# Aluminate Anions

# Steric Effects on the Structures, Reactivity, and Coordination Chemistry of Tris(2-pyridyl)aluminates

Raúl García-Rodríguez\* and Dominic S. Wright<sup>[a]</sup>

**Abstract:** Introducing substituents in the 6-position of the 2-pyridyl rings of tris(pyridyl)aluminate anions, of the type  $[EtAl(2-py')_3]^-$  (py' = a substituted 2-pyridyl group), has a large impact on their metal coordination characteristics. This is seen most remarkably in the desolvation of the THF solvate  $[EtAl(6-Me-2-py)_3Li]$  (1), containing a pyramidal, three-coordinate Li<sup>+</sup> cation. Similar monomeric complexes are observed for  $[EtAl(6-CF_3-2-py)_3Li]$  (2) and  $[EtAl(6-Br-2-py)_3Li]$  (3), which contain CF<sub>3</sub> and Br substituents (R). This steric influence can be exploited in the synthesis of a new class of terminal Al–

## Introduction

Over the last three decades, neutral tris(pyridyl) ligands of the general type  $[Y(Py)_3]$  (Py=2-pyridyl, Y=CR, COR, CH, N, P, P=O, As; **A** in Figure 1), have emerged as an important family of ligands.<sup>[1]</sup> These ligands, along with the related tris(pyrazolyl)borates and methanes, have found a vast range of applications in coordination, organometallic, and bioinorganic chemistry.<sup>[2]</sup> It is been only relatively recently, however, that attention has turned to ligands containing the heavier Group 13 and 14 atoms at the bridgehead.<sup>[3]</sup> This change from a non-metallic to a more metallic atom in particular opens up the possibility of redox activity and variable oxidation states at the bridgehead.<sup>[4]</sup> Of particular interest are tris(pyridyl)aluminates [RAI(2-



Figure 1. The framework found in the family of tris(2-pyridyl) ligands (A), the tris(2-pyridyl)aluminate family of ligands (B), and the oxo-pyridyl ligand set (C).

- [a] Dr. R. García-Rodríguez, Prof. D. S. Wright Department of Chemistry, University of Cambridge Lensfield Road, Cambridge CB2 1EW (UK) E-mail: rg489@cam.ac.uk
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OH complexes, as is seen in the controlled hydrolysis of **2** and **3** to give  $[EtAl(OH)(6-R-2-py)_2]^-$  anions, as in the dimer  $[EtAl(OH)(6-Br-2-py)_2Li]_2$  (**5**). Attempts to deprotonate the Al–OH group of **5** using  $Et_2Zn$  led only to the formation of the zincate complex  $[LiZn(6-Br-py)_3]_2$  (**6**), while reactions of the 6-Br substituted **3** and the unsubstituted complex  $[EtAl(2-py)_3Li]$  with MeOH give  $[EtAl(OMe)(6-Br-2-py)_2Li]_2$  (**7**) and  $[EtAl(OMe)(2-py)_2Li]_2$  (**8**), respectively, having similar dimeric arrangements to **5**. The combined studies presented provide key synthetic methods for the functionalization and elaboration of tris(pyridyl)aluminate ligands.

py')<sub>3</sub>]<sup>-</sup>, which are unusual in this area in that they are negatively charged instead of neutral (**B**; Figure 1).<sup>[3a]</sup> As one of the only anionic members of the tris(pyridyl) family,<sup>[5]</sup> the aluminates are particularly suitable for the coordination of metal cations. Indeed, aluminate ligands of this type have extensive coordination chemistry with a range of main-group and transition-metal ions.<sup>[6]</sup> The coordination of a tris(pyridyl) ligand to another metal provides a facile route to heterometallic complexes, such as the sandwich compound [{MeAl(2-py)<sub>3</sub>}<sub>2</sub>Fe], which is a highly selective styrene epoxidation catalyst in air.<sup>[7]</sup>

So far, studies of the coordination chemistry of tris(2-pyridyl) aluminate anions have focused almost exclusively on arrangements based on the unsubstituted 2-pyridyl ligand.<sup>[3a]</sup> We have found recently that the introduction of methyl groups at the 6-position of the 2-pyridyl rings has a large effect on the coordination character of the ligand.<sup>[8]</sup> For example, the [EtAl(6-Me-2-Py)<sub>3</sub>]<sup>-</sup> ligand is particularly useful in the steric stabilization of unusual metal oxidation states such as in [{EtAl(6-Me-2 $py_{3}_{2}Sm$ ], in which the  $Sm^{2+}$  cation is sterically shielded by the six Me-groups of the two aluminate ions. This results in an apparently large stabilization of the complex towards molecular oxygen as compared with the unsubstituted complex [{EtAl(2-py)<sub>3</sub>}<sub>2</sub>Sm], which rapidly scavenges molecular oxygen, giving the  $[EtAl(2-py)_2O]^{2-}$  dianion (C; Figure 1).<sup>[9]</sup> Relevant to the formation of a terminal Al-O ligand framework of this type, Roesky has shown that hydrolysis or hydroxylation of the sterically encumbered β-diketiminato AI<sup>Ⅲ</sup> complexes  $[HC{(CMe)(NDipp)}_2AIR_2]$  (Dipp=2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R=Cl, I or alkyl) produces terminal AI–OH compounds.<sup>[10]</sup>

In the study presented herein, we explore the synthesis and coordination properties of a series of sterically encumbered tris(pyridyl)aluminate ligands of the type D (Figure 2), having

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Figure 2. The steric effects introducing substituents at the 6-position of the tris(2-pyridyl) framework (D) and the resulting stabilisation of the hydroxo and alkoxide aluminate ions (E and F).

different substituents at the 6-position of the pyridyl ring (R = Me, CF<sub>3</sub>, Br). We then show that such aluminate ions can be used as simple precursors for the synthesis of a new family of terminal Al–OH (**E**; Figure 2) and related alkoxide complexes (**F**).

