lanthanum, elimination of “AlMe<sub>3</sub>” from  $I_1$  (route a in Scheme 4) yields the stable mono-TMA adduct **2** featuring truly bridging alkyl and aryloxy ligands (Table 2). Alternatively, complex **2** may be obtained by attack of monomeric “AlMe<sub>3</sub>” onto Ln(OAr)<sub>3</sub>. Note that TMA adducts are not produced from homoleptic Ln-[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> for steric reasons.<sup>34</sup> In the presence of the less bulky ortho-*i*Pr<sub>2</sub>-substituted aryloxy ligands, a bis-TMA adduct (**1**) is preferentially formed. This can occur via either intramolecular ligand reorientation in  $I_1$  (route b in Scheme 4) or addition of another “AlMe<sub>3</sub>” monomer to a mono-TMA adduct  $I_2$ .

The formation of mono(tetramethylaluminate) complexes **3** and **4** via aryloxy–alkyl interchange is the predominant pathway for smaller Ln metal centers carrying ortho-*t*Bu<sub>2</sub>-substituted aryloxy ligands. A possible *associative* mechanism requires the formation of intermediate  $I_1$  followed by cleavage of Me<sub>2</sub>AlOAr (route c in Scheme 4). The aluminum monoaryloxy may either dimerize to [Me<sub>2</sub>Al(μ-OAr)]<sub>2</sub><sup>6,35,36</sup> or dispro-

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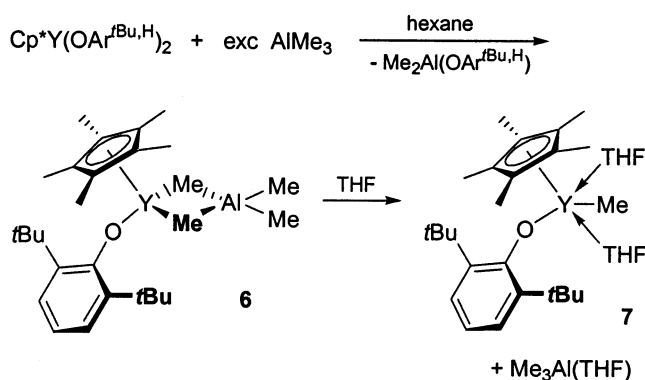
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Scheme 5



portionate to TMA and monomeric  $\text{MeAl}(\text{OAr})_2$ ,<sup>37</sup> counteracting reassociation with **I**<sub>1</sub>. However, not only for steric reasons do we favor a dissociative mechanism involving a mono-TMA adduct **I**<sub>2</sub> as an intermediate. For smaller rare-earth-metal centers, **I**<sub>2</sub> still displays steric oversaturation forcing  $\text{Me}_2\text{AlOAr}$  dissociation and generation of **I**<sub>3</sub>. This is in accord with the decreased oxophilicity of the smaller rare-earth-metal centers (disruption energy of metal monooxides,  $D_0(\text{MO})$ : La > Y > Lu >> Al).<sup>38</sup> Finally, sterically unsaturated **I**<sub>3</sub> is converted to heteroleptic tetramethylaluminates **3** and **4**. This may also proceed via the methyl-bridged intermediate **I**<sub>4</sub>. Such a sterically induced tetramethylaluminate formation is corroborated by (i) the kinetic lability of Ln–O(alkoxide/aryloxide) bonds,<sup>39,40</sup> (ii) the isolation of **I**<sub>2</sub> as the lanthanum derivative **2**, and (iii) the exclusive generation of mono(tetramethylaluminate) adduct and starting material from an equimolar reaction with Ln(OAr)<sub>3</sub>:TMA = 1:1. The kinetic control of this alkylation reaction is also evident from the formation of peralkylated species Ln[(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sub>3</sub> (**5**) in the presence of sterically less encumbered aryloxide ligands  $\text{OAr}^{\text{tPr,H}}$  as well as from the reaction behavior of Ln(II) aryloxides discussed in the following. The formation of homoleptic **5** probably proceeds via a series of other intermediates starting with **I**<sub>5</sub>.

**Alkylation of Cp\*-Supported Heteroleptic Yttrium(III) Aryloxides.** Aryloxide–tetramethylaluminate interchange is not restricted to homoleptic aryloxides. The reaction of TMA with  $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{OAr}^{\text{tBu,H}})_2$ , which was obtained via a salt metathesis reaction from  $\text{Y}(\text{OAr}^{\text{tBu,H}})_3$  and  $\text{NaCp}^*$ , yielded  $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{OAr}^{\text{tBu,H}})(\mu\text{-Me})_2\text{AlMe}_2$  (**6**). According to Scheme 5, again a single aryloxide ligand was eliminated as  $\text{Me}_2\text{Al}(\text{OAr}^{\text{tBu,H}})$ . Alkylated byproducts  $\text{Cp}^*\text{Y}(\text{AlMe}_4)_2$  and  $\text{Y}(\text{AlMe}_4)_3$  were not observed. Although crystals suitable for an X-ray structure determination were not obtained, microanalytical and NMR spectroscopic data are consistent with the molecular structure proposed in Scheme 5. At ambient temperature the tetramethylaluminate moiety in **6** exhibits a characteristic doublet at  $-0.15$  ppm (<sup>1</sup>H NMR, <sup>2</sup> $J_{\text{Y-H}} = 2.9$  Hz).

There is a distinct analogy to the reaction of  $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{OAr}^{\text{tBu,H}})_2$  with 1 equiv of methyl lithium, previously reported by Schaverien.<sup>41</sup> The methyl-bridged heteroleptic aryloxide  $[\text{Y}(\text{C}_5\text{Me}_5)(\text{OAr}^{\text{tBu,H}})(\mu\text{-Me})_2]_2$ , which was produced in the methyl lithium reaction, could be cleaved by addition of tetrahydrofuran to yield the monomeric complex  $(\text{C}_5\text{Me}_5)(\text{Ar}^{\text{tBu,H}}\text{O})\text{YMe}(\text{THF})_2$  (**7**), featuring a terminal methyl group (<sup>1</sup>H NMR  $\delta -0.33$  ppm (d, <sup>2</sup> $J_{\text{Y-H}} = 2.3$  Hz); <sup>13</sup>C NMR  $\delta 22.8$  ppm (d, <sup>1</sup> $J_{\text{Y-C}} = 60$  Hz)). Complex **7** was also formed via a donor-induced cleavage of complex **6**, as shown by the NMR spectrum of **6** recorded in *d*<sub>8</sub>-THF. The importance of the type of OR ligand for the outcome of the TMA-mediated alkylation is evident from the reaction of  $[\text{Cp}^*\text{Y}(\text{OR})_2]_2$  ( $\text{Cp}^* = \text{C}_5\text{H}_4\text{-SiMe}_3$ , R = *t*Bu) with TMA.<sup>4</sup> In this reaction, the bis-TMA adduct  $\text{Cp}^*\text{Y}[(\mu\text{-OR})(\mu\text{-Me})\text{AlMe}_2]_2$  was isolated in hexane solution after 8 h in high yield (90%).

