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Isolation and structural characterization of tetra- and pentaheterometallic neodymium 4-methylphenoxide complexes

William J. Evans,* Mohammad A. Ansari and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, Irvine, California 92697, U.S.A.

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Abstract—The compatibility of the special bridging abilities of the 4-methylphenoxide ligand, OC_6H_4Me-4, and alkylaluminum reagents have been examined. $NdCl_3$ reacts with KOC_6H_4Me-4 in THF to form $K_3Nd_2(\mu\text{-}OC_6H_4Me\text{-}4)_6(\mu_4\text{-}OC_6H_4Me\text{-}4)_3(THF)_7$, **1**, which has a trigonal bipyramidal arrangement of metal atoms with neodymium in the apical sites. Six doubly-bridging aryloxide ligands connect each apical metal to an equatorial metal and three quadruply-bridging aryloxide ligands connect the apical metals with two equatorial sites. Two potassium atoms have two terminal THF ligands and the other metals each have one terminal THF. A suspension of **1** in hexanes reacts with Al_2Me_6 to produce colorless crystals of $[Me_2Al(OC_6H_4Me\text{-}4)]_n$ and blue crystals which have been crystallographically characterized as $Nd[\mu\text{-}OC_6H_4Me\text{-}4)_2AlMe_2]_3$, **2**. The neodymium atom in **2** is surrounded by an octahedron of bridging aryloxide ligands and each aluminum is tetrahedral. © 1997 Elsevier Science Ltd

Keywords: neodymium; aluminum; heterometallic; aryloxide; polymetallic.

Recent studies of yttrium and lanthanide alkoxide and aryloxide chemistry have revealed that heterometallic complexes can often be obtained using the capacity of these OR and OAr ligands to bridge two different metals [1–6]. Although a variety of structural types and compositions have been identified, an extensive knowledge of synthetic routes to specific heterometallic species remains to be developed. The ability to make particular heterometallic combinations is desirable since yttrium and the lanthanide metals have often been found to be critical components in mixed metal solid state materials which exhibit unusual and useful physical properties [7]. Mixed metal complexes are also of interest with respect to catalysis, particularly when aluminum is one component [8].

In previous studies, we have found that both the 4-methylphenoxide ligand OC_6H_4Me-4 [2] and alkylaluminum reagents [3–6] can be useful in making mixed metal complexes. Since the 4-methylphenoxide ligand has no bulky groups near the donor atom, it is sterically well-suited for extensive bridging. The methyl group in the 4 position is useful for NMR characterization. The Lewis acidity of alkylaluminum complexes make them ideal for bridging as well. In this report, we examine a combination of these two approaches which shows that they are compatible and can be used together to extend their applicability.

EXPERIMENTAL

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were purified as previously described [9]. NMR spectra were recorded using a General Electric QE-300 300 MHz spectrometer at 25°C. Elemental analyses were determined on a Carlo Erba EA 1108 instrument or performed by Analytische Laboratorien, Gummersbach, Germany. 4-Methylphenol (Aldrich) was purified by sublimation prior to use.

$K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7$, 1

A freshly prepared sample of KOC_6H_4Me-4, obtained by reacting KH (200 mg, 4.5 mmol) with HOC_6H_4Me-4 (487 mg, 4.5 mmol) in 20 cm^3 of THF,

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* Author to whom correspondence should be addressed

was added to a suspension of $NdCl_3$ (250 mg, 1.0 mmol) in 10 cm^3 of THF. The reaction was stirred while heating at 60°C for 10 min and for an additional 48 h at ambient temperature. The $NdCl_3$ slowly went into solution. The blue solution was centrifuged to remove small amounts of pale blue insoluble material. The volume of the supernatant was reduced to about 10 cm^3 using a rotary evaporator and blue crystals of **1** (620 mg, 66%) formed after several days at room temperature. Anal. Found: Nd, 16.2. Calc. for $C_{91}H_{119}O_{16}K_3Nd_2$: Nd, 15.4%. IR (Nujol): 1610s, 1560w, 1505s, 1462s, 1458s, 1374m, 1296s, 1172m, 1108w, 1066w, 916w, 850w, 822s, 811m, 720w, 710w cm^{-1}. ^1H NMR (C_6D_6): δ 7.95 (br, $\Delta\nu_{1/2} = 210$ Hz), 7.41 (br, $\Delta\nu_{1/2} = 220$ Hz), 2.40 (br, $\Delta\nu_{1/2} = 70$ Hz), -4.05 (br, $\Delta\nu_{1/2} = 16$ Hz), -8.71 (br, $\Delta\nu_{1/2} = 40$ Hz).

