# Steric effects on the structures, reactivity and coordination chemistry of *tris*(2-pyridyl)aluminates

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**Abstract:** Introducing substituents in the 6-position of the 2-pyridyl rings of *tris*-pyridyl aluminate anions, of the type $[EtAl(2\text{-}py')_3]^-$ (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 $[EtAl(6\text{-}Me\text{-}2\text{-}py)_3Li{\cdot}THF]$ to give the monomer $[EtAl(6\text{-}Me\text{-}2\text{-}py)_3Li]$ (**1**), containing a pyramidal, three-coordinate $Li^+$ cation. Similar monomeric complexes are observed for $[EtAl(6\text{-}CF_3\text{-}2\text{-}py)_3Li]$ (**2**) and $[EtAl(6\text{-}Br\text{-}2\text{-}py)_3Li]$ (**3**), containing $CF_3$ and Br substituents (R). This steric influence can be exploited in the synthesis of a new class of terminal Al-OH complexes, as is seen in the controlled hydrolysis of **2** and **3** to give $[EtAl(OH)(6\text{-}R\text{-}2\text{-}py)_2]^-$ anions, as in the dimer $[EtAl(OH)(6\text{-}Br\text{-}2\text{-}py)_2Li]_2$ (**5**). Attempts to deprotonate the Al-OH group of **5** using $Et_2Zn$ led only to the formation of the zincate complex $[LiZn(6\text{-}Br\text{-}py)_3]_2$ (**6**), while reactions of the 6-Br substituted **3** and the unsubstituted complex $[EtAl(2\text{-}py)_3Li]$ with MeOH give $[EtAl(OMe)(6\text{-}Br\text{-}2\text{-}py)_2Li]_2$ (**7**) and $[EtAl(OMe)(2\text{-}py)_2Li]_2$ (**8**), respectively, having similar dimeric arrangements to **5**. The combined studies presented here provide key synthetic tools for the functionalization and elaboration of *tris*-pyridyl aluminate ligands.

## Introduction

In 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** Fig. 1), have emerged as an important family of ligands.[1] These ligands, along with the related tris(pyrazolyl)borates and methanes, have found a vast range of applications in coordination, organometallic and bioinorganic chemistry.[2] It is been only relatively recently, however, that attention has turned to ligands containing the heavier Group 13 and 14 atoms at the bridgehead.[3] 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.[4] Of particular interest are *tris*-pyridyl aluminates $[RAl(2\text{-}py')_3]^-$ which are unusual in this area in that they are negatively charged instead of neutral (**B**, Fig. 1).[3a] As one of the only anionic members of the *tris*-pyridyl family,[5] 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.[6] The coordination of a *tris*-pyridyl ligand to another metal provides a facile route to heterometallic complexes, such as the sandwich compound $[\{MeAl(2\text{-}py)_3\}_2Fe]$ which is a highly selective styrene epoxidation catalyst in air.[7]

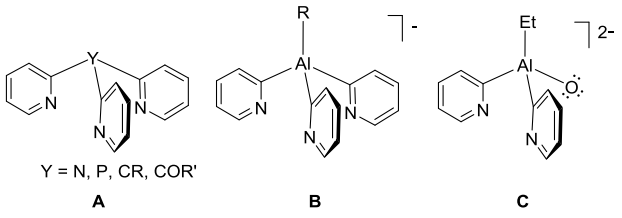



**Figure 1** (**A**) Framework found in the family of tris-2-pyridyl ligands, (**B**) the tris-2-pyridyl aluminate family of ligands, and (**C**) the oxo-pyridyl ligand set.

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.[3a] 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.[8] For

example, the $[EtAl(6\text{-}Me\text{-}2\text{-}Py)_3]^-$ ligand has proved to be particularly useful in the steric stabilization of unusual metal oxidations states such as in $[\{EtAl(6\text{-}Me\text{-}2\text{-}py)_3\}_2Sm]$, 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 $[\{EtAl(2\text{-}py)_3\}_2Sm]$, which rapidly scavenges molecular oxygen, giving the $[EtAl(2\text{-}py)_2O]^{2-}$ dianion (C, Fig.1).[9] 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 $Al^{III}$ complexes $[HC\{(CMe)(NDipp)\}_2AlR_2]$ (Dipp = 2,6-$^{i}Pr_2C_6H_3$, R = Cl, I or alkyl) produces terminal Al-OH compounds. [10]
In the study presented here we explore the synthesis and coordination properties of a series of sterically-encumbered *tris*-pyridyl aluminate ligands of the type **D** (Fig. 2), having different substituents at the 6-position of the pyridyl ring (R = Me, $CF_3$, 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**, Fig. 2) and related alkoxide complexes (**F**, Fig. 2).

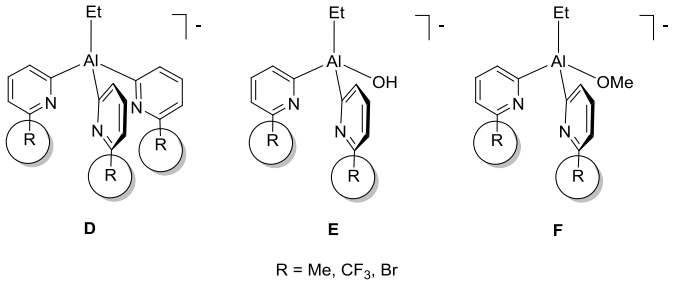
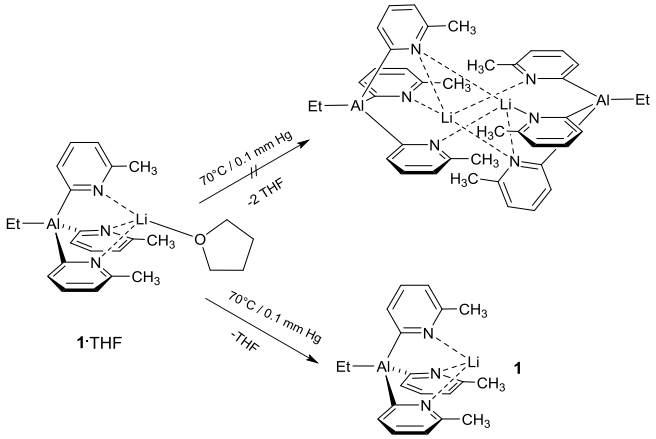



**Figure 2** (**D**) The steric effects introducing substituents at the 6-position of the tris-2-pyridyl framework, and (**E** and **F**) the resulting stabilization of the hydroxo and alkoxide aluminate ions.