## **Results and Discussion**

As noted above, the coordination chemistry of tris(pyridyl)ligands has been a major research theme in the past thirty years or so. Surprisingly, however, in contrast to the tris(pyrazolyl)borate ligands, there have been few systematic studies of the effects of introducing different substituents on the pyridyl ring.<sup>[8,11]</sup> We showed recently that methyl group substitution of the pyridyl ring units in the aluminate ion of [EtAl(6-Me-2py)<sub>3</sub>Li·THF] (1·THF) provided a sterically demanding metal coordination site that could be used to stabilize unusual oxidation states.<sup>[9]</sup> The extreme steric congestion of the aluminate ion is witnessed in the solid-state structure of 1.THF, which has a highly distorted Li-THF coordination environment. In light of this apparently weak coordination of THF to Li<sup>+</sup>, we decided in our preliminary studies to explore the desolvation of 1.THF, anticipating the formation of a dimeric complex [1]2, which would be analogous to the dimeric complex [MeAl(2-py)<sub>3</sub>Li]<sub>2</sub> formed by desolvation of THF using the unsubstituted complex [MeAl(2-py)<sub>3</sub>Li·THF] (Scheme 1).<sup>[6a]</sup>

Like the unsubstituted complex, 1.THF has a marked tendency to lose coordinated THF when placed under vacuum during isolation or when stored under an inert atmosphere for a prolonged period. Complete desolvation can be accomplished quantitatively by placing 1.THF under vacuum (0.1 mm Hg) for ca. 1.5 h at 70 °C, as seen by the absence of THF in solution <sup>1</sup>H NMR spectrum of the solid product produced. Crystals of the desolvated complex were grown from a concentrated toluene solution. Despite some difficulties with collection and refinement of single-crystal X-ray data (see the Experimental Section), the connectivity of the structure is determined unambiguously. Contrary to our expectations, the X-ray study shows that 1 is in fact a monomer, containing an unsolvated pyramidal Li<sup>+</sup> cation (Figure 3a). The steric protection that the three CH<sub>3</sub> groups in the 6-positions of the pyridyl rings provide to the Li<sup>+</sup> can be seen in the space filling view of the molecule (Figure 3 b). Additional Me C-H-Li contacts (range ca. 2.88-2.92 Å) may also contribute to the stabilisation of such an un-



**Scheme 1.** Desolvation of 1-THF, producing the monomeric complex 1 rather than the anticipated dimer [1]<sub>2</sub>.



**Figure 3.** a) Structure of the unsolvated monomer 1. Only one of two crystallographically independent (chemically identical) molecules is shown. b) space-filling view along the Li···Al axis, illustrating the sterically congested nature of the Li<sup>+</sup> cation. Owing to difficulties with the structure refinement (see the Experimental Section), no bond lengths or angles are quoted here.



usual coordination environment for Li. However, although these contacts are well below the sum of the van der Waals radii of H and Li (ca.  $3.02 \text{ Å})^{[12]}$  they are outside the range accepted for genuine C–H…Li agostic interactions (1.80–2.20 Å).<sup>[13]</sup>

In contrast to the behaviour of the dimeric unsubstituted complex  $[MeAl(2-py)_3Li]_2$ ,<sup>[6a]</sup> no evidence for a monomer/dimer equilibrium is detected in solution for desolvated **1**. Roomtemperature <sup>1</sup>H and <sup>7</sup>Li NMR spectroscopic studies in  $[D_8]$ toluene show the presence of a single compound in solu-



Scheme 2. Synthesis of the new complexes 2 and 3.

tion, with no variation in the spectra observed on changing the concentration. The monomeric nature of **1** in solution was also confirmed by variable-concentration cryoscopic molecular mass measurements in benzene, which give an association state (*n*) for  $[1]_n$  of 1.03–1.14 over the concentration range  $6.6 \times 10^{-3}$  to  $1.4 \times 10^{-3}$  mol L<sup>-1</sup> (Table 1).

Table 1. Cryoscopic molecular mass measurements of compounds $1-3$ . <sup>[a]</sup>				
Compound	Substituent at 6-position	Concentration $[mol L^{-1}]$	Mw	n
1	CH₃	1.4×10 <sup>-3</sup>	$349\pm9$	$1.03 \pm 0.03$
1	CH₃	$2.1 \times 10^{-3}$	$386\pm\!8$	$1.14 \pm 0.02$
1	CH₃	6.6×10 <sup>-3</sup>	$350\pm19$	$1.03\pm0.06$
2	CF <sub>3</sub>	$3.2 \times 10^{-3}$	$476\pm53$	$0.95\pm0.11$
2	CF <sub>3</sub>	7.8×10 <sup>-3</sup>	$525\pm25$	$1.05\pm0.05$
3	Br	$8.95 \times 10^{-3}$	$614\!\pm\!25$	$1.15\pm0.05$
3	Br	$1.3 \times 10^{-2}$	$577\pm\!17$	$1.08 \pm 0.05$
[a] All measurements were carried out in benzene.				

