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## ARTICLE

# Synthesis and Structures of *Tris*(2-pyridyl)aluminum Sandwich Compounds [ $\{\text{RAl}(2\text{-py}')_2\}_2\text{M}$ ] ( $\text{py}' = 2\text{-pyridyl}$ , $\text{M} = \text{Ca}, \text{Mn}, \text{Fe}$ )

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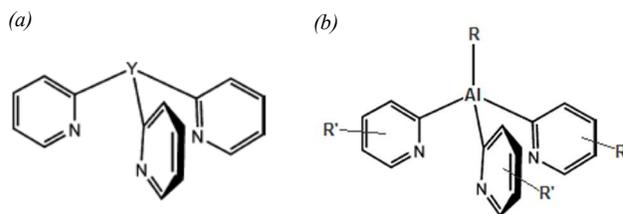
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Reactions of the lithium salts [ $\{\text{RAl}(2\text{-py}')_3\text{Li}\cdot\text{THF}$ ] [ $2\text{-py}' = 2\text{-py}$  (2-pyridyl),  $\text{R} = {}^n\text{Bu}$  (**1**),  $\text{R} = {}^{\text{sec}}\text{Bu}$  (**2**);  $\text{py}' = 5\text{-Me-2-py}$  (5-methyl-2-pyridyl),  $\text{R} = \text{Me}$  (**3**); 6-Me-2-py (6-methyl-2-pyridyl),  $\text{R} = \text{Et}$  (**4b**)] with the corresponding metal (II) halides give the new heterobimetallic sandwich compounds [ $\{\text{RAl}(2\text{-py}')_3\}_2\text{M}$ ] [ $\text{R} = {}^n\text{Bu}$ ,  $\text{M} = \text{Ca}$  (**5**),  $\text{Mn}$  (**6**),  $\text{Fe}$  (**7**);  $\text{R} = {}^{\text{sec}}\text{Bu}$ ,  $\text{M} = \text{Ca}$  (**8**),  $\text{Mn}$  (**9**)], [ $\{\text{MeAl}(5\text{-Me-2-py}')_3\}_2\text{Ca}$ ] (**10**) and [ $\{\text{EtAl}(6\text{-Me-2-py}')_3\}_2\text{Ca}$ ] (**11**) and the co-complex [ $\{\text{EtAl}(6\text{-Me-2-py}')_3\}_2\text{Mn}(\mu\text{-Cl})\text{Li}\{(\text{6-Me-2-py}')_3\text{AlEt}\}$ ] (**12**). While neither the bridgehead group (R) nor remote ring Me-groups have impact on metal coordination in **5-10**, the introduction of Me groups into the pyridyl substituent at the 6-position (*i.e.*, adjacent to the donor pyridyl-N atoms) has a marked effect on the ability of the ligands to form sandwich arrangements, as seen in the distorted structure of the sandwich compound **11** and in the formation of the co-complex **12**, consisting of a two half-sandwich arrangement linked by a  $\mu\text{-Cl}$  ion. The syntheses and solid-state structures of the new precursor **4b** and the new compounds **5-12** are reported.

## 1. Introduction

The coordination chemistry of *tris*(2-pyridyl) ligands of the type  $\text{Y}(2\text{-py})_3$  (Figure 1a), in which the bridgehead Y can be a variety of atoms or groups (*e.g.*, CH, COR, N, P, P=O, As), has been studied extensively in the past 20 years or so.<sup>1</sup> However, only relatively recently has attention turned to ligands containing heavier, more metallic main group bridgehead atoms.<sup>2</sup> One of the primary interests in these ligands is the ability to build a very large range of well-defined heterobimetallic complexes, simply through coordination of metal-based *tris*-pyridyl ligands to other metal ions. Unlike all other *tris*(2-pyridyl) ligands the iso-valent aluminium counterparts [ $\text{RAl}(2\text{-py}')_3$ ]<sup>-</sup> ( $\text{py}' = \text{a general pyridyl substituent}$ ) are negatively charged rather than neutral (Figure 1b).<sup>3-7</sup> As such, these 6e donors are ideally suited for the strong coordination of metal cations. Our studies in this area have focused almost exclusively on the parent ligand system [ $\text{MeAl}(2\text{-py})_3$ ]<sup>-</sup>. Although limited in their scope so far, these studies have shown that this ligand can be transferred *intact* to a range of transition or main group metals, forming neutral sandwich-type compounds [ $\{\text{MeAl}(2\text{-py}')_3\}_2\text{M}$ ] ( $\text{M} = \text{Ca}^{2+}$ ,<sup>5</sup>  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ <sup>4</sup>) or half-sandwich type compounds [ $\{\text{MeAl}(2\text{-py}')_3\}_2\text{MX}$ ] (*e.g.*,  $\text{M} = \text{Zn}^{2+}$ )<sup>5</sup> with divalent metal cations (depending on the metal and the reaction stoichiometry). Especially interesting is the observation that the  $\text{Fe}^{\text{II}}$  sandwich compound [ $\{\text{MeAl}(2\text{-py}')_3\}_2\text{Fe}$ ] is an efficient epoxidation catalyst for alkenes in the presence of air.<sup>5</sup>

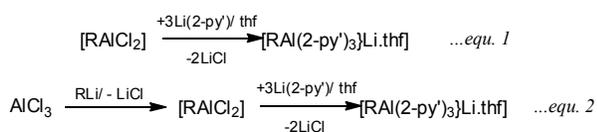
(a) Connectivity of the family of ligands  $[\text{E}(2\text{-py}')_3]$  and (b) the  $[\text{RAl}(2\text{-py}')_3]^-$ .



**Figure 1** (a) Connectivity of the family of ligands  $[\text{E}(2\text{-py}')_3]$  and (b) the  $[\text{RAl}(2\text{-py}')_3]^-$ .

The extensive elaboration of  $[\text{RE}(2\text{-py}')_3]^-$  ligands is easily achieved either using (i) the direct substitution of commercially available  $\text{RAlCl}_2$  with the lithio-pyridines  $\text{Li}(2\text{-py}')$  (equ. 1) or (ii) the stepwise *in situ* reactions of  $\text{AlCl}_3$  with  $\text{RLi}$  followed by addition of  $\text{Li}(2\text{-py}')$  (equ. 2).<sup>7</sup> These routes have allowed us to obtain a series of lithium salts of  $[\text{RAl}(2\text{-py}')_3]^-$  anions

containing different bridgehead substituents (R) and Me-substituents on the 3 to 6-positions of the 2-py' rings.



In the current paper we investigate the coordination behaviour of these ligands towards dications ( $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ ), showing that while the bridgehead group (R) or remote ring Me-groups have little or no impact on metal coordination, the introduction of Me groups into the pyridyl substituent at the 6-position (*i.e.*, adjacent to the pyridyl-N atoms) has a direct effect on the ability of the ligands to form sandwich arrangements.

