

# Post-functionalisation of *Tris*-pyridyl Aluminate Ligands: Chirality, Coordination and Supramolecular Chemistry

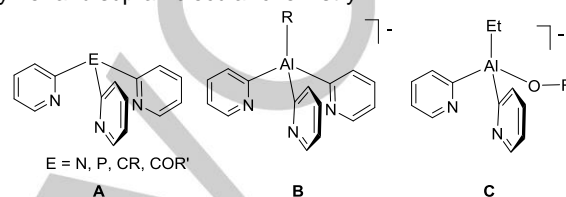
Álvaro García-Romero,<sup>[a]</sup> Alex J. Plajer,<sup>[b]</sup> Lucía Álvarez-Miguel,<sup>[a]</sup> Andrew D. Bond,<sup>[b]</sup> Dominic S. Wright<sup>[b]</sup> and Raúl García-Rodríguez<sup>\*[a]</sup>

**Abstract:** Post-functionalisation of the aluminate anion  $[\text{EtAl}(\text{6-Me-2-py})_3]^-$  (**1**) (2-py = 2-pyridyl) with alkoxide ligands can be achieved by the selective reactions of the lithium salt **1Li** with alcohols in the appropriate stoichiometry. This method can be used to introduce 3-py and 4-py functionality in the form of 3- and 4-alkoxymethylpyridyl groups, while maintaining the integrity of the aluminate framework, thereby giving entry to new supramolecular chemistry. Chirality can be introduced either by using a chiral alcohol as a reactant or by the step-wise reaction of **1Li** with two different non-chiral alcohols. The latter route has allowed the synthesis of a rare example of a chiral-at-aluminium aluminate.

## Introduction

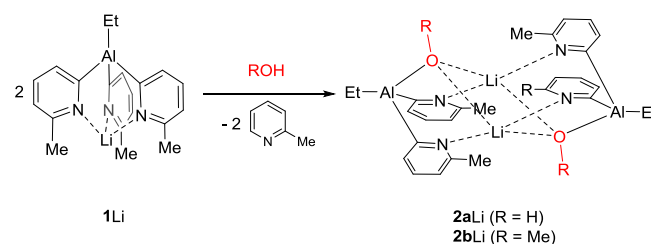
There has recently been a resurgence of interest in tripodal *tris*(2-pyridyl) ligands, particularly in their potential applications as spectator ligands in catalysis, but also in a range of other applications in coordination, organometallic and bioinorganic chemistry.<sup>[1]</sup> Most of the studies in the last 40 years or so have focused on neutral ligands with lighter bridgehead atoms E(2-py)<sub>3</sub> (E = CR, COR, CH, N, P, P=O, etc.; Figure 1 A).<sup>[2]</sup> More recently there has been growing interest in heavier, more metallic bridgehead ligands of Groups 13,<sup>[3]</sup> 14,<sup>[4]</sup> and 15.<sup>[5]</sup> Changing the bridgehead can have a large effect on the coordination and properties of the ligands. For instance, as Group 15 is descended, the Lewis acidity of the bridgehead atom of the neutral ligands  $[\text{E}(\text{2-py})_3]$  (E = N–Bi) increases, changing the donor properties of the ligand and the coordination mode. Thus, changing the bridgehead atom is a method that can be used to modulate the catalytic activity of the metal complexes.<sup>[5b]</sup> We have been particularly interested in Group 13 *tris*(2-pyridyl)aluminates ( $[\text{RAl}(\text{2-py})_3]^-$ ; Figure 1 B) as they are unusual in this area in having an overall negative charge (rather than being neutral).<sup>[3a]</sup> As one of the few anionic members of the *tris*-pyridyl family, they exhibit strong affinity for metal cations and have extensive coordination chemistry with a broad range of transition metals,<sup>[6]</sup> main-group metals<sup>[7]</sup> and lanthanides.<sup>[8]</sup> The closely related *tris*(2-pyridyl)borates<sup>[3b, 9]</sup> have also attracted

recent interest, stemming from their potential applications in polymer and supramolecular chemistry.<sup>[10]</sup>



**Figure 1** A conventional, neutral *tris*(2-pyridyl) ligands containing non-metallic bridgeheads, **B** *tris*(2-pyridyl)aluminates, **C** mono-substitution of a 2-pyridyl group by an RO group.

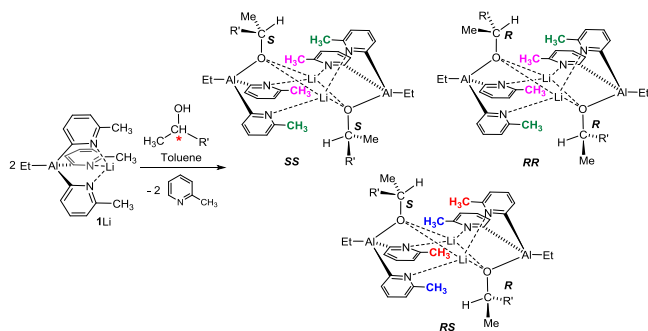
Our most recent interest in aluminates has turned to the elaboration of their frameworks *via* exchange of the 2-pyridyl groups of **B** with other donor groups (Figure 1 C). In contrast to B-bridged *tris*(2-pyridyl) borate ligands, the higher polarity of the Al-C bond enables easy exchange of the pyridyl groups. This is seen in the room-temperature reactions of the sterically hindered aluminate  $[\text{EtAl}(\text{6-Me-2-py})_3]^-$  (**1**) with ROH (R = H or Me), in which the exchange of just one of the 6-Me-py groups can be controlled (Scheme 1).<sup>[11]</sup> The reactions of **1** with racemic mixtures of the chiral alcohols R'(Me)CH(OH) (R' = C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>13</sub>, and C<sub>6</sub>H<sub>5</sub>) leads to mixtures of dimeric *SS/RS*- and *SR*-diastereomers. Owing to their different molecular symmetries, the *RR/SS* and *RS* dimers exhibit different signals in their <sup>1</sup>H and <sup>7</sup>Li NMR spectra, with the 6-Me groups acting as reporter groups (Scheme 2).<sup>[12]</sup>



**Scheme 1** Exchange of a 6-Me-py group of anion **1** for an RO group, forming dimers with Li<sub>2</sub>O<sub>2</sub> cores.

[a] Dr R. García-Rodríguez, Mr A. García-Romero, Lucía Álvarez-Miguel, GIR MIOMeT-IU Cinquima-Química Inorgánica Facultad de Ciencias, Universidad de Valladolid; Campus Miguel; Delibes, 47011 Valladolid; [raul.garcia.rodriguez@uva.es](mailto:raul.garcia.rodriguez@uva.es)

[b] Mr A. J. Plajer, Dr A. D. Bond, Prof. Dr D. S. Wright, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW; [dsw1000@cam.ac.uk](mailto:dsw1000@cam.ac.uk)

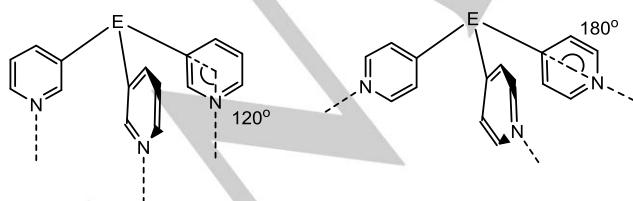


**Scheme 2** Reaction of **1Li** with chiral alcohols and the formation of *RR*, *SS* and *RS* dimers, with the magnetically-inequivalent 6-Me environments highlighted.

With the above background in mind, we present here a study of the ways in which ligand exchange of the 6-Me-py groups of **1** can be used to (i) access previously unexplored 3-py and 4-py functionality, leading to supramolecular assemblies, and (ii) build chirality at the Al centre by the incorporation of three different substituents.

