

Deprotonation, Insertion and Isomerisation in the Post-functionalisation of *Tris*-pyridyl Aluminates

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Post-functionalisation of the aluminate anion [EtAl(6-R-2-py)₃]⁻ (6-R-2-py = 6-R-2-pyridyl, R = Me or Br) can be accomplished *via* nucleophilic addition of the pyridyl groups to the electrophilic C=O group of aldehydes (RCH=O) or by deprotonation of carboxylic acids (RCO₂H). NMR spectroscopic and crystallographic studies show how 6-Me-2-py groups can detect chirality and reveal a new aspect of isomerism.

Introduction

Main group bridged *tris*-2-pyridyl ligands [E(2-py)₃] (Fig. 1a)¹ are an interesting class of ligands that are closely related to the extensively studied *tris*-pyrazolyl borate ligand family (Fig. 1b).² Their straightforward synthesis and the ease of tuning the donor properties, by modifying the steric and electronic properties of the 2-pyridyl substituents, has led to a broad range of applications in organometallic, coordination and bioinorganic chemistry. The vast majority of previous studies, however, have focused on the use of non- or semi-metallic bridgehead atoms, such as E = CX, N, P, As.¹ Moving to metallic group 13^{3,4} and 14⁵ congeners introduces, among other things, the possibility of redox activity and variable oxidation states at the bridgehead. We also showed recently that introducing heavier, metallic bridgeheads in the neutral group 15 ligands [E(6-Me-2-py)₃] (E = As, Sb, Bi) can allow fine tuning of the electronic character of the pyridyl substituents, with potential applications in catalysis.⁶

Tris-(2-pyridyl) aluminates [Al(2-py)₃]⁻ (Fig. 1c)⁴ and their

closely-related borate relatives³ are particularly interesting as rare examples of anionic *tris*-pyridyl arrangements which therefore have a stronger affinity for the coordination of metal cations than neutral *tris*-(2-pyridyl) counterparts, making them more conceptually similar to *tris*-pyrazolyl borates. Consequently, there has been considerable interest in the applications of these newly-introduced ligand sets as spectator ligands in catalysis as well as in polymer and supramolecular chemistry. For example, the Fe(II) sandwich complex [{MeAl(2-py)₃]₂Fe] has been shown to act as a highly selective alkene epoxidation catalyst under comparably mild reaction conditions using dry air, in the absence of an additional oxidant.⁷

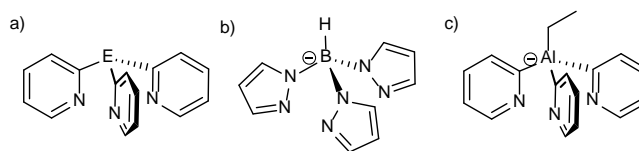


Figure 1 (a) Neutral *tris*-(2-pyridyl) ligands (E = RC, N, P, As), (b) *tris*-pyrazolyl borate ligands, and (c) *tris*-(2-pyridyl) aluminates.

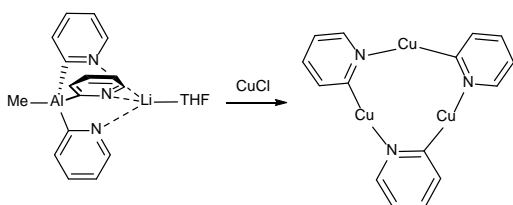
A further facet of the behaviour of *tris*-(2-pyridyl) aluminates, which is distinctly different from *tris*-(2-pyridyl) borates, is the more polar nature of the bridgehead Al-C bonds. This leads to the potential to act not only as ligands to a range of metals, but also (i) as storable sources of the 2-py⁻ anion^{4a,5f} and (ii) as precursors for further functionalisation in acid-base reactions.^{4f,8} The first of these features is illustrated by the reaction of [{MeAl(2-py)₃Li(thf)] with CuCl to give the organo-Cu^I trimer [Cu(2-py)₃] (Scheme 1), which is not formed by the direct reaction of the lithio-pyridine 2-Li-py with CuCl.^{4a} An interesting example of the second type of reactivity is shown in the retention of the aluminate framework of [EtAl(6-Me-2-py)₃]⁻ (**1**) on reaction with alcohols.⁸ In the case of racemic mixtures of chiral alcohols (R*OH), the formation of diastereomeric (*RR*, *SS* and *RS*) [{EtAl(6-Me-2-py)₂(OR*)]₂Li₂