## Results and Discussion

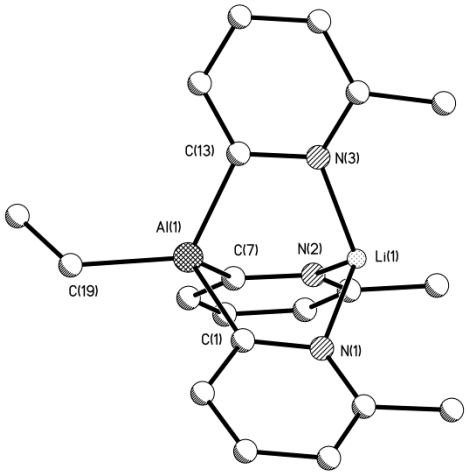
As noted in the introduction to this paper, the coordination chemistry of *tris*-pyridyl ligands has been a major research theme in the past thirty years or so. Surprisingly, however, in contrast to the *tris*-pyrazolylborate ligands there have been few systematic studies of the effects of introducing different substituents on the pyridyl ring.[8, 11] We showed recently that Me-substitution of the pyridyl ring units in the aluminate ion of $[EtAl(6\text{-}Me\text{-}2\text{-}py)_3Li{\cdot}THF]$ (**1**·THF) provided a sterically-demanding metal coordination site that could be used to stabilize unusual oxidation states.[9] 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 $Li^+$, we decided in our preliminary studies to explore the desolvation of **1**·THF, anticipating the formation of a dimeric complex $[\mathbf{1}]_2$ which would be analogous to the dimeric complex $[MeAl(2\text{-}py)_3Li]_2$ formed by desolvation of THF using the unsubstituted complex $[MeAl(2\text{-}py)_3Li{\cdot}THF]$ (Scheme 1).[6a]




**Scheme 1** Desolvation of **1**·THF, producing the monomeric complex 1 rather than the anticipated dimer $[\mathbf{1}]_2$.

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.* 1.5h at 70°C, as evidenced by the absence of THF in solution $^1$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 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 $Li^+$ cation (Fig. 3a). The steric protection that the three $CH_3$ groups in the 6-positions of the pyridyl rings provides to the $Li^+$ can be seen in the space filling view of the molecule (Fig. 3b). Additional Me C-H···Li contacts (range *ca.* 2.88-2.92 Å) may also contribute to the stabilisation of such an unusual 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 Å) [12] they are outside the range accepted for genuine C-H···Li agostic interactions (1.80-2.20 Å).[13]

(a)

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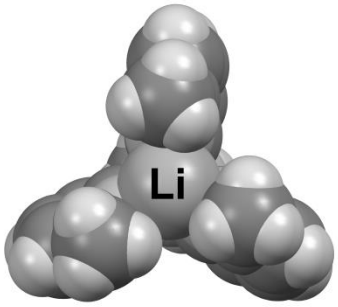



**Figure 3**. (a) Structure of the unsolvated monomer **1**. Only one of two crystallographically-independent (chemically-identical) molecules is shown. (b) space-filling view along the Li···Al axis, illustrating the sterically congested nature of the $Li^+$ cation. Owing to difficulties with the structure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

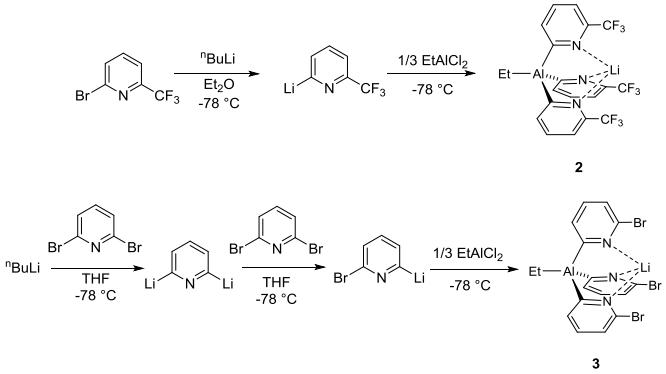
In contrast to the behavior of the dimeric unsubstituted complex $[MeAl(2\text{-}py)_3Li]_2$[6a] no evidence for a monomer/dimer equilibrium is detected in solution for desolvated **1**. Room-temperature $^1$H and $^7$Li NMR spectroscopic studies in $d_8$-toluene show the presence of a single compound in solution, 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 $[\mathbf{1}]_n$ of 1.03-1.14 over the concentration range 6.6 x $10^{-3}$ to 1.4 x $10^{-3}$ mol $L^{-1}$ (see Table 1).

**Table 1.** Cryoscopic molecular mass measurements of compounds **1-3**[a]

| Compound | Substituent at 6-position | Concentration (mol $L^{-1}$) | Mw | n |
|---|---|---|---|---|
| **1** | $CH_3$ | $1.4 \times 10^{-3}$ | 349 ± 9 | 1.03 ± 0.03 |
| **1** | $CH_3$ | $2.1 \times 10^{-3}$ | 386 ± 8 | 1.14 ± 0.02 |
| **1** | $CH_3$ | $6.6 \times 10^{-3}$ | 350 ± 19 | 1.03 ± 0.06 |
| **2** | $CF_3$ | $3.2 \times 10^{-3}$ | 476 ± 53 | 0.95 ± 0.11 |
| **2** | $CF_3$ | $7.8 \times 10^{-3}$ | 525 ± 25 | 1.05 ± 0.05 |
| **3** | Br | $8.95 \times 10^{-3}$ | 614 ± 25 | 1.15 ± 0.05 |
| **3** | Br | $1.3 \times 10^{-2}$ | 577 ± 17 | 1.08 ± 0.05 |

[a] All measurements were carried out in benzene.