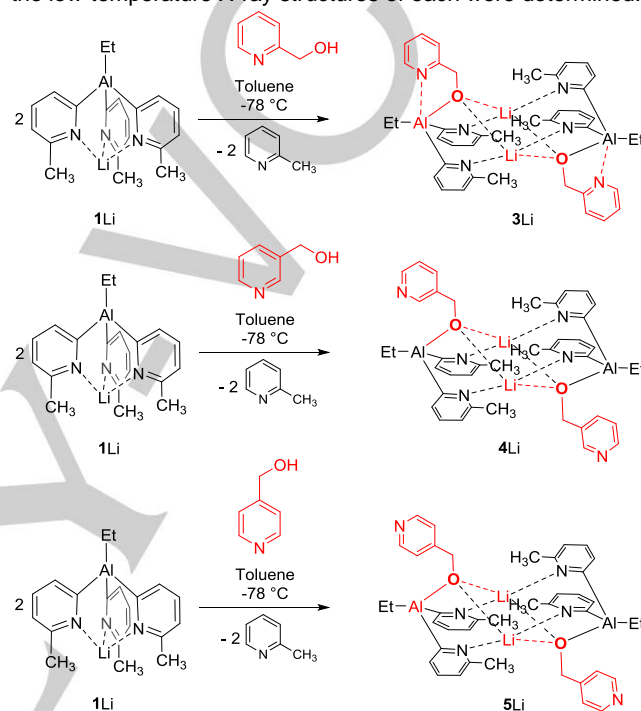
## Results and Discussion

One interesting idea in the general area of *tris*(pyridyl) ligands is the incorporation of donor functionality into the 3- and 4-positions, which should result in a fundamental change in the character of the ligand from intramolecular and tripodal for 2-py substituents to intermolecular for 3- and 4-py groups (Figure 2). A rare example illustrating this feature is observed with C(4-py)<sub>4</sub>, which functions as a tetrahedral node in the diamondoid lattice arrangement of [AgBF<sub>4</sub>{C(4-py)<sub>4</sub>}].<sup>[13]</sup> Despite their obvious potential as building blocks in supramolecular chemistry, the coordination chemistry of these ligands remains largely unexplored and only a few complexes containing neutral 3- and 4-py ligands with non-metallic C,<sup>[13-14]</sup> Si<sup>[15]</sup> and P<sup>[16]</sup> bridgeheads have been structurally characterized. The fundamental problem in developing any of the 3- or 4-py ligand systems of this type is the unreliability of the metal-halogen exchange reactions that generate the lithio-pyridine intermediates from the corresponding bromo-pyridines.<sup>[17]</sup> For this reason, despite our best efforts, we have been unable to obtain any of the metal-bridged *tris*(pyridyl) ligands containing 3-py or 4-py groups.



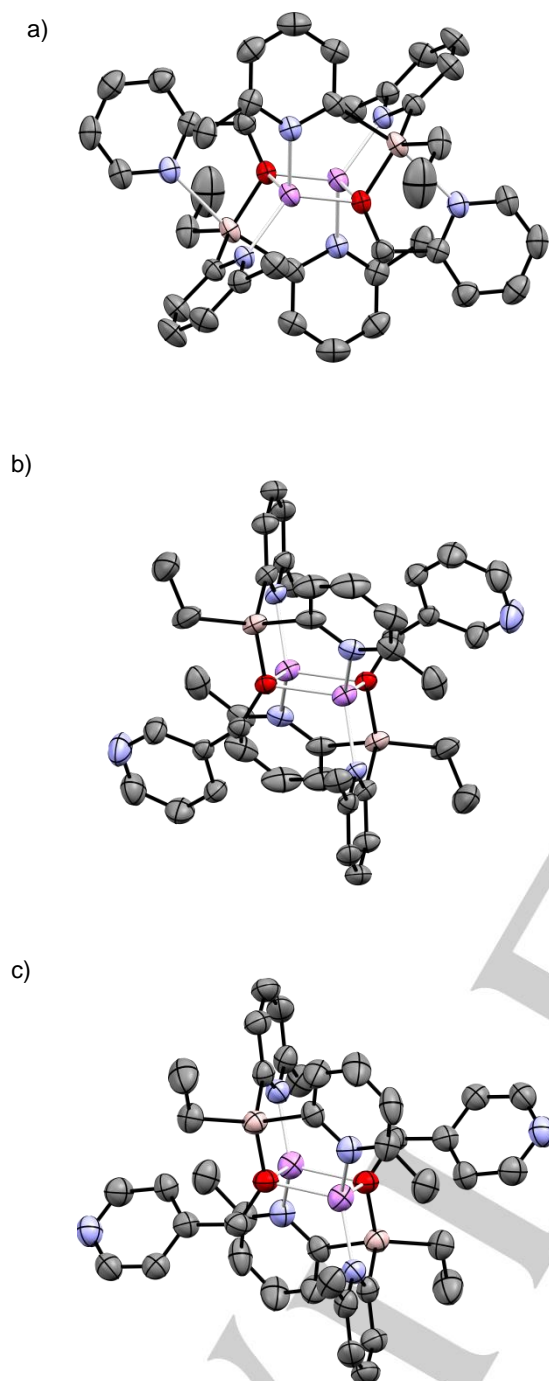
**Figure 2** *Tris*(pyridyl) ligand frameworks containing 3- and 4-py groups, allowing inter-molecular interactions, in contrast to more common 2-py ligands, which produce intra-molecular interactions (see for instance, **1Li** in Scheme 1).

We therefore decided to explore the incorporation of 3-OCH<sub>2</sub>py and 4-OCH<sub>2</sub>py groups using our previously established post-functionalisation strategy. The reactions of 2-(OH)CH<sub>2</sub>py, 3-(OH)CH<sub>2</sub>py and 4-(OH)CH<sub>2</sub>py (1 equivalent) with **1Li** at -78 °C in toluene led to the formation of the lithium complexes [Li{EtAl(2-OCH<sub>2</sub>py)(6-Me-2-py)<sub>2</sub>}]<sub>2</sub> (**3Li**), [Li{EtAl(3-OCH<sub>2</sub>py)(6-Me-2-py)<sub>2</sub>}]<sub>2</sub> (**4Li**), and [Li{EtAl(4-OCH<sub>2</sub>py)(6-Me-2-py)<sub>2</sub>}]<sub>2</sub> (**5Li**), containing the mono-substituted anions (Scheme 3). These can be isolated in crystalline form after workup of the reactions, and the low-temperature X-ray structures of each were determined.



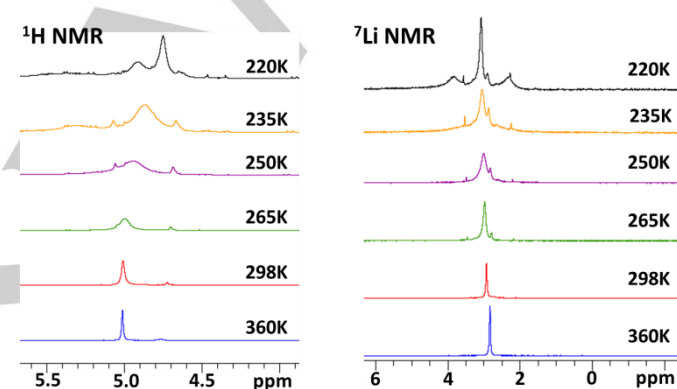
**Scheme 3** Syntheses of **3Li**, **4Li** and **5Li** incorporating 2-OCH<sub>2</sub>py, 3-OCH<sub>2</sub>py, and 4-OCH<sub>2</sub>py functionality, respectively.