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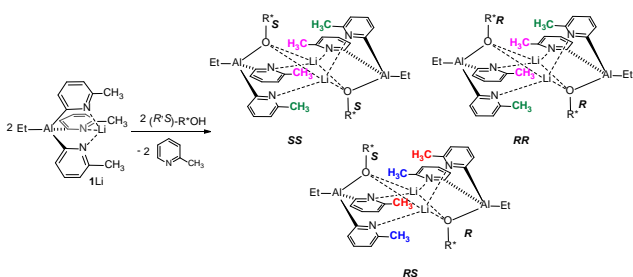
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dimers can be used as a rapid method of measuring the enantiomeric excess by NMR spectroscopy, with the 6-methyl-pyridyl substituent functioning as a reporter group (Scheme 2).^{8a} The stepwise reaction of the [EtAl(6-Me-2-py)₃]⁻ anion with two different alcohols also provides an interesting strategy to obtain 'chiral-at-aluminium' aluminates of the type [EtAl(6-Me-2-py)(OR¹)(OR²)]⁻.^{8b}



Scheme 1 Transfer of 2-py from the [MeAl(2-py)₃]⁻ anion to CuCl.



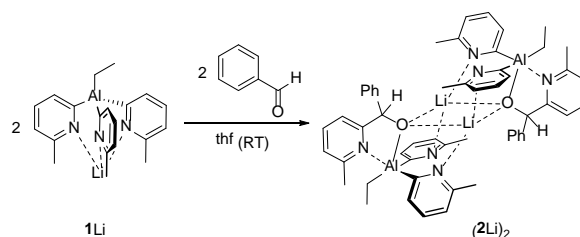
Scheme 2 Formation of diastereomeric dimers from reaction of a racemic mixture of chiral alcohols *R,S*-*R**OH. The magnetic inequivalence of the Me-substituents of the 6-Me-2-py groups (coloured according to environment) can be used to determine the enantiomeric excess.

Our broad aim in the current paper is to explore the acid-base and insertion reactions of aluminates further, with a view to their potential future applications in chiral discrimination beyond chiral alcohols. In this work we report the investigation of the reactions of the [EtAl(6-Me-2-py)₃]⁻ anion with aromatic aldehydes and carboxylic acids, showing that selective insertion (with ArCH=O) or deprotonation (with ArCO₂H) can occur to give the corresponding mono-substituted aluminates [EtAl(6-Me-2-py)₂{OCHAr(6-Me-2-py)}]⁻ and [EtAl(6-Me-2-py)₂(O₂CAr)]⁻.

Results and Discussion

We first explored the reactions of the lithium salt [EtAl(6-Me-2-py)₃Li] (1Li) with aldehydes. Monitoring the 1:1 stoichiometric reaction between 1Li and benzaldehyde (PhCH=O) by ¹H NMR in d₈-thf shows the exclusive formation of a single product (2Li)₂ after 5 min at room temperature (Scheme 3) (see ESI for NMR spectra). Several observations support the nucleophilic addition of the 6-Me-2-py group to the aldehyde carbonyl. In particular, the aldehyde CH proton of PhCH=O disappears completely and is replaced by a CH singlet at δ = 6.55 ppm, supporting the generation of a secondary alkoxide. In the ¹H-¹H NOESY NMR a cross-peak between the tertiary CH proton and the bridgehead Et-Al

group of the aluminate anion is also observed. There is little change in the ²⁷Al or ⁷Li NMR chemical shifts of (2Li)₂ in toluene (δ = 131 and 3.68 ppm, respectively) compared to those in 1Li in the same solvent (δ = 127 and 3.53 ppm, respectively)^{4f}.



Scheme 3 Selective reaction of the *tris*-pyridyl-aluminate 1Li with benzaldehyde.

X-ray quality crystals of the product [(EtAl(6-Me-2-Py)₂(OCHPh(6-Me-2-py))Li]₂ [(2Li)₂] were grown from a saturated toluene solution at -14°C in 40% yield (Figure 2).[‡] The single-crystal X-ray structure confirms the selective functionalisation of [EtAl(6-Me-2-py)₃][Li(thf)].[§] The solid-state structure is that of a centrosymmetric dimer containing a central Li₂O₂ core involving the O-atoms of the [EtAl(6-Me-2-Py)₂{OCHPh(6-Me-2-py)}]⁻ anions (2) [Li-O distances 1.941(4) and 2.320(4) Å]. The aluminate anions use their two 2-py-N atoms to coordinate the separate Li⁺ cations of the core [Li-N distances 2.018(4) and 2.023(4) Å], resulting in a pseudo-tetrahedral geometry at Li⁺. The pyridyl-N atom of the OCHPh(6-Me-2-py) group within each molecule of 2 is involved in a secondary N...Al interaction with the bridgehead Al^{III} atom [2.480(4) Å]. This results in a distorted trigonal bipyramidal coordination geometry for the Al atoms.