$Nd[Me_2Al(OC_6H_4Me\text{-}4)_2]_3$, **2**

In the glovebox, Al_2Me_6 (0.5 cm^3, 2.5 mmol) was added *via* syringe to a suspension of $K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7$ (200 mg, 0.12 moles) in 10 cm^3 of hexanes. After stirring overnight, the mixture was centrifuged and a small amount of insoluble material was discarded. Removal of solvent from the supernatant by rotary evaporation gave an oily product which showed a complicated NMR. After several days at ambient temperature, the oil produced a mixture of colorless crystals and blue crystals which had very similar solubilities. This procedure reproducibly gives this mixture, but separation of the products has not been achieved. Characterization has been done on crystals separated manually. The blue crystals were identified by X-ray diffraction as **2**. Found: C, 56.7; H, 6.4; Al, 8.2; Nd, 14.5. Calc. for $C_{48}N_{60}O_6Al_3Nd$: C, 60.2; H, 6.3; Al, 8.5; Nd, 15.1%. IR (Nujol): 1560w, 1541m, 1560s, 1465s, 1458s, 1418w, 1376s, 1217s, 1208w, 1188w, 1104w, 1017w, 824s, 764m, 722w, 685m, 668w cm^{-1}. ^1H NMR (C_6D_6): δ 5.65 (br, $\Delta\nu_{1/2} = 64$ Hz), 3.98 (br, $\Delta\nu_{1/2} = 50$ Hz), 1.24 (br, $\Delta\nu_{1/2} = 75$ Hz), 0.46 (br, $\Delta\nu_{1/2} = 25$ Hz) and -0.52 (s). Spectroscopic data for colorless crystals are as follows. IR (Nujol): 1612m, 1592w, 1506s, 1460s, 1374s, 1225s, 1190s, 1166m, 1105w, 1016w, 936w, 854w, 830m, 776w, 760m, 700s cm^{-1}. ^1H NMR (C_6D_6): δ 7.12 (d, 2H, C_6H_4Me), 6.94 (d, 2H, C_6H_4Me), 6.77 (t, 4H, C_6H_4Me), 1.99 (s, 3H, C_6H_4Me), 1.95 (s, 3H, C_6H_4Me), -0.27 (s, 6H, $AlMe_3$), -0.41 (s, 6H, $AlMe_3$).

Table 1. Crystallographic data for $K_3Nd_2(\mu\text{-}OC_6H_4Me\text{-}4)_6(\mu_4\text{-}OC_6H_4Me\text{-}4)_3(THF)_7$, **1** and $Nd\{(\mu\text{-}OC_6H_4Me\text{-}4)_2AlMe_2\}_3$, **2**

	1	2
Formula	$C_{91}H_{119}O_{16}K_3Nd_2$	$C_{48}H_{60}O_6Al_3Nd$
fw	1874.64	958.14
Space group	$P\bar{1}$	$C2/c$
a (Å)	14.043(3)	20.041(6)
b (Å)	17.334(4)	18.872(3)
c (Å)	18.951(2)	15.015(5)
α (°)	85.86(1)	
β (°)	85.99(1)	96.68(2)
γ (°)	87.56(2)	
V (Å^3)	4586(2)	5640(3)
Z	2	4
Radiation, λ (Å)	0.71073	0.71073
μ (mm^{-1})	1.316	1.005
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0354, 0.0771	0.0757, 0.2242
$R1$, $wR2$ (all data)	0.0521, 0.0850	0.1178, 0.2689
Temp (K)	163	163

$R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2)]^{1/2}$

X-ray data collection, structure determination and refinement for $K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7$, **1**

A pale blue crystal of approximate dimensions $0.46 \times 0.50 \times 0.50$ mm^3 was coated with Paratone oil, mounted on a glass fiber, 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 [10]. Details appear in Table 1.