The lithium salts **3Li**, **4Li**, and **5Li** were isolated in crystalline form after work up of the reactions in 29-57% yields and were characterized by elemental analysis and heteronuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li and <sup>27</sup>Al) NMR spectroscopy, in addition to obtaining their single-crystal X-ray structures. They all form dimeric structures in the solid state, which are similar to the previously reported dimers **2a** and **2b** (Scheme 1), containing central Li<sub>2</sub>O<sub>2</sub> cores (see Figure 3). However, while the 3-N and 4-N atoms of **4Li** and **5Li** are not involved in any secondary intra- or inter-molecular interactions, in the case of **3Li** the OCH<sub>2</sub>py arm is involved in intramolecular coordination through the 2-N atoms to the Al<sup>III</sup> centres of the [EtAl(6-Me-2-py)<sub>2</sub>(2-OCH<sub>2</sub>py)]<sup>-</sup> anion, resulting in a distorted trigonal bipyramidal geometry. This interaction [2.309(2) Å] is at the upper end of neutral donor-Al<sup>III</sup> interactions found in the Cambridge Structural Database.<sup>[18]</sup>

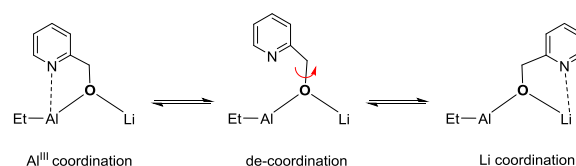


**Figure 3** Dimer structures of a) **3Li**, b) **4Li** and c) **5Li**. Displacement ellipsoids are drawn at the 50% probability level. H atoms and (in the cases of **2Li** and **5Li**) other chemically-equivalent independent molecules are omitted for clarity. A list of selected bond lengths and angles for each can be found in the supporting information. Colour key: oxygen (red), magenta (lithium), blue (nitrogen), pink (aluminium), carbon (grey).

An indication of the dynamic nature of the long-range  $A^{III}$ -N interactions in **3Li** is provided by  $^1H$  and  $^7Li$  NMR spectroscopy, carried out in toluene. Whereas the 360 K  $^1H$  spectra of **4Li** and **5Li** show sharp resonances, the  $OCH_2py$  and 2-py resonances of **3Li** exhibit significant broadening. Reducing the temperature from 360 K to 235 K results in the appearance of at least three resonances for the  $CH_2$  protons of the  $OCH_2py$  group (Figure 4a). The  $^7Li$  NMR spectrum also shows the appearance of several resonances over approximately the same temperature range, (Figure 4b). The fact that the  $^1H$  and  $^7Li$  NMR spectra do not change significantly with concentration suggests that the dynamic process involved is intramolecular (presumably involving the *intact* dimer units). On this basis, we tentatively suggest that the observed equilibrium process involves  $A^{III}/Li$  coordination by the N atoms of the 2-py groups of the pendant  $OCH_2py$  group (shown in idealised form in Scheme 4).



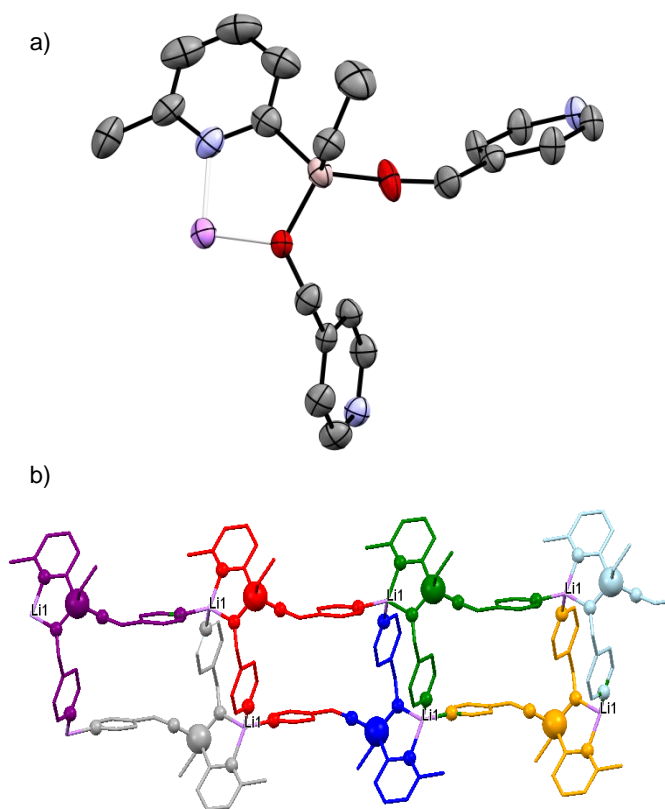
**Figure 4** Variable-temperature  $^1H$  (showing the region corresponding to the  $CH_2O$  protons) and  $^7Li$  spectra of **3Li** in toluene.



**Scheme 4** The proposed solution equilibrium in **3Li** involving  $A^{III}/Li$  coordination.

The reaction of **1Li** with further 4-(OH) $CH_2py$  was monitored by *in situ*  $^1H$  NMR spectroscopy. The addition of 1 equivalent of 4-(OH) $CH_2py$  occurs smoothly at room temperature, giving **3Li**. Although reaction with a further equivalent of 4-(OH) $CH_2py$  in thf leads to the formation of a number of 4- $OCH_2py$  containing products, the new complex  $Li[EtAl(4-OCH_2py)_2(6-Me-2-py)]$  (**6Li**) can be isolated from the scaled-up reaction in toluene, from which **6Li** precipitates (in 30% yield). This material was shown to be reasonably pure by elemental analysis and NMR spectroscopy. The solid-state structure of the monomer units of **6Li** is shown in Figure 5a. Apart from confirming the *bis*-substitution with the 4- $OCH_2py$  groups, the structure shows that

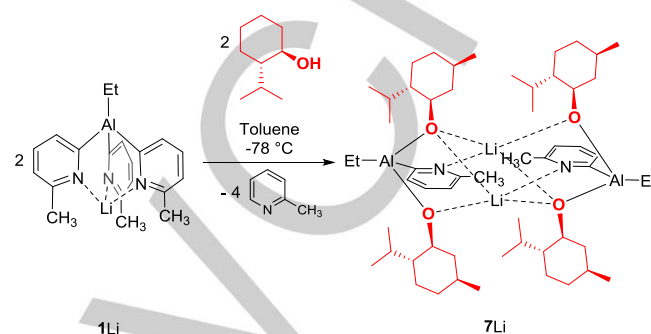
the donor-N atoms of the 4-py groups are orientated approximately perpendicular to each other. This allows the monomers of **6Li** to form a ribbon-like polymeric arrangement in which N-atoms of the 4-py groups bond to neighbouring Li<sup>+</sup> cations, resulting in a distorted four-coordinate geometry for Li<sup>+</sup> (Figure 5b). The supramolecular architecture of **6Li** demonstrates that substitution at the 4-position can indeed result in intermolecular association.



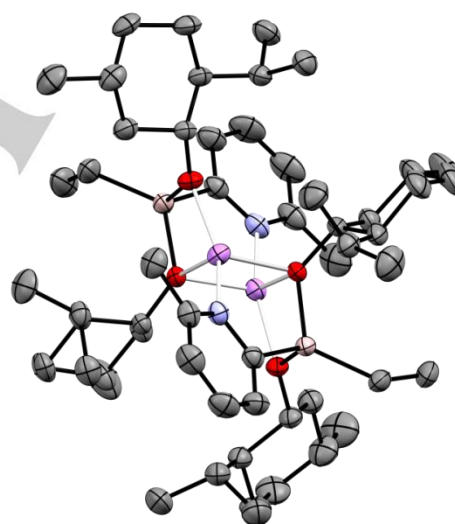
**Figure 5** a) The monomeric unit of **6Li** (with displacement ellipsoids at 50% probability), and b) association of the monomer units into a polymeric ribbon arrangement. In the solid state, toluene molecules occupy positions between the ribbons. The toluene molecules, as well as H atoms, are omitted for clarity. A list of selected bond lengths and angles can be found in the supporting information. Colour key: oxygen (red), magenta (lithium), blue (nitrogen), pink (aluminium), carbon (grey).