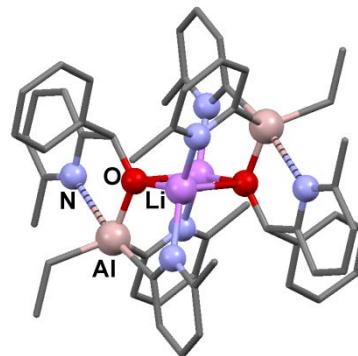


Figure 2 Structure of the dimer [(EtAl(6-Me-2-Py)₂(OCHPh(6-Me-2-py))Li]₂ in the toluene solvate [(2Li)₂].2.7toluene. H-atoms and the lattice toluene molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Li-O range 1.941(4)-2.320(4), Li-N range 2.018(4)-2.023(4), Al-O 1.8263(15), Al-C^{py} 2.025(2)-2.074(2), Al-C^{Et} 1.999(2), Al...N 2.480(4), Li-O-Li 85.88(14), O-Li-O 94.12(14). Colour code: O (red), Li (magenta), Al (pink), N (blue).

A chiral tertiary carbon atom is generated upon nucleophilic addition of the 6-Me-2-py substituent of 1 to the prochiral aldehyde carbonyl centre of PhCH=O. However, dimers of (2Li)₂ are non-chiral as a result of the presence of both *R*- and *S*-enantiomers of the OCHPh(6-Me-2-py) groups. The presence of the secondary N...Al interactions with the pyridyl-

N atoms of the OCHPh(6-Me-2-py) groups reinforces the rigidity of the system and restricts the free rotation of the C-O bond. This is probably largely responsible for the desymmetrization of the 6-Me-2-py groups of each of the anions **2** (Figure 3), although even without such interactions racemic dimers of the type $[\{EtAl(6-Me-2-py)_2(OR^*)\}Li]_2$ also exhibit NMR inequivalent 6-Me-2-py groups.^{8a} The room temperature 1H NMR spectra of $(2Li)_2$ in d_8 -toluene (ESI) and d_8 -thf both show two 6-Me-2-py environments. The corresponding 7Li NMR spectra, however, show a large change in chemical shift moving from toluene (sharp singlet at 3.68 ppm) to thf (broad singlet at 2.60 ppm), which we ascribe to the presence of a dimer in toluene and a (most likely thf solvated) monomer in thf. In either case, N/O-chelating OCHPh(6-Me-2-py) groups will still be present as well as desymmetrization of the 6-Me-2-py groups (as indicated in Figure 3). The observation of only two 6-Me-2-py groups in the 1H NMR spectrum and only a singlet in the 7Li NMR spectrum of dimeric $(2Li)_2$ in toluene strongly supports the retention of the *RS*-stereochemistry found in the solid-state structure, since equilibration to the *SS*- and *RR*-dimers would give additional 1H and 7Li resonances (as found previously in studies of the reactions of **1Li** with mixtures of chiral alcohols containing an enantiomeric excess of one isomer, Scheme 2^{8a}). The slow-exchange behaviour of pre-isolated *RS*- $(2Li)_2$ in toluene is therefore the same as that of pre-isolated *RS*- $[\{EtAl(6-Me-2-py)_2(OR^*)\}Li]_2$ dimers.^{8a}

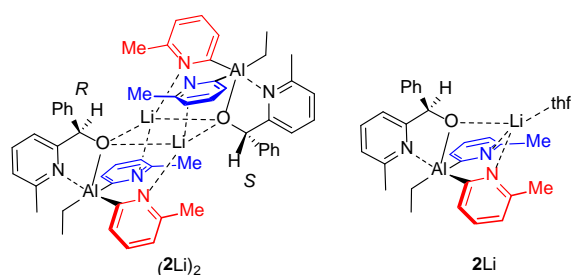


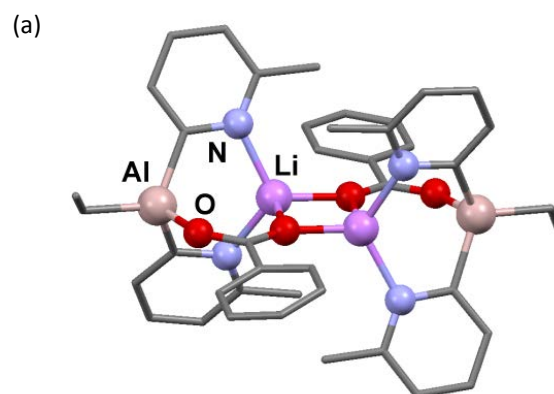
Figure 3 Desymmetrization of the 6-Me groups within the dimer $(2Li)_2$ and monomer $(2Li)$, resulting from the restricted rotation of the OCHPh(6-Me-2-py) groups.