All 16,856 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 no systematic extinctions nor any diffraction symmetry other than the Friedel condition. Of the two choices $P1$ and $P\bar{1}$, centrosymmetric $P\bar{1}$ was chosen and later proved to be correct by successful solution and refinement of the model.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares technique. The analytical scattering factors for neutral atoms were used throughout analysis. Intensity data were collected ($4 \leqslant 2\theta \leqslant 50°$) at 163 K using a 2Θ-ω scan technique with Mo-K_α radiation. The raw data were processed with a local version of CARESS [11]. All subsequent calculations were carried out using the SHELXL program set [12]. Hydrogen atoms were included using a riding model. Refinement of positional and thermal parameters led to convergence with $wR = 0.0850$ and GOF = 1.047 for 1009 variables refined against those 16,133 data. As a comparison on F, $R1 = 0.035$ for those with 12,938 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features, $\rho(\max) = 0.967$ e$Å^{-3}$. Important angles and distances are given in Table 2. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Center.

Table 2. Selected bond distances (Å) and angles (°) for $K_3Nd_2(\mu\text{-}OC_6H_4Me\text{-}4)_6(\mu_4\text{-}OC_6H_4Me\text{-}4)_3(THF)_7$, **1**

Nd(1)—O(1)	2.272(3)	K(1)—O(2)	2.847(3)	K(2)—C(33)	3.236(4)
Nd(1)—O(2)	2.494(3)	K(1)—O(3)	2.953(3)	K(2)—C(16)	3.338(4)
Nd(1)—O(3)	2.525(3)	K(1)—O(7)	2.674(3)	K(3)—O(1)	2.710(3)
Nd(1)—O(4)	2.561(3)	K(1)—O(8)	2.729(3)	K(3)—O(2)	2.938(3)
Nd(1)—O(5)	2.259(3)	K(1)—O(12)	2.670(3)	K(3)—O(6)	2.885(3)
Nd(1)—O(6)	2.493(2)	K(1)—O(13)	2.726(3)	K(3)—O(9)	2.835(3)
Nd(1)—O(7)	2.274(3)	K(1)—C(8)	3.229(4)	K(3)—C(1)	3.248(4)
Nd(2)—O(2)	2.518(2)	K(1)—C(15)	3.264(4)	K(3)—C(8)	3.076(4)
Nd(2)—O(3)	2.458(3)	K(1)—C(40)	3.270(3)	K(3)—C(54)	3.199(4)
Nd(2)—O(6)	2.540(2)	K(2)—O(3)	3.002(3)		
Nd(2)—O(8)	2.305(3)	K(2)—O(5)	2.810(3)		
Nd(2)—O(9)	2.244(3)	K(2)—O(6)	2.913(3)		
Nd(2)—O(10)	2.288(3)	K(2)—C(15)	3.275(4)		
Nd(2)—O(11)	2.592(3)	K(2)—C(26)	3.185(4)		
O(1)—Nd(1)—O(2)	79.24(9)	O(5)—Nd(1)—O(7)	110.44(10)		
O(1)—Nd(1)—O(3)	68.54(8)	O(6)—Nd(1)—O(7)	144.11(9)	O(6)—Nd(2)—O(8)	143.15(9)
O(1)—Nd(1)—O(6)	82.53(9)	O(2)—Nd(2)—O(3)	67.95(8)	O(6)—Nd(2)—O(9)	83.99(9)
O(1)—Nd(1)—O(7)	115.83(10)	O(2)—Nd(2)—O(10)	141.45(9)	O(6)—Nd(2)—O(10)	79.29(9)
O(2)—Nd(1)—O(3)	67.31(8)	O(2)—Nd(2)—O(6)	67.90(8)	O(8)—Nd(2)—O(9)	109.04(10)
O(2)—Nd(1)—O(4)	134.62(9)	O(2)—Nd(2)—O(10)	141.45(9)		
O(3)—Nd(1)—O(4)	143.55(9)	O(2)—Nd(2)—O(9)	87.93(9)		
O(3)—Nd(1)—O(5)	86.41(9)	O(2)—Nd(2)—O(8)	78.02(9)		
O(3)—Nd(1)—O(7)	79.75(9)	O(2)—Nd(2)—O(11)	144.27(9)		
O(4)—Nd(1)—O(5)	77.56(10)	O(3)—Nd(2)—O(6)	68.83(8)		
O(4)—Nd(1)—O(6)	140.18(9)	O(3)—Nd(2)—O(8)	86.01(9)		
O(4)—Nd(1)—O(7)	75.71(10)	O(3)—Nd(2)—O(9)	148.66(9)		
O(5)—Nd(1)—O(6)	84.60(9)	O(3)—Nd(2)—O(10)	81.95(9)		