The ability to incorporate a chiral alkoxy group into these aluminates has been demonstrated in previous work, through the reaction of [EtAl(6-Me-2-py)<sub>3</sub>]<sup>-</sup> (**1**) with chiral alcohols (Scheme 2).<sup>[12]</sup> So far, however, **6Li** is the only example in which the controlled incorporation of two alkoxy groups has been witnessed (although in this case, these are non-chiral). Interestingly, during the current work we found that the reaction of (-)-menthol ((1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexan-1-ol) with **1Li** in toluene at room temperature leads to clean precipitation of the disubstituted product [Li{EtAl(OC<sub>10</sub>H<sub>19</sub>)<sub>2</sub>(6-Me-2-py)}<sub>2</sub>] (**7Li**) directly from the reaction in 62% isolated yield (Scheme 5). In contrast to the polymeric arrangement observed for **6Li**, the solid-state structure of **7Li** is dimeric, with the

association of the two monomer units occurring through a central Li<sub>2</sub>O<sub>2</sub> ring. This arrangement is clearly similar to that in the structures of the mono-substituted complexes **2Li**-**5Li**. The bonding of the Li<sup>+</sup> cations in **7Li** to three alkoxy O-atoms and to a py-N atom also results in a similar tetrahedral geometry for these metal centres (Figure 6).



**Scheme 5** Reaction of **1Li** with menthol, giving the dimer **7Li**.

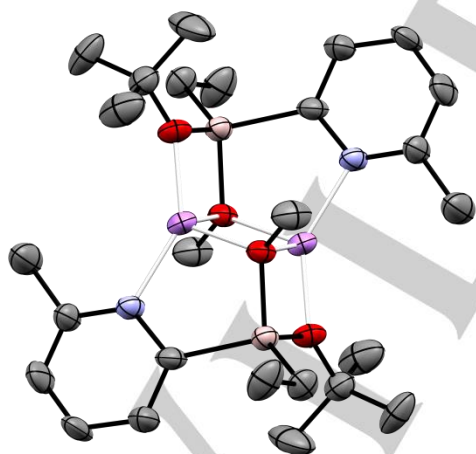


**Figure 6** Solid-state structure of **7Li**. Displacement ellipsoids are drawn at the 50% probability level. The menthol molecule is disordered over two orientations in the crystal structure, related approximately by a 180° rotation around the C–O bond. This disorder, as well as H atoms, is omitted for clarity. A list of selected bond lengths and angles can be found in the supporting information. Colour key: oxygen (red), magenta (lithium), blue (nitrogen), pink (aluminium), carbon (grey).

The final area of study was to investigate the possibility of introducing chirality at the Al centre of an aluminate anion. Although octahedral Al ions with chelate ligands can produce helical chirality,<sup>[19]</sup> chiral-at-Al tetrahedral aluminates, the analogues of iconic asymmetric carbon, are extremely rare. Indeed, the only example that we are aware of is the anion

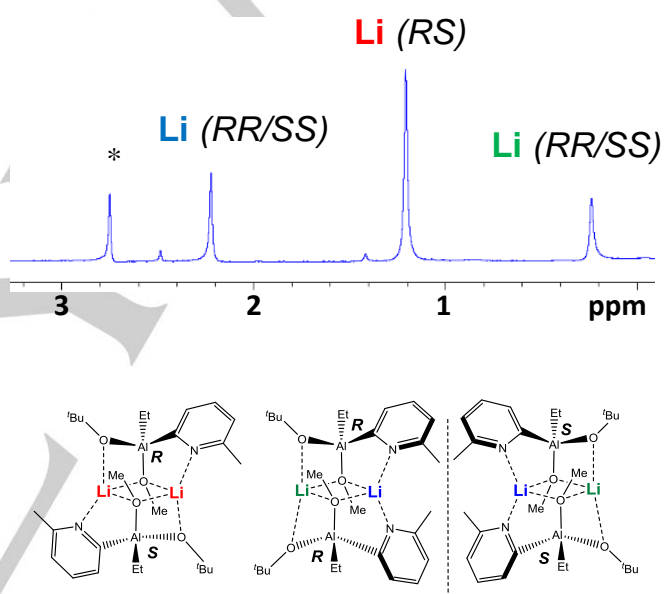
$[R_1R_2Al(\mu-CH_2)(\mu-CHSiMe_3)SiMe_2]^- [R_1 = CH(SiMe_3)_2, R_2 = Me_2Si]^-$ .<sup>[20]</sup> The strategy was to use stepwise replacement of the 6-Me-2-py groups of **1** with two different non-chiral alkoxy groups. The reactions of the MeO-substituted complex  $[Li\{EtAl(OMe)(6-Me-2-py)_2\}]_2$  (**2bLi**) (Scheme 1) with <sup>t</sup>BuOH or the <sup>t</sup>BuO-substituted complex  $[Li\{EtAl(O^tBu)(6-Me-2-py)_2\}]_2$  (**8Li**) with MeOH in toluene at -78 °C generate complex mixtures of products, as revealed by *in situ* <sup>1</sup>H and <sup>7</sup>Li NMR spectroscopy (see Supporting Information for the synthesis and structure of the new compound **8Li**). The new complex  $[Li\{EtAl(OMe)(O^tBu)(6-Me-2-py)_2\}]_2$  (**9Li**) was crystallised in low yield (7%) from the reaction of **2bLi** with <sup>t</sup>BuOH, but was shown spectroscopically (<sup>1</sup>H and <sup>7</sup>Li NMR) to be formed in both of these reactions. Interestingly, the reaction involving **8Li** also produces the *bis*-pyridyl complex  $[Li\{EtAl(OMe)(6-Me-2-py)_2\}]_2$  (**2bLi**), suggesting ligand redistribution during the course of this reaction. Contamination of isolated solid samples of **9Li** with **2bLi** resulted in poor elemental analysis, although it was fully characterised by multinuclear NMR spectroscopy. Attempts to obtain **9Li** through equilibration reactions between **8Li** and **2bLi** did not succeed. No reaction was observed after mixing equimolar amounts of **8Li** and **2bLi** (in toluene or THF) for 48 h at room temperature.

Like most of the alkoxy complexes investigated previously and in the current work, the solid-state structure of **9Li** is that of a dimer containing a central Li<sub>2</sub>O<sub>2</sub> core arrangement (Figure 7). The core arrangement of **9Li** is very similar to the di-substituted complex **7Li** in particular. The Al centres of the two  $[EtAl(6-Me-2-py)(OMe)(O^tBu)]^-$  anions in the dimer have *R* and *S* absolute configurations so that overall, the complex is non-chiral in the solid state.



**Figure 7** Solid-state structure of **9Li**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Another chemically-equivalent independent molecule is present in the lattice and omitted for clarity. The structure exhibits apparent layer-stacking disorder, as described in the supporting information. A list of selected bond lengths and angles can also be found in the Supporting Information. Colour key: oxygen (red), magenta (lithium), blue (nitrogen), pink (aluminium), carbon (grey).