The unusual monomeric behavior 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 which 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-$CF_3$-2-py)$_3$Li] (**2**) and [EtAl(6-Br-2-py)$_3$Li] (**3**) were prepared in moderate yields (of 41 and 51%, respectively) using a similar synthetic procedure to **1**·THF, involving the reactions of $EtAlCl_2$ with the corresponding 2-lithio-pyridines (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 $^n$BuLi (1 equiv.) *to* the bromo-pyridine at -78$^o$C, the lithiation of 2,6-dibromo-2-pyridine is most effective if the bromo-pyridine is added to the solution of $^n$BuLi. Although there is some debate as to the reasons for this in the literature, 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-$Li_2$-py) which is subsequently involved in the formation of the monolithiate (2-Li-6-Br-2-py).[14] Significantly, even though the syntheses of **2** and **3** are undertaken in THF and $Et_2O$ as the solvents no coordination of the $Li^+$ 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-$CF_3$ and 6-Br groups compared to 6-Me. For **2**, this is in-line with the greater van der Waals' radius of the $CF_3$ group (2.74 Å for $CF_3$ *vs* 2.23 Å for $CH_3$).[15] However, for **3** this appears to be counterintuitive since the van der Waals' radius of Br is smaller than that for a Me-group (1.85 Å).[12, 15]

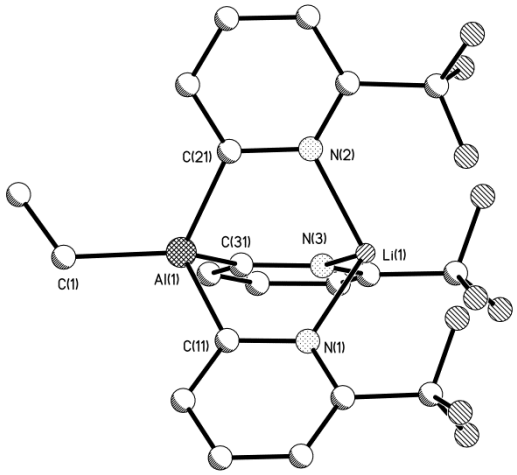



**Scheme 2** Synthesis of the new complexes **2** and **3**.

Both **2** and **3** were characterized by chemical analysis and multi-nuclear NMR spectroscopy. Their monomeric natures in solution were further supported by variable-concentration cryoscopy in benzene (Table 1). The room-temperature $^1$H and $^7$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** (Figs. 4a and 4b, respectively). Both complexes feature three-coordinate, pyramidal $Li^+$ 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)$^o$ in **3**

are similar in both complexes, despite the different steric influence of the $CF_3$ and Br groups in the 6-positions of the 2-py rings.

(a)

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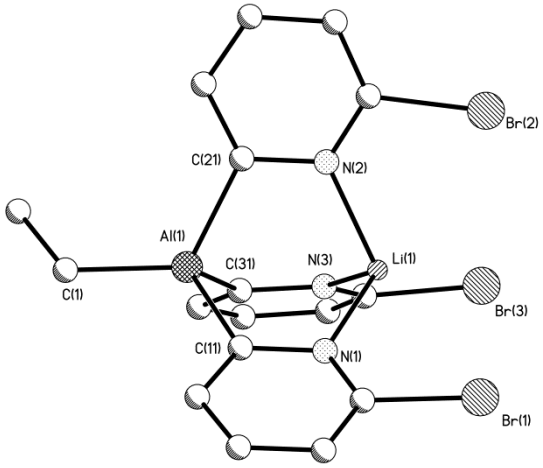
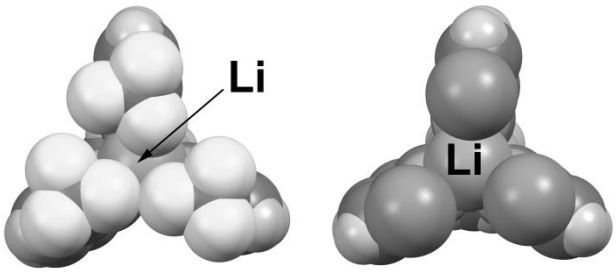



**Figure 4** Solid-state structures of the monomeric complexes (a) **2** and (b) **3**. H-atoms and the disorder of the $CF_3$ groups in **2** are removed for clarity. Selected bond lengths (Å) and angles (°): **2**, Cpy–Al(1) range 2.015(3)–2.001(3), N(1)-Li(1) 2.024(5), N(2)-Li(1) 2.028(6), N(3)-Li(1) 2.027(6), Cpy–Al(1)–Cpy range 102.92(12)–103.94(12), Al(1)–Cpy–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**, Cpy–Al(1) range 2.019(3)–2.034(3), N(1)-Li(1) 2.020(6), N(2)-Li(1) 2.016(5), N(3)-Li(1) 2.016(5), Cpy–Al(1)–Cpy range 101.78(11)-105.10(11), Al(1)–Cpy–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).