The room-temperature 2:1 reaction of **1Li** with benzaldehyde in thf only results in the formation of $(2Li)_n$, presumably because the remaining 6-Me-2-py groups are less nucleophilic due to the increase in the electronegativity of the Al centre and the lower polarity of the Al-C(py) bonds. Increasing the temperature only led to a complicated mixture of products. In addition, no reaction of alkoxy aluminates of the type $[EtAl(6-Me-2-py)_2(OR)Li]$ ($R = Me, ^tBu$) with benzaldehyde is observed at room temperature.

Although **1Li** reacts with benzaldehyde, ketones (such as benzophenone, $PhMeC=O$), isonitriles (such as $PhNC$) and imines (such as $PhCH=NMe$), which contain less electrophilic C-centres, do not react. However, unsurprisingly on the basis of previous studies, carboxylic acids react readily with **1Li**

even at low temperature. The 1H NMR spectrum of the room-temperature 1:1 reaction of **1Li** with benzoic acid ($PhCO_2H$) in thf showed the formation of a mixture of products. Significantly, these included 6-Me-pyH and EtH, indicating that both the 6-Me-2-py and bridgehead Et groups of **1** are involved in deprotonation of the acid. Although the same reaction at $-78^\circ C$ in toluene leads to a *ca.* 1:1:1 mixture of unreacted **1Li** and the mono- and disubstituted anions $[EtAl(6-Me-2-py)_2(PhCO_2)]^-$ (**3**) and $[EtAl(6-Me-2-py)(PhCO_2)_2]^-$ (**4**), respectively, the reaction of the bridgehead Et group is largely suppressed. The 1H NMR spectrum shows that the 1:2 reaction of **1Li** with $PhCO_2H$ at $-78^\circ C$ in toluene leads to exclusive formation of **4**.

On the basis of the previous NMR experiments, we scaled up the 1:1 and 1:2 reactions using the same conditions to obtain the solid lithium salts $[\{EtAl(6-Me-2-py)_2(PhCO_2)\}Li]_2$ (**3Li**)₂ and $[\{EtAl(6-Me-2-py)(PhCO_2)_2\}Li]_n$ (**4Li**)_n (in 23% and 34% yields, respectively).[‡] Although $(4Li)_n$ could only be obtained as a powder (which was characterised by multinuclear NMR and elemental analysis), in the case of $(3Li)_2$ crystals of the mono-toluene solvate were obtained directly from the reaction mixture by layering with *n*-hexane and storage at $-15^\circ C$ for 16h.[§] The single-crystal X-ray structure reveals an approximately centrosymmetric dimeric arrangement and confirms the substitution of one of the 6-Me-2-py groups (Figure 4a). Interestingly, the coordination mode of the anions $[EtAl(6-Me-2-py)_2(PhCO_2)]^-$ (**3**) is distinctly different from that of the anions $[EtAl(6-Me-2-py)_2\{OCHPy(6-Me-Py)\}]^-$ (**2**) in $(2Li)_2$ and in previously reported alkoxyaluminum dimers of the type $[\{EtAl(6-Me-2-py)_2(OR)\}Li]_2$.⁸ Whereas in all the latter the two 6-Me-2-py groups coordinate separate Li^+ cations within their Li_2O_2 cores, in $(3Li)_2$ both of the 6-Me-2-py groups of each anion are coordinated to a single Li^+ cation of the Li_2O_2 ring unit. The formation of the dimer effectively results from the 'side-on' association of $2Li$ monomers, with the Li_2O_2 ring, $PhCO_2$ groups and Al atoms of the aluminate ligands being almost coplanar.