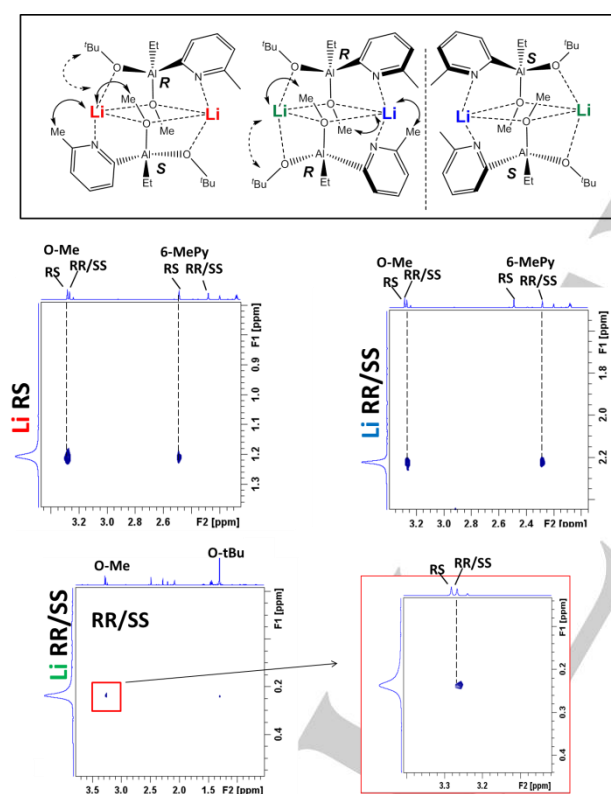
Despite the observation of only the *R/S*-dimer in the solid-state structure of **9Li**, it appears that the *R/R*- and *S/S* dimers are also present in bulk samples and/or in solution. The <sup>7</sup>Li NMR spectrum of isolated samples of crystalline **9Li** at room temperature in toluene (Figure 8, top) reveals the presence of three distinct singlets at  $\delta = 2.22, 1.20$  and  $0.24$  with relative integrals of 1 : 2 : 1. Isolated samples also contain variable amounts of the starting material **2bLi** at  $\delta = 2.75$ . The observation of three 1 : 2 : 1 Li resonances for **9Li** is strikingly similar to the mixture of *RR/SS*- and *RS*-dimers formed in the 1 : 1 reactions of racemic alcohols with **1aLi** (Scheme 2), which generate statistical mixtures of the *RR/SS*- and *RS*-dimers in which there are two distinct (overlapping) Li environments in the *RR* and *SS*-dimers but only one environment in the *RS*.



**Figure 8** (top) Room-temperature <sup>7</sup>Li NMR spectrum of **9Li**. The three different environments observed at  $\delta = 2.22, 1.20$  and  $0.24$  correspond to *bis*-O, *tris*-O and *tetra*-O environments. The black asterisk is unreacted starting complex **2bLi** which is always present in the samples. (bottom) The isomers of **9Li**: a centrosymmetric *9-RS* dimer and a pair of enantiomers *9-RR/SS*.

The observed <sup>7</sup>Li NMR spectrum of **9Li** is consistent with the theoretical statistical distribution expected for the three possible *RS* and *SS/RR* isomers of **9Li** (Figure 8, bottom), having a total of three Li environments as a consequence of the different coordination environments of the Li<sup>+</sup> cations. The central resonance at  $\delta = 1.20$  corresponds to the *mono*-pyridyl coordination site from the single magnetic environment of *9-RS* (which is centrosymmetric) while *9-RR/SS* (which is present as a pair of enantiomers) has two Li environments: a *bis*-pyridyl coordination environment ( $\delta = 2.22$ ) and an all-O coordination environment ( $\delta = 0.24$ ). Further confirmation for this assignment comes from a <sup>1</sup>H-<sup>7</sup>Li HOESY experiment, which can be used to

assess the spatial proximity between  $^7\text{Li}$  and  $^1\text{H}$  nuclei (Figure 9). The  $^1\text{H}$ - $^7\text{Li}$  HOESY shows cross-peaks between the  $^7\text{Li}$  resonance of the centrosymmetric *RS* dimer ( $\delta = 1.20$  ppm, in red), the O-CH<sub>3</sub> resonance at  $\delta = 3.28$ , the py-CH<sub>3</sub> resonance at  $\delta = 2.49$ , and a weaker cross peak (not shown in the figure) with the O<sup>t</sup>Bu resonance at  $\delta = 1.30$ . For the homochiral *SS/RR* dimers, the two lithium atoms are in different environments. One Li atom ( $\delta = 2.22$ ) faces the 6-Me-2-py group (marked in blue in Figure 9) while the other one ( $\delta = 0.24$ ) faces the O<sup>t</sup>Bu group (marked in green in Figure 9). This is consistent with the  $^1\text{H}$ - $^7\text{Li}$  HOESY experiment in which the  $^7\text{Li}$  resonance at  $\delta = 2.22$  ppm for the *RR/SS* dimers has cross-peaks with the O-CH<sub>3</sub> resonance at  $\delta = 3.27$  and the CH<sub>3</sub> resonance of the 6-Me-Py at  $\delta = 2.49$ , while the other  $^7\text{Li}$  resonance for the *RR/SS* dimers at  $\delta = 0.24$  ppm has cross-peaks with the O-CH<sub>3</sub> group at  $\delta = 3.27$  and a weaker cross-peak with the O<sup>t</sup>Bu group at  $\delta = 1.30$  ppm, but no cross peaks with the 6-Me-Py protons.



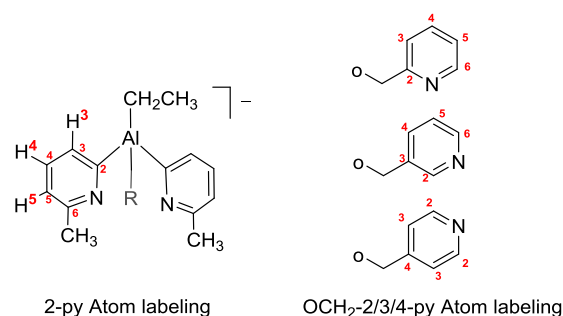
**Figure 8**  $^1\text{H}$ - $^7\text{Li}$  HOESY (298 K,  $d_6$ -toluene, 500 MHz, mixing time of 100 ms) spectrum of **9Li**. The isomers of **9Li** are shown above with the three different Li environments highlighted in different colours. The NOE signals observed in the experiment are shown with arrows. The dotted arrow represents the weaker NOE signal observed between Li and O<sup>t</sup>Bu groups (which are further away). The dotted lines in the spectrum are guides for the eye.

## Conclusions

Using our previously developed post-functionalisation methodology, we have shown that the exchange of the 6-Me-2-py ligands for appropriate alkoxide ligands can be used to (i) introduce 3-py and 4-py functionality (which in the case of **6Li** leads to intermolecular association), (ii) introduce chiral substituents into the frameworks of aluminate ligands (and for the first time, two such groups in the new complex **7Li**), and (iii) build chiral-at-the-metal arrangements (as in the case of **9Li**), which cannot be accessed by conventional equilibration reactions. Further exploration of this research direction will continue in future studies in this area.