(a)

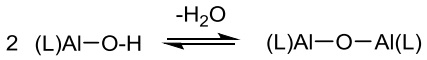



(b)

**Figure 5** Views of the $Li^+$ cation along the Li···Al axis, (a) **2** and (b) **3**.

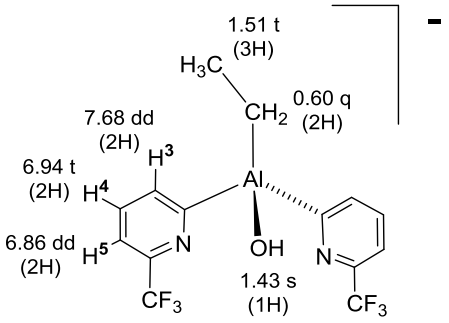
Views of **2** and **3** along the Al···Li axes of each of the monomers are presented in Fig. 5, from which it can be seen that the blocking of the $Li^+$ coordination site appears to be greatest in the $CF_3$ derivative **2**. It can be noted, however, that in the case of **2** and **3** the low coordination number of $Li^+$ 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)].[12] The extent to which these secondary interactions contribute to the coordination of $Li^+$ is unclear at this stage. In the case of **3**, for example, variable-temperature $^{19}F$ and $^{7}Li$ NMR spectroscopy (298-213K) indicated no Li···F coupling and the presence of a singlet in the $^{19}F$ NMR spectrum at all temperatures shows that the $CF_3$ 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 $FeCl_2$ which produces a green solution presumably of the half-sandwich compound [{EtAl(2-py)$_3$}FeCl],[8] neither **2** nor **3** coordinate $FeCl_2$. Further attempts to coordinate other metal ions with **2** and **3** also failed. It therefore appears that the introduction of the $CF_3$ 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 $Al^{III}$ 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, since lower steric demands of the ligand set and higher acidity of the O-H bond will encourage dimerization (Scheme 3).[16]




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

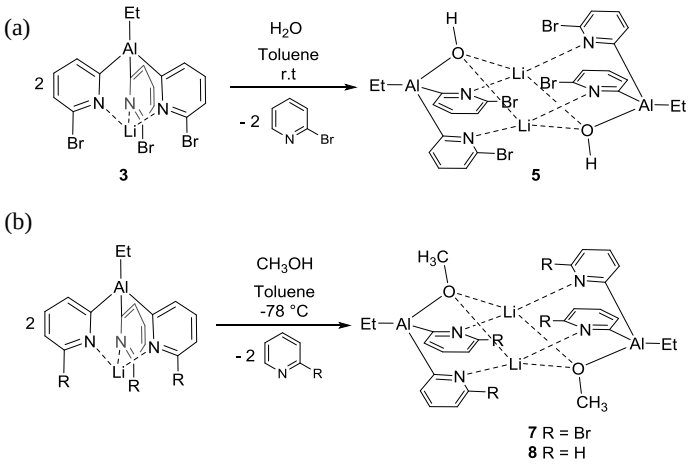
With this background in mind we decided to explore the use of **2** and **3** as scaffolds for the synthesis of terminal Al-OH compounds. The reaction of **2** with 1-2 equivalents of $H_2O$ in $d_8$-toluene was investigated in an *in situ* multinuclear NMR study. Within 5 minutes of mixing at room temperature the $^{7}Li$ 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 $^{1}H$ NMR spectrum confirms the formation of a single new species which can be identified as the $[EtAl(OH)(6\text{-}CF_3\text{-}2\text{-}py)_2]^-$ anion (**4**) (Scheme 4), observed as minor pyridyl-C-H and Et-Al resonances next to the corresponding resonances for **2**. In addition, free 6-$CF_3$-2-py-H and ethane (singlet, $\delta$ = 0.81 ppm) are also observed, suggesting that the hydrolysis of **2** is not selective, i.e., that either the Al-(6-$CF_3$-2-py) or Et-Al groups can be involved in intramolecular deprotonation of $H_2O$. The optimal reaction time was found to be *ca.* 1.5 h, by which time the resonances for **4** amount to only *ca.* 10% of the total integrated $^{1}H$ NMR resonances.




**Scheme 4** Assignment of the $^{1}H$ NMR spectrum of the anion **4** from the *in situ* NMR spectrum.

An *in situ* NMR spectroscopic study of the reaction of **3** with $H_2O$ indicated the formation of a closely related terminal Al-OH complex (**5**) in solution, but now quantitatively. The reaction is complete after 30 mins, giving a mixture of **5**, 2-Br-2-py-H and a small amount of ethane. Compound **5** has a similar $^{1}H$ NMR spectrum to the anion **4**, with 6-Br-pyridyl and

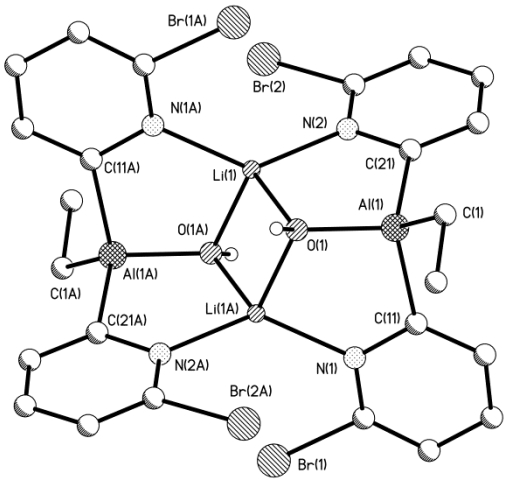
Et-Al resonances in 1 : 2 ratio along with a singlet characteristic of Al-OH at $\delta = 1.12$ ppm. The reaction was scaled up, allowing the preparation of **5** in 25% crystalline yield after workup (Scheme 5a). The presence of the OH group in solid **5** is shown by a sharp O-H stretching band at 3641 $cm^{-1}$ in the IR spectrum. This can be compared to values of greater than 3700 $cm^{-1}$ for terminal Al-OH, indicating weakening of the O-H bond. Full assignment of the $^{1}H$ NMR resonances and confirmation of the presence of the Et-Al-OH and Et−Al-Py linkages were obtained using 2-D NMR $^{1}H$-$^{13}C$ HMQC, $^{1}H$-$^{1}H$ NOESY and $^{1}H$-$^{13}C$ HMBC experiments (see SI).




**Scheme 5** Synthesis of the terminal Al-OH complex **5** and the alkoxides **6** and **7**.

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 $[\{EtAl(6\text{-}Br\text{-}2py)_2(OH)\}Li]_2$ in which the OH groups of the $[EtAl(6\text{-}Br\text{-}2py)_2(OH)]^-$ anions bridge the two $Li^+$ cations together in a central $Li_2O_2$ ring unit (Fig. 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 $H_2O$ 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 O-H group within a 'cleft' in the molecular arrangement, bounded by an Al-bonded Et group and two 6-Br-2-py groups, as seen in the space-filling diagram shown in Fig. 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).[17] 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•••Br H-bonds in the complex.