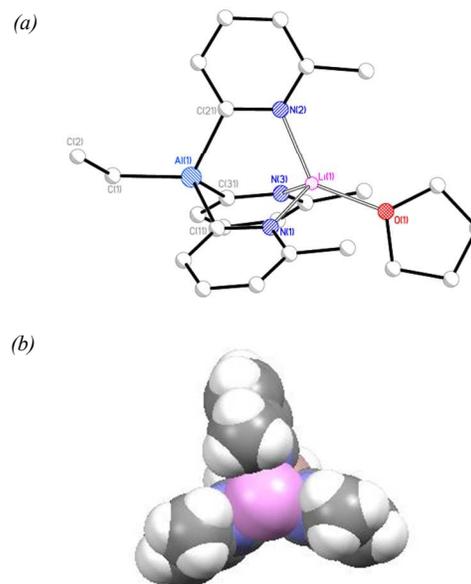
## 2. Results and Discussion

### 2.1 Synthesis of *Tris*(2-pyridyl)aluminate lithium Precursors

The previously reported lithium reagents  $[\text{RAI(2-py)'}_3\text{Li}\cdot\text{THF}]$  [ $2\text{-py}' = 2\text{-py}$  (2-pyridyl),  $\text{R} = {}^n\text{Bu}$  (**1**),  $\text{R} = {}^{\text{sec}}\text{Bu}$  (**2**);  $\text{py}' = 5\text{-Me-2-py}$  (5-methyl-2-pyridyl),  $\text{R} = \text{Me}$  (**3**)] were prepared using the literature procedures.<sup>7</sup> The precursors  $[{}^n\text{BuAl(2-py)}_3\text{Li}\cdot\text{THF}]$  (**1**) and  $[{}^{\text{sec}}\text{BuAl(2-py)}_3\text{Li}\cdot\text{THF}]$  (**2**) were obtained using the stepwise *in situ* route in THF (equ. 2) in which  $\text{AlCl}_3$  was firstly reacted with the appropriate organolithium reagents (RLi;  $\text{R} = {}^n\text{Bu}$  for **1**,  ${}^{\text{sec}}\text{Bu}$  for **2**) followed by reaction of the intermediate  $\text{RAICl}_2$  with 3 equivalents of  $\text{Li(2-py)}$ .  $[\text{MeAl(5-Me-2-py)}_3\text{Li}\cdot\text{THF}]$  (**3**) was obtained from the reaction of  $\text{MeAlCl}_2$  in THF with 3 equivalents of  $\text{Li(5-Me-2-py)}$  (equ. 1). It was found, however, that the previously reported 6-Me-substituted derivative  $[\text{MeAl(6-Me-2-py)}_3\text{Li}\cdot\text{THF}]$  (**4a**) was particularly difficult to obtain in sufficient yield or purity to facilitate further investigations of the coordination chemistry its  $[\text{MeAl(6-Me-2-py)}_3]^-$  anion. In addition, during the current study the starting material  $\text{MeAlCl}_2$  became no longer commercially available. These problems were easily circumvented simply by preparing the new Et-bridgehead derivative  $[\text{EtAl(6-Me-2-py)}_3\text{Li}\cdot\text{THF}]$  (**4b**) using the reaction of commercially-available  $\text{EtAlCl}_2$  with 3 equivalents of  $\text{Li(6-Me-2-py)}$  in THF (equ. 1).<sup>†</sup> The product readily crystallises in a total yield of 43% yield on storage of the reaction solution (for supporting spectra of **4b** see ESI, Figures SI-S6).

The new precursor **4b** is of particular interest to the current study since it contains the most sterically hindered  $[\text{RAI(2-py)'}_3]$  ligand set. This is seen in the single-crystal X-ray structure of the complex, shown in Figure 2a.‡ Most notably, unlike all of the other complexes **1**, **2** or **3**,<sup>7</sup> the THF ligand is tilted away from the axis of the C-Al...Li vector [ $\text{Al(1)}\cdots\text{Li(1)-O(1)}$  161.1(1)°] as a result of the steric congestion within the coordination site. Connected with this, the two pyridyl rings associated with N(1) and N(3) are twisted with respect to the Al...Li axis by 5.8-9.6° so as to reduce steric contact with the

three adjacent 6-Me substituents [*cf.* the ring associated with N(2) which is almost in the same plane as Al(1) and Li(1)]. The net effect of these distortions is a large increase in the N(1)...N(3) bite distance to 3.64 Å compared to those of N(2)...N(1) and N(2)...N(3) [3.14 and 3.30 Å, respectively] in order to accommodate the THF ligand. The highly strained nature of the coordination in **4b** is also evident in the extremely distorted geometry of the  $\text{Li}^+$  cation, with the O-Li-N and N-Li-N angles varying over a large range of 95.5(1)-132.6(1)°, and in the unsymmetrical N-Li bond lengths, with N(1,3) being *ca.* 0.50 Å longer than N(2)-Li(1). A space-filling view of **4b** along the Li...Al axis (with the coordinated THF ligand omitted) illustrates the highly congested environment of  $\text{Li}^+$  cation. A similar situation occurs in the solid-state structure of the Me-analogue **4a**.<sup>7</sup>

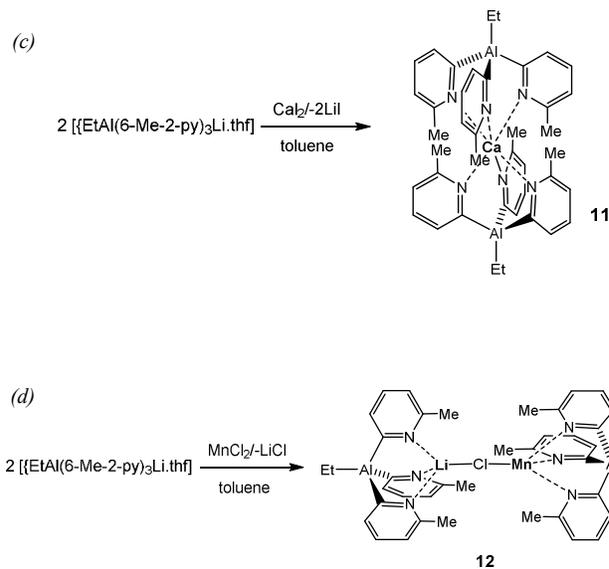
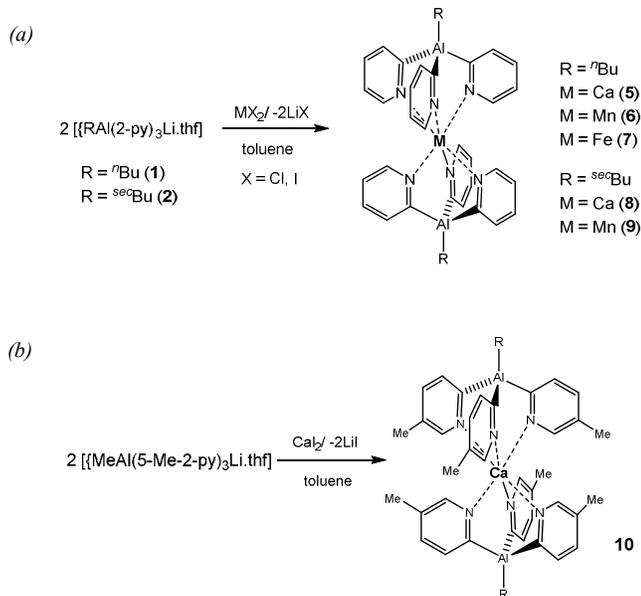


**Figure 2** (a) Structure of molecules of  $[\text{EtAl(6-Me-2-py)}_3\text{Li}\cdot\text{THF}]$  (**4b**). H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-C(1) 1.984(1), C<sub>py</sub>-Al(1) 2.015(1)-2.030(1), Al(1)...Li(1) 3.029(2), N(2)-Li(1) 2.098(2), N(1)-Li(1) 2.151(3), N(3)-Li(1) 2.154(3), Li(1)-O(1) 1.990(2), C<sub>py</sub>-Al(1)-C<sub>py</sub> range 101.27(5)-107.81(5), Al(1)-C<sub>py</sub>-N range 116.22(9)-118.30(9), N-Li-N range 95.5(1)-115.6(1), O(1)-Li(1)-N range 104.1(1)-132.6(1), Al(1)...Li(1)-O(1) 161.1(1); (b) Space-filling view of the molecule down the Al...Li axis (with the THF ligand omitted).

### 2.2 Synthesis of New Complexes of new *Tris*(2-pyridyl)aluminate Compounds of Ca, Mn and Fe

We next investigated the formation of sandwich compounds of the type  $[\{\text{RAI(2-py)'}_3\}_2\text{M}]$  with divalent metal ions (M) using **1**, **2**, **3** and **4b** as sources of the  $[\text{RAI(2-py)'}_3]^-$  ligands. Synthetic studies focused on complexes of the third-period ions  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  since this selection of ions would allow the assessment of the effects of decreased ionic size and, most obviously in the case of  $\text{Fe}^{2+}$ , the potential effect of a low-spin ion on the formation of sandwich compounds. The reactions performed and products obtained in these synthetic studies are summarised in Scheme 1.