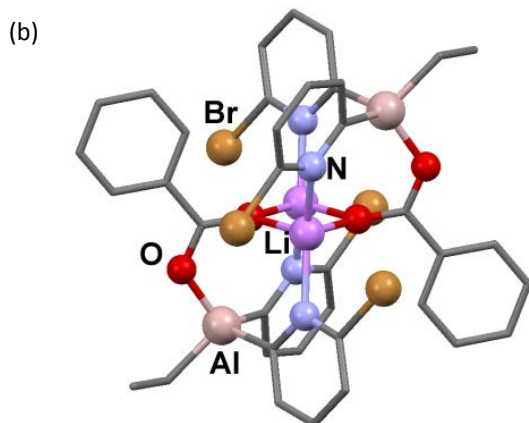


Figure 4 Dimeric structures of (a) $[\{EtAl(6\text{-Me-}2\text{-py})_2(\text{PhCO}_2)\}Li]_2$ $[(3Li)_2]$ (in the solvate $(3Li)_2 \cdot \text{toluene}$) and (b) $[\{EtAl(6\text{-Br-}2\text{-py})_2(\text{PhCO}_2)\}Li]_2$ $[(7Li)_2]$. The H-atoms and the toluene molecules present in the lattices of the solvates $[(3Li)_2] \cdot \text{toluene}$ and $[(7Li)_2] \cdot \text{toluene}$ have been omitted for clarity. Only one of two crystallographically-independent molecules of $(7Li)_2$ is shown (the data for $(7Li)_2$ are given as ranges over both molecules). Selected bond lengths (Å) and angles ($^\circ$): $(3Li)_2$, Li-O range 1.943(3)–1.998(3), Li-N range 2.081(4)–2.101(4), Al-O range 1.8366(15)–1.8404(14), Al-C^{py} range 1.995(2)–2.007(2), Al-C^{Et} range 1.973(2)–1.974(2), Li-O-Li 85.54(13), O-Li-O 94.28(14)–94.47(14). $(7Li)_2$, Li-O range 1.930(6)–1.956(7), Li-N range 2.093(6)–2.124(6), Al-O range 1.814(2)–1.833(2), Al-C^{py} range 2.015(3)–2.030(4), Al-C^{Et} range 1.976(4)–1.999(4), Li-O-Li range 88.3(3)–90.2(3), O-Li-O 88.3(3)–90.1(3). Colour code: O (red), Li (magenta), Al (pink), N (blue), Br (orange).

As background to this study, we also explored the selectivity of the reactions of benzoic acid with other aluminate ions $[\{EtAl(6\text{-R-}2\text{-py})_3\}Li]$ [R = CF₃ (**5**), Br (**6**)].^{4f} The presence of electron-withdrawing substituents on the pyridyl rings makes these anions considerably less reactive than **1** and a greater amount of EtH was observed by ¹H NMR in their 1:1 and 1:2 reactions with PhCO₂H at -78°C in toluene. The observed order of reactivity (**1**Li > **6**Li > **5**Li) is in line with the electron-withdrawing ability of the substituent on the pyridyl ring units (and the resulting reduction in the polarity of the C^{py}-Al bonds). A ca. 3:1 mixture of unreacted anion **1** and the new anion $[\{EtAl(6\text{-Br-}2\text{-py})_2(\text{PhCO}_2)\}]^-$ (**7**) is formed under these conditions, from which a low yield of the crystalline salt $[\{EtAl(6\text{-Br-}2\text{-py})_2(\text{PhCO}_2)\}Li]_2$ $[(7Li)_2]$ was isolated.¶ Owing to the low yield, the complex was only characterised using X-ray crystallography.§ The solid-state structure again shows a centrosymmetric dimer arrangement (Figure 4b), with the overall structural features being similar to those found in $(2Li)_2$ and $(4Li)_2$. However, a particular point of interest is the coordination mode of the anion $[\{EtAl(6\text{-Br-}2\text{-py})_2(\text{PhCO}_2)\}]^-$ (**7**) to the Li⁺ cations, which involves bonding of the pyridyl-N atoms to the two separate Li⁺ cations within the Li₂O₂ ring, and is therefore like that found in $(2Li)_2$ rather than that in the more chemically-related dimer $(3Li)_2$. The ‘face-on’ association of the monomer units of $(7Li)_2$ places the Al atoms of the aluminate ligands above and below the Li₂O₂ ring unit, with the PhCO₂ groups being perpendicular to the ring [cf. the coplanar arrangement noted previously in $(3Li)_2$].

The origin of the coordination isomerism observed in $(3Li)_2$ and $(7Li)_2$ may in part be due to the presence of stabilising Br...Li interactions which are in the range 3.040(6)–3.066(6) Å

in $(7Li)_2$, although this is not fully understood at this stage (Figure 5, left).⁹ The side-on mode found in $(3Li)_2$ (Figure 5, right) not only results in greater steric congestion around the Li⁺ cations, but also places the substituent at the 6-position in near proximity to the O atoms of the Li₂O₂ ring. Interestingly, the ¹H-⁷Li HOESY NMR of $(3Li)_2$ in toluene nonetheless shows a through-space correlation between the Li ions and the protons of the 6-Me substituents of the 6-Me-2-py ligands and *ortho*-H atom of the PhCO₂⁻ groups (ESI). These protons are in close proximity to the Li⁺ cations in the solid-state structure of the dimer (as indicated in Figure 5, right), with Li...H-C contacts in the range ca. 2.67–3.05 Å suggesting that further (weak) stabilisation by inter-monomer agostic interactions may be occurring.¹⁰

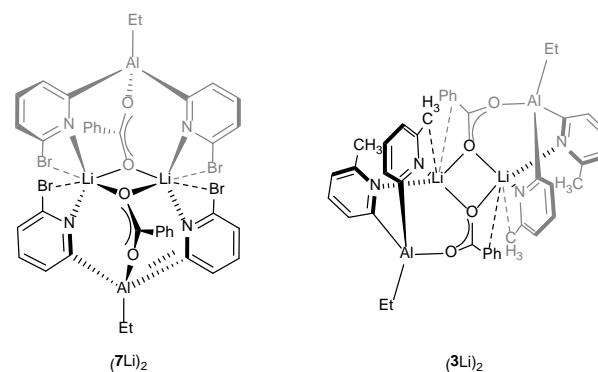


Figure 5 Schematics of the structures of $(7Li)_2$ (*face-on*) and $(3Li)_2$ (*side-on*), showing the coordination modes of the aluminate ligands with respect to the Li₂O₂ cores.