(a)



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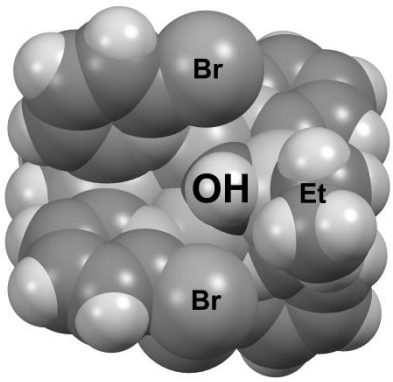



**Figure 6** Structure of the hydroxo *bis*–pyridylaluminate dimer **5** featuring a terminal Al-OH group. H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-O(1) 1.790(3), $C_{py}$–Al(1) 2.016(4)-2.019(4), N(1)-Li(1) 2.037(7), N(2)-Li(1) 2.046(7), O(1)-Li(1A) 1.964(7), O(1)-Li(1) 1.980(7), $C_{py}$-Al(1)-$C_{py}$ 104.28(15), $C_{py}$-Al(1)-O(1) 101.41(14)-101.65(14), Al(1)–$C_{py}$–N 113.9(3)-115.0(3), O-Al(1)-Li 36.4(2)-36.6(2), O(1)-Li(1)-N(1A) 112.6(4), O(1A)-Li(1)-N(2) 113.7(4), N(2)-Li(1)-N(1A) 135.3(4), N(2)-Li(1)-O(1) 96.8(3), O1-Li(1)-O(1A) 95.7(3), O(1)-Li(1)-N(2) 96.8(3). (b) Space-filling diagram, showing the environment around the OH group.

Roesky and coworkers have shown previously that the terminal Al-OH retains its Brønsted acidity, reacting for example with $Cp_3Ln$ (Ln = lanthanides) to give heterometallic Al-O-Ln bridged compounds.[18] In order to assess the acidity of the Al-OH groups in **5** we first explored its thermal behavior in solution. A solution of **5** in $d_8$-toluene was heated at 80°C for 3h, resulting in the elimination of free 6-Br-2-py-H and ethane, presumably *via* intramolecular deprotonation of the OH group (see SI $^1$H NMR studies). In a follow-up experiment, **5** was reacted with $ZnEt_2$ as an external base (1 : 1 equivalents). A mixture of compounds is observed by *in situ* $^1$H and $^{13}$C NMR spectroscopy. However, the *ca.* 20 ppm increase in chemical shifts of the C(2) of the 2-py group in the $^{13}$C NMR spectrum compared to **5** suggested that at least some transfer of the 2-py group onto $Zn^{2+}$ had occurred.[19] This was confirmed by the isolation of a few crystals of dimeric $[LiZn(6\text{-Br-py})_3]_2$ (**6**) from the NMR scale reaction and their structural characterization (see Fig. 7). Compound **6** consists of a dimeric zincate $[Zn(6\text{-Br-2-py})_3]_2^{2-}$ dianion ion-paired with two $Li^+$ cations, in which full transfer of the 6-Br-2-py groups has occurred from Al to Zn.

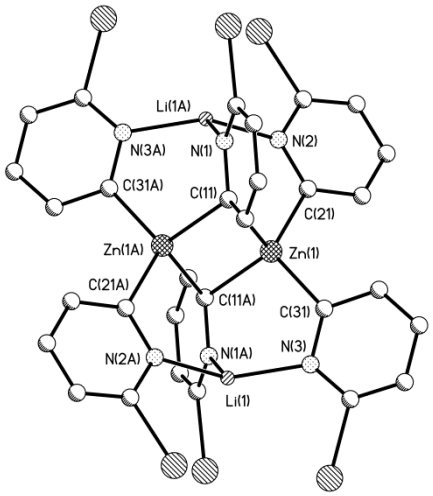



**Figure 7** Structure of the 2-Br-py complex zinc complex **6**. H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): $C_{py}$–Zn range 2.019(8)- 2.279(8), N-Li range 1.965(14)- 2.022(14), N–Li–N range 103.6(6)- 134.0(8), Zn–$C_{py}$–N range 116.7(5)-124.8(6).

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 $[EtAl(2\text{-py})_3Li{\cdot}THF]$ or 6-Br substituted **3** with MeOH (1.3 equivalents) in toluene at 0°C give the closely related heteroleptic compounds $[\{EtAl(2\text{-py})_2(OMe)\}Li]_2$ (**7**) and $[\{EtAl(6\text{-Br-2-py})_2(OMe)\}Li]_2$ (**8**) in 20-30% crystalline yields (Scheme 5b). 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 (Figs. 8a and b). The retention of these dimeric structures in solution along with the full assignment of their resonances are supported by extensive 1-D and 2-D multinuclear NMR investigations (see SI).