**Reaction of TMA with Ytterbium(II) and Samarium(II) Aryloxides.** Although the reactivity of TMA toward various divalent ytterbium and samarium compounds has been examined,<sup>42</sup> aryloxide derivatives apparently escaped that attention. For example,  $\text{YbCp}^*_2(\text{THF})_2$  simply forms the organoaluminum adduct complex  $\text{Cp}^*_2\text{Yb}(\mu\text{-Et})\text{AlEt}_2(\text{THF})$ ,<sup>43</sup> while samarocene(II) complexes reduce  $\text{AlR}_3$  compounds to yield samarocene(III) tetraalkylaluminate complexes.<sup>24,44</sup> Depending on the amount of  $\text{AlR}_3$  reagent, silylamide complexes of Yb(II) and Sm(II) form bis- $\text{AlR}_3$  adducts or bis(tetraalkylaluminate) complexes of composition  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2(\text{AlMe}_3)_2$ <sup>17b</sup> and  $[\text{Ln}(\text{AlR}_4)_2]_n$ ,<sup>45</sup> respectively.

In the present study, we found that excess TMA (6 equiv) reacts (16 h, ambient temperature) with aryloxides  $\text{Ln}(\text{OAr}^{\text{tBu,R}})_2(\text{THF})_x$  ( $x = 1, 2$ ) to afford the bis-TMA adducts  $\text{Ln}[(\mu\text{-OAr}^{\text{tBu,R}})(\mu\text{-Me})\text{AlMe}_2]_2$  in good yields (Scheme 6). Complexes **8–10** are quite soluble in aromatic solvents and can be crystallized from *n*-hexane/toluene mixtures as yellow to orange (Yb) and brown to grayish (Sm) solids. Depending on the type of aryloxide substituent at the 4-position (H vs Me vs *t*Bu), varying amounts of the peralkylated Yb(II) aluminate  $[\text{Yb}(\text{AlMe}_4)_2]_n$  (**11a**)<sup>45</sup> could be separated off and identified in the synthesis of **8a** (23%) and **8b** (2%) as the only lanthanide-containing byproduct. To investigate the correlation between excess TMA, (prolonged) reaction time, and Yb(II) aluminate formation, the reaction of  $\text{Yb}(\text{OAr}^{\text{tBu,H}})_2(\text{THF})_2$  with TMA was examined in greater detail. By using a 6-fold excess of TMA, 40% of insoluble Yb(II) aluminate **11a** was obtained after 96 h at ambient temperature via **8a**, while a 24 equiv reaction produced 53% of **11a** within 16 h. For the most soluble complex **8c** and the corresponding Sm(II) compounds peralkylation did not occur within 16 h at ambient temperature. Interestingly, treatment of the least soluble precursor system,  $\text{Yb}(\text{OAr}^{\text{Ph,H}})_2(\text{THF})_2$ , with TMA also affords the bis-TMA adducts **10** exclusively.

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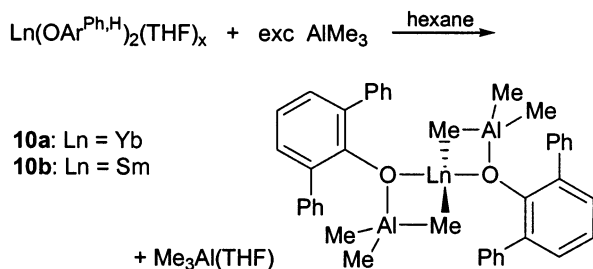
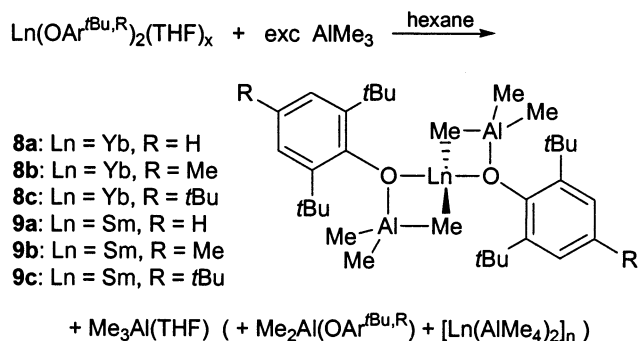
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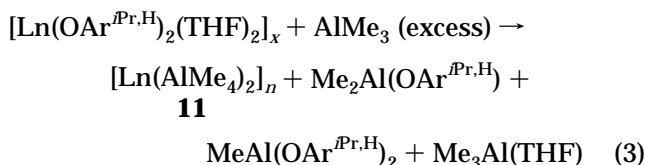
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Scheme 6



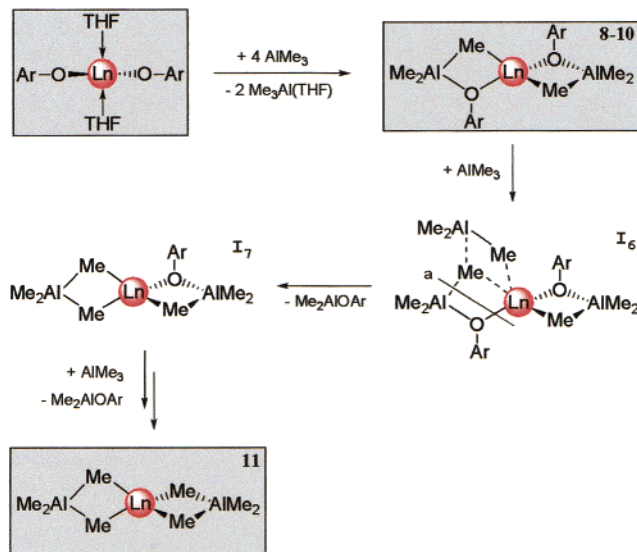
Elemental analysis and NMR spectroscopic data confirmed the formation of bis-TMA adducts **8–10**. Complexes **8** and **10a** exhibit a single  $^1\text{H}$  NMR resonance for the aluminum methyl groups (**8**,  $\delta$   $-0.10$  to  $-0.13$  ppm; **10a**,  $\delta$   $-0.76$  ppm) in the temperature range  $+20$  to  $-90$  °C. The ambient-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR signal of their aluminum methyl groups ( $\delta$   $-0.6$  to  $-4.5$  ppm) appears as a quartet with  $^1J_{\text{C-H}}$  coupling constants of about 110 Hz. The  $^1\text{H}$  NMR  $\text{AlMe}$  resonances of the paramagnetic samarium(II) derivatives **9** and **10b** showed a considerable shift to higher field and were found in the narrow range of  $-20.6$  to  $-20.9$  ppm and at  $-23.0$  ppm, respectively.