Conclusions

We have shown that the aluminate anion **1** can function either as a nucleophile, adding to polar C=O groups of aldehydes, or as a base, deprotonating the OH groups of carboxylic acids. The observed desymmetrization of the 6-Me-2-py groups on reaction with benzaldehyde is of interest with regard to potential future applications of **1** in chiral discrimination. Perhaps of more direct interest, however, is the observation of two distinct (*side-on* and *face-on*) bonding modes of the aluminate anions generated in the reactions of **1** with carboxylic acids, which appear to be subtly influenced by the presence of the secondary Li-interactions.

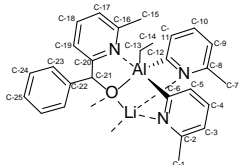
Acknowledgements: We thank the Spanish MINECO-AEI and the EU (ESF) for a Ramon y Cajal contract (RG-R, RYC-2015-19035), the Leverhulme Trust (postdoctoral grant for ALC, DSW and RG-R) and the Cambridge Trust (Chancellor’s Scholarship for AJP) for funding.

Conflicts of interest

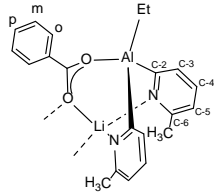
There are no conflicts to declare.

Notes and references

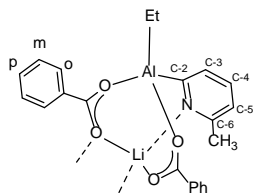
‡ **Synthesis of (2Li)₂**: To a stirred solution of 1Li (300 mg, 0.89 mmol) in 5 mL of thf was added neat benzaldehyde (89 μ L, 0.89 mmol). The mixture was stirred for 10 min and the solvent was then removed *in vacuo*. The oily residue was dissolved in 2 mL of toluene and stored at -15 °C for 1 week to yield (2Li)₂ as colourless crystals. Isolation under vacuum (10⁻¹ atm., ca. 15 mins) results in removal of the toluene solvation found in the lattice in the later structural characterisation of (2Li)₂·2.7toluene. The following data refer to the unsolvated complex (2Li)₂. Yield 160 mg, 0.36 mmol, 40%. ¹H NMR (298K, 500 MHz, d₈-toluene), δ [ppm] = 7.66 (d, J = 7.2 Hz, 1H, H-5), 7.58 (d, J = 7.2 Hz, 1H, H-11), 7.27 (d, J = 7.3 Hz, 2H, H-23), 7.15 – 7.00 (m, 5H, H-4, H-10, H-24, H-25), 6.82 (t, J = 7.7 Hz, 1H, H-18), 6.62 (d, J = 7.7 Hz, 1H, H-3), 6.55 (pt, J = 8.5 Hz, 2H, H-9, H-17), 6.41 (d, J = 7.8 Hz, 1H, H-19), 5.73 (s, 1H, H-21), 2.62 (s, 3H, H-15), 2.50 (s, 3H, H-1), 2.36 (s, 3H, H-15), 1.46 (t, J = 8.2 Hz, 3H, H-14), 0.55 (q, J = 8.1 Hz, 2H, H-13). ¹³C NMR (298K, 126 MHz, d₈-toluene), δ [ppm] = 187.97, 167.41, 155.50, 155.08, 154.90, 146.09, 136.67, 132.45, 129.86, 129.35, 128.80, 128.68, 127.90, 127.75, 126.97, 120.61, 119.64, 119.61, 119.50, 77.08, 25.04, 24.61, 24.59, 9.59, -1.99. ²⁷Al NMR (298K, 130 MHz, d₈-toluene), δ [ppm] = 130.9. ⁷Li NMR (194 MHz, d₈-toluene, 25 °C) δ [ppm] = 3.68. Elemental analysis (%), calcd. for (2Li)₂: C 72.8%, H 6.6%, N 9.4%; found C 72.8%, H 7.2%, N 8.9%.