Reactions of the Ca, Mn and Fe dihalides (1 equivalent) with the appropriate lithium *tris*(pyridyl)aluminate precursor (2 equivalents) in toluene followed by filtration, reduction of the solvent volume under vacuum and crystallisation at ambient temperature to  $-15^{\circ}\text{C}$  gave the crystalline complexes sandwich-type compounds  $[\{^n\text{BuAl}(2\text{-py})_3\}_2\text{M}] \cdot x(\text{toluene})$  [ $\text{M} = \text{Ca}$  (**5**),  $x = 1$ ;  $\text{M} = \text{Mn}$  (**6**),  $x = 1$ ;  $\text{Fe}$  (**7**)],  $[\{\text{sec}^i\text{BuAl}(2\text{-py})_3\}_2\text{M}] \cdot x(\text{toluene})$  [ $\text{M} = \text{Ca}$  (**8**),  $x = 1$ ;  $\text{M} = \text{Mn}$  (**9**),  $x = 1$ ],  $[\{\text{MeAl}(5\text{-Me-2-py})_3\}_2\text{Ca}]$  (**10**),  $[\{\text{EtAl}(6\text{-Me-2-py})_3\}_2\text{Ca}]$  (**11**) and the co-complex  $[\{\text{EtAl}(6\text{-Me-2-py})_3\}\text{Mn}(\mu\text{-Cl})\text{Li}\{\{6\text{-Me-2-py}\}_3\text{AlEt}\}]$  (**12**).<sup>†</sup> The formation of toluene *mono*-solvates in the cases of **5**, **6**, **8** and **9** was shown by a combination of elemental analysis,  $^1\text{H}$  NMR spectroscopy and single-crystal X-ray crystallography. Although the crystalline yields of the complexes are generally low (8-29 % based on the lithium aluminate supplied), their syntheses and crystallisation proved to be completely reproducible. One reason for these low yields is the poor solubility of the metal halides in toluene. Presumably for this reason, it was found that the optimum synthesis of the Fe complex **7** involved the 1 : 1 stoichiometric reaction of the lithium *tris*(2-pyridyl) aluminate **1** with  $\text{FeCl}_2$  (which is particularly insoluble in toluene). Use of THF as the solvent in these reactions (in place of toluene) resulted in significant problems with contamination of the products with lithium halide byproducts. A further possible reason for the observed low yields of **5-12** is that of alkyl transfer from the bridgeheads of the *tris*(2-pyridyl)aluminate ions to the metal salts ( $\text{MX}_2$ ), although we have found no evidence for this in these or related reactions so far.



**Scheme 1** Reaction schemes showing the synthesis of the new sandwich and co-complexes in this study.

The room-temperature solution  $^1\text{H}$  NMR spectra of the Mn (**6** and **9**) and Fe (**7**) sandwich compounds revealed extensive broadening of the resonances, indicating the presence of paramagnetic components. These observations are the same as previously seen in the solution NMR spectra of  $[\{\text{MeAl}(2\text{-py})_3\}_2\text{M}]$  ( $\text{M} = \text{Mn}, \text{Fe}$ ).<sup>5</sup> In contrast, the Ca compounds **5**, **8**, **10** and **11** showed sharp, well-resolved resonances which could be fully assigned on the basis of COSY spectra and other 2-D experiments (ESI, Figure S9 and S10). For **11**, a  $^1\text{H}$ - $^1\text{H}$  NOESY NMR study was also highly informative, showing the close proximity of the C(3)-*H* proton of the 6-Me-2-py rings to the bridgehead *Et*-Al group (ESI, Figure S12).

No solid products could be isolated from the reaction of  $[\text{EtAl}(6\text{-Me-2-py})_3\text{Li}\cdot\text{THF}]$  (**4b**) with  $\text{FeCl}_2$ . However, the formation of a deep-green solution in this case hinted at a different outcome to that seen in the sandwich compounds  $[\{^n\text{BuAl}(2\text{-py})_3\}_2\text{Fe}]$  (**5**) and  $[\{\text{MeAl}(2\text{-py})_3\}_2\text{Fe}]$ , which are both deep-red in colour. Although only obtained in low yield, the isolated product of the reaction of  $\text{MnCl}_2$  with **4b** is the unusual co-complex  $[\{\text{EtAl}(6\text{-Me-2-py})_3\}\text{Mn}(\mu\text{-Cl})\text{Li}\{\{6\text{-Me-2-py}\}_3\text{AlEt}\}]$  (**12**), in which mono-substitution of the  $\text{Mn}^{\text{II}}$  has occurred. The same compound is isolated even if the reaction mixture is heated to reflux (in toluene), suggesting that the formation of a sandwich arrangement like that seen for compounds **5-11** is disfavoured on steric grounds (see later discussion of the structure of **12**). A similar structural arrangement to **12** is also the likely result in the case of  $\text{Fe}^{\text{II}}$ , with an even smaller ionic radius than  $\text{Mn}^{\text{II}}$ . Interestingly, although they are broadened by the presence of paramagnetic  $\text{Mn}^{\text{II}}$  in **12**, the room-temperature  $^1\text{H}$  and  $^{27}\text{Al}$  NMR are otherwise identical to the corresponding spectra for the precursor **4b** (with the exception that the THF resonances in **4b** are absent in the  $^1\text{H}$  NMR spectrum **12**) (ESI, Figure S14). The Et and 6-Me-2-py resonances for the  $\text{Mn}^{\text{II}}$ -

coordinated ligand are presumably paramagnetically-broadened to such an extent as to no longer be visible.

Only poor quality crystals of **5**, **6**, **7** and **8** could be obtained despite repeated X-ray single-crystal analyses on several samples in each case, as a result only relatively low quality data could be collected on these compounds (with  $R1$  in the range 0.105-0.143). In addition, again despite repeated data collections on different crystals from several batches, only relatively low-angle X-ray data on compounds **11** and **12** could be obtained. Despite the poor quality of the data on several of the compounds reported here, their structures are determined unambiguously. Details of the data collections on compounds **5-11** are collected in Table 2.<sup>‡</sup> Compound **12** exhibits two polymorphs, a high-temperature form [rhombohedral,  $R3$ ; data collected at 250(2) K] and a low-temperature form [trigonal,  $P3(1)$ ; data collected at 180(2) K]. Both polymorphs exhibit very similar structural features and disorder of the Li-( $\mu$ -Cl)-Mn unit, but only the data on the low-temperature  $P3(1)$  form is discussed in this paper because of its better quality.

The low-temperature [180(2) K] solid-state structures of **5**, **6** and **7** (Figure 3), **8** and **9** (Figure 4), **10** (Figure 5) and **11** (Figure 7) show that they are all sandwich complexes of the type  $[\{RAl(2-py)_3\}_2M]$ ,<sup>8</sup> containing six-coordinate, octahedral metal ions (M). The complexes are closely related to the previously reported Me-bridgehead counterparts  $[\{MeAl(2-py)_3\}_2M]$  ( $M = Ca^{II}$ ,<sup>4</sup>  $Mn^{II}$ ,  $Fe^{II}$ <sup>5</sup>). Table 1 presents selected bond lengths and angles for all of these compounds. Despite the short-comings in the X-ray data for **5**, **6**, **7**, **8** and **11** (mentioned above), taken together as a closely related series of compounds their structural parameters can be used to demonstrate some general trends. However, before moving on to discuss this series in more detail, one of the issues that the now more extensive structural data available helps to resolve is the determination of whether the  $Mn^{II}$  and  $Fe^{II}$  ions in **6**, **7** and **9** are in a high-spin or low-spin electronic state.<sup>9</sup> From these data, the Mn-N bond lengths in **6** [2.268(4)-2.317(4) Å] and **9** [2.295(4)-2.308(4) Å] are consistent with the presence of high-spin  $Mn^{II}$  ions.<sup>9</sup> However, the Fe-N bond lengths in **7** [2.017(6)-2.063(6) Å] strongly suggest the presence of low-spin  $Fe^{II}$  ( $d^6$ ) at the temperature of the X-ray structure determination.<sup>9</sup> The fact that **7** is paramagnetic in solution at ambient temperature is probably due to the presence of a high-spin component, resulting from high-spin/low-spin equilibrium in the temperature range 180 and 298 K. Precedents for this behaviour are well known in closely related  $Fe^{II}$  tris-pyrazolylborate sandwich compounds of the type  $[\{RB(pz)_3\}_2Fe]$ .<sup>8b,10</sup> In the light of the new structural evidence described in this paper, we now believe that the previously reported sandwich compound  $[\{MeAl(2-py)_3\}_2Fe]$ , which is paramagnetic in solution and the solid state at ambient temperature but has similar Fe-N bond lengths to **7** [2.054(3) Å at 180(2) K],<sup>5</sup> also exhibits temperature-dependent high-spin/low-spin equilibrium.