The unusual monomeric behaviour found for 1 in the solid and solution states motivated us to explore other related sterically constrained tris(pyridyl)aluminate ligands. A further potential issue that we also wanted to explore was the effect of electron-withdrawing effects on the coordination ability of the tris(pyridyl) ligand set. The new monomeric complexes [EtAl(6-CF<sub>3</sub>-2-py)<sub>3</sub>Li] (2) and [EtAl(6-Br-2-py)<sub>3</sub>Li] (3) were prepared in moderate yields (of 41 and 51%, respectively) using a similar synthetic procedure to 1.THF, involving the reactions of EtAlCl<sub>2</sub> with the corresponding 2-lithiopyridines (Scheme 2). However, one important modification was introduced in the case of 3 in regard to the lithiation of 2,6-dibromopyridine. Instead of the lithiation being accomplished by the addition of nBuLi (1 equiv) to the bromopyridine at -78 °C, the lithiation of 2,6dibromo-2-pyridine is most effective if the bromopyridine is added to the solution of *n*BuLi. Although there is some debate as to the reasons for this, it is thought that the presence of excess *n*BuLi at the beginning of the addition results in the formation of the dilithiate (2,6-Li<sub>2</sub>-py), which is subsequently involved in the formation of the monolithiate (2-Li-6-Br-py).<sup>[14]</sup> Significantly, even though the syntheses of **2** and **3** are undertaken in THF and Et<sub>2</sub>O as the solvents, no coordination of the Li<sup>+</sup> cations in either of the complexes was seen in the analytical or spectroscopic analyses of the isolated solid products. This gave us a preliminary indication of the apparently greater steric influence of the 6-CF<sub>3</sub> and 6-Br groups compared to 6-Me. For **2**, this is in line with the greater van der Waals radius of the CF<sub>3</sub> group (2.74 Å for CF<sub>3</sub> versus 2.23 Å for CH<sub>3</sub>).<sup>[15]</sup> However, for **3** this appears to be counterintuitive because the van der Waals radius of Br is smaller than that for a Me group (1.85 Å).<sup>[12,15]</sup>

Both 2 and 3 were characterized by chemical analysis and multinuclear NMR spectroscopy. The monomeric nature of these compounds in solution was further supported by variable-concentration cryoscopy in benzene (Table 1). The roomtemperature <sup>1</sup>H and <sup>7</sup>Li NMR spectra also only showed sharp concentration-independent resonances. Final confirmation of this is given by the single-crystal X-ray structures of 2 and 3 (Figure 4a and b, respectively). Both complexes feature threecoordinate, pyramidal Li<sup>+</sup> coordination geometries that are similar to that found in 1. A few salient features of the molecular structures of both complexes are worth mentioning here. In particular, the Li-N bond lengths (range 2.024(5)-2.027(6) in 2 and 2.020(6)-2.016(5) Å in 3) and N-Li-N angles (range 100.2(2)–105.8(2) in **2** and 101.3(2)–107.8(2) $^{\circ}$  in **3** are similar in both complexes, despite the different steric influence of the CF<sub>3</sub> and Br groups in the 6-positions of the 2-py rings.

Views of **2** and **3** along the Al···Li axes of each of the monomers are presented in Figure 5, from which it can be seen that the blocking of the Li<sup>+</sup> coordination site appears to be greatest in the CF<sub>3</sub> derivative **2**. It can be noted, however, that in the case of **2** and **3** the low coordination number of Li<sup>+</sup> may also stem from the presence of Li···F and Li···Br interactions. Illustrating this, the Li···F contacts in **2** are in the range 2.50–2.55 Å, while the Li···Br contacts in **3** are in the range 3.27–3.38 Å (both well within the sums of the van der Waals radii of Li and F (ca. 3.29 Å) and Li and Br (ca. 3.67 Å)).<sup>[12]</sup> The extent to which these secondary interactions contribute to the coordina-



Figure 4. Solid-state structures of the monomeric complexes a) 2 and b) 3. Hydrogen atoms and the disorder of the CF<sub>3</sub> groups in 2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: 2:  $C_{py}$ -Al1 range 2.015(3)-2.001(3), N1-Li1 2.024(5), N2-Li1 2.028(6), N3-Li1 2.027(6); Cpy-Al1-Cpy range 102.92(12)-103.94(12), Al1-C<sub>py</sub>-N range 114.8(2)-116.5(2), N-Li-N range 100.2(2)-105.8(2), Li-Br range 2.343(18)-2.55(2). 3: C<sub>py</sub>-Al1 range 2.019(3)-2.034(3), N1-Li1 2.020(6), N2-Li1 2.016(5), N3-Li1 2.016(5); Cpy-Al1-Cpy range 101.78(11)-105.10(11), Al1-C<sub>py</sub>-N range 114.11(19)-116.9(2), N-Li-N range 101.3(2)-107.8(2), Li-Br range 3.272(6)-3.384(6).

tion of Li<sup>+</sup> is unclear at this stage. In the case of 3, for example, variable-temperature <sup>19</sup>F and <sup>7</sup>Li NMR spectroscopy (298-213 K) indicated no Li-F coupling and the presence of a singlet in the <sup>19</sup>F NMR spectrum at all temperatures shows that the CF<sub>3</sub> groups rotate freely.

We next moved on to explore the coordination chemistry of the new aluminate ligands of 2 and 3. In contrast to the reaction of 1 with FeCl<sub>2</sub>, which produces a green solution presumably of the half-sandwich compound [{EtAl(2-py)<sub>3</sub>}FeCl],<sup>[8]</sup> neither 2 nor 3 coordinate FeCl<sub>2</sub>. Further attempts to coordinate other metal ions with 2 and 3 also failed. It therefore appears that the introduction of the CF<sub>3</sub> and Br groups into the 6-positions completely blocks their coordination behaviour. This steric effect can potentially be turned to an advantage, however, in the stabilization of unusual Al<sup>III</sup> complexes. It has been suggested that the stabilization of a terminal Al-OH group relies on the steric influence of the supporting ligand groups (L) and their impact on the acidity of the O-H bond, because lower steric demands of the ligand set and higher acidity of the O–H bond will encourage dimerization (Scheme 3).<sup>[16]</sup>

-H<sub>2</sub>O 2 (L)AI-O-H (L)AI-O-AI(L)

Scheme 3. Dimerisation of a terminal Al–OH complex to give Al–O–Al.