The enhanced steric unsaturation of the larger divalent metal centers compared to the La(III) system ensures the coordination of two TMA molecules. The formation of similar bis-TMA adduct complexes has been previously observed in Yb(II) and Sm(II) bis-(trimethylsilyl)amides,  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2(\text{AlMe}_3)_2$ .<sup>17b</sup> An additional experiment was performed to investigate the reaction behavior of the sterically less crowded divalent lanthanide aryloxides  $[\text{Ln}(\text{OAr}^{\text{Pr,H}})_2(\text{THF})_2]_x$  (Ln = Yb, Sm). According to eq 3, use of excess TMA afforded the



homoleptic peralkylated aluminates  $[\text{Ln}(\text{AlMe}_4)_2]_n$  (**11**) in quantitative yield after 16 h. Note that under identical reaction conditions the bulkier 2,6-di-*tert*-butylphenoxide ligand gave only 23% of Yb(II) aluminate **11a** and the putative Sm(II) aluminate **11b** did not form.

Finally, possible pathways for the formation of the bis-TMA adducts and peralkylated Ln(II) species are summarized in Scheme 7. Addition of TMA to mixtures

Scheme 7. Formation of Bis-TMA Adducts (**8–10**) and Homoleptic Tetramethylaluminates (**11**) from Lanthanide(II) Aryloxides<sup>a</sup>

<sup>a</sup> Fully characterized complexes are shown in boxes.

of the lanthanide(II) precursors in hexane led to displacement of the coordinated THF molecules, which preferentially coordinate to the harder Lewis acid center Al(III) in  $\text{Me}_3\text{Al}(\text{THF})$ . The next steps principally resemble the scenario which has been discussed for the Ln(III) derivatives in Scheme 4. Stable bis-TMA adducts **8–10** formed in the presence of another 2 equiv of TMA. Subsequent association with TMA to give intermediates such as **I**<sub>6</sub> could be a prevalent route for the relatively larger Ln(II) centers (compared to Ln(III)). Furthermore, a less pronounced Ln–O(Ar) interaction and hence dissociation of  $\text{Me}_2\text{Al}(\text{OAr})$  from **I**<sub>6</sub> (route a in Scheme 7) to yield **I**<sub>7</sub> should be favored for the smaller less oxophilic Yb center. Another TMA addition/ $\text{Me}_2\text{Al}(\text{OAr})$  dissociation sequence produces homoleptic tetramethylaluminate derivatives **11**, the insolubility of which drives the reaction to completion (enhanced kinetic control).

## Conclusions

Aryloxide ligands provide a rigid and variable ancillary ligand set for studying the multifunctional reactivity of trimethylaluminum, TMA, toward Ln–OR moieties. The conversion of divalent and trivalent rare-earth-metal aryloxides either to TMA-adduct complexes  $\text{Ln}(\text{OAr})_x(\text{AlMe}_3)_y$  ( $x = 2, 3$ ;  $y = 1, 2$ ) or to tetramethylaluminate derivatives of types  $(\text{Ar}^{\text{tBu,RO}})_2\text{Ln}[\mu\text{-Me}_2\text{AlMe}_2]$  and  $[\text{Ln}(\text{AlMe}_4)_2]_n$  ( $x = 2, 3$ ) by reaction with TMA once more demonstrates the importance of steric and, concomitantly, electronic factors in rare-earth-metal chemistry. This intrinsic alkylation capability of TMA, which has to be rationalized on the basis of the unique stereoelectronic situation implied by aryloxide ligation, is certainly not directly transferable and applicable to catalytically more relevant alkoxide-based systems. However, since the outcome of the TMA reactions seems to be predominantly under kinetic control, one can easily predict that factors such as  $\text{Ln}(\text{OAr})_x/\text{AlR}_3$  molar ratios and contact time of the different components are crucial for the uniform forma-



tion of the catalytically active (alkylated) species in rare-earth-metal-based "Ziegler Mischkatalysatoren". In light of these findings it is certainly worthwhile to examine alkoxide-based alkylation reactions in more detail; that is, the reactivity of TMA toward homoleptic alkoxide complexes of the type Ln(OR)<sub>x</sub> (*x* = 2, 3; R = *i*Pr, *t*Bu, neopentyl, etc.). Not unexpectedly, preliminary studies on the system Yb(OC*t*Bu)<sub>3</sub>/AlMe<sub>3</sub> reveal peralkylation, that is, exclusive generation of [Yb(AlMe<sub>2</sub>)<sub>2</sub>]<sub>*n*</sub> in the presence of excess of TMA, while alkylation of [Ln(O*i*Pr)<sub>3</sub>] with TMA was found to come to a halt at the stage of the tris-TMA adduct Ln(O*t*Bu)<sub>3</sub>(AlMe<sub>3</sub>)<sub>3</sub> (Ln = Y, Nd).<sup>2,3</sup>

## Experimental Section

**General Considerations.** All operations were performed with rigorous exclusion of air and water, using high-vacuum and glovebox techniques (MB Braun MB150B-G-II; <1 ppm O<sub>2</sub>, <1 ppm H<sub>2</sub>O). Solvents were predried and distilled from Na/K alloy (benzophenone ketyl) under argon. Deuterated solvents were obtained from Deutero GmbH and degassed and dried over Na/K alloy. All phenolic ligands were purchased from Aldrich and distilled or sublimed before use. Trimethylaluminum, TMA, was purchased from Aldrich and used without further purification. The lanthanide aryloxides Ln(OAr)<sub>3</sub>,<sup>14</sup> Ln(OAr)<sub>2</sub>(THF)<sub>*x*</sub><sup>15</sup> and (C<sub>5</sub>Me<sub>5</sub>)Y(OAr<sup>*t*Bu,H</sup>)<sub>2</sub><sup>19</sup> were synthesized according to slightly modified literature procedures. NMR spectra were recorded on a Bruker DPX-400 (FT, 400 MHz <sup>1</sup>H; 100 MHz <sup>13</sup>C) spectrometer in C<sub>6</sub>D<sub>6</sub> at 25 °C unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Perkin-Elmer 1650-FTIR spectrometer as Nujol mulls. Elemental analyses were performed in the microanalytical laboratory of the institute.

