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Utility of Mixed-Ligand Alkylaluminum Reagents in the Formation of Mixed-Metal Yttrium and Lanthanide Aluminum Compounds

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$[(ArO)_2(THF)Y(\mu\text{-}OAr)]_2$ ($Ar = C_6H_3Me_2\text{-}2,6$) reacts with Al_2Me_6 or $AlEt_3$ in toluene or hexanes to form the mixed-metal products $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlR_2$ [R − Me (**1**), Et (**2**)]. These complexes can be obtained in quantitative yield from $[AlR_2(OAr)]_2$ and $Y(OAr)_3(THF)_3$ in toluene. Yb and Nd analogs of **1** and **2** can be obtained similarly, and the representative complexes $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, **3**, and $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, **4**, were crystallographically characterized. Complexes **1**−**4** all crystallize from benzene in the same space group *C*2/*c*. Unit cell parameters at 298 K follow: **1**, $a = 24.148(3)$ Å, $b = 12.396(3)$ Å, $c = 18.677(2)$ Å, $\beta = 118.68(8)°$, $V = 4704(1)$ Å^3, $Z = 4$; **2**, $a = 21.790$ Å, $b = 13.039$ Å, $c = 19.434$ Å, $\beta = 111.68°$, $V = 5128$ Å^3; **3**, $a = 23.881(9)$ Å, $b = 12.035(7)$ Å, $c = 18.676(6)$ Å, $\beta = 118.74(2)°$, $V = 4706(3)$ Å^3, $Z = 4$; **4**, $a = 23.185(2)$ Å, $b = 13.128(1)$ Å, $c = 18.905(2)$ Å, $\beta = 117.65(1)°$, $V = 5096(1)$ Å^3, $Z = 4$. In the case of **3**, least-squares refinement of the model based on 2500 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final $R_F = 7.6\%$. For **4** the model based on 2243 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final $R_F = 7.2\%$. Complexes **1**, **3**, and **4** have distorted octahedral and tetrahedral coordination environments around lanthanide and aluminum, respectively.

Introduction

In recent years, yttrium and the lanthanide metals were often found to be desirable components of mixed-metal solid state materials which exhibit unusual and useful physical properties.[1] Since the synthetic chemistry of mixed-metal compounds containing the lanthanides has not been extensively developed, it is often not possible to locate a molecular precursor with the appropriate combination and stoichiometry of metals for a specific application. Similarly, although mixed-metal complexes containing early transition metals and aluminum are of interest in regard to the development of single-component olefin polymerization catalysts,[2] an extensive knowledge of synthetic routes to such compounds is not available.

Recent studies of the chemistry of yttrium *tert*-butoxide complexes showed that these compounds react readily with alkylaluminum reagents to form mixed-metal yttrium aluminum complexes with variable metallic ratios such as YAl_3, YAl_2, and YAl.[3] To extend this chemistry to metals other than yttrium and to develop more controlled, higher yield reactions leading to compounds with specific metal:aluminum ratios, we have examined the chemistry of the 2,6-dimethylphenoxide complexes of yttrium and representative lanthanides. Halide-free 2,6-dimethylphenoxide−yttrium complexes are readily available from YCl_3 and exist either as the bridged species $[(ArO)_2(THF)Y(\mu\text{-}OAr)]_2$ or as $Y(OAr)_3(THF)_3$ ($OAr = OC_6H_3Me_2\text{-}2,6$), both of which have been fully characterized by X-ray crystallography.[4] In this report, we describe the reactivity of these species with trimethyl- and triethylaluminum, the utility of the mixed-ligand aluminum reagent $[AlR_2(OAr)]_2$ in forming mixed-metal complexes, and the extension of the yttrium results to both smaller and larger lanthanides.

Experimental Section

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum-line, and glovebox techniques. Solvents were purified as previously described.[5] $Nd_2(OAr)_6(THF)_4$,[6] $Y_2(OAr)_6(THF)_2$,[4] and $Y(OAr)_3(THF)_3$,[4] were prepared as previously reported. NMR spectra were recorded using a General Electric QE 300 spectrometer. Elemental analyses were determined on a Carlo Erba EA 1108 instrument or performed by the Analytische Laboratorien, Gummersbach, Germany. 2,6-Dimethylphenol (Aldrich) was purified by sublimation prior to use.