With this background in mind we decided to explore the use of 2 and 3 as scaffolds for the synthesis of terminal Al-OH compounds. The reaction of 2 with 1–2 equiv of  $H_2O$  in [D<sub>8</sub>]toluene was investigated in an in situ multinuclear NMR spectroscopy study. Within 5 min of mixing at room temperature, the <sup>7</sup>Li NMR spectrum showed the presence of unreacted **2** (singlet,  $\delta = 2.87$  ppm) along with a new minor resonance (singlet,  $\delta = 2.54$  ppm). The <sup>1</sup>H NMR spectrum confirms the formation of a single new species which can be identified as the  $[EtAl(OH)(6-CF_3-2-py)_2]^-$  anion (4; Scheme 4), observed as minor pyridyl-C-H and Et-Al resonances next to the corresponding resonances for 2. Furthermore, free 6-CF<sub>3</sub>-2-py-H and ethane (singlet,  $\delta = 0.81$  ppm) are also observed, suggesting that the hydrolysis of 2 is not selective, that is, that either the Al-(6-CF<sub>3</sub>-2-py) or Et-Al groups can be involved in deprotonation of  $H_2O$ . The optimal reaction time was found to be about 1.5 h, by which time the resonances for 4 amount to only ca. 10% of the total integrated <sup>1</sup>H NMR resonances.



Figure 5. Views of the Li $^+$  cation along the Li $\cdots$ Al axis: a) 2 and b) 3.

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Scheme 4. Assignment of the <sup>1</sup>H NMR spectrum of the anion 4 from the in situ NMR spectrum.

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An in situ NMR spectroscopic study of the reaction of **3** with H<sub>2</sub>O indicated the formation of a closely related terminal Al–OH complex (**5**) in solution, but now quantitatively. The reaction is complete after 30 min, giving a mixture of **5**, 6-Br-2-py-H and a small amount of ethane. Compound **5** has a similar <sup>1</sup>H NMR spectrum to the anion **4**, with 6-Br-pyridyl and Et–Al resonances in 1:2 ratio along with a singlet characteristic of Al–OH at  $\delta = 1.12$  ppm. The reaction was scaled up, allowing the preparation of **5** in 25% crystalline yield after workup (Scheme 5a). The presence of the OH group in solid **5** is



Scheme 5. Synthesis of the terminal Al–OH complex 5 and the alkoxides  ${\bf 6}$  and  ${\bf 7}.$ 

shown by a sharp O–H stretching band at 3641 cm<sup>-1</sup> in the IR spectrum. This can be compared to values of greater than 3700 cm<sup>-1</sup> for terminal Al–OH, indicating weakening of the O–H bond. Full assignment of the <sup>1</sup>H NMR resonances and confirmation of the presence of the Et-Al-OH and Et-Al-Py linkages were obtained using 2D NMR <sup>1</sup>H–<sup>13</sup>C HMQC, <sup>1</sup>H–<sup>1</sup>H NOESY, and <sup>1</sup>H–<sup>13</sup>C HMBC experiments (see the Supporting Information).

The single-crystal X-ray structure of 5 confirms all of the conclusions drawn from spectroscopic data. Molecules of 5 have a centrosymmetric dimer structure [{EtAl(6-Br-2py)<sub>2</sub>(OH)}Li]<sub>2</sub> in which the OH groups of the [EtAl(6-Br-2py)<sub>2</sub>(OH)]<sup>-</sup> anions bridge the two  $Li^+$  cations together in a central  $Li_2O_2$  ring unit (Figure 6a). The H atom of the OH group was located in the difference Fourier map (then OH was refined as a rigid group). Overall, the most interesting feature of 5 is the stabilization of the Al-OH functionality within a dimeric arrangement of this type, in which elimination of H<sub>2</sub>O and the formation of an Al-O-Al bridge appears to be set up. One explanation for the stability of the complex is the location of the OH group within a cleft in the molecular arrangement, bounded by an Albonded Et group and two 6-Br-2-py groups, as seen in the space-filling diagram shown in Figure 6b. The Al–O bonds in 5 (1.790(3) Å) are noticeably longer than typically found in monomeric terminal Al-OH complexes (ca. 1.73 Å).<sup>[17]</sup> The acute intramolecular Br···H–O(Al) angles (89.7° and 103.1°) and the Br...H (3.842 Å and 3.664 Å) and Br...O distances (3.965(3) Å and





4.010(3) Å) in **5** argue against the presence of significant stabilizing H $\cdots$ Br H-bonds in the complex.

Br

Figure 6. a) Structure of the hydroxo bis(pyridyl)aluminate dimer 5 featuring a terminal Al–OH group. Hydrogen atoms are omitted for clarity. Selected

bond lengths [Å] and angles [°]: Al1-O1 1.790(3), C<sub>py</sub>-Al1 2.016(4)-2.019(4),

N1-Li1 2.037(7), N2-Li1 2.046(7), O1-Li1A 1.964(7), O1-Li1 1.980(7); C<sub>py</sub>-Al1-

C<sub>DV</sub> 104.28(15), C<sub>DV</sub>-Al1-O1 101.41(14)-101.65(14), Al1-C<sub>DV</sub>-N 113.9(3)-115.0(3),

O-Al1-Li 36.4(2)-36.6(2), O1-Li1-N1A 112.6(4), O1A-Li1-N2 113.7(4), N2-Li1-N1A 135.3(4), N2-Li1-O1 96.8(3), O1-Li1-O1A 95.7(3), O1-Li1-N2 96.8(3).

b) Space-filling diagram, showing the environment around the OH group.