X-ray data collection, structure determination and refinement for $Nd[Me_2Al(OC_6H_4Me\text{-}4)_2]_3$, **2**

A blue crystal of approximate dimensions $0.40 \times 0.50 \times 0.53$ mm^3 was transferred as described above to the Siemens *P*4 rotating-anode diffractometer. 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* was found to be correct choice.

Intensity data were collected at 163K ($4 \leqslant 2\theta \leqslant 60°$) using a 2Θ-ω scan technique. Structure solution and refinement was carried out as reported above for **1**. The molecule is located about a site of a two fold symmetry. The Nd atom lies directly on a two fold rotation axis. Refinement of positional and thermal parameters led to convergence with $wR = 0.2689$ and GOF = 1.075 for 263 variables refined against all 8226 data. As a comparison on *F*, $R1 = 0.0757$ for those 5039 data with $|F_o| > 4.0\sigma(|F_0|)$. Large thermal parameters resulted from the poor quality of the crystal. Important angles and distances are given in Table 3. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

$K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7$, **1**

The reaction of 3 equivalents of KOC_6H_4Me-4 with $NdCl_3$ in THF formed a blue paramagnetic complex identified by X-ray crystallography as $K_3Nd_2(\mu\text{-}OC_6H_4Me\text{-}4)_6(\mu_4\text{-}OC_6H_4Me\text{-}4)_3(THF)_7$, **1**, Fig. 1. To improve the yield of this product, KOC_6H_4Me-4 was reacted with $NdCl_3$ in a 9 : 2 ratio to give **1** in > 60% isolated yield according to eq. (1).

$$9KOC_6H_4Me\text{-}4 + 2NdCl_3 \xrightarrow{THF} K_3Nd_2(\mu\text{-}OC_6H_4Me\text{-}4)_6(\mu_4\text{-}OC_6H_4Me\text{-}4)_3(THF)_7 + 6KCl \quad (1)$$

The structure of **1** is very similar to that of the product of the reaction of 9 equivalents of $NaOC_6H_4Me$-4 with 2 equivalents of $LaCl_3$, namely $La_2Na_3(\mu_4\text{-}OC_6H_4Me)_3(\mu\text{-}OC_6H_4Me)_6(THF)_5$, **3**, and its dioxane derivative $\{(La_2Na_3(\mu_4\text{-}OR)_3(\mu\text{-}OR)_6](\mu\text{-}dioxane)_2(dioxane)_3](dioxane)\}_n$, **4** [2]. Complex **3** was first identified from a 3 : 1 ligand to metal ratio reaction which gave a pentametallic product.

1, **3**, and **4** each have a trigonal bipyramidal arrangement of metals with the seven coordinate lan-

Table 3. Selected bond distances (Å) and angles (°) for Nd$\{(\mu\text{-OC}_6\text{H}_4\text{Me-4})_2\text{AlMe}_2\}_3$, **2**

Nd(1)—O(1)	2.349(4)	O(1)—Nd(1)—O(1′)	102.3(2)
Nd(1)—O(2)	2.350(6)	O(1)—Nd(1)—O(2)	63.7(2)
Nd(1)—O(3)	2.368(4)	O(1)—Nd(1)—O(3)	100.3(2)
Al(2)—C(24)	1.845(7)	O(2)—Nd(1)—O(3)	104.8(2)
Al(1)—O(1)	1.845(7)	O(1)—Al(1)—C(15)	113.2(4)
Al(1)—O(2)	1.846(5)	O(1)—Al(1)—C(16)	108.6(4)
Al(1)—C(15)	1.934(8)	O(2)—Al(1)—C(15)	111.5(3)
Al(1)—C(16)	1.948(8)	O(2)—Al(1)—C(16)	112.1(3)
Al(2)—O(3)	1.839(5)	O(3)—Al(1)—C(24)	113.2(4)