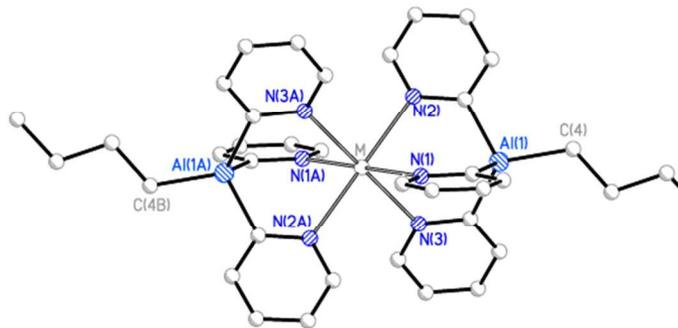
Comparison of the bond lengths and angles within the frameworks of the  $[\{^nBuAl(2-py)_3\}]$  ligands of **5** ( $M = Ca$ ), **6** ( $M = Mn$ ) and **7** ( $M = Fe$ ) (Figure 4) and those of the  $[\{^{sec}BuAl(2-py)_3\}]$  ligands of **8** ( $M = Ca$ ) and **9** ( $M = Mn$ )

(Figure 5) (Table 1) shows that there are only small changes in any of the parameters, despite the difference in the ionic radii of the coordinated metal cations [ $Ca^{2+}$  1.14 Å;  $Mn^{2+}$  0.97 Å (high spin);  $Fe^{2+}$  0.75 Å (low-spin)<sup>11</sup>] and the bridgehead R-group. In addition, the key structural parameters found in the  $[\{MeAl(5-Me-2-py)_3\}_2Ca]$  (**10**) (Figure 5), the other  $Ca^{II}$  sandwich compounds **5** and **8**, and the previously reported compound  $[\{MeAl(2-py)_3\}_2Ca]$ <sup>4</sup> are almost identical. Thus, somewhat expectedly, the placement of the Me-group at the 5-position of the pyridyl rings in the  $[MeAl(5-Me-2-py)_3]^-$  ligands of **10** has no obvious effect on its coordination behaviour compared to the unsubstituted ligands. However, there is clear evidence of steric strain in the formation of the sandwich arrangement in the case of **11**, in which the Me-substituents are at the 6-positions of the 2-pyridyl rings (Figure 6). This is seen most obviously in the large increase in the N-Ca bond lengths [range 2.534(2)-2.614(2) Å] compared to the other  $Ca^{II}$  compounds **5**, **8** and **10** [overall range 2.460(3)-2.490(3) Å] and the previously reported sandwich compound  $[\{MeAl(2-py)_3\}_2Ca]$  [2.476(2)-2.489(2) Å].<sup>4</sup> There is also a noticeable increase in the Al- $C_{py}$ -N angle [range 121.4(2)-123.9(2)°] compared to the other Ca complexes [range 115.3(4)-118.9(4)°<sup>4</sup>]. The distortions in **11** appear to be the direct result of the steric clash of the Me-groups of either of the  $[EtAl(6-Me-2-py)_3]^-$  ligands with the pyridyl rings of each other. This is seen in the space-filling view of the sandwich structure of **11** (Figure 6b), in which the Me- and 2-py-group interdigitate, producing a number of particularly short interligand (methyl)C-H... $N_{py}$  contacts (range *ca.* 2.42-2.68 Å) which are well below the sum of the van der Waals radii of H and N (2.75 Å<sup>9</sup>).

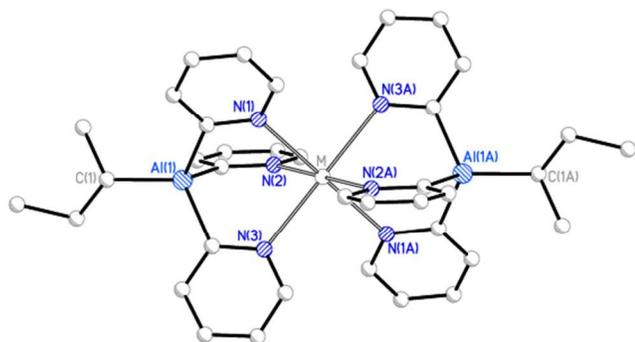
With the previous discussion in mind, the apparent inability of the  $[EtAl(6-Me-2-py)_3]^-$  ligand to form a  $Mn^{II}$  sandwich compound of the type  $[\{EtAl(6-Me-2-py)_3\}_2Mn]$  is perhaps not surprising, because the reduction in the size of the coordinated cation from  $Ca^{2+}$  (1.14 Å<sup>9</sup>) to  $Mn^{2+}$  [0.97 Å (high spin)<sup>9</sup>] would require far too close approach of the two ligands. Instead, the more favourable alternative is *mono*-substitution of one Cl for a  $[EtAl(6-Me-2-py)_3]^-$  ligand and the formation of the co-complex  $[\{EtAl(6-Me-2-py)_3\}Mn(\mu-Cl)Li\{6-Me-2-py\}_3AlEt]$  (**12**), in which the other  $[\{EtAl(6-Me-2-py)_3\}Li]$  precursor molecule remains *intact* (Figure 7a). In this sense, the structure of **12** can be regarded as a model intermediate in the reactions producing sandwich compounds like **5-11**. The co-complex arrangement of **12** keeps the 6-Me substituents spatially separated, as can be seen from the space-filling view of the structure (Figure 7b). The situation with **12** is related to that seen in a previous study of the reaction of  $ZnCl_2$  with  $[MeAl(2-py)_3]Li\cdot THF$ , which only results in *mono*-substitution to give the half-sandwich compound  $[\{MeAl(2-py)_3\}ZnCl]$  as a result of the small ionic radius of  $Zn^{2+}$ .<sup>4</sup>

It is interesting to note that the  $[\{EtAl(6-Me-2-py)_3\}_2Li]$  subunit of **12** does not exhibit the same gross distortion of the  $Li^+$  coordination geometry as was seen in the precursor **4b**, presumably due to the presence of the almost linear Li-Cl-Mn bridge (as opposed to the more sterically congested THF complexation). The reduction of the ligand  $C_{py}$ -Al(2)- $C_{py}$

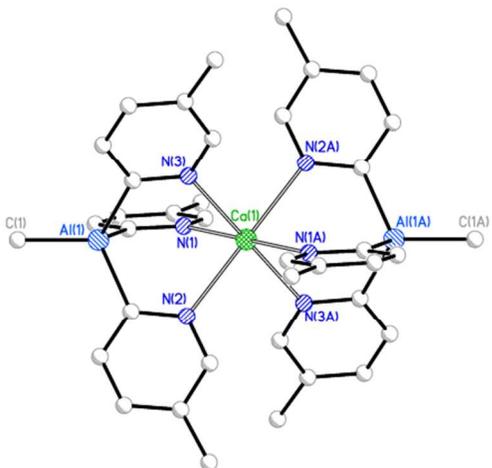
[102.6(4)-104.1(4) $^\circ$ ] and Al(2)-C<sub>py</sub>-N [118.6(6)-120.5(7) $^\circ$ ] angles in the Mn-coordinating ligand compared to those in the Ca complex **11** [105.8(1)-109.1(1) and 121.4(2)-123.9(2) $^\circ$ ] also indicates reduced ligand strain.



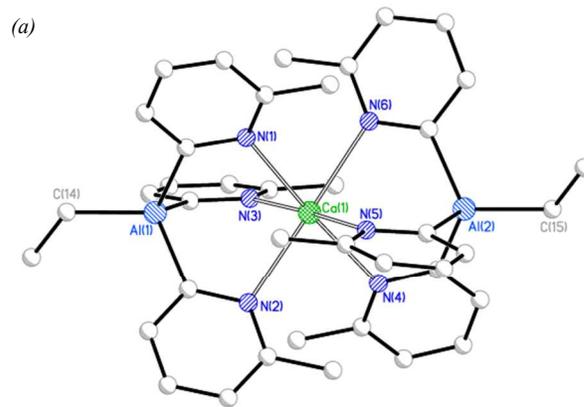
**Figure 3** Structure of [ $t\text{BuAl}(2\text{-py})_3$ ]<sub>2</sub>M [M = Ca (**5**), Mn (**6**), Fe (**7**)]. H-atoms are omitted for clarity. The data from **5** has been used to generate the picture.



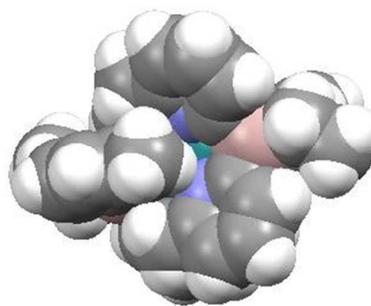
**Figure 4** Structure of [ $t\text{BuAl}(2\text{-py})_3$ ]<sub>2</sub>M [M = Ca (**8**), Mn (**9**)]. H-atoms are omitted for clarity. The data from **8** has been used to generate the picture.