Roesky and co-workers have shown previously that the terminal Al–OH retains its Brønsted acidity, reacting for example with Cp<sub>3</sub>Ln (Ln=lanthanides) to give heterometallic Al-O-Ln bridged compounds.<sup>[18]</sup> To assess the acidity of the Al–OH groups in **5** we first explored its thermal behaviour in solution. A solution of **5** in [D<sub>8</sub>]toluene was heated at 80 °C for 3 h, resulting in the elimination of free 6-Br-2-py-H and ethane, presumably via intramolecular deprotonation of the OH group (see <sup>1</sup>H NMR studies the Supporting Information). In a followup experiment, **5** was reacted with ZnEt<sub>2</sub> as an external base (1 equiv). A mixture of compounds is observed by in situ <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. However, the ca. 20 ppm increase

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**Figure 7.** Structure of the 2-Br-py zinc complex **6.** Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C<sub>py</sub>–Zn range 2.019(8)–2.279(8), N–Li range 1.965(14)–2.022(14); N-Li-N range 103.6(6)–134.0(8), Zn-Cpy-N range 116.7(5)–124.8(6).

in the chemical shifts of C2 of the 2-py group in the <sup>13</sup>C NMR spectrum compared to **5** suggested that at least some transfer of the 2-py group onto  $Zn^{2+}$  had occurred.<sup>[19]</sup> This was confirmed by the isolation of a few crystals of dimeric [LiZn(6-Br-py)<sub>3</sub>]<sub>2</sub> (**6**) from the NMR-scale reaction and their structural characterization (see Figure 7). Compound **6** consists of a dimeric zincate [Zn(6-Br-2-py)<sub>3</sub>]<sub>2</sub><sup>2-</sup> dianion ion-paired with two Li<sup>+</sup> cations, in which full transfer of the 6-Br-2-py groups has occurred from Al to Zn.

The use of tris(2-pyridyl)aluminates as general precursors for the preparation of heteroleptic variants, demonstrated in the synthesis of the mixed-ligand 2-py/OH complexes 4 and 5, is an attractive one. To carry this idea further we explored the reactions of alcohols (ROH) with aluminates. Reactions of the unsubstituted complex [EtAl(2-py)<sub>3</sub>Li<sup>-</sup>THF] or 6-Br substituted 3 with MeOH (1.3 equivalents) in toluene at 0°C give the closely related heteroleptic compounds [{EtAl(6-Br-2-py)<sub>2</sub>(OMe)}Li]<sub>2</sub> (7) and [{EtAl(2-py)<sub>2</sub>(OMe)}Li]<sub>2</sub> (8) in 20-30% yields of crystalline product (Scheme 5 b). These new compounds were characterized by analytical and spectroscopic techniques prior to their X-ray structural characterization. Both complexes have dimeric structures that are similar to that of 5 in the solid state, but now with the OH group replaced by OMe (Figure 8 a,b). The retention of these dimeric structures in solution along with the full assignment of their resonances are supported by extensive 1D and 2D multinuclear NMR investigations (see the Supporting Information).

Both **7** and **8** are much more thermally stable than their Al– OH relatives **4** and **5**, presumably because there is now no longer any possibility of intramolecular deprotonation of the OH group by the Al-bonded 2-py' or Et groups. As far as ligand properties are concerned, our preliminary studies have so far shown that the unsubstituted aluminate ligand of **7** can



**Figure 8.** Structure of the heteroleptic alkoxide aluminates a) **7** and b) **8**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **7**: Al1–O1 1.808(2),  $C_{py}$ –Al1 2.012(3) and 2.021(3), N1–Li1 2.048(6), N2–Li1A 2.045(6), O1–Li1 2.011(6), O1–Li1A 2.010(6);  $C_{py}$ -Al1- $C_{py}$  105.60(14),  $C_{py}$ -Al1-O1 101.92(12) and 102.16(12), Al1- $C_{py}$ -N 115.3(2) and 115.6(2), O-Al-Li1 33.08(11)-33.33(11), O1-Li1-N2A 115.8(3), N2A-Li1-N1 132.3(3), O1–Li1-N1 96.7(2), O1A-Li1-O1 95.7(2). **8**: Al1–O1 1.8012(11),  $C_{py}$ –Al1 2.0175(16) and 2.0188(17), N1–Li1 2.029(3), N2–Li1A 2.023(3), O1–Li1 1.999(3), O1–Li1A 1.989(3);  $C_{py}$ -Al1- $C_{py}$  106.71(6),  $C_{py}$ -Al1-O1 102.17(6) and 102.34(6), Al1– $C_{py}$ -N 116.36(11) and 116.50(11), O1–Al1-Li1 38.50(6), O1–Li1-A1 34.12(5), O1–Li1-N2A 114.43(14), O1-Li1-N1 99.24(13), N2A-Li1-N1 127.81(15), O1A-Li1-O1 96.42(12).

readily be transferred to other metals (such as  $Fe^{II}$ ), whereas the more sterically congested ligand of **8** cannot be.

## Conclusion

The introduction of steric congestion at the 6-position of the pyridyl ring units of tris(2-pyridyl)aluminate ligands has a profound effect on their coordination properties. This is shown most dramatically in the current work by the labile loss of coordinated THF from the 6-Me substituted complex [EtAl(6-Me-2-py)<sub>3</sub>Li-THF] (1-THF), which gives the highly unusual monomer



1, as opposed to the expected dimeric arrangement that would have a coordination number of four rather than three for Li<sup>+</sup>. The steric effect of substituents at the 6-position is also seen in the behaviour of the 6-Br substituted ligand framework, which reacts with  $H_2O$  to give a room-temperature stable heteroleptic aluminium 2-py/OH complex. This type of reaction, using the tris(pyridyl) ligand as a scaffold to build heteroleptic systems selectively, is an important synthetic step because it allows for extremely extensive elaboration of the steric and donor character of the ligands and for the potentially facile incorporation of chiral alcohols or amines into heteroleptic 2-py ligand arrangements. Our studies are continuing in this area, particularly with a view to obtaining families of simply prepared chiral aluminates for catalysis.