**Y(OC<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)(μ-OC<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (1).** To a suspension of [Y(OAr<sup>*t*Bu,H</sup>)<sub>3</sub>]<sub>2</sub> (0.397 g, 0.64 mmol) in *n*-hexane was slowly added a *n*-hexane solution of 6 equiv of TMA (0.277 g, 3.84 mmol), and the mixture was stirred at ambient temperature overnight. Then, the solvent and the excess TMA were removed in vacuo. The remaining solid was dissolved in *n*-hexane and crystallized at -45 °C to yield the TMA adduct as colorless crystals (0.226 g, 0.30 mmol, 46%). IR: 1588 w, 1439 s, 1363 m, 1321 s, 1260 s, 1245 m, 1204 m, 1168 s, 1098 m, 1054 w, 1042 m, 934 w, 891 m, 870 w, 835 s, 798 m, 755 s, 707 s, 697 s, 603 m, 570 w, 475 w, 470 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.11 (d, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 2 H, Ar *H*), 7.03 (d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 2 H, Ar *H*), 6.97–6.90 (m, 5 H, Ar *H*), 3.64 (septet, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.57 (septet, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.44 (septet, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41 (d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 6 H, CHH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 6 H, CHH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, <sup>3</sup>J<sub>H,H</sub> = 6.3 Hz, 6 H, CHH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 6 H, CHH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (d, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 6 H, CHH(CH<sub>3</sub>)<sub>2</sub>), 0.94 (d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 6 H, CHH(CH<sub>3</sub>)<sub>2</sub>), -0.29 (s, 18 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 156.8 (d, <sup>2</sup>J<sub>Y,C</sub> = 6.2 Hz, C<sub>ipso</sub>), 148.4, 139.2, 136.7, 125.6, 125.2, 125.1, 123.6, 120.6, 27.4, 27.3, 26.6, 26.4, 26.2, 25.6, 25.1, 24.2, 23.7, -2.8 ((μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>42</sub>H<sub>69</sub>Al<sub>2</sub>O<sub>3</sub>Y: C, 65.95; H, 9.09; Al, 7.06. Found: C, 65.89; H, 9.04; Al, 6.3.

**General Procedure for the Formation of Mono-TMA Adducts of Lanthanum(III) Aryloxides.** To a suspension of La(OAr<sup>*t*Bu,R</sup>)<sub>3</sub> in *n*-hexane was slowly added a *n*-hexane solution of 4 equiv of TMA, and the mixture was stirred at ambient temperature overnight. Then, the solvent and excess TMA were removed in vacuo. The remaining solid was dissolved in *n*-hexane and crystallized at -45 °C to give the TMA adducts as amorphous solids in good yields.

**La(OC<sub>6</sub>H<sub>3</sub>*t*Bu<sub>2</sub>-2,6)(μ-OC<sub>6</sub>H<sub>3</sub>*t*Bu<sub>2</sub>-2,6)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (2a).** Following the procedure described above, La(OAr<sup>*t*Bu,H</sup>)<sub>3</sub> (0.226 g, 0.30 mmol) and TMA (0.087 g, 1.20 mmol) yielded **2a** as a

colorless solid (0.208 g, 0.25 mmol, 84%). IR: 1588 w, 1405 s, 1348 m, 1263 m, 1236 s, 1218 s, 1190 s, 1123 m, 1099 w, 882 w, 856 s, 818 m, 745 s, 720 m, 701 m, 688 m, 652 m, 544 w, 503 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.20 (m, br, 6 H, Ar *H*<sub>meta</sub>), 6.80 (m, br, 3 H, Ar *H*<sub>para</sub>), 1.48 (s, 18 H, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 1.44 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.14 (s, br, 9 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR: δ 162.0 (s, C<sub>ipso</sub>), 153.9 (s, <sup>TMA</sup>C<sub>ipso</sub>), 140.8 (s), 136.9 (s), 127.8 (d, <sup>1</sup>J<sub>C,H</sub> = 155 Hz), 125.6 (d, <sup>1</sup>J<sub>C,H</sub> = 154 Hz), 122.5 (d, <sup>1</sup>J<sub>C,H</sub> = 159 Hz), 118.8 (d, <sup>1</sup>J<sub>C,H</sub> = 159 Hz), 35.9 (s, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 34.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.7 (q, <sup>1</sup>J<sub>C,H</sub> = 125 Hz, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 32.5 (q, <sup>1</sup>J<sub>C,H</sub> = 125 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.9 (q, <sup>1</sup>J<sub>C,H</sub> = 109 Hz, (μ-Me)AlMe<sub>2</sub>). <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, -90 °C): δ 7.15 (d, <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz, 4 H, Ar *H*<sub>meta</sub>), 7.04 (d, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2 H, <sup>TMA</sup>Ar *H*<sub>meta</sub>), 6.75 (t, <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz, 2 H, Ar *H*<sub>para</sub>), 6.66 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 1 H, <sup>TMA</sup>Ar *H*<sub>para</sub>), 1.36 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.33 (s, 18 H, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 0.20 (s, 9 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>45</sub>H<sub>72</sub>AlLaO<sub>3</sub>: C, 65.36; H, 8.78. Found: C, 65.38; H, 8.76.