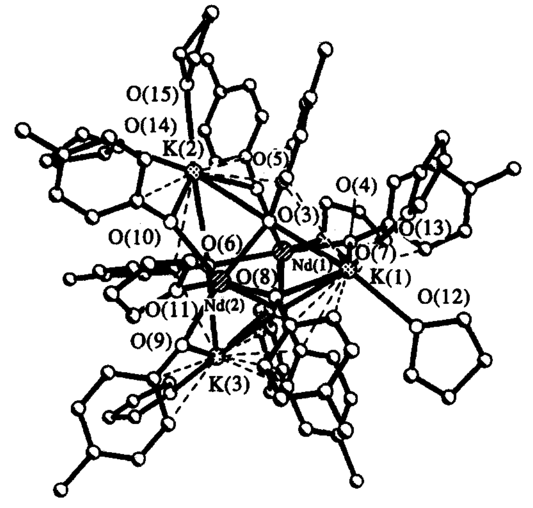

Fig. 1. Ball and stick diagram of the full structure of $\text{K}_3\text{Nd}_2(\mu\text{-OC}_6\text{H}_4\text{Me-4})_6(\mu_4\text{-OC}_6\text{H}_4\text{Me-4})_3(\text{THF})_7$, **1** showing some short potassium arene contacts with dotted lines.

thanide metals in the axial positions, Fig. 2. In each complex, all of the 4-methylphenoxide ligands are bridging: six are doubly bridging and three are quadruply bridging, which is rather unusual. In each of these complexes, each lanthanide metals is terminally ligated with one ether molecule.

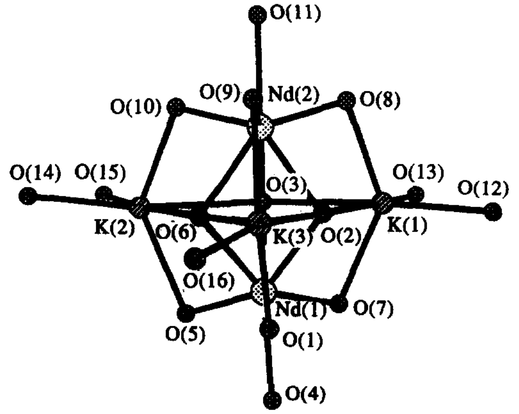

Fig. 2. Ball and stick diagram of the trigonal bipyramidal metal framework of $\text{K}_3\text{Nd}_2(\mu\text{-OC}_6\text{H}_4\text{Me-4})_6(\mu_4\text{-OC}_6\text{H}_4\text{Me-4})_3(\text{THF})_7$, **1**, with the oxygen donor atoms included.

The difference between **1**, **3** and **4** is the ligation of the alkali metals. In **3**, each sodium has one terminal THF ligand. In **1** and **4**, two of the three equatorial alkali metal atoms are coordinated to two terminal ether groups and the third is coordinated to only one ether molecule. The structure of **1** differs from that of **4** in that it has some close aryl ring alkali metal interactions.

The structure of **1** is best compared with **4** since the crystal data on **3** were of limited quality. Since the main point of difference between **1** and **4** involves the aryl ring coordination, the potassium–carbon distances will be discussed first. Calibration on these distances can be obtained by considering that the K—C(arene) distances in KBPh_4 average 3.191(5) Å [13], a 3.097(10)–3.473(11) Å range is found in $\{\text{K}[\text{Nd}(\text{OC}_6\text{H}_3{}^i\text{Pr-2,6})_4]\}_n$ [14], 3.17(2) to 3.93(2) Å distances are found in $\{\text{K}[(\mu\text{-C}_5\text{H}_5)_2\text{Nd}(\mu\text{-O-C}_6\text{H}_3\text{Me}_2\text{-2,6})_2]\}_n$ [15] and 3.31 and 3.42 Å average distances are found in $(\text{MeC}_6\text{H}_5)_2\text{K}(\mu\text{-Cl})\text{Lu}[\text{CH}(\text{SiMe}_3)_2]_3$ [16]. In **1** there are 18 K—C distances less than 3.42 Å. Each of these involves either an *ipso* carbon or a carbon adjacent to one of these *ipso* carbon atoms. K(3) which is attached to only one THF ligand, has the shortest K—C(arene ring) distances which include lengths of 3.074(4), 3.076(4), 3.199(4), and 3.248(4) Å. K(1) and K(2) each have 3 lengths between 3.18 and 3.28 Å.