## **Experimental Section**

#### Materials and general methods

All of the syntheses were carried out on a vacuum line under an argon atmosphere. Products were isolated and handled with the aid of a N<sub>2</sub>-filled glove box (Saffron type  $\alpha$ ). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 QNP or Bruker Avance 500 MHz Cryo spectrometer. <sup>7</sup>Li and <sup>27</sup>Al NMR NMR spectra were re-

corded on a Bruker Avance 500 MHz

Cryospectrometer. Elemental analysis

was obtained on a PerkinElmer 240

Elemental Analyser. The unambigu-

ous assignment of NMR resonances was accomplished by additional 2D

NMR experiments (1H-1H COSY, 1H-1H

NOESY, <sup>1</sup>H-<sup>13</sup>C HMQC, and <sup>1</sup>H-<sup>13</sup>C

HMBC experiments (see (Scheme 6)

for atom labelling and the Support-

ing Information for details). [EtAl(6-

Me-2-py)<sub>3</sub>Li·THF], 1·THF, was synthe-

sized as described previously.<sup>[9]</sup>



**Scheme 6.** Atom labelling used in the NMR studies for the pyridyl aluminate ligands.

#### Synthesis of [EtAl(6-Me-2-py)<sub>3</sub>Li] (1)

[EtAl(6-Me-2-py)<sub>3</sub>Li-THF] (250 mg, 0.608 mmol) was placed under vacuum (0.1 mm Hg) for ca. 1.5 h at 70 °C, affording 1 as a white solid in quantitative yield: 205 mg, 0.604 mmol, 99%. Colourless crystals of 1 were obtained from a saturated solution of 1 in toluene at 20 °C. <sup>1</sup>H NMR (298 K, [D<sub>8</sub>]toluene, 500 MHz),  $\delta$  = 7.69 (d,  $J_{\rm HH}$  = 7.3 Hz, 3 H, H3 py), 7.00 (t,  $J_{\rm HH}$  = 7.5 Hz, 3 H, H<sup>4</sup> py), 6.46 (d,  $J_{\rm HH}$  = 7.8 Hz, 3 H, H5 py), 2.26 (s, 9H, C6 CH<sub>3</sub>), 1.98 (t,  $J_{\rm HH}$  = 8.1 Hz, 3 H, Al-CH<sub>2</sub>CH<sub>3</sub>), 1.09 (q,  $J_{\rm HH}$  = 8.1 Hz, 3 H, Al-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]toluene, 100.6 MHz),  $\delta$  = 188.62 (br, C<sub>2</sub> py), 154.93 (C6 py), 133.32 (C4 py), 130.61 (C3 py), 119.79 (C5 py), 24.89 (C6 CH<sub>3</sub>), 11.23 (Al-CH<sub>2</sub>CH<sub>3</sub>), -2.54 (br, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (298 K, [D<sub>8</sub>]toluene, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O),  $\delta$  = 126.55 (br, s). <sup>7</sup>Li NMR (298 K, [D<sub>8</sub>]toluene, 194.4 MHz, ref. solution of LiCl/D<sub>2</sub>O),  $\delta$  = 3.53 (s). Elemental analysis (%) calcd. for 1: C 70.8, H 6.8 N, 12.4; found: C 69.9, H 6.8, N 12.6.

#### Synthesis of [EtAl(6-CF<sub>3</sub>-2-py)<sub>3</sub>Li] (2)

2-Bromo-6-(trifluoromethyl)pyridine (2.00 g, 8.85 mmol) was dissolved in Et<sub>2</sub>O (40 mL). *n*BuLi (5.6 mL, 8.96 mmol, 1.6  $\mu$  in hexanes) was added to the solution dropwise at -78 °C over a period of 20 min. The resulting orange solution was stirred at -78 °C for 3 h.

EtAlCl<sub>2</sub> (2.95 mL, 2.95 mmol, 1.0 м in hexanes) was added dropwise to the solution over 20 min. The resulting mixture was allowed slowly to reach ambient temperature overnight. The solvent was removed in vacuo and toluene (30 mL) and THF (10 mL) were added and the yellow-brown mixture was stirred at room temperature for 3 h and filtrated over Celite. The solvent was removed in vacuo until the precipitation of a white solid was observed, which was redissolved by gentle heating. Storage at -15 °C afforded colourless crystals of 2, which were dried in a glovebox. Total yield of isolated crystalline product: 600 mg, 1.2 mmol, 41%. Note: If the lithiation step is carried out in THF at -78 °C rather than in Et<sub>2</sub>O, then compound 2 was obtained in lower yield (10–20%). <sup>1</sup>H NMR (298 K, [D\_8]toluene, 500 MHz),  $\delta\!=\!7.74$  (d,  $J_{\rm HH}\!=\!7.4$  Hz, 3 H, H3 py), 6.81 (t,  $J_{\rm HH}$  = 7.7 Hz, 3 H, H4 py), 6.74 (dd,  $J_{\rm HH}$  = 7.8 and 0.9 Hz, 3 H, H5 py), 1.88 (t,  $J_{\rm HH} = 8.2$  Hz, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.99 (q,  $J_{\rm HH} = 8.2$  Hz, 3 H, Al-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]toluene, 100.6 MHz),  $\delta$  = 189.0 (br, C2 py), 146.19 (q, <sup>2</sup>J<sub>CF</sub> = 32.5 Hz, C6 py), 135.94 (C3 py), 133.92 (C4 py), 123.89 (q,  ${}^{1}J_{CF} = 273$  Hz, CF<sub>3</sub>), 117.35 (C5 py), 10.93 (Al-CH<sub>2</sub>CH<sub>3</sub>), -2.91 (br, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (298 K, [D<sub>8</sub>]toluene,130.3 MHz, ref. solution of AlCl<sub>3</sub>·6 H<sub>2</sub>O/D<sub>2</sub>O),  $\delta = 127.11$  (br, s). <sup>7</sup>Li NMR (298 K,  $[D_8]$ toluene, 194.4 MHz, ref. solution of LiCl/D<sub>2</sub>O),  $\delta = 2.87$  (s). Elemental analysis (%) calcd for 2: C 47.9, H 2.8, N 8.4; found C 47.6, H 2.8, N 8.1.