**La(OC<sub>6</sub>H<sub>3</sub>*t*Bu<sub>2</sub>-2,6-Me-4)<sub>2</sub>(μ-OC<sub>6</sub>H<sub>3</sub>*t*Bu<sub>2</sub>-2,6-Me-4)(μ-Me)AlMe<sub>2</sub>] (2b).** Following the procedure described above, La(OAr<sup>*t*Bu,Me</sup>)<sub>3</sub> (0.239 g, 0.30 mmol) and TMA (0.087 g, 1.20 mmol) yielded **2b** as a colorless solid (0.225 g, 0.26 mmol, 86%). IR: 1600 w, 1415 vs, 1362 m, 1350 m, 1263 s, 1225 vs, 1212 vs, 1190 s, 1118 m, 1022 w, 950 w, 920 w, 887 m, 862 m, 830 s, 822 vs, 803 s, 776 m, 696 s, 601 m, 575 w, 527 s cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.08 (s, 2 H, <sup>TMA</sup>Ar *H*<sub>meta</sub>), 7.06 (s, 4H, Ar *H*<sub>meta</sub>), 2.22 (s, 6 H, CH<sub>3</sub>), 2.12 (s, 3H, <sup>TMA</sup>CH<sub>3</sub>), 1.48 (s, br, 54 H, C(CH<sub>3</sub>)<sub>3</sub>, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 0.18 (s, br, 9 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 160.0 (C<sub>ipso</sub>), 151.2 (<sup>TMA</sup>C<sub>ipso</sub>), 141.0, 136.7, 131.1, 129.7, 126.6, 126.2, 36.0 (<sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 34.9 (C(CH<sub>3</sub>)<sub>3</sub>), 32.7 (<sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 32.6 (C(CH<sub>3</sub>)<sub>3</sub>), 21.3 (CH<sub>3</sub>), 21.1 (<sup>TMA</sup>CH<sub>3</sub>), 2.0 (br, (μ-Me)AlMe<sub>2</sub>). <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, -90 °C): δ 7.04 (s, 4 H, Ar *H*<sub>meta</sub>), 7.00 (s, 2 H, Ar *H*<sub>meta</sub>), 2.22 (s, 6 H, CH<sub>3</sub>), 2.05 (s, 3 H, CH<sub>3</sub>), 1.40 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.37 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.24 (s, 9 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (*d*<sub>8</sub>-toluene, -90 °C): δ 160.1 (s, C<sub>ipso</sub>), 151.3 (s, <sup>TMA</sup>C<sub>ipso</sub>), 141.5 (s), 136.3 (s), 131.8 (s), 130.0 (s), 127.8 (d, <sup>1</sup>J<sub>C,H</sub> = 154 Hz), 125.7 (d, <sup>1</sup>J<sub>C,H</sub> = 154 Hz), 36.0 (s, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 35.0 (s, C(CH<sub>3</sub>)<sub>3</sub>), 32.3 (q, <sup>1</sup>J<sub>C,H</sub> = 126 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 31.8 (q, <sup>1</sup>J<sub>C,H</sub> = 125 Hz, <sup>TMA</sup>C(CH<sub>3</sub>)<sub>3</sub>), 21.5 (q, CH<sub>3</sub>), 21.2 (q, <sup>TMA</sup>CH<sub>3</sub>), 2.7 (q, <sup>1</sup>J<sub>C,H</sub> = 110 Hz, (μ-Me)AlMe<sub>2</sub>). Anal. Calcd for C<sub>48</sub>H<sub>78</sub>AlLaO<sub>3</sub>: C, 66.34; H, 9.05. Found: C, 66.50; H, 9.13.

**General Procedure for the Alkylation of Yttrium(III) and Lutetium(III) Aryloxides.** Ln(OAr)<sub>3</sub> was suspended in *n*-hexane. Then, a *n*-hexane solution of 6 equiv of TMA was slowly added at ambient temperature. After the mixture was stirred for 16 h, the solvent and excess TMA were removed in vacuo. The remaining solid was dissolved in *n*-hexane and crystallized at -45 °C to give the aluminate complexes as colorless solids in moderate yields.

**Y(OC<sub>6</sub>H<sub>3</sub>*t*Bu<sub>2</sub>-2,6)(μ-Me)<sub>2</sub>AlMe<sub>2</sub>] (3a).** Following the procedure described above, Y(OAr<sup>*t*Bu,H</sup>)<sub>3</sub> (0.317 g, 0.45 mmol) and TMA (0.195 g, 2.70 mmol) yielded **3a** (0.164 g, 0.28 mmol, 62%) as colorless crystals. IR: 1582 w, 1412 s, 1350 m, 1263 s, 1241 s, 1215 m, 1193 m, 1125 w, 1100 w, 874 s, 820 m, 796 w, 750 s, 720 s, 695 m, 666 m, 578 m, 550 m, 454 m cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.21 (d, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 4 H, Ar *H*<sub>meta</sub>), 6.83 (t, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 2 H, Ar *H*<sub>para</sub>), 1.40 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.02 (d, <sup>2</sup>J<sub>Y,H</sub> = 3.7 Hz, 12 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 160.5 (d, <sup>2</sup>J<sub>Y,C</sub> = 5.2 Hz, C<sub>ipso</sub>), 137.2, 125.5, 119.1, 34.7 (C(CH<sub>3</sub>)<sub>3</sub>), 31.7 (C(CH<sub>3</sub>)<sub>3</sub>), 2.7 (br, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>32</sub>H<sub>54</sub>AlO<sub>2</sub>Y: C, 65.51; H, 9.28, Al, 4.60. Found: C, 65.37; H, 9.13; Al, 4.5.

**Y(OC<sub>6</sub>H<sub>3</sub>*t*Bu<sub>2</sub>-2,6-Me-4)<sub>2</sub>(μ-Me)<sub>2</sub>AlMe<sub>2</sub>] (3b).** Following the procedure described above, Y(OAr<sup>*t*Bu,Me</sup>)<sub>3</sub> (0.298 g, 0.40 mmol) and TMA (0.173 g, 2.40 mmol) yielded **3b** (0.135 g, 0.22 mmol, 55%) as colorless crystals. IR: 1600 w, 1416 s, 1354 m, 1251 s, br, 1226 s, 1213 s, 1182 s, 1117 m, 1106 m, 1034 w, 1021 w, 949 w, 888 w, 865 m, 844 s, 828 s, 806 m, 775 m, 722 m, 699 s, 674 s, 642 w, 608 w, 574 w, 544 m, 534 s, 478 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.07 (s, 4 H, Ar *H*<sub>meta</sub>), 2.26 (s, 6 H, CH<sub>3</sub>), 1.44 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.04 (d, <sup>2</sup>J<sub>Y,H</sub> = 3.7 Hz, 12 H, (μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 158.5 (d, <sup>2</sup>J<sub>Y,C</sub> = 7.6 Hz, C<sub>ipso</sub>),