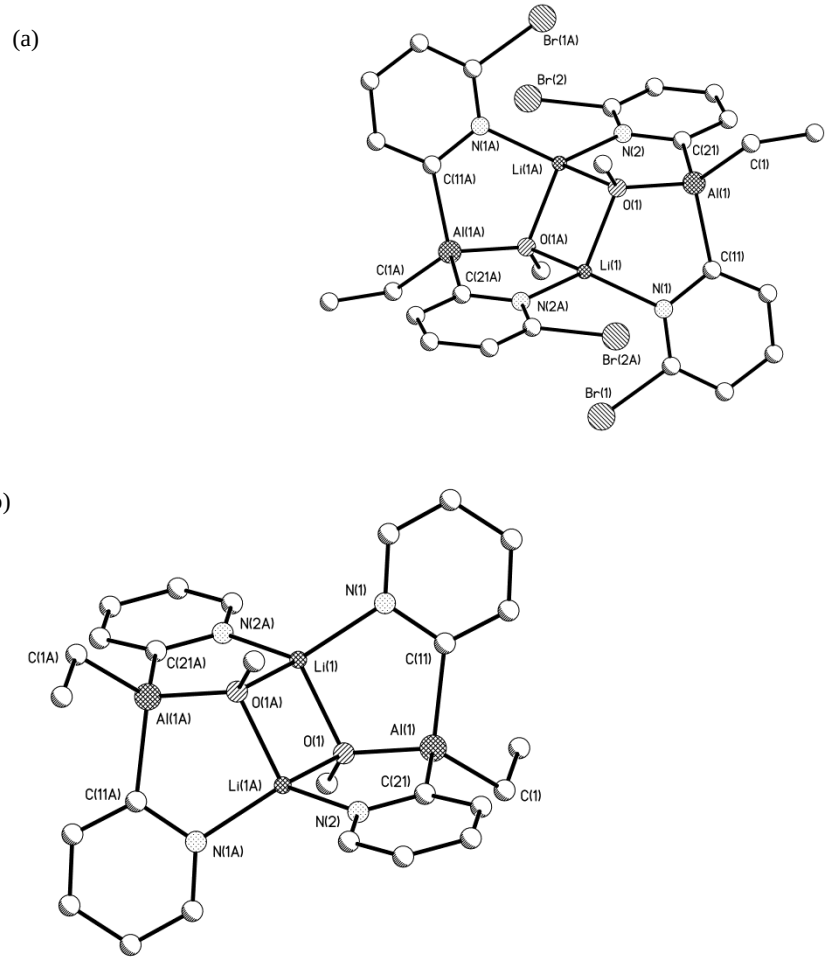



**Figure 8**. Structure of the heteroleptic alkoxide aluminates (a) **7** and (b) **8**. H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **7**, Al1-O1 1.808(2), $C_{py}$–Al(1) 2.012(3) and 2.021(3), N(1)-Li(1) 2.048(6), N(2)-Li(1A) 2.045(6), O(1)-Li(1) 2.011(6), O(1)-Li(1A) 2.010(6),$C_{py}$-Al(1)-$C_{py}$ 105.60(14), $C_{py}$-Al(1)-O(1) 101.92(12) and 102.16(12), Al(1)–$C_{py}$–N 115.3(2) and 115.6(2), O-Al-Li(1) 33.08(11)-33.33(11), O(1)-Li(1)-N(2A) 115.8(3), N(2A)-Li(1)-N(1) 132.3(3), O(1)-Li(1)-N(1) 96.7(2), O(1A)-Li(1)-O(1) 95.7(2). **8**, Al1-O1 1.8012(11), $C_{py}$–Al(1) 2.0175(16) and 2.0188(17), N(1)-Li(1) 2.029(3), N(2)-Li(1A) 2.023(3), O(1)-Li(1) 1.999(3), O(1)-Li(1A) 1.989(3), $C_{py}$-Al(1)-$C_{py}$ 106.71(6), $C_{py}$-Al(1)-O(1) 102.17(6) and 102.34(6), Al(1)–$C_{py}$–N 116.36(11) and 116.50(11), O(1)-Al(1)-Li(1) 38.50(6), O(1)-Li(1)-Al(1) 34.12(5), O(1)-Li(1)-N(2A) 114.43(14), O(1)-Li(1)-N(1) 99.24(13), N(2A)-Li(1)-N(1) 127.81(15), O(1A)-Li(1)-O(1) 96.42(12).

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

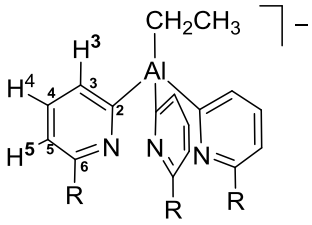
## Conclusions

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)$_3$Li·THF] (**1**·THF), which gives the highly

unusual monomer **1**, as opposed to the expected dimeric arrangement which would have a four- rather than three-coordination number for $Li^+$. The steric effect of substituents at the 6-position is also seen in the behavior 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 amides 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 syntheses were carried out on a vacuum-line under argon atmosphere. Products were isolated and handled with the aid of a $N_2$-filled glove box (Saffron type $\alpha$). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 QNP or Bruker Avance 500 MHz Cryo spectrometer. $^7$Li and $^{27}$Al NMR NMR spectra were recorded on a Bruker Avance 500 MHz Cryo-spectrometer. Elemental analysis was obtained on a Perkin Elmer 240 Elemental Analyser. The unambiguous assignment of NMR resonances was accomplished by additional 2D NMR experiments ($^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, $^1$H-$^{13}$C HMQC and $^1$H-$^{13}$C HMBC experiments (see SI for details). [EtAl(6-Me-2-py)$_3$Li·THF], **1**·THF, was synthesized as described previously.[9]