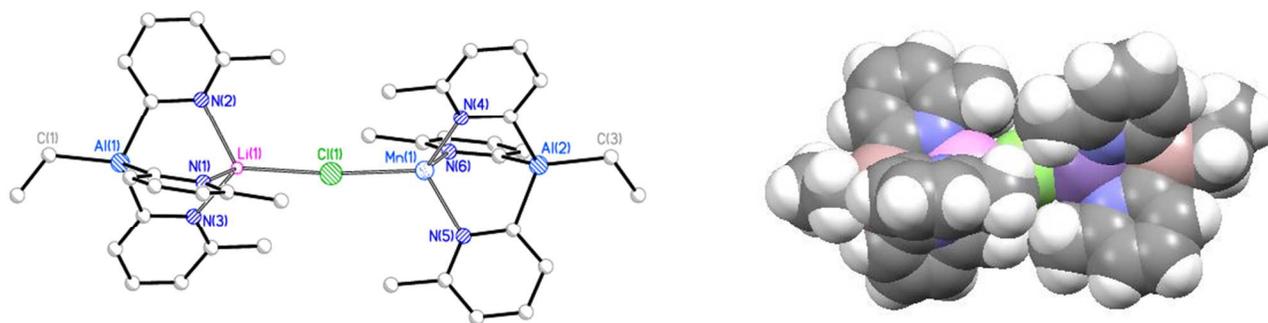
**Figure 5** Structure of [ $\text{MeAl}(5\text{-Me-2-py})_3$ ]<sub>2</sub>Ca (**10**). H-atoms are omitted for clarity.



(b)



**Figure 6** (a) Structure of [ $\text{EtAl}(6\text{-Me-2-py})_3$ ]<sub>2</sub>Ca (**11**). H-atoms are omitted for clarity; (b) Space-filling view of the molecule, with H-atoms included.



**Figure 7** (a) Structure of  $[\{\text{EtAl}(6\text{-Me-2-py})_3\}\text{Mn}(\mu\text{-Cl})\text{Li}\{\{6\text{-Me-2-py}\}_3\text{AlEt}\}]$  (**12**) (low-temperature  $P3(1)$ ). Only the major  $\text{Mn}(1)\text{-Cl}(1)\text{-Li}(1)$  component of the disorder of the  $\text{Mn}(\mu\text{-Cl})\text{-Li}$  bridge is shown. H-atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ):  $\text{Al}(1)\text{-C}(1)$  1.95(1),  $\text{Al}(1)\text{-C}_{\text{py}}$  range 2.015(8)-2.026(8),  $\text{Al}(1)\cdots\text{Li}(1)$  3.082(8),  $\text{Li}(1)\text{-N}$  range 2.120(9)-2.160(9),  $\text{Li}(1)\text{-Cl}(1)$  2.878(8),  $\text{Mn}(1)\text{-Cl}(1)$  2.344(3),  $\text{Mn}(1)\text{-N}$  range 2.165(7)-2.182(6),  $\text{Al}(2)\text{-C}(3)$  1.986(9),  $\text{Al}(2)\text{-C}_{\text{py}}$  2.010(8)-2.026(8),  $\text{Al}(2)\cdots\text{Mn}(1)$  3.171(8),  $\text{C}_{\text{py}}\text{-Al}(1)\text{-C}_{\text{py}}$  103.6(3)-105.2(3),  $\text{Al}(1)\text{-C}_{\text{py}}\text{-N}$  range 116.4(6)-117.7(7), range  $\text{N-Li}(1)\text{-N}$  range 98.2(3)-100.4(3),  $\text{N-Li}(1)\text{-Cl}$  range 114.4(3)-115.7(3),  $\text{Li}(1)\text{-Cl}(1)\text{-Mn}(1)$  173.4(2),  $\text{C}_{\text{py}}\text{-Al}(2)\text{-C}_{\text{py}}$  range 102.7(3)-104.0(3),  $\text{Al}(2)\text{-C}_{\text{py}}\text{-N}$  range 119.0(5)-120.4(6),  $\text{N-Mn}(1)\text{-N}$  range 100.8(2)-101.9(2),  $\text{N-Mn}(1)\text{-Cl}(1)$  range 115.5(2)-117.6(2); (b) Space-filling view of the molecule, with H-atoms included.

**Table 1** Selected bond lengths (Å) and angles ( $^\circ$ ) in the sandwich compounds  $[\{\text{BuAl}(2\text{-py})_3\}_2\text{M}]$  [ $\text{M} = \text{Ca}$  (**5**),  $\text{Mn}$  (**6**),  $\text{Fe}$  (**7**)],  $[\{\text{secBuAl}(2\text{-py})_3\}_2\text{M}]$  [ $\text{M} = \text{Ca}$  (**8**),  $\text{Mn}$  (**9**)], of  $[\{\text{MeAl}(5\text{-Me-2-py})_3\}_2\text{Ca}]$  (**10**) and  $[\{\text{EtAl}(6\text{-Me-2-py})_3\}_2\text{Ca}]$  (**11**).

compound	5	6	7	8	9	10	11
$\text{C}_{\text{alkyl}}\text{-Al}$	mean 1.99*	1.965(8)	1.876(1)	1.99(1)	1.986(8)	1.970(2)	mean 1.983*
$\text{C}_{\text{py}}\text{-Al}$	2.016(4)- 2.025(3)	2.006(5)- 2.017(5)	1.802(9)- 1.88(1)	2.027(4)- 2.039(3)	2.015(5)- 2.016(5)	2.011(2)- 2.034(2)	2.019(3)- 2.035(3)
$\text{Al}\cdots\text{M}$	3.637(1)	3.503(5)	mean 3.22*	3.646(4)	3.514(5)	3.596(6)	mean 3.46*
$\text{N-M}$	2.462(4)- 2.489(4)	2.268(4)- 2.317(4)	2.017(6)- 2.063(6)	2.448(3)- 2.466(3)	2.295(4)- 2.308(4)	2.466(2)- 2.481(2)	2.528(3)- 2.613(3)
$\text{C}_{\text{py}}\text{-Al-C}_{\text{py}}$	104.4(2)- 107.2(2)	103.2(2)- 105.0(2)	103.8(3)- 104.6(3)	104.6(2)- 107.1(2)	102.6(2)- 105.2(2)	105.39(8)- 106.95(8)	105.7(1)- 109.1(1)
$\text{Al-C}_{\text{py}}\text{-N}$	118.0(4)- 118.9(4)	116.0(2)- 117.7(3)	115.3(4)- 117.7(4)	116.0(2)- 116.8(2)	116.4(3)- 117.2(3)	118.1(1)- 118.6(1)	121.1(2)- 123.9(2)
$\text{N-M-N}$	87.6(1)- 92.4(1)	88.8(2)- 91.2(2)	84.3(3)- 95.5(2)	87.4(1)- 92.6(1)	89.4(1)- 90.5(1)	88.53(5)- 91.47(5)	84.11(9)- 94.94(9)

\*Mean values of bond lengths result from disorder of the bridgehead substituents R in the cases of **5**, **6** and **7** and/or from the presence of two independent Al centres in the structure of **7** and **11**.

## Conclusions

The current study has shown that a series of *tris*(2-pyridyl) aluminate ligands [ $\{RAl(2-py')_3Li\cdot THF\}$ ], containing different bridgehead groups (R) and substituted or non-substituted 2-pyridyl groups (2-py') can be applied in transition metal coordination chemistry. While neither the bridgehead group (R) nor remote ring Me-groups appear to have any steric or electronic impact on metal coordination, the introduction of Me groups into the pyridyl substituent at the 6-position has a marked effect on the ability of the ligands to form sandwich arrangements of the type [ $\{RAl(2-py')_3\}_2M$ ].

In the light of the 'frustrated' ligand properties of the  $[EtAl(6-Me-2-py)_3]^-$  anion, we are currently exploring the stabilisation of unusual metal-metal bonds using this ligand.