Table 4. Crystal Data and Data Collection Parameters of Complexes 1, 3a, and 4a

	1	3a	4a
chem formula	C <sub>42</sub> H <sub>69</sub> Al <sub>2</sub> O <sub>3</sub> Y	C <sub>32</sub> H <sub>54</sub> AlO <sub>2</sub> Y	C <sub>32</sub> H <sub>54</sub> AlO <sub>2</sub> Lu
fw	764.84	586.64	672.70
color/shape	colorless/fragment	colorless/fragment	colorless/fragment
cryst size (mm)	0.94 × 0.64 × 0.20	0.51 × 0.30 × 0.20	0.71 × 0.25 × 0.13
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	11.7263(1)	19.6670(1)	19.6660(1)
<i>b</i> (Å)	18.1264(1)	14.4580(2)	14.4500(2)
<i>c</i> (Å)	20.7998(1)	23.3750(3)	23.2530(2)
<i>V</i> (Å <sup>3</sup> )	4421.11(5)	6646.58(13)	6607.89(11)
<i>Z</i>	4	8	8
<i>T</i> (K)	123	183	183
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.149	1.173	1.352
$\mu$ (mm <sup>-1</sup> )	1.392	1.805	3.038
<i>F</i> <sub>000</sub>	1640	2512	2768
$\theta$ range (deg)	2.07–25.34	2.47–26.37	1.75–27.48
data collected ( <i>h, k, l</i> )	±14, ±21, ±25	±24, ±17, ±29	±25, ±18, ±30
no. of rflns collected	102 626	77 434	51 909
no. of indep rflns/ <i>R</i> <sub>int</sub>	7990/0.053	6669/0.036	7578/0.041
no. of obsd rflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	7757	4981	6138
no. of params refined	710	325	325
<i>R</i> 1 (obsd/all)	0.0197/0.0212	0.0497/0.0837	0.0320/0.0495
w <i>R</i> 2 (obsd/all)	0.0466/0.0471	0.0966/0.1124	0.0870/0.1080
GOF (obsd/all)	1.048/1.048	1.096/1.096	1.192/1.192
max/min $\Delta\rho$ (e Å <sup>-3</sup> )	+0.22/−0.21	+0.86/−0.33	+0.86/−1.81

136.9, 127.1, 126.0, 34.7 (*C*(CH<sub>3</sub>)<sub>3</sub>), 31.7 (*C*(CH<sub>3</sub>)<sub>3</sub>), 21.5 (CH<sub>3</sub>), 2.6 (br, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>34</sub>H<sub>58</sub>AlO<sub>2</sub>Y: C, 66.43; H, 9.51. Found: C, 66.20; H, 9.43.

**Y(OC<sub>6</sub>H<sub>2</sub>tBu<sub>3</sub>-2,4,6)<sub>2</sub>[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (3c).** Following the procedure described above, Y(OAr<sup>tBu,tBu</sup>)<sub>3</sub> (0.350 g, 0.40 mmol) and TMA (0.173 g, 2.40 mmol) yielded a yellow oil. <sup>1</sup>H NMR:  $\delta$  7.37 (s, 4 H, Ar *H*<sub>meta</sub>), 1.45 (s, 36 H, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.36 (s, 18 H, *p*-C(CH<sub>3</sub>)<sub>3</sub>), 0.03 (d, <sup>2</sup>*J*<sub>Y,H</sub> = 3.7 Hz, 12 H, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  158.3 (d, <sup>2</sup>*J*<sub>Y,C</sub> = 5.4 Hz, *C*<sub>ipso</sub>), 140.2, 136.3, 122.1, 35.2 (*o*-C(CH<sub>3</sub>)<sub>3</sub>), 35.1 (*p*-C(CH<sub>3</sub>)<sub>3</sub>), 32.0 (*o*-C(CH<sub>3</sub>)<sub>3</sub>), 31.8 (*p*-C(CH<sub>3</sub>)<sub>3</sub>), 2.6 (br, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>).

**Lu(OC<sub>6</sub>H<sub>3</sub>tBu<sub>2</sub>-2,6)<sub>2</sub>[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (4a).** Following the procedure described above, Lu(OAr<sup>tBu,H</sup>)<sub>3</sub> (0.356 g, 0.45 mmol) and TMA (0.195 g, 2.70 mmol) yielded **4a** (0.211 g, 0.31 mmol, 70%) as colorless crystals. IR: 1583 w, 1414 vs, 1351 m, 1264 s, 1242 vs, 1219 m, 1195 m, 1125 w, 1099 w, 878 vs, 821 m, 796 w, 750 vs, 720 s, 700 m, 666 s, 579 m, 551 m, 453 m cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.23 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.7 Hz, 4 H, Ar *H*<sub>meta</sub>), 6.83 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.7 Hz, 2 H, Ar *H*<sub>para</sub>), 1.42 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.30 (s, 12 H, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  161.1 (*C*<sub>ipso</sub>), 137.5, 125.5, 119.1, 34.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.8 (C(CH<sub>3</sub>)<sub>3</sub>), 4.9 (br, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>-Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>32</sub>H<sub>54</sub>AlLuO<sub>2</sub>: C, 57.13; H, 8.09; Al, 4.01. Found: C, 57.18; H, 8.14; Al, 4.1.

**Lu(OC<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-2,6-Me-4)<sub>2</sub>[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (4b).** Following the procedure described above, Lu(OAr<sup>tBu,Me</sup>)<sub>3</sub> (0.342 g, 0.41 mmol) and TMA (0.177 g, 2.46 mmol) yielded **4b** (0.166 g, 0.24 mmol, 58%) as colorless crystals. IR: 1423 s, 1352 m, 1292 w, 1250 s, br, 1216 m, 1194 m, 1120 m, 1022 w, 950 w, 920 w, 889 w, 860 s, 850 s, 806 w, 776 m, 723 s, 702 s, 632 w, 579 m, 565 m, 548 s, 460 w, 443 m cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.09 (s, 4 H, Ar *H*<sub>meta</sub>), 2.26 (s, 6 H, CH<sub>3</sub>), 1.45 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.31 (s, 12 H, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  159.0 (*C*<sub>ipso</sub>), 137.2, 127.0, 126.0, 34.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.9 (C(CH<sub>3</sub>)<sub>3</sub>), 21.4 (CH<sub>3</sub>), 4.8 (br, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>34</sub>H<sub>58</sub>AlLuO<sub>2</sub>: C, 58.27; H, 8.34; Al, 3.85. Found: C, 58.18; H, 8.24; Al, 4.0.