#### Synthesis of [EtAl(6-Br-2-py)<sub>3</sub>Li] (3)

A solution of nBuLi (12.5 mL, 20 mmol, 1.6 m in hexanes) in THF (12 mL) was cooled at -78 °C. To this solution was added dropwise over 30 min a solution of 2,6-dibromopyridine (4.74 g, 20 mmol) in THF (28 mL). The resulting dark green mixture was stirred (40 min at -78 °C). EtAlCl<sub>2</sub> (6.6 mL, 6.6 mmol, 1.0 M in hexanes) was added to the solution of 2-lithio-6-bromopyridine over 15 min. The resulting mixture was allowed slowly to reach ambient temperature overnight and stirred for a further 36 h. The solvent was removed in vacuo. The addition of toluene (40 mL) and THF (10 mL) afforded a pale yellow-brown mixture (dark brown mixtures were associated with lower yields) which was filtrated over Celite. The solvent was removed in vacuo until the precipitation of a white solid was observed, which was redissolved by gentle heating. Storage at ambient temperature (24 h) afforded colourless crystals of 3. Further concentration of the solution and storage at  $-15\,^\circ\text{C}$  afforded more colourless crystals of 3. Total yield of isolated product: 1.80 g, 3.37 mmol, 51 %.  $^1\text{H}$  NMR (298 K, [D\_8]toluene, 500 MHz),  $\delta\!=\!7.49$ (dd,  $J_{\rm HH}\!=\!6.1$  and 2.1 Hz, 3 H, H3 py), 6.66–6.52 (m, 6 H, H4 and H5 py), 1.82 (t,  $J_{HH} = 8.2$  Hz, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.89 (q,  $J_{HH} = 8.2$  Hz, 3H, Al-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]toluene, 100.6 MHz),  $\delta = 191.9$  (br, C2 py), 142.95 (C6 py), 136.07 (C4 py), 131.94 (C3 py), 123.71 (C5 py), 10.93 (Al-CH $_2CH_3$ ), -2.90 (br, Al-CH $_2$ ).  $^{27}\text{Al}$  NMR (298 K,  $[D_{s}]$ toluene, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O),  $\delta$  = 125.30 (br, s). <sup>7</sup>Li NMR (298 K, [D<sub>8</sub>]toluene, 194.4 MHz, ref. solution of LiCl/ D<sub>2</sub>O),  $\delta = 1.58$  (s). Elemental analysis (%) calcd. for **3**: C 38.2, H 2.6, N 7.9; found: C 38.2, H 2.7, N 7.8.

#### Synthesis of [EtAl(OH)(6-Br-2-py)<sub>2</sub>Li]<sub>2</sub> (5)

H<sub>2</sub>O (76  $\mu$ L, 4.2 mmol, 1.4 equiv) was added at room temperature to a solution of **3** (1.40 g, 2.62 mmol) in toluene (50 mL). The progress of the reaction can be monitored by <sup>7</sup>Li NMR. The mixture was stirred at room temperature for 3 h and subsequently filtered over Celite to afford a colourless solution. The solution was concentrated under vacuum (ca. 3 mL) and n-pentane was added until turbidity was observed. Storage at -15 °C afforded colourless crystals of **5** (258 mg, 0.327 mmol, 25% yield of crystalline product). Note: The compound is highly soluble in toluene; however, if the solvent

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is evaporated under vacuum and the resulting residue is dried under prolongated vacuum to remove 2-bromopyridine and H<sub>2</sub>O, 440 mg of compound **5** (0.558 mmol, 43% yield) containing 5% of **3** was obtained. IR (Nujol), v(OH): 3641 cm<sup>-1</sup>. <sup>1</sup>H NMR (298 K, [D<sub>8</sub>]toluene, 500 MHz),  $\delta = 7.47$  (dd,  $J_{\rm HH} = 7.0$  and 1.1 Hz, 2H, H3 py), 6.82–6.78 (m, 2H, H5 py), 6.78–6.72 (m, 2H, H4 py), 1.46 (t,  $J_{\rm HH} = 8.1$  Hz, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>), 1.07 (s, 1H, Al-OH), 0.50 (q,  $J_{\rm HH} = 8.1$  Hz, 3H, Al-CH<sub>2</sub>). <sup>13</sup>C[<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]toluene, 100.6 MHz),  $\delta = 191.8$  (br, C2 py), 143.76 (C6 py), 136.02 (C4 py), 131.29 (C3 py), 125.0 (C5 py, overlapped with residual toluene solvent signal), 10.08 (Al-CH<sub>2</sub>CH<sub>3</sub>), -0.30 (br, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (298 K, [D<sub>8</sub>]toluene, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O),  $\delta = 138.0$  (br, s). <sup>7</sup>Li NMR (298 K, [D<sub>8</sub>]toluene, 194.4 MHz, ref. solution of LiCl/D<sub>2</sub>O),  $\delta = 1.94$  (s). Elemental analysis (%) calcd. for **5**: C 36.6, H 3.1, N 7.1; found C 35.6, H 3.1, N 6.8.

#### Synthesis of [EtAl(OMe)(6-Br-2-py)<sub>2</sub>Li]<sub>2</sub> (7)

Methanol (120 µL, 3.04 mmol, 1.25 equiv) was added at 0 °C to a solution of 3 (1.30 g, 2.435 mmol) in toluene (50 mL). The mixture was stirred (1.5 h at 0 °C) and subsequently allowed to reach room temperature. The resulting cloudy solution was stirred for 1 h at room temperature and filtered over Celite. The colourless solution produced was concentrated (to ca. 5 mL) and was layered with npentane. Storage at -15°C afforded colourless crystals of 7. Total yield of isolated crystalline product: 220 mg, 0.27 mmol, 22%.  $^1\text{H}$  NMR (298 K,  $[\text{D}_{\text{8}}]$  toluene, 500 MHz),  $\delta\!=\!7.47$  (dd,  $J_{\text{HH}}\!=\!7.0$  and 1.1 Hz, 2H, H3 py), 6.79-6.83 (m, 2H, H5 py), 6.77-6.71 (m, 2H, H4 py), 3.52 (s, 3 H, OCH<sub>3</sub>), 1.54 (t, J<sub>HH</sub> = 8.1 Hz, 3 H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.64 (q,  $J_{HH} = 8.1 \text{ Hz}, 3 \text{ H}, \text{Al-CH}_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, [D<sub>8</sub>]toluene, 100.6 MHz),  $\delta =$  191.3 (br, C2 py), 143.60 (C6 py), 136.07 (C4 py), 131.62 (C3 py), 125.32 (C5 py, overlapped with residual toluene solvent signal), 51.52 (OCH<sub>3</sub>,), 10.29 (Al-CH<sub>2</sub>CH<sub>3</sub>), -1.25 (br, Al-CH<sub>2</sub>,). <sup>27</sup>Al NMR (298 K, [D<sub>8</sub>]toluene, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6 H<sub>2</sub>O/D<sub>2</sub>O),  $\delta$  = 139.27 (br, s). <sup>7</sup>Li NMR (298 K, [D<sub>8</sub>]toluene, 194.4 MHz, ref. solution of LiCl/D<sub>2</sub>O),  $\delta = 1.98$  (s). Elemental analysis (%) calcd. for 5: C 38.3, H 3.5, N 6.9; found: C 38.6, H 3.5, N 6.8.