## Acknowledgements

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## Notes and references

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† **Synthesis of 4b, 5, 6, 7, 8, 9, 10, 11 and 12:** All syntheses were carried out on a vacuum-line under argon atmosphere. Products were isolated and handled with the aid of a N<sub>2</sub>-filled glove box (Saffron type  $\alpha$ ). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance 400 QNP or Bruker Advance 500 MHz Cryo spectrometer. <sup>7</sup>Li and <sup>27</sup>Al NMR spectra were recorded on a Bruker Advance 500 MHz Cryo spectrometer. Elemental analysis was obtained on a Perkin Elmer 240 Elemental Analyser. The unambiguous assignment of NMR resonances was accomplished in selected cases by additional 2D NMR experiments (<sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>1</sup>H NOESY, <sup>1</sup>H-<sup>13</sup>C HMQC and <sup>1</sup>H-<sup>13</sup>C HMBC experiments). Elemental analyses on all of the compounds were complicated by their air sensitivity and potentially by the formation of metal carbides during their combustion. The latter is indicated by the experimentally determined C contents obtained for compounds **4b**, **7**, **10** and **11**, which were consistently *ca.* 1-2 % lower than the calculated values over several analyses. The values reported here are the best obtained over several analyses on a single sample.

*Synthesis of [EtAl(6-Me-2-py)<sub>3</sub>Li·THF] (4b);* 2-Bromo-6-methylpyridine (2.28 ml, 20 mmol) was dissolved in THF (40 ml). <sup>n</sup>BuLi (12.5 ml, 20 mmol, 1.6 M in hexanes) was added to the solution dropwise at -78 °C over a period of 25-30min. The resulting orange solution was stirred (3 h at -78 °C). EtAlCl<sub>2</sub> (6.6 ml, 6.6 mmol, 1.0 M in hexanes) was added to the solution of 2-lithio-pyridine over 30 min. The resulting mixture was allowed to reach ambient temperature and stirred for a further 20h. The solvent was removed *in vacuo*. The addition of toluene (40 ml) and THF (10ml) afforded an orange mixture which was heated to gentle reflux prior to filtration 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 large colourless crystalline blocks of **4b**. Further concentration of the solution and storage at -15°C afforded more colourless crystals of **4b**. Total isolated crystalline Yield 1.17 g, 2.84mmol, 43%. <sup>1</sup>H NMR (+25°C, d<sub>8</sub>-THF, 500 MHz),  $\delta$  = 7.43 (d,  $J_{HH} = 7.2$  Hz, 3H, C(3)-H py),

7.19 (t,  $J_{HH} = 7.5$  Hz, 3H, C(4)-H py), 6.76 (d,  $J_{HH} = 7.7$  Hz, 3H, C(5)-H py), 3.62 (m, 4H, -CH<sub>2</sub>-O, THF), 2.57 (s, 9H, C(6)-Me), 1.77 (m, 4H, -CH<sub>2</sub>-O, THF), 1.42 (t,  $J_{HH} = 8.0$  Hz, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.50 (q,  $J_{HH} = 8.0$  Hz, 3H, Al-CH<sub>2</sub>). A <sup>1</sup>H-<sup>1</sup>H NOESY experiment on **4b** showed the close proximity of the C(3)-H py protons to the protons of Al-CH<sub>2</sub>CH<sub>3</sub>, confirming the presence of an Et-Al-Py linkage. <sup>13</sup>C{<sup>1</sup>H} NMR (25°C, d<sub>8</sub>-THF, 100.6 MHz),  $\delta$  = 189.80 (br, C(2)), 156.37 (C(6)), 132.54 (C(4)), 130.47 (C(3)), 120.04 (C(5)), 68.02 (CH<sub>2</sub>O, THF), 26.18 (-CH<sub>2</sub>-, THF), 24.48 (C(6)-Me), 10.93 (Al-CH<sub>2</sub>CH<sub>3</sub>), -1.20 (br, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (130.3 MHz, 298K, rel solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O),  $\delta$  = 126.94 (br, s). <sup>7</sup>Li NMR (+25°C, 194.4 MHz, rel solution of LiCl/D<sub>2</sub>O),  $\delta$  = 1.27 (s) Elemental analysis, calcd. for **4b** C 70.1, H 7.6, N 10.2%; Found C 68.3, H 7.4, N 10.2%.

The syntheses of **5**, **6**, **7**, **8**, **9**, **10**, **11** and **12** all involve closely similar methods. Therefore a general synthetic method is provided below. Specific quantities of reagents, crystallisation conditions and characterisation data are provided separately for each compound.

*General synthetic method;* To a Schlenk tube were added the solid lithium precursor (**1** for **5**, **6** and **7**; **2** for **8** and **9**; **3** for **10**; **4b** for **11** and **12**) and the metal dihalide in a glove box. The Schlenk tube was transferred to a vacuum line and the solids dissolved in toluene at ambient temperature. The resulting suspension was stirred (16h for **5**, **6**, **7**, **8**, **9**, **10**; 24 h for **11**; 48h for **12**) before filtration through Celite to give a solution. The majority of the solvent was removed *in vacuo* until the precipitation of a solid was observed. This solid was heated gently back into solution. The solution was then stored at ambient temperature to -15°C to give crystals of the product.

*Synthesis of [<sup>n</sup>BuAl(2-py)<sub>3</sub>Ca]·toluene (5-toluene);* Using **1** (0.310 g, 0.77 mmol) and Ca<sub>2</sub> (0.114 g, 0.39 mmol) in 25 ml of toluene. A cloudy yellow solution was produced after reaction. Storage of the solution at -15°C (24h) gave colourless crystalline rectangular blocks of **5-toluene** (0.02 g, 0.03 mmol, 8%). <sup>1</sup>H NMR (298 K, d<sub>6</sub>-benzene, 400 MHz),  $\delta$  = 8.11 (6H, dt,  $J_{HH} = 1.4$ , 1.4, 7.5 Hz, C(6)-H py), 7.90 (6H, ddd,  $J_{HH} = 1.4$ , 1.7, 5.2 Hz, C(3)-H py), 7.07 (6H, td,  $J_{HH} = 1.7$ , 7.5, 7.5 Hz, C(5)-H py), 6.28 (6H, ddd,  $J_{HH} = 1.4$ , 5.2, 7.5 Hz, C(4)-H 2-py), 2.51-2.34 (4H, m, AlCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.08-1.97 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.43-1.22 (6H, m, CH<sub>2</sub>-CH<sub>3</sub>), 0.30 (4H, s, Al-CH<sub>2</sub>CH<sub>2</sub>-). IR (Nujol, NaCl windows, 4000-625 cm<sup>-1</sup>),  $\nu$ /cm<sup>-1</sup> = 3063(w) (aryl C-H str.), 1595(w) 1578(s) 1548 (m) (aryl). Satisfactory elemental analysis could not be obtained.

*Synthesis of [<sup>n</sup>BuAl(2-py)<sub>3</sub>Mn]·toluene (6-toluene);* Using **1** (0.350 g, 0.87 mmol) and MnCl<sub>2</sub> (0.055 g, 0.44 mmol) in 20 ml of toluene. A cloudy yellow solution was produced after reaction. Storage of the solution at -15°C (48h) gave colourless crystalline plates of **6-toluene** (0.03 g, 0.043 mmol, 10%). Isolation under vacuum (10<sup>-1</sup> atm., *ca.* 10 mins) gave amorphous material which was found to contain no toluene solvation. The spectroscopic and analytic results listed correspond to this material. <sup>1</sup>H NMR (298 K, d<sub>6</sub>-benzene, 500 MHz),  $\delta$  = 8.55-6.33 (24H, collection of br.s), 2.49-0.91 (18H, collection of br. s). IR (Nujol, NaCl windows, 4000-625 cm<sup>-1</sup>),  $\nu$ /cm<sup>-1</sup> = 3058 (w) (aryl C-H str.), 1595 (w), 1579 (s), 1549 (m) (aryl). Elemental analysis, calcd. for **6** C 66.0, H 6.1, N 12.2; found C 66.6, H 6.3, N 12.5.

*Synthesis of [<sup>n</sup>BuAl(2-py)<sub>3</sub>Fe] (7);* Using **1** (0.400 g, 1.00 mmol) and FeCl<sub>2</sub> (0.127 g, 1.00 mmol) in 30 ml of toluene. A cloudy deep-red solution was produced after reaction. Storage of the solution at ambient temperature (48h) gave colourless crystalline plates of **7** (0.030g, 0.043mmol, 11%). <sup>1</sup>H NMR (298 K, d<sub>6</sub>-benzene, 400 MHz),  $\delta$  = 8.47-6.10 (24H, collection of br. s), 2.34-0.99 (collections of br. s). IR (Nujol, NaCl windows, 4000-625 cm<sup>-1</sup>),  $\nu$ /cm<sup>-1</sup> = 3073 (w) (aryl C-H str.), 1594 (w), 1509 (s), 1439 (m) (aryl). Elemental analysis, calcd. for **7** C 65.9, H 6.1, N 12.1; found C 64.4, H 6.1, N 12.6.