**(C<sub>5</sub>Me<sub>5</sub>)Y(OC<sub>6</sub>H<sub>3</sub>tBu<sub>2</sub>-2,6)<sub>2</sub>[( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>] (6).** Following the procedure described above, Cp\*Y(OAr<sup>tBu,H</sup>)<sub>2</sub> (0.222 g, 0.35 mmol) and TMA (0.101 g, 1.40 mmol) yielded **6** (0.091 g, 0.18 mmol, 51%) as an amorphous solid. IR: 1582 w, 1410 m, 1303 w, 1245 s, 1210 w, 1193 w, 1169 w, 1153 w, 1127 w, 1102 w, 1021 w, 871 m, 748 m, 697 m, 663 m, 582 w, 459 w cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.25 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.7 Hz, 2 H, Ar *H*<sub>meta</sub>), 6.85 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.7 Hz, 1 H, Ar *H*<sub>para</sub>), 1.80 (s, 15 H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.36 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), -0.15 (d, <sup>2</sup>*J*<sub>Y,H</sub> = 2.9 Hz, 12 H, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  161.1 (d, <sup>2</sup>*J*<sub>Y,C</sub> = 5.4 Hz, *C*<sub>ipso</sub>), 137.4, 125.2,

121.8, 118.2 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 34.9 (C(CH<sub>3</sub>)<sub>3</sub>), 31.7 (C(CH<sub>3</sub>)<sub>3</sub>), 11.5 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.4 (br, ( $\mu$ -CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>28</sub>H<sub>48</sub>-AlOY: C, 65.10; H, 9.37. Found: C, 65.50; H, 9.52.

#### General Procedure for the Synthesis of Bis-TMA Adducts of Ytterbium(II) and Samarium(II) Aryloxides.

Ln(OAr)<sub>2</sub>(THF)<sub>*x*</sub> was dissolved in *n*-hexane and a *n*-hexane solution of 6 equiv of TMA slowly added. The mixture was stirred at ambient temperature overnight. Then, the solvent and excess TMA were removed in vacuo. The remaining solid was dissolved in toluene and the solution centrifuged, filtered through a Celite pad to separate insoluble parts, and finally crystallized from *n*-hexane or *n*-hexane/toluene mixtures at -45 °C to give the TMA adducts as yellow (Yb) or reddish brown (Sm) solids in good yields.

**Yb[( $\mu$ -OC<sub>6</sub>H<sub>3</sub>tBu<sub>2</sub>-2,6)( $\mu$ -Me)AlMe<sub>2</sub>]<sub>2</sub> (8a).** Following the procedure described above, Yb(OAr<sup>tBu,H</sup>)<sub>2</sub>(THF)<sub>2</sub> (0.255 g, 0.35 mmol) and TMA (0.151 g, 2.10 mmol) yielded **8a** as an orange solid (0.06 g, 0.08 mmol, 23%). <sup>1</sup>H NMR:  $\delta$  7.11 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.9 Hz, 4 H, Ar *H*<sub>meta</sub>), 6.75 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.9 Hz, 2 H, Ar *H*<sub>para</sub>), 1.30 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), -0.13 (s, 18 H, ( $\mu$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  154.2 (*C*<sub>ipso</sub>), 140.1, 127.4, 121.6, 35.6 (C(CH<sub>3</sub>)<sub>3</sub>), 32.8 (C(CH<sub>3</sub>)<sub>3</sub>), -0.6 (( $\mu$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>).

**Yb[( $\mu$ -OC<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-2,6-Me-4)( $\mu$ -Me)AlMe<sub>2</sub>]<sub>2</sub> (8b).** Following the procedure described above, Yb(OAr<sup>tBu,Me</sup>)<sub>2</sub>(THF)<sub>2</sub> (0.219 g, 0.29 mmol) and TMA (0.125 g, 1.74 mmol) yielded **8b** as yellow crystals (0.162 g, 0.21 mmol, 74%). IR: 1411 m, 1265 w, 1255 w, 1229 m, 1204 m, 1189 m, 1117 w, 863 w, 830 w, 818 w, 804 w, 774 w, 721 m, 965 m, br, 601 w, 525 w cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.00 (s, 4 H, Ar *H*<sub>meta</sub>), 2.10 (s, 6 H, CH<sub>3</sub>), 1.32 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), -0.10 (s, 18 H, ( $\mu$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  151.7 (*C*<sub>ipso</sub>), 140.0, 130.0, 127.6, 35.6 (C(CH<sub>3</sub>)<sub>3</sub>), 32.5 (C(CH<sub>3</sub>)<sub>3</sub>), 21.0 (CH<sub>3</sub>), -0.6 (( $\mu$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>36</sub>H<sub>64</sub>-Al<sub>2</sub>O<sub>2</sub>Yb: C, 57.20; H, 8.53. Found: C, 57.29; H, 8.58.

**Yb[( $\mu$ -OC<sub>6</sub>H<sub>2</sub>tBu<sub>3</sub>-2,4,6)( $\mu$ -Me)AlMe<sub>2</sub>]<sub>2</sub> (8c).** Following the procedure described above, Yb(OAr<sup>tBu,tBu</sup>)<sub>2</sub>(THF)<sub>2</sub> (0.302 g, 0.36 mmol) and TMA (0.156 g, 2.16 mmol) yielded **8c** (0.181 g, 0.21 mmol, 60%) as a light yellow solid. IR: 1601 w, 1420 s, 1362 s, 1292 w, 1273 m, 1227 s, 1196 s, 1152 w, 1116 m, 882 w, 836 m, 820 w, 776 m, 750 m, 720 s, 691 s, 596 w, 542 w cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.33 (s, 4 H, Ar *H*<sub>meta</sub>), 1.37 (s, 36 H, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (s, 18 H, *p*-C(CH<sub>3</sub>)<sub>3</sub>), -0.13 (s, 18 H, ( $\mu$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  151.9 (*C*<sub>ipso</sub>), 142.9, 139.3, 124.1, 35.9 (*o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.5 (*p*-C(CH<sub>3</sub>)<sub>3</sub>), 32.6 (*o*-C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (*p*-C(CH<sub>3</sub>)<sub>3</sub>), -0.7 ( $\mu$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>42</sub>H<sub>76</sub>Al<sub>2</sub>O<sub>2</sub>Yb: C, 60.05; H, 9.12. Found: C, 60.42; H, 9.31.

**Sm[(μ-OC<sub>6</sub>H<sub>3</sub>tBu<sub>2</sub>-2,6)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (9a).** Following the procedure described above, Sm(OAr<sup>tBu,H</sup>)<sub>2</sub>(THF)<sub>2</sub> (0.303 g, 0.43 mmol) and TMA (0.186 g, 2.58 mmol) yielded **9a** as a reddish brown solid (0.150 g, 0.21 mmol, 50%). IR: 1581 w, 1402 s, 1365 s, 1348 m, 1308 w, 1253 m, 1238 s, 1225 s, 1190 s, 1126 m, 1098 w, 877 w, 864 m, 818 m, 797 w, 754 m, 718 m, 696 s, br, 657 w, 636 w, 596 m, 494 m cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.73 (d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 4 H, Ar *H*<sub>meta</sub>), 7.47 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 2 H, Ar *H*<sub>para</sub>), 3.45 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), -20.93 (s, 18 H, (μ-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>34</sub>H<sub>60</sub>Al<sub>2</sub>O<sub>2</sub>Sm: C, 57.91; H, 8.58. Found: C, 57.17; H, 8.41.