$[Me_2Al(OAr)]_2$. $[Me_2Al(OC_6H_3Me_2)]_2$ was obtained from 2,6-dimethylphenol (1.22 g, 10 mmol) and Al_2Me_6 (1 mL, 5.2 mmol) in 20 mL of hexane. Evaporation of the solvent produced a highly crystalline product (1.77 g, 99%). Anal. Calcd for $C_{20}H_{30}O_2Al_2$: C, 67.39; H, 8.48. Found: C, 67.06; H, 8.36. ^1H NMR (C_6D_6): δ 6.82 (m, 3H, $Me_2C_6H_3$), 2.40 (s, 6H, $Me_2C_6H_3$), −0.40 (s, 6H, $AlMe_2$). EI-MS: 341 (M^+ − Me, 4%), 178 ($M^+/2$, 7%), 122 ($OC_6H_3Me_2$, 100%).

$[Et_2Al(OAr)]_2$. $[Et_2Al(OC_6H_3Me_2)]_2$ was obtained from 2,6-dimethylphenol (1.22 g, 10 mmol) and $AlEt_3$ (1.14 g, 10 mmol) in 20 mL of hexane. Evaporation of the solvent produced a microcrystalline powder (2.0 g, 97%). Anal. Calcd for $C_{24}H_{38}O_2Al_2$: C, 69.90; H, 9.22. Found: C, 69.57; H, 9.26. ^1H NMR (C_6D_6): δ 6.83 (m, 3H, $Me_2C_6H_3$), 2.41 (s, 6H, $Me_2C_6H_3$), 1.05 (t, 6H, $Al(CH_2CH_3)_2$), 0.31 (q, 4H, $Al(CH_2CH_3)_2$). EI-MS: 383 (M^+ − Et, 4%), 122 ($OC_6H_3Me_2$, 100%).

$Yb(OAr)_3(THF)_3$. Since this Yb analog of the previously described $Y(OAr)_3(THF)_3$[4] was made in a different way, its synthesis is described

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here. To a flask containing $Yb[N(SiMe_3)_2]_3$ (1.0 g, 1.53 mmol) in 20 mL of THF was added 2,6-dimethylphenol (560 mg, 4.6 mmol), and the mixture was stirred for 18 h. The resultant solution was centrifuged, and a small amount of insoluble solid was discarded. The supernatant was dried on a rotary evaporator to produce a light yellow crystalline powder (1.05 g, 90%). Anal. Calcd for $C_{36}H_{51}O_6Yb$: Yb, 22.98. Found: Yb, 23.5.

$(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$, 1. In the glovebox, $Y_2(OAr)_6(THF)_2$ (605 mg, 0.5 mmol) was dissolved in 8 mL of toluene, and Al_2Me_6 (0.6 mL, 3 mmol) was added via syringe. After being stirred overnight, the mixture was centrifuged and a small amount of insoluble material was discarded. The solvent was removed in vacuo, and the residue was extracted with hexanes. The hexane-insoluble fraction (ca. 300 mg) was found to be starting material. Removal of solvent from the supernatant by rotary evaporation gave an oily product which was found by NMR spectroscopy to contain three components which were later identified as **1**, $Y_2(OAr)_6(THF)_2$, and $[Me_2Al(OAr)]_2$. After several days at ambient temperature, the oil produced colorless crystals (56 mg) which were identified by X-ray diffraction as **1**.