*Synthesis of [<sup>n</sup>BuAl(2-py)<sub>3</sub>Ca]·toluene (8-toluene);* Using **2** (0.200 g, 0.50 mmol) and Ca<sub>2</sub> (0.074 g, 0.25 mmol) in 15 ml of toluene. A cloudy

yellow solution was produced after reaction. Storage of the solution at -15°C (24h) gave colourless crystalline rectangular blocks of **8**-toluene (0.055 g, 0.072 mmol, 29%). <sup>1</sup>H NMR (298 K, d<sub>6</sub>-benzene, 400 MHz),  $\delta$  = 8.17 (6H, m, C(6)-H 2-py), 7.94 (6H, m, C(3)-H 2-py), 7.09 (6H, m, C(5)-H 2-py), 6.30 (6H, m, C(4)-H 2-py), 2.85-1.36 (18H, overlapping m, <sup>sec</sup>Bu) (samples also showed contamination with trace quantities of pyridine). IR (Nujol, NaCl windows, 4000-625 cm<sup>-1</sup>),  $\nu$ /cm<sup>-1</sup> = 3064 (w) (aryl C-H str.), 1596 (w), 1578 (s), 1548 (m) (aryl). Satisfactory elemental analysis could not be obtained owing to the presence of pyridine contamination in samples (as seen in the <sup>1</sup>H NMR spectrum).

**Synthesis of [<sup>sec</sup>BuAl(2-py)<sub>3</sub>]<sub>2</sub>Mn-toluene (**9**-toluene);** Using **2** (0.200 g, 0.50 mmol) and MnCl<sub>2</sub> (0.031 g, 0.25 mmol) in 15 ml of toluene. A cloudy yellow solution was produced after reaction. Storage of the solution at 4°C (48h) gave colourless crystalline plates of **9**-toluene (0.025 g, 0.032 mmol, 13%). Isolation under vacuum (10<sup>-1</sup> atm., ca. 10 mins) gave amorphous material which was found to contain no toluene solvation. The spectroscopic and analytic results listed correspond to this material. <sup>1</sup>H NMR (298 K, d<sub>6</sub>-benzene, 400 MHz),  $\delta$  = 8.51-6.65 (24H, collection of br. s), 2.68-0.85 (18H, collection of br. s). IR (Nujol, NaCl windows, 4000-625 cm<sup>-1</sup>),  $\nu$ /cm<sup>-1</sup> = 3065 (w) (aryl C-H str.), 1596 (w), 1579 (s), 1549 (m) (aryl). Elemental analysis, calcd. for **9** C 66.0, H 6.1, N 12.2; found C 65.6, H 6.2, N 13.4.

**Synthesis of [MeAl(5-Me-2-py)<sub>3</sub>]<sub>2</sub>Ca (**10**);** Using **3** (0.200 g, 0.50 mmol) and Ca<sub>2</sub> (0.074 g, 0.25 mmol) in 15 ml of toluene. A colourless suspension was produced after reaction. Storage of the solution at 4°C (24h) gave colourless crystalline rectangular blocks of **10** (0.035 g, 0.052 mmol, 21%). <sup>1</sup>H NMR (298 K, d<sub>6</sub>-benzene, 400 MHz),  $\delta$  = 8.49 (6H, d, J<sub>HH</sub> = 5.0 Hz, C(3)-H py), 6.91 (6H, d, J<sub>HH</sub> = 7.6 Hz, C(6)-H py), 6.71 (6H, dd, J<sub>HH</sub> = 5.0, 7.4 Hz, C(4)-H py), 1.82 (18H, m, C(4)-Me 4-Me-2-py), 0.63 (3H, s, Al-Me). Elemental analysis, calcd. for **10** C 67.4, H 6.2, N 12.4, found C 65.4, H 6.0, N 10.4.

**Synthesis of [EtAl(6-Me-2-py)<sub>3</sub>]<sub>2</sub>Ca (**11**);** Using **4b** (0.200 g, 0.49 mmol) and Ca<sub>2</sub> (0.072 g, 0.25 mmol) in toluene (15ml)/ THF (3ml). A cloudy colourless solution was produced after reaction. Storage of the filtrate at ambient temperature (24h) gave colourless crystals of **11** (0.020 g, 0.028mmol, 12%). <sup>1</sup>H NMR (298 K, d<sub>8</sub>-THF, 500 MHz),  $\delta$  = 7.69 (d, J<sub>HH</sub> = 7.1 Hz, 6H, C(3)-H py), 7.37 (t, J<sub>HH</sub> = 7.5 Hz, 6H, C(4)-H py), 6.71 (d, J<sub>HH</sub> = 7.6 Hz, 6H, C(5)-H py), 1.57 (t, J = 8.0 Hz, 6H, Al-CH<sub>2</sub>CH<sub>3</sub>), 1.42 (s, 18H, C(6)-Me), 0.78 (q, J<sub>HH</sub> = 8.0 Hz, 4H, Al-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, d<sub>8</sub>-THF, 125.8 MHz),  $\delta$  = 188.15 (br, C(2)), 159.01 (C(6)), 134.16 (C(4)), 131.76 (C(3)), 122.50 (C(5)), 22.94 (C(6)-Me), 10.67 (Al-CH<sub>2</sub>CH<sub>3</sub>), -0.28 (br, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (298 K, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O),  $\delta$  = 132.37 (br, s). Elemental analysis, calcd. for **11**, C 68.2, H 6.6, N 11.9%; Found C 66.6, H 6.2, N 12.3%.

**Synthesis of [EtAl(6-Me-2-py)<sub>3</sub>]<sub>2</sub>Mn( $\mu$ -Cl)Li{(6-Me-2-py)<sub>3</sub>AlEt} (**12**);** Using **4b** (0.200 g, 0.49 mmol) and MnCl<sub>2</sub> (0.031 g, 0.25 mmol) in toluene (15ml)/ THF (3ml). A cloudy pale yellow solution was produced after reaction. Storage of the filtrate at ambient temperature (24h) gave colourless crystals of **12** (ca. 0.005g, 3 %). <sup>1</sup>H NMR (298 K, d<sub>8</sub>-THF, 500 MHz),  $\delta$  = 7.43 (br, 3H, C(3)-H py), 7.20 (br, 3H, C(4)-H py), 6.77 (br, 3H, C(5)-H py), 2.54 (br, 9H, C(6)-Me), 1.42 (br, 3H, Al-CH<sub>2</sub>CH<sub>3</sub>), 0.50 (br, 3H, Al-CH<sub>2</sub>). <sup>27</sup>Al NMR (298 K, d<sub>8</sub>-THF, 130.3 MHz, ref. solution of AlCl<sub>3</sub>·6H<sub>2</sub>O/D<sub>2</sub>O),  $\delta$  = 126.84 (br, s). <sup>7</sup>Li NMR (+25°C, d<sub>8</sub>-THF, 194.4 MHz, ref. solution of LiCl/D<sub>2</sub>O),  $\delta$  = 1.80 (s). Despite repeated attempts satisfactory elemental analysis could not be obtained.

‡ **X-ray Crystallographic Studies of 4b, 5, 6, 7, 8, 9, 10, 11 and 12:** All data (except that for **11** and the R3 polymorph of **12**) were collected on a Nonius KappaCCD Diffractometer equipped with an Oxford Cryostream cooling device. The data for **11** the R3 polymorph of **12** were collected on a Bruker D8 QUEST diffractometer. Crystals were mounted directly from solution using perfluorohydrocarbon oil<sup>12</sup> to prevent atmospheric oxidation, hydrolysis and solvent loss. Data were solved by direct methods and refined by full-matrix least squares on F<sup>2</sup>.<sup>13</sup> Details of the data collections and structural refinements are given in Table 2.

Further details of the methods of refinement of the structures are as follows:

**Compounds 5 and 6:** The <sup>n</sup>Bu group (disordered over two sites) and the toluene solvent molecule are both poorly resolved (both were modelled with bond length restraints and common isotropic displacement parameters for the carbon atoms). Anisotropic displacement parameters were assigned to the Al and Ca atoms only. An all-anisotropic refinement does behave and does converge but the resulting extra displacement parameters have no apparent physical significance.