**Sm[(μ-OC<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-2,6-Me-4)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (9b).** Following the procedure described above, Sm(OAr<sup>tBu,Me</sup>)<sub>2</sub>(THF)<sub>2</sub> (0.257 g, 0.35 mmol) and TMA (0.151 g, 2.10 mmol) yielded **9b** as a reddish brown solid (0.225 g, 0.31 mmol, 88%). IR: 1601 w, 1409 s, 1366 s, 1347 m, 1266 m, 1251 m, 1234 s, 1210 s, 1185 s, 1118 m, 884 w, 864 m, 832 m, 821 m, 805 m, 772 m, 720 s, 696 s, br, 632 w, 598 m, 526 w, 491 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.87 (s, 4 H, Ar *H*<sub>meta</sub>), 3.39 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.72 (s, 6 H, CH<sub>3</sub>), -20.88 (s, 18 H, (μ-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>36</sub>H<sub>64</sub>Al<sub>2</sub>O<sub>2</sub>Sm: C, 58.97; H, 8.80; Al, 7.36. Found: C, 58.59; H, 8.67; Al, 7.5.

**Sm[(μ-OC<sub>6</sub>H<sub>2</sub>tBu<sub>3</sub>-2,4,6)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (9c).** Following the procedure described above, Sm(OAr<sup>tBu,tBu</sup>)<sub>2</sub>(THF)<sub>2</sub> (0.335 g, 0.41 mmol) and TMA (0.177 g, 2.46 mmol) yielded **9c** as a reddish brown solid (0.147 g, 0.18 mmol, 44%). IR: 1600 w, 1418 s, 1363 s, 1344 m, 1292 w, 1273 m, 1235 s, 1203 s, 1189 s, 1152 w, 1118 s, 917 w, 884 m, 841 s, 819 w, 772 w, 751 m, 691 vs, br, 645 w, 598 m, 536 w, 504 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 8.18 (s, 4 H, Ar *H*<sub>meta</sub>), 6.38 (s, 36 H, *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.94 (s, 18 H, *p*-C(CH<sub>3</sub>)<sub>3</sub>), -20.61 (s, 18 H, (μ-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>42</sub>H<sub>76</sub>Al<sub>2</sub>O<sub>2</sub>Sm: C, 61.72; H, 9.37; Al, 6.60. Found: C, 62.21; H, 9.26; Al, 6.8.

**Yb[(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (10a).** Following the procedure described above, Yb(OAr<sup>Ph</sup>)<sub>2</sub>(THF) (0.213 g, 0.29 mmol) and TMA (0.125 g, 1.74 mmol) yielded **10a** as a yellow solid (0.223 g, 0.28 mmol, 95%). IR: 1591 w, 1560 w, 1454 vs, 1419 m, 1313 w, 1277 w, 1237 m, 1181 w, 1085 w, 1070 w, 1028 w, 934 w, 856 m, 800 mw, 776 m, 764 s, 755 s, 705 s, br, 610 w, 598 w, 576 w, 522 w, 507 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.39 (d, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 8 H, Ar *H*), 7.08–6.97 (m, 16 H, Ar *H*), 6.83 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 2 H, Ar *H*<sub>para</sub>), -0.76 (s, 18 H, (μ-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 153.3 (C<sub>ipso</sub>), 140.2, 133.0, 131.5, 130.5, 129.8, 128.7, 121.3, -4.5 ((μ-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>42</sub>H<sub>44</sub>Al<sub>2</sub>O<sub>2</sub>Yb: C, 62.45; H, 5.49; Al, 6.68. Found: C, 61.57; H, 5.40; Al, 6.0.

**Sm[(μ-OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)(μ-Me)AlMe<sub>2</sub>]<sub>2</sub> (10b).** Following the procedure described above, Sm(OAr<sup>Ph</sup>)<sub>2</sub>(THF) (0.257 g, 0.36 mmol) and TMA (0.156 g, 2.16 mmol) yielded **10b** as a grayish brown solid (0.249 g, 0.32 mmol, 88%). IR: 1592 w, 1582 w, 1565 w, 1490 m, 1419 s, 1314 m, 1276 m, 1236 s, 1201 m, 1176 s, 1084 w, 1070 w, 1028 w, 861 s, 854 s, 800 w, 771 m, 764 s, 754 s, 705 vs, 691 vs, 680 sh, 630 w, 610 m, 596 m, 576 w, 522 w, 506 w, 497 w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 13.56 (s), 12.69 (s), 10.93 (s), 6.06 (m), -23.01 (s, 18 H, (μ-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd

for C<sub>42</sub>H<sub>44</sub>Al<sub>2</sub>O<sub>2</sub>Sm: C, 64.25; H, 5.65; Al, 6.87. Found: C, 63.88; H, 5.64; Al, 6.6.

**X-ray Crystallography. General Procedure.** Crystals suitable for diffraction experiments were selected in a glovebox, coated with perfluorinated ether, and fixed in a capillary. Preliminary examination of the crystal quality and data collection were carried out on a Nonius KappaCCD diffractometer in combination with a rotating-anode X-ray generator and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) employing the COLLECT software package.<sup>46</sup>

**Crystal Structure Determination of 1, 3a, and 4a.** A total of 1032 (311, 380) collected images were processed using Denzo.<sup>47</sup> Data for compounds **3a** and **4a**, respectively, are specified in parentheses. Absorption and/or decay effects were corrected during the scaling procedure.<sup>47</sup> The structures were solved by direct methods<sup>48</sup> and refined with standard difference Fourier techniques.<sup>49</sup> All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were placed in calculated positions and included in the structure factor calculation but not refined for **3a** and **4a**. In **1** all hydrogen atoms were found in the difference Fourier maps and refined freely with individual isotropic thermal displacement. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  employing the SHELXL-97 weighting scheme and stopped at a maximum shift/error of <0.002 (0.001, 0.001). As demonstrated by the Flack parameter  $\epsilon = 0.156(2)$ , the crystal of compound **1** is partly twinned. In the final model, including twin refinement for **1**, 710 (325, 325) parameters were refined to wR2 = 0.0471 (0.1124, 0.1080) based on all 7990 (6669, 7578) data. For details see Table 4.

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**Supporting Information Available:** Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles for complexes **1**, **3a** and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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