Synthesis of (3Li)₂: 1Li (200 mg, 589 μ mol) was dissolved in toluene (5 mL) and the solution was cooled to -78 °C. After addition of benzoic acid (72 mg, 590 μ mol, 1.00 eq.), the reaction mixture was stirred at -78 °C for 3 min and subsequently allowed to warm up to room temperature. The resulting clear solution was stirred at room temperature for a further 4 h. The solution was concentrated *in vacuo* until the precipitation of a colourless solid was observed. The precipitate was redissolved by gently heating the solution. Layering with hexane and storage at -15 °C overnight afforded colourless crystals of (3Li)₂. Isolation under vacuum (10⁻¹ atm., ca. 15 mins) results in removal of the toluene solvation found in the lattice in the later structural characterisation of (3Li)₂·toluene. The following data refer to the unsolvated complex (3Li)₂. (50 mg, 136 μ mol, 23%). IR (Nujol), $\nu_{\text{sym}}(\text{C}=\text{C py})$: 1603 cm⁻¹, $\nu_{\text{asym}}(\text{CO}_2)$: 1568 cm⁻¹, $\nu_{\text{sym}}(\text{CO}_2)$: 1413 cm⁻¹. ¹H-NMR (298 K, d₈-toluene, 500 MHz), δ [ppm] = 8.18 (d, J = 5.1 Hz, 2H, *o*-C₆H₅), 7.80 (d, J = 7.1 Hz, 2H, H-3 py), 7.11 (t, J = 7.6 Hz, 2H, H-4 py), 6.91 (t, J = 6.7 Hz, 1H, *p*-C₆H₅), 6.73 (m, 2H, *m*-C₆H₅), 6.47 (t, J = 7.6 Hz, 2H, H-5 py), 1.90–1.87 (m, 9H, 2-py-CH₃ and Al-CH₂-CH₃), 1.02 (q, J = 8.0 Hz, 2H, Al-CH₂) ppm. ¹³C-NMR (298 K, d₈-toluene, 126 MHz), δ [ppm] = 184.4 (br, C_q, C-2 py), 174.4 (br, C_q, COO), 158.2 (C_q, C-6 py), 135.6 (C_q, C₆H₅), 133.8 (CH, C-4 py), 133.0 (CH, *p*-C₆H₅), 131.1 (CH, *o*-C₆H₅), 131.0 (CH, C-3 py), 125.6 (CH, *m*-C₆H₅), 122.1 (CH, C-5 py), 23.7 (CH₃, py), 10.4 (CH₃, Al-CH₂-CH₃), -1.4 (CH₂, Al-CH₂) ppm. ⁷Li-NMR (298 K, d₈-toluene, 194 MHz), δ [ppm] = 3.03 ppm. Elemental analysis: calcd. for [EtAl(O₂CPh)(6-Me-2-py)₂Li], C 68.5%, H 6.0%, N 7.6%, found: C 68.5%, H 6.1%, N 7.0%.



Synthesis of (4Li)_n: 1Li (200 mg, 589 μ mol) was dissolved in toluene (5 mL) and the solution was cooled to -78 °C. After addition of benzoic acid (144 mg, 1.18 mmol, 2.00 eq.), the reaction mixture was stirred at -78 °C for 3 min and subsequently allowed to warm to room temperature. The resulting clear solution was stirred at room temperature for a further 4 h. The solution was concentrated *in vacuo* to a volume of 1 mL and layered with *n*-hexane. Storage at -15 °C overnight afforded (4Li)_n as a colourless solid (80 mg, 201 μ mol, 34%). IR (Nujol), $\nu_{\text{sym}}(\text{C}=\text{C py})$: 1630 cm⁻¹, $\nu_{\text{sym}}(\text{C}=\text{C py})$: 1602 cm⁻¹, $\nu_{\text{asym}}(\text{CO}_2)$: 1566 cm⁻¹, $\nu_{\text{sym}}(\text{CO}_2)$: 1417 cm⁻¹. ¹H-NMR (298 K, d₈-toluene, 500 MHz), δ [ppm] = 8.47 (m, 4 H, *o*-C₆H₅), 7.69 (d, J = 7.2 Hz, 1H, H-3 py), 7.11–7.07 (m, 5H, *m*-C₆H₅ and H-4 py), 7.02–7.00 (m, 2H, *p*-C₆H₅), 6.30 (d, J = 7.3 Hz, 1H, H-5 py), 1.85 (t, J = 8.2 Hz, 3H, Al-CH₂-CH₃), 1.69 (br s, 3H, 2-py-CH₃), 0.89 (q, J = 8.1 Hz, 2 H, Al-CH₂). ¹³C-NMR (298 K, d₈-toluene, 126 MHz), δ [ppm] = 180.0 (br, C_q, C-2 py), 173.9 (br, C_q, COO), 158.2 (C_q, C-6 py), 134.0 (CH, C-4 py), 133.3 (C_q, C₆H₅), 133.0 (CH, *p*-C₆H₅), 131.7 (CH, C-3 py), 128.5 (CH, *o*-C₆H₅), 125.4 (CH, *m*-C₆H₅), 122.3 (CH, C-5 py), 23.5 (CH₃, py), 9.9 (CH₃, Al-CH₂-CH₃), -1.5 (br, CH₂, Al-CH₂) ppm. ⁷Li-NMR (298 K, d₈-toluene, 194 MHz), δ [ppm] = 2.55 ppm. Elemental analysis: calcd. for (4Li)_n, C 66.5%, H 5.3%, N 3.5%, found: C 66.3%, H 5.7%, N 3.5%.