#### Synthesis of [EtAl(OMe)(2-py)<sub>2</sub>Li]<sub>2</sub> (8)

Methanol (63  $\mu$ L, 1.56 mmol, 1.25 equiv) was added at -78 °C to a solution of [EtAl(2-py)<sub>3</sub>Li·THF] (480 mg, 1.30 mmol) in toluene (28 mL). The mixture was stirred at -78 °C for 5 min and subsequently transferred to an ice bath and allowed to reach 0°C. The mixture was slowly allowed to reach room temperature overnight and the resulting pale yellow cloudy solution was filtered over Celite. The solution produced was concentrated (to ca. 3 mL). Addition of n-pentane (ca. 5 mL) and storage at -15 °C afforded colourless crystals of 8. Total yield of isolated crystalline product: 100 mg, 0.20 mmol, 31 %.  $^1\text{H}$  NMR (298 K, [D\_g]toluene, 500 MHz),  $\delta\!=\!8.22-$ 8.19 (m, 2H, H6 py), 7.78–7.74 (m, 2H, H3 py), 7.15 (td, J<sub>HH</sub>=7.6 and 1.7 Hz, 2 H, H4 py), 6.69-6.64 (m, 2 H, H5 py), 3.20 (s, 3 H, OCH<sub>3</sub>), 1.57 (t, J<sub>HH</sub>=8.1 Hz, 3 H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.62 (q, J<sub>HH</sub>=8.1 Hz, 3 H, Al-CH\_2).  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (298 K, [D\_8]toluene, 100.6 MHz),  $\delta\!=\!$  187.90 (br, C2 py), 148.80 (C6 py), 133.42 (C3 py), 133.30 (C4 py), 121.29 (C5 py), 51.11 (OCH<sub>3</sub>,), 10.61 (Al-CH<sub>2</sub>CH<sub>3</sub>), -0.48 (br, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (298 K, [D<sub>8</sub>]toluene, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6 H<sub>2</sub>O/D<sub>2</sub>O),  $\delta =$ 141.22 (br, s). <sup>7</sup>Li NMR (298 K, [D<sub>8</sub>]toluene, 194.4 MHz, ref. solution of LiCl/D<sub>2</sub>O),  $\delta = 2.56$  (s). Elemental analysis (%) calcd. for 8: C 62.4, H 6.4, N 11.2; found: C 62.5, H 6.5, N 10.8.

#### X-ray crystallographic studies

Data were collected for 1 on a Nonius Kappa CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation, for 3, 5, 7, and 8 on a Bruker D8 QUEST diffractometer with an Incoatec IµS Cu microfocus source, and for 2 and 6 on a Bruker SMART X2S diffractometer with a monochromatic MoK $\alpha$  microfocus source. Crystals were mounted directly from solution using perfuorohydrocarbon oil to prevent atmospheric oxidation, hydrolysis, and solvent  $\mathsf{loss},^{\scriptscriptstyle[20]}$  and the temperature was held between 180 and 250 K using an Oxford Cryosystems N<sub>2</sub> cryostat. Data were collected using Bruker Apex2 or GIS, processed using SAINT and SADABS and refined using SHELXL.<sup>[21]</sup> Details of the data collections and structural refinements are given in the Supporting Information, Table S1. Further details of the methods of refinement of the structures are as follows. 1: After several crystallization attempts, all crystals obtained for 1 were relatively weakly diffracting and frequently showed multiple spots indicative of several crystalline domains. It is noted that the reported triclinic lattice has approximately monoclinic metric symmetry, which may indicate a likelihood for twinning, but we were not able to implement any effective multicomponent integration or refinement. The refinement reported for 1 is the best of five datasets collected from five different crystals. The molecular geometry is generally satisfactory, with restraints applied to the ethyl groups to maintain sensible bond distances. Several of the atoms exhibit relatively prolate displacement ellipdoids. 2: The CF<sub>3</sub> groups exhibit rotational disorder and were modelled over two positions with restrained geometry. The site occupancy factors were initially refined, then constrained to the values 0.58:0.42 for the final refinement cycles. 5: the H atom of the OH group was included in a position taken from the difference Fourier map, then the OH group was treated as a rigid body for subsequent refinement, with an individual isotropic displacement parameter refined for H. 7: the toluene solvent molecule is disordered about an inversion centre. It was modelled with a constrained benzene ring and common isotropic displacement parameters for the C atoms. Compounds 2 and 3 are isostructural (that is, the Br atoms in 3 occupy essentially the same space as the disordered CF<sub>3</sub> groups in 2).

CCDC 1404218 (1), 1404219 (2), 1404220 (3), 1404222 (5), 1404221 (6), 1404223 (7), and 1404224 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: aluminates  $\cdot$  lithium  $\cdot$  N ligands  $\cdot$  steric effects  $\cdot$  terminal hydroxide ligands

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