## Experimental Section

**Materials and general methods:** All syntheses were carried out on a vacuum-line under argon or N<sub>2</sub> atmosphere. Products were isolated and handled under N<sub>2</sub> or argon atmosphere. Elemental analysis was obtained on a Perkin Elmer 240 Elemental Analyser. All NMR solvents were stored over molecular sieves and degassed by three freeze-pump-thaw cycles under nitrogen prior to use. The chemical shift values are given in ppm.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced to TMS.  $^7\text{Li}$  and  $^{27}\text{Al}$  NMR experiments are referenced to a solution of LiCl/D<sub>2</sub>O and a solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O, respectively. The unambiguous assignment of NMR resonances was accomplished by additional 2D NMR experiments [ $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^1\text{H}$  NOESY,  $^1\text{H}$ - $^{13}\text{C}$  HMQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC experiments (see SI for details)]. Li[EtAl(6-Me-2-py)<sub>3</sub>] (**1Li**)<sup>[5a]</sup> and [Li{EtAl(OMe)(6-Me-2-py)<sub>2</sub>}]<sub>2</sub> (**2bLi**)<sup>[12]</sup> were synthesized as described previously. X-ray data were collected on a Bruker D8 QUEST diffractometer with an Incoatec  $\mu\text{S}$  Cu microfocus source. Crystals were mounted directly from their mother liquor using perfluorohydrocarbon oil to prevent atmospheric oxidation, hydrolysis, and solvent loss, and the temperature was held at 180(2) K using an Oxford Cryosystems N<sub>2</sub> cryostat (see ESI for details). CCDC 1849411-1849417 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.



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

**Synthesis of [Li{EtAl(2-OCH<sub>2</sub>-py)(6-Me-2-py)<sub>2</sub>}]<sub>2</sub> (**3Li**):** Li[EtAl(6-Me-2-py)<sub>3</sub>] (200 mg, 0.589 mmol) was dissolved in toluene (5 mL), and to this cloudy solution 1 eq. of HOCH<sub>2</sub>-2-py (57  $\mu\text{L}$ , 0.589 mmol) was added at -78 °C. The mixture was allowed to reach room temperature, and then further stirred at room temperature for 3 h to give a clear solution. The solvent was evaporated under vacuum and the residue was dried under vacuum to remove free 6-CH<sub>3</sub>-2-pyH. 4 mL of toluene was added to the resulting residue. Filtration, concentration of the solution, and slow diffusion with n-hexane as the non-solvent at -15 °C afforded colorless

crystals of **3Li**. Total yield 100-120 mg 48-57% Elemental analysis, calcd. for **3Li**, C 67.6, H 6.5, N 11.8%; Found C 67.7, H 6.6, N 11.9%.  $^1\text{H}$  NMR (298 K,  $d_8$ -toluene, 500 MHz),  $\delta$  = 7.75 (br, 1H,  $\text{H}^6$  py'), 7.59 (d, J = 7.0 Hz, 2H,  $\text{H}^3$  py), 7.09 (t, J = 7.6 Hz, 2H,  $\text{H}^4$  py), 6.84 (t, J = 7.4 Hz, 1H,  $\text{H}^4$  py'), 6.67 (br, 1H,  $\text{H}^3$  py'), 6.54 (d, J = 7.5 Hz, 2H,  $\text{H}^5$  py), 6.30 (t (br), J = 5.5 Hz, 1H,  $\text{H}^5$  py'), 4.96 (s(br), 2H,  $\text{OCH}_2$ ), 2.21 (s, 6H,  $\text{C}^6$ - $\text{CH}_3$ ), 1.40 (t, J = 7.7 Hz, 3H,  $\text{Al-CH}_2\text{CH}_3$ ), 0.43 (q, J = 7.7 Hz, 2H,  $\text{Al-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K,  $d_8$ -toluene, 100.6 MHz),  $\delta$  = 188.7 (br,  $\text{C}^2$  py), 162.93 ( $\text{C}^2$  py'), 156.55 ( $\text{C}^6$  py), 147.59 ( $\text{C}^6$  py'), 136.95 ( $\text{C}^4$  py'), 132.68 ( $\text{C}^4$  py), 130.15 ( $\text{C}^3$  py), 122.12 (br,  $\text{C}^3$  py'), 121.97 ( $\text{C}^5$  py'), 120.12 ( $\text{C}^5$  py), 66.56 ( $\text{OCH}_2$ ), 24.60 ( $\text{C}^6$ - $\text{CH}_3$ ), 11.01 ( $\text{Al-CH}_2\text{CH}_3$ ), 1.19 (br,  $\text{Al-CH}_2$ ).  $^{27}\text{Al}$  NMR (298K,  $d_8$ -toluene, 130.3 MHz, ref solution of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$ ),  $\delta$  = 137 (very br, s).  $^7\text{Li}$  NMR (298K,  $d_8$ -toluene, 194.4 MHz, ref solution of  $\text{LiCl}/\text{D}_2\text{O}$ ),  $\delta$  = 2.92 (s).

**Synthesis of  $[\text{Li}\{\text{EtAl}(\text{3-OCH}_2\text{-py})(\text{6-Me-2-py})_2\}]_2$  (**4Li**):**  $\text{Li}\{\text{EtAl}(\text{6-Me-2-py})_3\}$  (200 mg, 0.589 mmol) was dissolved in toluene (4 mL), and to this cloudy solution 1 eq. of  $\text{HOCH}_2\text{-3-py}$  (57  $\mu\text{L}$ , 0.589 mmol) was added at  $-78^\circ\text{C}$ . The mixture was allowed to reach room temperature and then further stirred at room temperature for 2 h. The solvent was evaporated under vacuum, the residue was dried under vacuum and 5 ml of toluene was added. Filtration over Celite, concentration (to ca. 2 ml), and slow diffusion of n-hexane (ca. 5 ml) as the non-solvent at  $-15^\circ\text{C}$  afforded colorless crystals of **4Li**. 70 mg first batch. 33% yield. Elemental analysis, calcd. for **4Li**, C 67.6, H 6.5, N 11.8%; Found C 67.9, H 6.5, N 11.8%.  $^1\text{H}$  NMR (298 K,  $d_8$ -toluene, 500 MHz),  $\delta$  = 8.21 (d, J = 1.8 Hz, 1H,  $\text{H}^2$  py'), 8.18 (dd, J = 4.8 and 1.8 Hz, 1H,  $\text{H}^5$  py'), 7.63 (d, J = 7.0 Hz, 2H,  $\text{H}^3$  py), 7.09 (t, J = 7.5 Hz, 2H,  $\text{H}^4$  py), 6.75 (dt, J = 7.8 and 1.8 Hz, 1H,  $\text{H}^4$  py'), 6.50 (d, J = 7.8 Hz, 2H,  $\text{H}^5$  py), 6.30 (dd, J = 7.8 and 4.8 Hz, 1H,  $\text{H}^2$  py'), 4.59 (s, 2H,  $\text{OCH}_2$ ), 2.05 (s, 6H,  $\text{C}^6$ - $\text{CH}_3$ ), 1.40 (t, J = 8.1 Hz, 3H,  $\text{Al-CH}_2\text{CH}_3$ ), 0.53 (q, JHH = 8.1 Hz, 3H,  $\text{Al-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K,  $d_8$ -toluene, 100.6 MHz),  $\delta$  = 186.3 (br,  $\text{C}^2$  py), 157.15 ( $\text{C}^6$  py), 149.69 ( $\text{C}^2$  py'), 148.62 ( $\text{C}^6$  py'), 134.46 ( $\text{C}^4$  py'), 133.84 ( $\text{C}^4$  py), 130.84 ( $\text{C}^3$  py), 122.57 ( $\text{C}^5$  py'), 121.66 ( $\text{C}^5$  py), 64.32 ( $\text{OCH}_2$ ), 24.32 ( $\text{C}^6$ - $\text{CH}_3$ ), 10.61 ( $\text{Al-CH}_2\text{CH}_3$ ), 1.14 (br,  $\text{Al-CH}_2$ ).  $^{27}\text{Al}$  NMR (298 K,  $d_8$ -toluene, 130.3 MHz, ref solution of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$ ),  $\delta$  = 145 (very br, s).  $^7\text{Li}$  NMR (298K,  $d_8$ -toluene 194.4 MHz, ref solution of  $\text{LiCl}/\text{D}_2\text{O}$ ),  $\delta$  = 2.55 (s).