Synthesis of (7Li)₂: Compound (7Li)₂ was only isolated as a few crystals that were characterised by X-ray crystallography and no NMR data could be recorded. In a glove box, 6Li (40 mg, 0.075 mmol) and benzoic acid (9.1 mg, 0.075 mmol, 1.00 eq) were dissolved in toluene (0.6 mL). The solution was concentrated and stored at -15 °C overnight, affording (7Li)₂ as a few colourless crystals.

§ Crystal data for (2Li)₂·2.7toluene; Formula [C₅₄H₅₈Al₂Li₂N₆O₂].2.7toluene, *M* = 1140.05 triclinic, space group P-1, *Z* = 2, *a* = 10.7764(4), *b* = 11.6195(4), *c* = 15.5555(6) Å, α = 72.5308(19), β = 75.6187(18), γ = 68.8699(16)°, *V* = 1711.41(11) Å³, $\mu(\text{Cu-K}\alpha)$ = 0.742 mm⁻¹, ρ_{calc} = 1.106 g cm⁻³, *T* = 180(2) K. Total reflections 34421, unique 5992 (*R*_{int} = 0.059), *R*₁ = 0.103 [*I* > 2 σ (*I*)] and *wR*₂ = 0.306 (all data). The toluene molecules are disordered and the stated quantity is approximate. The refinement was also carried out with the toluene molecules omitted and a continuous solvent-area model applied using SQUEEZE.¹¹ This produced *R*₁ = 0.056 [*I* > 2 σ (*I*)] and *wR*₂ = 0.155 (all data), with 171 electrons corrected for per unit cell (\approx 3.4 toluene molecules). The bond distances and angles given in the main text refer to the SQUEEZED structure, since the precision is improved. CCDC 1897739 and 1897741 (SQUEEZED) contain the supplementary crystallographic data for (2Li)₂·toluene.

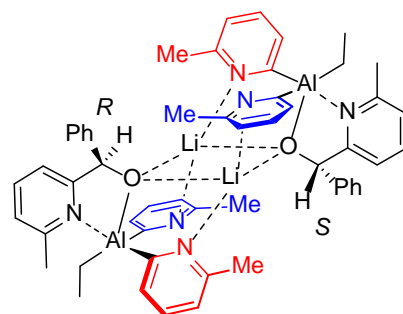
Crystal data for (3Li)₂·toluene; Formula [C₄₂H₄₄Al₂Li₂N₄O₄].C₇H₈, *M* = 828.78, monoclinic, space group P2₁/*n*, *Z* = 2, *a* = 11.9268(3), *b* = 25.7178(7), *c* = 15.3307(4) Å, β = 100.0816(13)°, *V* = 4629.8(2) Å³, $\mu(\text{Cu-K}\alpha)$ = 0.933 mm⁻¹, ρ_{calc} = 1.189 g cm⁻³, *T* = 180(2) K. Total reflections 56906, unique 8164 (*R*_{int} = 0.045), *R*₁ = 0.045 [*I* > 2 σ (*I*)] and *wR*₂ = 0.121 (all data). CCDC 1897740 contains the supplementary crystallographic data for (3Li)₂·toluene.

Crystal data for (7Li)₂; Formula C₃₈H₃₂Al₂Br₄Li₂N₄O₄, *M* = 996.15, triclinic, space group P-1, *Z* = 2, *a* = 10.4621(3), *b* = 13.0873(4), *c* = 16.4267(6) Å, α = 86.2550(15), β = 71.9417(15), γ = 71.1903(14)°, *V* = 2022.67(11) Å³, $\mu(\text{Cu-K}\alpha)$ = 5.636 mm⁻¹, ρ_{calc} = 1.636 g cm⁻³, *T* = 180(2) K. Total reflections 57695, unique 7182 (*R*_{int} = 0.044), *R*₁ = 0.037 [*I* > 2 σ (*I*)] and *wR*₂ = 0.092 (all data). CCDC 1897742 contains the supplementary crystallographic data for (7Li)₂.

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Deprotonation, Insertion and Isomerisation in the Post-functionalisation of *Tris*-pyridyl Aluminates



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Reactions of aluminate anions $[\text{EtAl}(6\text{-R-2-py})_3]^-$ (6-R-2-py = 6-R-2-pyridyl, R = Me or Br) with aldehydes (RCH=O) or carboxylic acids (RCO_2H) reveal how these species can be used to sense chirality and show a new aspect of isomerism in this area.