Complex **1** was obtained in quantitative yield by adding a toluene solution of $[Me_2Al(OAr)]_2$ (178 mg, 1 mmol) to $Y(OAr)_3(THF)_3$ (667 mg, 1 mmol) in 8 mL of toluene and warming to 100 °C for 30 min. Removal of solvent produced **1**, identified by ^1H NMR spectroscopy, as a white powder in 96% yield (810 mg). Anal. Calcd for $C_{42}H_{58}O_6AlY$: C, 65.11; H, 7.55; Al, 3.48; Y, 11.48. Found: C, 64.91; H, 7.41; Al, 3.36; Y, 11.20. IR (Nujol): 2924 m, br, 2910 s, 2722 w, 1592 m, 1376 s, 1290 s, 1265 m, 1219 s, 1194 w, 1159 w, 1092 m, 1029 m, 858 m, 760 w, 727 w cm^{-1}. ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 6.80 (m, 8H, $C_6\mathit{H}_3Me_2$), 6.66 (m, 4H, $C_6\mathit{H}_3Me_2$), 3.26 (s, 8H, $C_4\mathit{H}_8O$), 2.60 (s, 12H, $C_6H_3\mathit{Me}_2$), 2.40 (s, 12H, $C_6H_3\mathit{Me}_2$), 0.73 (s, 8H, $C_4\mathit{H}_8O$), −0.33 ($Al\mathit{Me}_2$). ^{13}C NMR (C_6D_6, 300 MHz): δ 129.2, 128.9, 128.8, 128.2, 125.3, 125.7, 122.3, 117.1 ($\mathit{C}_6H_3Me_2$), 24.1, 21.1 ($C_6H_3\mathit{Me}_2$), 19.1, 18.7 ($Al\mathit{Me}_2$).

A single crystal of **1** was mounted in a glass capillary and transferred to a Siemens P3 diffractometer, and data were collected at room temperature. Although crystallographic analysis identified the overall structure of the molecule, accurate bond distances and angles could not be obtained due to the poor quality of the crystal. Details are given in the supplementary material.

$(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlEt_2$, 2. $AlEt_3$ (1 mL of a 1 M solution in hexanes) was added dropwise to $Y_2(OAr)_6(THF)_2$ (605 mg, 0.5 mmol) in 10 mL of toluene. After the solution was stirred for 2 days, the solvent was removed by rotary evaporation and the solids were extracted with hexanes. From this solution precipitated colorless crystals of **2** (210 mg, 26% yield) after several days at ambient temperature. Anal. Calcd for $C_{42}H_{62}O_6AlY$: C, 65.82; H, 7.78. Found: C, 65.73; H, 7.86. IR (Nujol): 1590 m, 1377 m, 1280 w, 1273 s, 1232 s, 1187 s, 1095 m, 1019 s, 976 m, 955 w, 915 w, 850 m, 840 m, 768 m, 740 w, 694 m, 643 m cm^{-1}. ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 6.80 (m, 8H, $C_6\mathit{H}_3Me_2$), 6.69 (m, 4H, $C_6\mathit{H}_3Me_2$), 3.34 (s, 8H, $C_4\mathit{H}_8O$), 2.63 (s, 12H, $C_6H_3\mathit{Me}_2$), 2.42 (s, 12H, $C_6H_3\mathit{Me}_2$), 0.88 (s, 8H, $C_4\mathit{H}_8O$), 1.08 (t, 6H, $CH_2\mathit{CH}_3$), 0.42 (q, 4H, CH_2CH_3). ^{13}C NMR (C_6D_6, 300 MHz, 25 °C): δ 161.1 ($\mathit{C}_6H_3Me_2$), 152.9 ($\mathit{C}_6H_3Me_2$), 129.0 ($\mathit{C}_6H_3Me_2$), 128.7 ($\mathit{C}_6H_3Me_2$), 128.0 ($\mathit{C}_6H_3Me_2$), 127.7 ($\mathit{C}_6H_3Me_2$), 127.3 ($\mathit{C}_6H_3Me_2$), 125.6 ($\mathit{C}_6H_3Me_2$), 122.2 ($\mathit{C}_6H_3Me_2$), 117.0 ($\mathit{C}_6H_3Me_2$), 70.2 (THF), 24.1 (THF), 18.7 ($C_6H_3\mathit{Me}_2$), 18.9 ($C_6H_3\mathit{Me}_2$), 8.6 (CH_2CH_3), 2.2 (CH_2CH_3).