**Compound 7:** Refined as a racemic twin with final BASF=0.41. Strenuous attempts to refine the structure in a higher symmetry rhombohedral group were unsuccessful. The two <sup>n</sup>Bu groups are very poorly resolved, modelled as disordered about a triad axis with bond length restraints and common isotropic displacement parameters for the carbon atoms. Anisotropic displacement parameters were assigned to the Al and Fe atoms only, common isotropic displacement parameters were assigned to the C and N atoms of the 2-py rings. The AFIX command was used in the refinement of the 2-py rings in order to produce sensible bond distances.

**Compounds 8 and 9:** The <sup>sec</sup>Bu group and the toluene solvent molecule are both poorly resolved, the toluene is disordered about an inversion centre. Both were modelled with bond length restraints and common isotropic displacement parameters for the carbon atoms. Anisotropic displacement parameters were assigned to the Al and Ca atoms only. For **8**, the AFIX command was used in the refinement of the 2-py rings in order to produce sensible bond distances.

**Compound 12:** The Mn,  $\mu$ -Cl and Li atoms are disordered over two sites (each of the metal sites occupied either by an Mn or an Li atom). The Mn(1)-Cl(1)-Li(1) fragment (occupancy 0.89) and the Li(2)-Cl(2)-Mn(2) fragment (occupancy 0.11) were restrained to have the same geometry. The Mn and Li atoms were assigned a common isotropic displacement parameter, the Cl atoms another. The final refinement gives reasonable bond lengths and (Mn-Cl distances 2.34 Å, Li-Cl distances 2.88 Å, <sup>14</sup>U(iso) = 0.05 for Mn/Li, U(iso) = 0.07 for Cl), very similar to that obtained for the high-temperature rhombohedral form. Except for the Al atoms (which were assigned anisotropic displacement parameters) all other non-H atoms were assigned common isotropic parameters. So, with the Mn/Li occupancy factor etc., 12 extra LS parameters (SHELXL 'free variables') were used for this refinement giving a total of 192 LS parameters and a respectable parameter/data ratio of 18:1.

**Table 2** Details of the data collections and structural refinements of **4b**, **5**-toluene, **6**-toluene, **7**, **8**-toluene, **9**-toluene, **10**, **11** and **12**.

Compound*	<b>4b</b>	<b>5</b> -toluene	<b>6</b> -toluene	<b>7</b>	<b>8</b> -toluene	<b>9</b> -toluene	<b>10</b>	<b>11</b>	<b>12</b>
Chemical formula	C <sub>24</sub> H <sub>31</sub> AlLiN <sub>3</sub> O	C <sub>38</sub> H <sub>42</sub> Al <sub>2</sub> CaN <sub>6</sub> •C <sub>7</sub> H <sub>8</sub>	C <sub>38</sub> H <sub>42</sub> Al <sub>2</sub> MnN <sub>6</sub> •C <sub>7</sub> H <sub>8</sub>	C <sub>38</sub> H <sub>42</sub> Al <sub>2</sub> FeN <sub>6</sub>	C <sub>38</sub> H <sub>42</sub> Al <sub>2</sub> CaN <sub>6</sub> •C <sub>7</sub> H <sub>8</sub>	C <sub>38</sub> H <sub>42</sub> Al <sub>2</sub> MnN <sub>6</sub> •C <sub>7</sub> H <sub>8</sub>	C <sub>38</sub> H <sub>42</sub> Al <sub>2</sub> CaN <sub>6</sub>	C <sub>40</sub> H <sub>46</sub> Al <sub>2</sub> CaN <sub>6</sub>	C <sub>40</sub> H <sub>46</sub> Al <sub>2</sub> CaLiMnN <sub>6</sub>
<i>FW</i>	411.44	768.95	783.81	692.59	768.95	783.81	676.82	704.87	762.12
Crystal system	monoclinic	triclinic	triclinic	trigonal	triclinic	triclinic	monoclinic	monoclinic	trigonal
Unit cell dimensions	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>R</i> 3	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 3(1)
<i>a</i> (Å)	10.7216(3)	9.5264(3)	9.4064(5)	12.432(2)	9.5380(4)	9.4224(2)	10.2800(8)	11.7465(6)	12.457(2)
<i>b</i> (Å)	16.9280(5)	9.6015(3)	9.5770(5)	12.432(2)	9.5762(5)	9.4959(2)	10.297(1)	19.5696(9)	12.457(2)
<i>c</i> (Å)	13.0438(4)	12.4043(5)	12.3360(7)	19.172(4)	12.4193(7)	12.3300(3)	18.271(2)	16.2852(8)	22.235(4)
$\alpha$ (°)	-	84.746(2)	86.303(2)	-	89.456(2)	90.491(2)	-	-	-
$\beta$ (°)	100.930(1)	71.733(2)	72.415(3)	-	72.848(2)	106.116(2)	102.983(3)	96.215(2)	-
$\gamma$ (°)	-	88.276(2)	89.284(2)	-	86.782(3)	93.0150(10)	-	-	-
<i>V</i> (Å <sup>3</sup> )	2324.44(12)	1072.89(6)	1057.13(10)	2566.0(7)	1082.16(9)	1058.09(4)	1884.6(3)	3721.5(3)	2988.1(9)
<i>z</i>	4	1	1	3	1	1	2	4	3
$\rho_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.176	1.190	1.231	1.345	1.180	1.230	1.193	1.258	1.271
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	0.899	0.225	0.392	0.529	0.223	0.392	0.247	2.193	0.478
reflections collected	19156	12584	11362	6085	11281	14981	9723	19391	10346
independent reflections ( <i>R</i> <sub>int</sub> )	4463 (0.020)	4867 (0.080)	4710 (0.046)	1957 (0.033)	4841 (0.059)	3332 (0.046)	5475 (0.031)	3315 (0.030)	3476 (0.074)
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.040	0.105	0.110	0.138	0.143	0.073	0.051	0.043	0.065
<i>wR</i> 2 (all data)	0.101	0.258	0.307	0.446	0.403	0.200	0.1382	0.126	0.1655

\* Additional data: for compounds **4b**, **5**-toluene, **6**-toluene, **7**, **8**-toluene, **9**-toluene, **10** and **12** (low-temperature *P*3(1) polymorph) Mo-K $\alpha$  radiation was used ( $\lambda = 0.71073$  nm). For compounds **11** and **12** (high-temperature *R*3 polymorph) Cu-K $\alpha$  ( $\lambda = 1.54184$  nm). Only the data on the low-temperature *P*3(1) form of **12** is shown. For the crystal data on the high-temperature *R*3 polymorph of **12** see ESI. For all data collections shown in Table 2 *T* = 180(2) K.

Electronic Supplementary Information (ESI) available. Selected <sup>1</sup>H, <sup>27</sup>Al and <sup>13</sup>C NMR spectra on compounds (showing representative data); CCDC numbers 993333 (**5**), 993334 (**6**), 993335 (**8**), 993336 (**9**), 993337 (**7**), 993338 (**10**), 993339 (**4b**), 1015853 and 1015854 (*P*3(1) and *R*3 phases, **12**), 9933341 (**11**) contain the crystallographic files. See DOI: 10.1039/b000000x/

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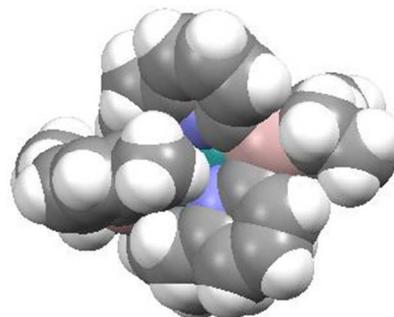
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Graphical Abstract

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**Synthesis and Structures of *Tris*(2-pyridyl)aluminate Sandwich Compounds  $[\{RAl(2-py')_2\}_2M]$  ( $py' = 2$ -pyridyl,  $M = Ca, Mn, Fe$ )**



While neither the bridgehead group (R) nor remote ring Me-groups have impact on metal coordination of *tris*(2-pyridyl) aluminate ligands  $[RAl(2-py')_3]^-$ , introduction of Me groups into the pyridyl substituent at the 6-position (*i.e.*, adjacent to the donor pyridyl-N atoms) has a marked effect on the ability of the ligands to form sandwich arrangements.

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