The Nd—(μ-O) distances in **1** range from 2.244(3) to 2.305(3) Å and average 2.27(2) Å. The analogous La—(μ-O) values for **4**, 2.326(4)–2.349(4) Å with a 2.34(1) Å average are similar, considering that Nd is 0.05 Å smaller than La [17]. The Nd—(μ_4-O) distances in **1** are larger as expected and span a wider range, 2.458(3)–2.540(2) Å, than those in **4**, 2.527(4)–2.575(4) Å. However, the averages for the two compounds, 2.50(3) Å for **1** and 2.55(2) Å for **4**, are consistent with the difference in their radii.

The K—O and Na—O distances are more difficult to compare since their coordination numbers differ due to the arene interactions and since the difference in K and Na radii using Shannon radii [17] varies from 0.31–0.38 depending on the coordination number. The K—(μ-O) distances in **1** range from 2.668(3) to 2.835(3) Å with a 2.74(6) Å average compared to a

2.371(5)–2.539(5) Å range and 2.44(6) Å average for **4**. Using the difference in six coordinate radii of sodium and potassium of 0.36 Å, a 2.73–2.90 Å range and an average of 2.80 Å would have been expected for **1**. The K—(μ_4-O) distances in **1** range from 2.847(3)–3.002(3) Å with an average of 2.92(4) Å compared to a 2.469(5)–2.842(5) range and 2.67(5) Å average for **4** which translates to an expected range of 2.83–3.20 Å and average of 3.03 Å for **1** when radial differences are considered. The shorter distances in **1** are unusual since the additional interactions of the arene rings would be expected to lead to longer distances. Evidently, a range of distances can be accommodated in this structural type.

The similarity of **1**, **3**, and **4** attests to the preferred nature of this type of structure. This structure has also been seen in different variations in the La/Na system in structures which have one metal less in the skeleton, but which maintain the basic form: $[Na(DME)_3][La_2Na_2(\mu_3\text{-}OR)_3(\mu\text{-}OR)_4(OR)_2(THF)_2(DME)_2](DME)$, **5**, and $[Me_4N][La_2Na_2(\mu_4\text{-}OR)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(THF)_5](THF)$, **6** [2]. The structure of **1** shows that this structural type can accommodate a larger alkali metal ion. The prevalence of this structure is surprising considering that three of the aryloxide ligands must bridge four metal centers. With the larger potassium ions, the bridging oxygen is even more stretched than in **3**–**6**. However, the shorter than expected K—O distances in **1** may occur because these distances in **1** represent an upper limit on the metal oxygen bond lengths in structures of this type.

$Nd[Me_2Al(OC_6H_4Me\text{-}4)_2]_3$, 2

Given the propensity of 4-methylphenoxide ligands to form and retain $Ln_2M_3(OC_6H_4Me\text{-}4)_9$ structures, it was uncertain if alkylaluminum reagents would break open this polymetallic framework. However, alkylaluminum reagents are known to break up trimetallic yttrium *tert*-butoxide units [3, 4, 18], for example as shown in eqn (2),

$$Y_3(OCMe_3)_9(THF)_2 + \text{excess } Al_2Me_6 \rightarrow Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_3 \qquad (2)$$

and to solubilize intractable solids derived from the insoluble product made from $LnCl_3$ and 3 equivalents of $MNMe_2$ [5], as exemplified in eqn. (3).

$$NdCl_3 + 3LiNMe_2 \rightarrow [Nd(NMe_2)_3(LiCl)_3]\downarrow + 1.5Al_2Me_6 \rightarrow [Nd(NMe_2)_3(AlMe_3)_3] + 3LiCl \qquad (3)$$

In this aryloxide ligand case, the alkylaluminum reaction is also successful as shown in eqn (4).

$$K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7 + Al_2Me_6(xs) \rightarrow Nd[(\mu\text{-}OC_6H_4Me\text{-}4)_2AlMe_2]_3 + \text{other products} \qquad (4)$$