Complex **2** was obtained in high yield by addition of $[Et_2Al(OAr)]_2$ (206 mg, 1 mmol) to $Y(OAr)_3(THF)_3$ (667 mg, 1 mmol) in 8 mL of toluene and warming to 100 °C for 90 min. Removal of the solvent produced **2**, identified by ^1H NMR, as a white powder in 80% yield (320 mg).

A single crystal of **2** was mounted in a glass capillary and transferred to a Siemens $P2_1$ diffractometer, and data were collected at room temperature. The unit cell was found to be isomorphous with that of **4** (see below). Due to the poor quality of the crystal, uncertainties in the cell parameters were large and complete data collection was not pursued.

$(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, 3. Reaction of $[Me_2Al(OAr)]_2$ (178 mg, 1 mmol) with $Yb(OAr)_3(THF)_3$ (751 mg, 1 mmol) in 8 mL of toluene as described above for the yttrium analog formed **3** as a light yellow powder, which was recrystallized from benzene (840 mg, 98%). Anal. Calcd for $C_{42}H_538O_6AlYb$: C, 58.80; H, 6.81. Found: C, 57.48; H, 6.61. IR (Nujol): 1593 m, 1282 w, 1275 s, 1231 m, 1200 m, 1093 s, 1025 w, 945 w, 875 s, 850 w, 837 m, 762 s, 737 m, 712 w, 681 m, 668 w cm^{-1}.

Table 1. Crystallographic Data for $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, **3**, and $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, **4**[a]

formula	$C_{48}H_{60}AlO_6Yb$	$C_{50}H_{64}AlO_6Nd$
mol wt	933.0	932.2
space group	*C*2/*c*	*C*2/*c*
a, Å	23.881(9)	23.185(2)
b, Å	12.035(7)	13.1283(12)
c, Å	18.676(6)	18.905(2)
β, deg	118.74(2)	117.658(7)
V, $Å^3$	4706(3)	5096.8(9)
Z	4	4
D_{calcd}, g cm^{-3}	1.317	1.215
temp, K	296	296
abs coeff, μ, cm^{-1}	2.050	1.078
min−max transm coeff	0.73−0.91	0.80−0.85
R_F, %	7.6	7.2
R_{wF}, %	9.4	9.2
GOF	1.57	1.56

[a] Radiation was Mo Kα; $\lambda = 0.710\,73$ Å.

X-ray Data Collection, Structure Determination, and Refinement for $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, 3. All of the complexes described here produced crystals which crack in a cold stream at temperatures of about 165 K. X-ray data were therefore collected at room temperature. In the glovebox, a colorless crystal of approximate dimensions 0.20 × 0.23 × 0.27 mm^3 was mounted in a capillary and transferred to a Siemens $P2_1$ diffractometer. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of intensity data were carried out using standard techniques similar to those of Churchill.[7] Details appear in Table 1.

All data were corrected for absorption and for Lorentz and polarization effects, merged to yield a unique data set, and placed on an approximately absolute scale. A careful examination of a preliminary data set revealed the systematic extinctions *hkl* for $h + k = 2n + 1$, *h*0*l* for $l = 2n + 1$, and *hk*0 for $h + k = 2n + 1$. Of the two possible space groups *Cc* and *C*2/*c*, the centrosymmetric monoclinic space group *C*2/*c* [C_{2h}^6; No.]15 was found to be correct choice.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[8] or the SHELXTL PLUS program set.[9] The analytical scattering factors for neutral atoms were used throughout the analysis;[10a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[10b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o| + 0.002(|F_o|)^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. One of the phenyl rings was refined as a rigid group. Hydrogen atoms were included using a riding model with $d(C{-}H) = 0.96$ Å and $U(\text{iso}) = 0.08$ $Å^2$. There is a benzene molecule per formula unit as a solvent of crystallization. Refinement of positional and thermal parameters led to convergence with $R_F = 7.6\%$, $R_{wF} = 9.4\%$, and GOF = 1.57 for 110 variables refined against those 2500 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features, $\varrho(\max) = 1.94$ e $Å^{-3}$. Important angles and distances are given in Table 2.