**Synthesis of  $[\text{Li}\{\text{EtAl}(\text{4-OCH}_2\text{-py})(\text{6-Me-2-py})_2\}]_2$  (**5Li**):**  $\text{Li}\{\text{EtAl}(\text{6-Me-2-py})_3\}$  (215 mg, 0.63 mmol) was dissolved in toluene (5 mL), and to this cloudy solution 1 eq. of  $\text{HOCH}_2\text{-4-py}$  (69 mg, 0.63 mmol) was added at  $-78^\circ\text{C}$ . The mixture was allowed to reach room temperature, then further stirred at room temperature for 16 h. The solvent was evaporated under vacuum and the residue was dried under vacuum for 2 h in order to completely removed 6- $\text{CH}_3\text{-2-pyH}$ . To the white residue, 5 mL of toluene was added. After filtration of the resulting suspension, the solution was concentrated under vacuum (to ca. 2-3 mL), and slow diffusion of n-hexane as the non-solvent (ca. 5 mL) at  $-15^\circ\text{C}$  afforded colorless crystals of **5Li**. 60 mg. 29% yield. Elemental analysis, calcd. for **5Li**, C 67.6, H 6.5 N, 11.8%; Found C 67.0, H 6.6, N 11.8%.  $^1\text{H}$  NMR (298 K,  $d_8$ -toluene, 500 MHz),  $\delta$  = 8.08 (m, 2H,  $\text{H}^2$  py'), 7.61 (d, J = 7.2 Hz, 2H,  $\text{H}^3$  py), 7.09 (t, J = 7.5 Hz, 2H,  $\text{H}^4$  py), 6.54-6.46 (m, 4H, 2H,  $\text{H}^5$  py and 2H  $\text{H}^3$  py'), 4.56 (s, 2H,  $\text{OCH}_2$ ), 2.05 (s, 6H,  $\text{C}^6$ - $\text{CH}_3$ ), 1.35 (t, J = 8.1 Hz, 3H,  $\text{Al-CH}_2\text{CH}_3$ ), 0.46 (q, J = 8.1 Hz, 3H,  $\text{Al-CH}_2$ ).  $^1\text{H}$  NMR (298K,  $d_8$ -THF, 500 MHz),  $\delta$  = 8.37 (m, 2H,  $\text{H}^2$  py'), 7.37 (m, 2H,  $\text{H}^3$  py'), 7.33 (d, J = 7.2 Hz, 2H,  $\text{H}^3$  py), 7.21 (t, J = 7.7 Hz, 2H,  $\text{H}^4$  py), 6.78 (d, J = 7.7 Hz, 2H,  $\text{H}^5$  py), 4.88 (s, 2H,  $\text{OCH}_2$ ), 2.42 (s, 6H,  $\text{C}^6$ - $\text{CH}_3$ ), 1.07 (t, J = 8.1 Hz, 3H,  $\text{Al-CH}_2\text{CH}_3$ ), 0.89 (q, J = 8.1 Hz, 3H,  $\text{Al-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K,  $d_8$ -toluene, 100.6 MHz),  $\delta$  = 186.2 (br,  $\text{C}^2$  py), 157.20 ( $\text{C}^6$  py), 149.92 ( $\text{C}^4$  py'), 149.80 ( $\text{C}^2$  py'), 133.95 ( $\text{C}^4$  py), 130.81 ( $\text{C}^3$  py), 121.69 ( $\text{C}^5$  py), 65.68 ( $\text{OCH}_2$ ), 24.44 ( $\text{C}^6$ - $\text{CH}_3$ ), 10.61 ( $\text{Al-CH}_2\text{CH}_3$ ), 1.01 (br,  $\text{Al-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K,  $d_8$ -toluene, 100.6 MHz),  $\delta$  = 188.8 (br,  $\text{C}^2$  py), 156.47 ( $\text{C}^6$  py), 154.63 ( $\text{C}^4$  py'), 150.06 ( $\text{C}^2$  py'), 132.54 ( $\text{C}^4$  py), 130.43 ( $\text{C}^3$  py), 122.69 ( $\text{C}^3$  py'), 120.08 ( $\text{C}^5$  py), 65.09 ( $\text{OCH}_2$ ), 24.69 ( $\text{C}^6$ - $\text{CH}_3$ ), 10.69 ( $\text{Al-CH}_2\text{CH}_3$ ), 0.90

(br,  $\text{Al-CH}_2$ ).  $^{27}\text{Al}$  NMR (298 K,  $d_8$ -toluene, 130.3 MHz, ref solution of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$ ),  $\delta$  = 130 (very br, s).  $^7\text{Li}$  NMR (298K,  $d_8$ -toluene, 194.4 MHz, ref solution of  $\text{LiCl}/\text{D}_2\text{O}$ ),  $\delta$  = 0.93 (s).  $^{27}\text{Al}$  NMR (298K,  $d_8$ -toluene, 130.3 MHz, ref solution of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$ ),  $\delta$  = 144.8 (very br, s).  $^7\text{Li}$  NMR (298 K,  $d_8$ -toluene, 194.4 MHz, ref solution of  $\text{LiCl}/\text{D}_2\text{O}$ ),  $\delta$  = 2.55 (s).

**Synthesis of  $[\text{Li}\{\text{EtAl}(\text{4-OCH}_2\text{-py})_2(\text{6-Me-2-py})\}]_2$  (**6Li**):**  $\text{Li}\{\text{EtAl}(\text{6-Me-2-py})_3\}$  (215mg, 0.63 mmol) was dissolved in toluene (5 mL) and to this cloudy solution 2 eq. of  $\text{HOCH}_2\text{-4-py}$  (140 mg, 1.28 mmol) was added at room temperature. The mixture was further stirred at room temperature for 16 h. At this point a white precipitate was observed. An additional 5 mL of toluene was added, and the precipitate was isolated by filtration and dried under vacuum to give **6Li** as a waxy solid (65mg, 30% Yield). The analytical results listed below correspond to this material. Colourless crystals of **6Li**-toluene suitable for X-ray experiments were obtained from a saturated solution of **6Li** in a 3:1 mixture of toluene/THF after 24h at  $-15^\circ\text{C}$ . Elemental analysis, calcd. for **6Li**, C 64.7, H 6.2 N, 11.3%; Found C 65.4, H 6.3, N 10.2%.  $^1\text{H}$  NMR (298K,  $d_8$ -THF, 500 MHz),  $\delta$  = 8.33 (m, 4H,  $\text{H}^2$  py'), 7.41 (d, J = 7.1 Hz, 1H,  $\text{H}^3$  py), 7.35 (t, J = 7.6 Hz, 1H,  $\text{H}^4$  py), 7.30 (m, 4H,  $\text{H}^3$  py'), 6.92 (d, J = 7.7 Hz, 1H,  $\text{H}^5$  py), 4.83 (s, 4H,  $\text{OCH}_2$ ), 2.40 (s, 3H,  $\text{C}^6$ - $\text{CH}_3$ ), 1.03 (t, J = 8.1 Hz, 3H,  $\text{Al-CH}_2\text{CH}_3$ ), -0.87 (q, J = 8.1 Hz, 3H,  $\text{Al-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298K,  $d_8$ -toluene, 100.6 MHz),  $\delta$  = 187.40 (br,  $\text{C}^2$  py), 156.62 ( $\text{C}^6$  py), 155.90 ( $\text{C}^4$  py'), 149.95 ( $\text{C}^2$  py'), 133.69 ( $\text{C}^4$  py), 131.10 ( $\text{C}^3$  py), 122.05 ( $\text{C}^3$  py'), 121.16 ( $\text{C}^5$  py), 64.52 ( $\text{OCH}_2$ ), 24.16 ( $\text{C}^6$ - $\text{CH}_3$ ), 10.46 ( $\text{Al-CH}_2\text{CH}_3$ ), -0.65 (br,  $\text{Al-CH}_2$ ).  $^{27}\text{Al}$  NMR (298 K,  $d_8$ -toluene, 130.3 MHz, ref solution of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$ ),  $\delta$  = 120 (very br, s).  $^7\text{Li}$  NMR (298K,  $d_8$ -toluene, 194.4 MHz, ref solution of  $\text{LiCl}/\text{D}_2\text{O}$ ),  $\delta$  = 0.75 (s).