This reaction proceeds in a manner similar to that of eq. (3) in that the starting material, $K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7$, is insoluble in the hexane solvent and Al_2Me_6 takes the neodymium into solution. In this system some ligand redistribution must take place as was also observed in the yttrium 2,6-dimethylphenoxide reaction shown in eq. (5)

$$[(2,6\text{-}Me_2C_6H_3O)_2(THF)Y(\mu\text{-}OC_6H_3Me_2\text{-}2,6)]_2 + 3Al_2Me_6 \rightarrow (2,6\text{-}Me_2C_6H_3O)_2(THF)_2Y(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2\text{-}AlMe_2 + [AlMe_2(OC_6H_3Me_2\text{-}2,6)]_2 + \text{other products} \qquad (5)$$

in which one methyl on aluminum is exchanged for an aryloxide [6]. Spectral data on the colorless byproduct of reaction (4) are consistent with the formation of a mixed aryloxide methyl aluminum complex [19] as was observed in the 2,6-dimethylphenoxide reaction [6].

$Nd[(\mu\text{-}OC_6H_4Me\text{-}4)_2AlMe_2]_3$, **2**, can be considered a derivative of the crystallographically characterized $Nd[(\mu\text{-}Me)_2AlMe_2]_3$ [5] in which bridging methyl groups have been substituted with 4-methylphenoxide ligands. The structural features of **2** can also be compared with those in $(2,6\text{-}Me_2C_6H_3O)_2(THF)_2Nd(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2AlEt_2$ [6].

Complex **2** possesses a crystallographically imposed two-fold symmetry axis passing through Nd(1) and Al(2). Nd is in a distorted octahedral environment (Fig. 3) with O—Nd—O angles ranging from 63.7(2) to 108.8(2)°. The Nd—(μ-O) distances in **2** vary from 2.349(4) to 2.368(3) Å which are longer than Nd—(μ-O) distances but shorter than Nd—(μ_4-O) distances found in the precursor $K_3Nd_2(OC_6H_4Me\text{-}4)_9(THF)_7$. As expected, these distances are longer than the 2.194(11)—2.206(12) Å and 2.21(2) Å Nd—O distances in $\{K[(\mu\text{-}C_5H_5)_2Nd(\mu\text{-}OAr)_2]\}_n$ [15] and $K[Nd(OC_6H_3{}^iPr_2\text{-}2,6)_4]$ [14], respectively, which do not have bridging oxygen donor atoms. The Nd—(μ-O) distances in **2** are closer to the 2.447(7) Å bridging

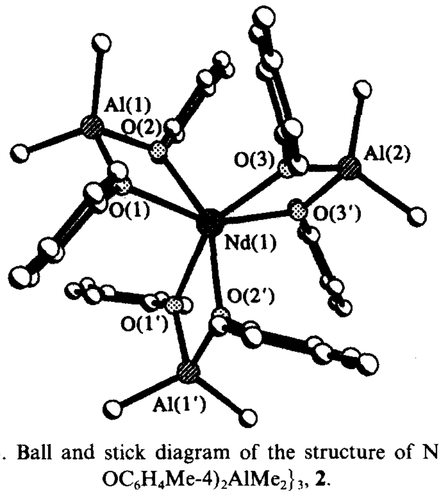

Fig. 3. Ball and stick diagram of the structure of $Nd\{(\mu\text{-}OC_6H_4Me\text{-}4)_2AlMe_2\}_3$, **2**.

Nd—O distance than to the 2.153(9) Å non-bridging Nd—O distance in $(2,6\text{-}Me_2C_6H_3O)_2(THF)_2Nd(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2AlEt_2$ [6].

The geometry around aluminum is distorted tetrahedral with donor atom—Al—donor atom angles ranging from 84.4(2) to 121.2(4)°. The Al—O distances span the narrow range from 1.839(5) to 1.846(5) Å and are similar to the 1.810(8) and 1.846(10) Å Al—O distances in $(2,6\text{-}Me_2C_6H_3O)_2(THF)_2Nd(\mu\text{-}OC_6H_3Me_2\text{-}2,6)AlEt_2$ and $(2,6\text{-}Me_2C_6H_3O)_2(THF)_2Yb(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2AlMe_2$ [6].

CONCLUSION

The capacities of 4-methylphenoxide ligands and alkylaluminum moieties to form bridged heterometallic complexes have been shown to be compatible. Hence, these two approaches to heterometallic lanthanide complexes can be combined to provide another synthetic option for generating compounds containing desirable mixtures of metal.

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