$(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, 4. Addition of $AlEt_3$ (1 mL, 1 M solution in hexanes) to $[Nd(OAr)_3(THF)_2]_2$ (605 mg, 0.5 mmol) in 10 mL of toluene caused an immediate blue to red color change. Removal of solvent after stirring for 2 days and extraction with hexanes

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Table 2. Important Interatomic Distances and Angles for $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, **3**, and $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, **4**

	3	**4**
Ln(1)−Al(1)	3.298(7)	3.411(6)
Ln(1)−O(1)	2.306(8)	2.447(7)
Ln(1)−O(2)	2.056(12)	2.153(9)
Ln(1)−O(3)	2.371(9)	2.493(7)
Al(1)−O(1)	1.846(10)	1.810(8)
Al(1)−C(21)	1.996(29)	1.991(28)
O(1)−C(1)	1.387(18)	1.383(15)
O(2)−C(9)	1.369(27)	1.343(17)
C(21)−C(22)		1.717(82)
C(21)−C(23)		1.424(43)
O(1)−Ln(1)−O(2)	105.8(4)	111.2(3)
O(1)−Ln(1)−O(3)	80.2(3)	79.7(3)
O(2)−Ln(1)−O(3)	82.2(4)	81.5(3)
O(1)−Ln(1)−O(1A)	65.6(4)	61.5(3)
O(3)−Ln(1)−O(2A)	83.5(4)	83.4(3)
O(1)−Al(1)−C(21)	113.1(7)	114.3(6)
O(1)−Al(1)−O(1A)	85.1(6)	87.4(5)
C(21)−Al(1)−O(1A)	114.3(9)	114.4(8)
C(21)−Al(1)−C(21A)	113.9(16)	110.5(15)
Nd(1)−O(1)−Al(1)	104.7(4)	105.5(3)
Nd(1)−O(2)−C(9)	165.5(12)	169.0(8)
Al(1)−C(21)−C(22)		100.3(33)

gave a red solution. Evaporation of solvent on a rotary evaporator gave an oil which was redissolved in benzene. Slow evaporation gave large block-shaped crystals after several days at ambient temperature (210 mg, 24%). The crystals appeared red to the naked eye but were blue in the light of the microscope. Anal. Calcd for $C_{42}H_{62}O_6AlNd$: C, 61.58; H, 7.28. Found: C, 61.25; H, 7.18. IR (Nujol): 1592 m, 1279 w, 1269 s, 1229 s, 1195 s, 1095 s, 1023 m, 975 w, 949 w, 918 w, 870 w, 853 m, 841 s, 765 s, 746 m, 695 s, 638 s, br cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, 4. Complex **4** was found to be isomorphous with **3**. A blue crystal of approximate dimensions 0.37 × 0.37 × 0.30 mm^3 was mounted in a capillary and transferred to a Siemens P_4 diffractometer. The data collection, structure solution, and refinement were carried out as described above. This structure also contains a benzene molecule per formula unit as a solvent of crystallization. Refinement of positional and thermal parameters led to convergence with $R_F = 7.2\%$, $R_{wF} = 9.2\%$, and GOF = 1.56 for 142 variables refined against those 2438 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features, $\varrho(\max) = 0.67$ e Å^{-3}.

Results and Discussion

Synthesis. The reaction of Al_2Me_6 with either $[(ArO)_2(THF)Y(\mu\text{-}OAr)]_2$ or $Y(OAr)_3(THF)_3$ in hexanes or toluene gives complicated reaction mixtures. $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$, **1**, was crystallized from the system shown in reaction 1 and was definitively identified by X-ray crystallography.

$$[(ArO)_2(THF)Y(\mu\text{-}OAr)]_2 + 3Al_2Me_6 \rightarrow \underset{\mathbf{1}}{(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2} + [AlMe_2(OAr)]_2 + \text{other products} \quad (1)$$

The formation of the dimethyl tetrakis(aryloxide) product must involve a ligand redistribution which leads to other products richer in alkyl groups. A similar ligand redistribution product, $(Me_3CO)Cl(THF)_2Y(\mu\text{-}OCMe_3)_2(AlMe_2)$, was observed in a *tert*-butoxide system involving the reaction of $Y_3(OCMe_3)_7Cl_2(THF)_2$ with $AlMe_3$.[3] The ligand redistribution appears to be more prevalent with the 2,6-dimethylphenoxide system.