**Synthesis of  $[\text{Li}\{\text{EtAl}(\text{OC}_{10}\text{H}_{19})_2(\text{6-Me-2-py})\}]_2$  (**7Li**):**  $\text{Li}\{\text{EtAl}(\text{6-Me-2-py})_3\}$  (200 mg, 0.589 mmol) was dissolved in toluene (5 mL) and (-)-menthol (184 mg, 1.179 mmol) was added at room temperature. The mixture was stirred at room temperature for 4 h. At this point a white precipitate had formed. The addition of n-hexane (5 mL) and storage at  $-15^\circ\text{C}$  afforded more white precipitate. The mother liquor was syringed off and the white solid was dried under vacuum to give **7Li** as a white solid. 160 mg. 62% yield. Colorless crystals of **7Li** were obtained from a saturated solution of **7Li** in toluene at  $-20^\circ\text{C}$ . Elemental analysis, calcd. for **7Li**, C 72.2, H 10.6 N, 3.0%; Found C 72.3, H 10.6, N 3.3%.  $^1\text{H}$  NMR (298K,  $d_8$ -thf, 500 MHz),  $\delta$  = 7.40 (d, J = 7.0 Hz, 1H,  $\text{H}^3$  py), 7.27 (t, J = 7.5 Hz, 1H,  $\text{H}^4$  py), 6.81 (d, J = 7.5 Hz, 1H,  $\text{H}^5$  py), 3.47 (m, 2H,  $\text{OCH}$  menthol), 2.60 (m, 1H,  $\text{CH}$  menthol), 2.43 (m, 1H,  $\text{CH}$  menthol), 2.40 (s, 3H,  $\text{C}^6$ - $\text{CH}_3$ ), 2.18 (m, 1H,  $\text{CH}_2$  menthol), 1.97 (m, 1H,  $\text{CH}_2$  menthol), 1.62 (m, 2H,  $\text{CH}_2$  menthol), 1.53 (m, 2H,  $\text{CH}_2$  menthol), 1.36 (m, 2H,  $\text{CH}_2$  menthol), 0.97 (t, J = 8.0 Hz, 3H,  $\text{Al-CH}_2\text{CH}_3$ , partially overlapped with menthol resonances), 0.97-0.75 (m, 23H, menthol), 0.64 (d, J = 7.0 Hz, 3H,  $\text{CH}_3$  menthol), -0.08 to -0.24 (m, 2H,  $\text{Al-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K,  $d_8$ -thf, 100.6 MHz),  $\delta$  = 190.6 (br,  $\text{C}^2$  py), 155.84 ( $\text{C}^6$  py), 132.87 ( $\text{C}^4$  py), 130.96 ( $\text{C}^3$  py), 120.27 ( $\text{C}^5$  py'), 71.56 ( $\text{OCH}$ ), 71.17 ( $\text{OCH}$ ), 53.23 (C menthol), 53.13 (C menthol), 49.40 (C menthol), 48.90 (C menthol), 36.37 (C menthol), 32.98 (C menthol), 32.94 (C menthol), 25.80 (C menthol), 25.58 (C menthol), 23.88 ( $\text{C}^6$ - $\text{CH}_3$ ), 23.82 (C menthol), 23.18 (C menthol), 23.14 (C menthol), 22.34 (C menthol), 22.25 (C menthol), 16.62 (C menthol), 16.40 (C menthol), 10.93 ( $\text{Al-CH}_2\text{CH}_3$ ), 1.36 (br,  $\text{Al-CH}_2$ ).  $^{27}\text{Al}$  NMR (298K,  $d_8$ -thf, 130.3 MHz, ref solution of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{D}_2\text{O}$ ),  $\delta$  = 111.0 (very br, s).  $^7\text{Li}$  NMR (298K,  $d_8$ -thf, 194.4 MHz, ref solution of  $\text{LiCl}/\text{D}_2\text{O}$ ),  $\delta$  = 0.52 (s).

**Synthesis of  $[\text{Li}\{\text{EtAl}(\text{OMe})(\text{O}^i\text{Bu})(\text{6-Me-2-py})_2\}]_2$  (**9Li**):**  $[\text{Li}\{\text{EtAl}(\text{OMe})(\text{6-Me-2-py})_2\}]_2$  (**2bLi**) (200 mg, 0.72 mmol) was dissolved in toluene (5 mL), and to this cloudy solution 1 eq. of  $^i\text{BuOH}$  (69 $\mu\text{L}$ , 0.72 mmol) was added at  $-78^\circ\text{C}$ . After 1.5 h at  $-78^\circ\text{C}$ , the mixture was allowed to reach room temperature and was then further stirred at room temperature for 16 h.

The solvent was evaporated under vacuum, and the residue was dried under vacuum for 2 h in order to completely remove 6-CH<sub>3</sub>-2-pyH. To the white residue 5 mL of toluene was added, and the resulting cloudy solution was filtered and concentrated under vacuum to ca. 0.5 mL. 3 mL of n-hexane was added, and the solution was concentrated under vacuum until the precipitation of a white solid was observed, which was dissolved by gentle heating. Slow diffusion of n-hexane (ca. 3 mL) as the non-solvent at -15°C afforded a few colorless crystals of **9Li** (ca. 10 mg, 7% yield). Additionally, **9Li** could be prepared by reacting [Li{EtAl(OtBu)(6-Me-2-py)}<sub>2</sub>] (8Li) and MeOH in a similar manner as indicated above. <sup>1</sup>H NMR (298 K, d<sub>8</sub>-toluene, 500 MHz), δ = 7.50-7.43 (m, 1H, H<sup>3</sup> py, RS and RR/SS), 7.14-7.09 (m, 1H, H<sup>4</sup> py, RS and RR/SS), 6.64-6.59 (m, 1H, H<sup>5</sup> py, RS and RR/SS), 3.28 (s, 3H, OCH<sub>3</sub>, RS), 3.27 (s, 3H, OCH<sub>3</sub>, RR/SS), 2.49 (s, 3H, Py-CH<sub>3</sub>, RS), 2.28 (s, 3H, Py-CH<sub>3</sub>, RR/SS), 1.47-1.41 (m, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>, RS and RR/SS), 1.32-1.29 (m, 9H, C(CH<sub>3</sub>)<sub>3</sub>, RS and RR/SS), 0.51-0.36 (m, 2H, Al-CH<sub>2</sub>, RS and RR/SS). <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), δ = 124 (very 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), δ = 2.22 (s, RR/SS), 1.20 (s, RS), 0.24 (s, RR/SS). Elemental analysis, calcd. for **9Li** C 60.2, H 8.9, N, 5.4%; Found C 59.8, H 8.7, N 6.3%. As noted in the paper, the samples contained small amounts of the starting complex **2bLi**, which was difficult to separate. The values reported here are the best obtained over several analyses on a single sample.

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