R = $CH_3$, $CF_3$, Br, H

**Scheme 6.** Atom labeling scheme used in the NMR studies for the pyridyl aluminates ligands.

**Synthesis of [EtAl(6-Me-2-py)$_3$Li] (1):** [EtAl(6-Me-2-py)$_3$Li·THF] (250 mg, 0.608 mmol) was placed under vacuum (0.1 mm Hg) for *ca.* 1.5h at 70 °C affording **1** as a white solid in quantitative yield: 205 mg, 0.604 mmol, 99%. Colorless crystals of **1** were obtained from a saturated solution of **1** in toluene at 20$^o$C. $^1$H NMR (298K, $d_8$-toluene, 500 MHz), $\delta$ = 7.69 (d, JHH = 7.3 Hz, 3H, H$^3$ py), 7.00 (t, JHH = 7.5 Hz, 3H, H $^4$py), 6.46 (d, JHH = 7.8 Hz, 3H, H$^5$py), 2.26 (s, 9H, C$^6$–CH$_3$), 1.98 (t, J HH= 8.1 Hz, 3H, Al–CH$_2$C<u>H</u>$_3$), 1.09 (q, JHH = 8.1Hz, 3H, Al–CH$_2$). $^{13}$C{$^1$H} NMR (298K, $d_8$-toluene, 100.6 MHz), $\delta$ =188.62 (br, C$^2$ py), 154.93 (C$^6$ py), 133.32 (C$^4$ py), 130.61 (C$^3$ py), 119.79 (C$^5$ py), 24.89 (C$^6$–CH$_3$), 11.23 (Al–CH$_2$<u>C</u>H$_3$), -2.54 (br, Al–CH$_2$). $^{27}$Al NMR (298K, $d_8$-toluene ,130.3 MHz, ref solution of $AlCl_3.6H_2O/D_2O$), $\delta$ = 126.55 (br, s). $^7$Li NMR (298K, $d_8$-toluene ,194.4 MHz, ref solution of $LiCl/D_2O$), $\delta$ = 3.53 (s). Elemental analysis, cald. 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$_3$-2-py)$_3$Li] (2):** 2-Bromo-6-(trifluoromethyl)pyridine (2.00 g, 8.85 mmol) was dissolved in $Et_2O$ (40 ml). $^n$BuLi (5.6 ml, 8.96 mmol, 1.6 M 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. $EtAlCl_2$ (2.95 ml, 2.95 mmol, 1.0 M 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 (10ml) were added and the yellow-brown mixture was stirred at room temperature for 3h 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 isolated crystalline yield, 600 mg, 1.2 mmol, 41%. Note: If the lithiation step is carried out in THF at -78°C rather than in $Et_2O$ then compound **2** was obtained in lower yield (10-20%). $^1$H NMR (298K, $d_8$-toluene, 500 MHz), $\delta$ = 7.74 (d, JHH = 7.4 Hz, 3H, H$^3$ py), 6.81 (t, JHH = 7.7 Hz, 3H, H$^4$ py), 6.74 (dd, JHH = 7.8 and 0.9 Hz, 3H, H$^5$ py), 1.88 (t, J HH= 8.2 Hz, 3H, Al–CH$_2$C<u>H</u>$_3$), 0.99 (q, JHH = 8.2Hz, 3H, Al–CH$_2$). $^{13}$C{$^1$H} NMR (298K, $d_8$-toluene, 100.6 MHz), $\delta$ = 189.0 (br, C$^2$ py), 146.19 (q, $^2$JCF = 32.5 Hz, C$^6$ py), 135.94 (C$^3$ py), 133.92 (C$^4$ py), 123.89 (q, $^1$JCF = 273 Hz, $CF_3$), 117.35 (C$^5$ py), 10.93 (Al–CH$_2$<u>C</u>H$_3$), -2.91 (br, Al–CH$_2$). $^{27}$Al NMR (298K, $d_8$-toluene ,130.3 MHz, ref. solution of $AlCl_3.6H_2O/D_2O$), $\delta$ = 127.11 (br, s). $^7$Li NMR (298K, $d_8$-toluene ,194.4 MHz, ref. solution of $LiCl/D_2O$), $\delta$ = 2.87 (s). Elemental analysis, cald. 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)$_3$Li] (3):** A solution of $^n$BuLi (12.5 ml, 20 mmol, 1.6 M in hexanes) in THF (12mL) was cooled at -78°C. To this solution was added dropwise over 30min a solution of 2,6-dibromopyridine (4.74 g, 20 mmol) in THF (28mL). The resulting dark green mixture was stirred (40 min at -78 °C). $EtAlCl_2$ (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 36h. The solvent was removed *in vacuo*. The addition of toluene (40 ml) and THF (10ml) 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°C afforded more colourless crystals of **3**. Total isolated yield, 1.80 g, 3.37 mmol, 51%. $^{1}$H NMR (298K, $d_8$-toluene, 500 MHz), δ = 7.49 (dd, JHH = 6.1 and 2.1 Hz, 3H, $H^3$ py), 6.66-6.52 (m, 6H, $H^4$ and $H^5$ py), 1.82 (t, J HH= 8.2 Hz, 3H, Al–$CH_2C\underline{H}_3$), 0.89 (q, JHH = 8.2Hz, 3H, Al–$CH_2$). $^{13}C\{^1H\}$ NMR (298K, $d_8$-toluene, 100.6 MHz), δ = 191.9 (br, $C^2$ py), 142.95 ($C^6$ py), 136.07 ($C^4$ py), 131.94 ($C^3$ py), 123.71 ($C^5$ py), 10.93 (Al–$CH_2\underline{C}H_3$), -2.90 (br, Al–$CH_2$). $^{27}$Al NMR (298K, $d_8$-toluene ,130.3 MHz, ref. solution of $AlCl_3.6H_2O/D_2O$), δ = 125.30 (br, s). $^{7}$Li NMR (298K, $d_8$-toluene ,194.4 MHz, ref. solution of $LiCl/D_2O$), δ = 1.58 (s). Elemental analysis, cald. 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)$_2$Li]$_2$ (5):** $H_2O$ (76uL, 4.2 mmol, 1.4 eqv) was added at room temperature to a solution of **3** (1.40g, 2.62 mmol) in toluene (50mL). The progress of the reaction can be monitored by $^{7}$Li NMR. The mixture was stirred at room temperature for 3h and subsequently filtered over Celite to afford a colorless solution. The solution was concentrated under vacuum (*ca* 3ml) and n-pentane was added until turbidly was observed. Storage at -15°C afforded colorless crystals of **5** (258 mg, 0.327 mmol, 25% crystalline yield). Note: The compound is highly soluble in toluene, however, if the solvent is evaporated under vacuum and the resulting residue is dried under prolongated vacuum to remove 2-bromopyridine and $H_2O$, 440mg of compound **5** (0.558 mmol, 43% yield) containing 5% of **3** were obtained. IR (Nujol), ν(OH): 3641 $cm^{-1}$. $^{1}$H NMR (298K, $d_8$-toluene, 500 MHz), δ = 7.47 (dd, JHH = 7.0 and 1.1 Hz, 2H, $H^3$ py), 6.82-6.78 (m, 2H, $H^5$ py), 6.78-6.72 (m, 2H, $H^4$ py), 1.46 (t, J HH= 8.1 Hz, 3H, Al–$CH_2C\underline{H}_3$), 1.07 (s, 1H, Al–OH), 0.50 (q, JHH = 8.1 Hz, 3H, Al–$CH_2$). $^{13}C\{^1H\}$ NMR (298K, $d_8$-toluene, 100.6 MHz), δ = 191.8 (br, $C^2$ py), 143.76 ($C^6$ py), 136.02 ($C^4$ py), 131.29 ($C^3$ py), 125.0 ($C^5$ py, overlapped with residual toluene solvent signal), 10.08 (Al–$CH_2\underline{C}H_3$), -0.30 (br, Al–$CH_2$,). $^{27}$Al NMR (298K, $d_8$-toluene ,130.3 MHz, ref. solution of $AlCl_3.6H_2O/D_2O$), δ = 138.0 (br, s). $^{7}$Li NMR (298K, $d_8$-toluene, 194.4 MHz, ref. solution of $LiCl/D_2O$), δ = 1.94 (s) . Elemental analysis, cald. 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)$_2$Li]$_2$ (7)**: Methanol (120uL, 3.04 mmol, 1.25 eqv) was added at 0°C to a solution of **3** (1.30g, 2.435mmol) in toluene (50mL). The mixture was stirred (1.5h at 0°C) and subsequently allowed to reach room temperature. The resulting cloudy solution was stirred for 1h at room temperature and filtered over Celite. The colorless solution produced was concentrated (to *ca.* 5mL) and was layered with n-pentane. Storage at -15°C afforded colorless crystals of **7**. Total isolated crystalline yield 220 mg, 0.27 mmol, 22%. $^{1}$H NMR (298K, $d_8$-toluene, 500 MHz), δ = 7.47 (dd, JHH = 7.0 and 1.1 Hz, 2H, $H^3$ py), 6.79-6.83 (m, 2H, $H^5$ py), 6.77-6.71 (m, 2H, $H^4$ py), 3.52 (s, 3H, $OCH_3$), 1.54 (t, J HH= 8.1 Hz, 3H, Al–$CH_2C\underline{H}_3$), 0.64 (q, JHH = 8.1 Hz, 3H, Al–$CH_2$). $^{13}C\{^1H\}$ NMR (298K, $d_8$-toluene, 100.6 MHz), δ = 191.3 (br, $C^2$ py), 143.60 ($C^6$ py), 136.07 ($C^4$ py), 131.62 ($C^3$ py), 125.32 ($C^5$ py, overlapped with residual toluene solvent signal), 51.52 ($OCH_3$,), 10.29 (Al–$CH_2\underline{C}H_3$), -1.25 (br, Al–$CH_2$,). $^{27}$Al NMR (298K, $d_8$-toluene ,130.3 MHz, ref. solution of $AlCl_3.6H_2O/D_2O$), δ = 139.27 (br, s). $^{7}$Li NMR (298K, $d_8$-toluene, 194.4 MHz, ref. solution of $LiCl/D_2O$), δ = 1.98 (s). Elemental analysis, cald. 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)$_2$Li]$_2$ (8):** Methanol (63uL, 1.56 mmol, 1.25 eqv) was added at -78°C to a solution of [EtAl(2-py)$_3$Li·THF] (480 mg, 1.30 mmol) in toluene (28mL). The mixture was stirred at -78°C for 5min 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.* 3mL). Addition of n-pentane (*ca.* 5ml) and storage at -15°C afforded colorless crystals of **8**. Total isolated crystalline yield 100 mg, 0.20 mmol, 31%. $^{1}$H NMR (298K, $d_8$-toluene, 500 MHz), δ = 8.22-8.19 (m, 2H, $H^6$ py), 7.78-7.74 (m, 2H, $H^3$ py), 7.15 (td, J HH= 7.6 and 1.7 Hz, 2H, $H^4$ py), 6.69-6.64 (m, 2H, $H^5$ py), 3.20 (s, 3H, $OCH_3$), 1.57 (t, J HH= 8.1 Hz, 3H, Al–$CH_2C\underline{H}_3$), 0.62 (q, JHH = 8.1 Hz, 3H, Al–$CH_2$). $^{13}C\{^1H\}$ NMR (298K, $d_8$-toluene, 100.6 MHz), δ = 187.90 (br, $C^2$ py), 148.80 ($C^6$ py), 133.42 ($C^3$ py), 133.30 ($C^4$ py), 121.29 ($C^5$ py), 51.11 ($OCH_3$,), 10.61 (Al–$CH_2\underline{C}H_3$), -0.48 (br, Al–$CH_2$,). $^{27}$Al NMR (298K, $d_8$-toluene ,130.3 MHz, ref. solution of $AlCl_3.6H_2O/D_2O$), δ = 141.22 (br, s). $^{7}$Li NMR (298K, $d_8$-toluene, 194.4 MHz, ref. solution of $LiCl/D_2O$), δ = 2.56 (s). Elemental analysis, cald. 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 KappaCCD diffractometer with graphite-monochromated MoKα 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 MoKα microfocus source. Crystals were mounted directly from solution using perfuorohydrocarbon oil to prevent atmospheric oxidation, hydrolysis, and solvent loss,[20] and the temperature was held between 180 and 250 K using an Oxford Cryosystems $N_2$ cryostat. Data were collected using Bruker Apex2 or GIS, processed using SAINT and SADABS and refined using SHELXL.[21] Details of the data collections and structural refinements are given in Table S1 in the Supporting Information. 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 multi-component 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 in order to maintain sensible bond distances. Several of the atoms exhibit relatively prolate displacement ellipdoids. **2**: The $CF_3$ 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 center. It was modelled with a constrained benzene ring and common isotropic displacement parameters for the C atoms. Compounds **2** and **3** are isostructural (i.e. the Br atoms in **3** occupy essentially the same space as the disordered $CF_3$ groups in **2**).

CCDC 1 1404218, **2** 1404219, **3**, 1404220, **6** 1404221, **5** 1404222, **7** 1404223 and **8** 1404224.

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**Keywords:** *tris*-pyridyl aluminate • steric effects • terminal Al-OH • lithium• NMR

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