Since this mixture did not provide a clean route to a 1:1 Y:Al product and since ligand redistribution seemed to be preferred, the use of the mixed-ligand aluminum reagent $[AlMe_2(OAr)]_2$ was investigated. This complex is readily obtained from the reaction of Al_2Me_6 with HOAr.

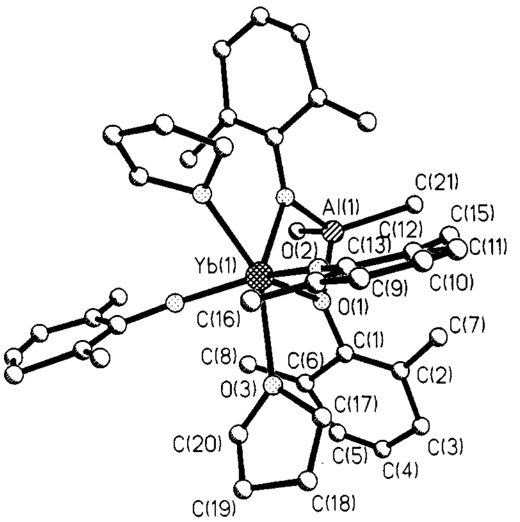

Figure 1. Molecular structure of $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, **3**.

$$Al_2Me_6 + 2HOAr \rightarrow [AlMe_2(OAr)]_2 + 2CH_4 \quad (2)$$

The reaction of $[AlMe_2(OAr)]_2$ with $Y(OAr)_3(THF)_3$ forms $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$ in >90% yield according to eq 3.

$$Y(OAr)_3(THF)_3 + {}^1/_2[AlMe_2(OAr)]_2 \rightarrow \underset{\mathbf{1}}{(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2} + THF \quad (3)$$

$(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$ is readily isolated in pure form by simple removal of solvent.

Although the crystallographic data revealed the identity of $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$, the poor diffraction and fast decay of the crystal on the diffractometer provided only low-quality X-ray data. To obtain crystals of an analog which could provide better data, the ytterbium analog $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, **3**, was prepared. This required the preparation of the ytterbium 2,6-dimethylphenoxide complex $Yb(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ as shown in eq 4. $Yb(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$

$$Yb[N(SiMe_3)_2]_3 + 3HOAr \rightarrow Yb(OAr)_3(THF)_3 + 3HN(SiMe_3)_2 \quad (4)$$

reacts with $AlMe_3$ in a reaction analogous to that observed with $Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$, and good X-ray data were obtainable on $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$ (Figure 1).

Extension of these results to ethylaluminum analogs and to a larger lanthanide was studied to establish the generality of this approach to mixed-metal species. The reaction of the 2,6-dimethylphenoxide neodymium complex $[Nd(OC_6H_3Me_2\text{-}2,6)_3(THF)_2]_2$ with $AlEt_3$ was examined, and as shown in eq 5, the

$$[Nd(OC_6H_3Me_2\text{-}2,6)_3(THF)_2]_2 + AlEt_3 \rightarrow \underset{\mathbf{4}}{(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2} \quad (5)$$

$(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$ product analogous to $(ArO)_2(THF)_2(\mu\text{-}OAr)_2AlMe_2$ was isolated. X-ray crystallography revealed that $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$ is isomorphous with $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$ and $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$.

Reactions analogous to eq 3 were studied with the diethylaluminum reagent $[AlEt_2(OAr)]_2$ prepared from $AlEt_3$ and ArOH as described above for $[AlMe_2(OAr)]_2$. The $(ArO)_2(THF)_2Y(\mu$-

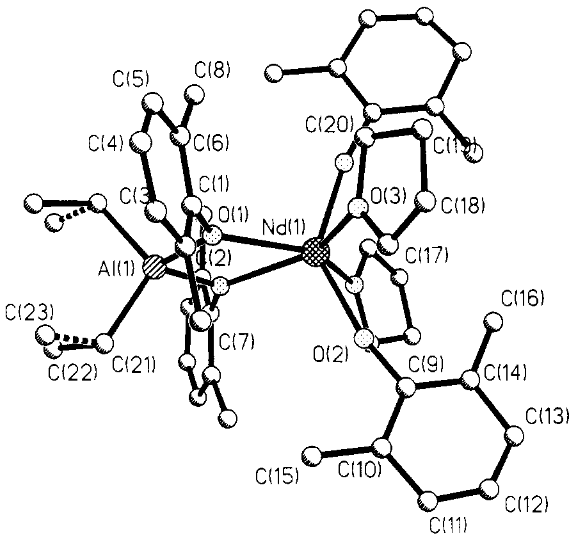

Figure 2. Molecular structure of $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, **4**.

$OAr)_2AlEt_2$ product, **2**, was also found to be isomorphous with $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$ and $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$. As in the case of the other yttrium complex $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlMe_2$, the quality of data on $(ArO)_2(THF)_2Y(\mu\text{-}OAr)_2AlEt_2$ was poor and only the unit cell could be determined definitely. In this case, the Nd analog $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, **4**, was used to obtain better structural data on an ethyl derivative.

Structural Studies. The structure of $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$ (Figure 1) contains an ytterbium center in a severely distorted octahedral coordination environment with O−Yb−O angles ranging from 65.4(4) to 145.8(4)°. As expected, the Yb−O(bridging) distance of 2.306(8) Å is larger than the Yb−O(terminal) distance of 2.057(11) Å, and this observation is consistent with those for other complexes containing dimethylphenoxide ligands. For example, in $[(ArO)_2(THF)Y(\mu\text{-}OAr)]_2$,[4] the Y−O distances involving terminal oxygen atoms are 2.075(6) and 2.045(6) Å and the bridging distances are 2.277(5) and 2.275(5) Å.

The aluminum center has a distorted tetrahedral geometry with local angles of 85.3(6)−121.0(8)°. The 1.970(26) Å Al−C distance is in the range of Al−C distances in known complexes, e.g. 1.946(23) and 2.014(33) Å in $Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_3$ and 1.966(10) and 1.983(10) Å in $(Me_3CO)Cl(THF)_2Y[(\mu\text{-}OCMe_3)_2AlMe_2]$.[3] The Yb−O−Al angle, 105.5(3)°, is comparable to the analogous 102.2 and 104.4° angles in $(Me_3CO)(THF)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$.

$(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$, **4**, is isomorphous with $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$, **3**. The distances and angles in $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$ follow the trends discussed above for **3**. The only significant difference in the structures of $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$ and $(ArO)_2(THF)_2Yb(\mu\text{-}OAr)_2AlMe_2$ is that the methyl carbons of the ethyl group are disordered in two different orientations in $(ArO)_2(THF)_2Nd(\mu\text{-}OAr)_2AlEt_2$.

Conclusion

Yttrium and lanthanide 2,6-dimethylphenoxide complexes react with trialkylaluminum reagents to generate 1:1 mixed-metal complexes, but facile ligand redistribution processes that form mixtures containing $(ArO)_2(THF)_2Ln(\mu\text{-}OAr)_2AlR_2$ complexes in which the metal is surrounded by oxygen donor ligands decrease the utility of this reaction. The type of ligand redistribution and byproduct formation can be avoided by using mixed-ligand aluminum starting reagents such as $[AlR_2(OAr)]_2$ which can be readily synthesized in quantitative yield for R = Me and Et. $(ArO)_2(THF)_2Ln(\mu\text{-}OAr)_2AlR_2$ products can be isolated in high yield simply by removal of solvent. These 1:1 mixed-metal Ln:Al species are accessible for a large metal like neodymium as well as for small metals like yttrium or ytterbium.

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Supplementary Material Available: Listings of crystal data, data collection, solution, and refinement parameters, atomic coordinates, thermal parameters, and interatomic distances and angles and additional structural diagrams (27 pages). Ordering information is given on any current masthead page.

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