Pyridyl 'ring-flipping' in the dimers $[Me_2E(2\text{-py})]_2$ (E = B, Al, Ga; 2-py = 2-pyridyl)

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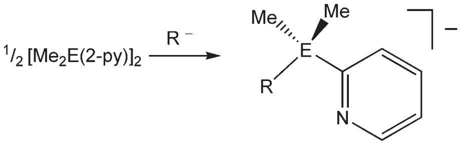
The boron and aluminium dimers $[Me_2E(\mu\text{-py})]_2$ [E = B (1); Al (2)] are formed as mixtures of two isomers in which the group 13 centres are coordinated by the bridging 2-py ligands in a *cis* or *trans* manner, however, in contrast to previous studies, we find that simply heating the mixtures of these isomers of 1 and 2 gives the more thermodynamically stable (synthetically useful) *trans* isomers exclusively (the *trans* isomer being the only product in the case of the gallium analogue 3).

Our interest in pyridyl ligands of the type $[Y(2\text{-py})_3]^{x-}$ has focused on little-studied species containing metal bridgeheads (Y).[1,2] The incorporation of metal bridgeheads gives rise to larger ligand bites than normally found in non-metallic counterparts (*e.g.*, Y = CR, N, P),[3] and to the potential for the involvement of the metal centres in redox chemistry. We found recently that the group 13 homologues $[RE(2\text{-py})_3]^-$ have an extensive coordination chemistry with a range of main group and transition metals and that they are highly effective ligands in catalysis.[2c,d] Our current interest in group 13 dimers of the type $[Me_2E(2\text{-py})]_2$ stems from their use as potential precursors to unsymmetrical multidentate anionic ligands of the type $[Me_2E(2\text{-py})R]$, generated by nucleophilic addition (eqn (1)), and from the potential applications of $[Me_2E(2\text{-py})]_2$ to act simultaneously as a Lewis acid and Lewis base (Fig. 1).



(1)

A major stumbling block to the development of this area was highlighted in earlier studies by Hodgkins and Powell who showed that the reaction of 2-lithiopyridine (2-Li-py) with Me_2BBr gives rise to two isomers of $[Me_2B(2\text{-py})]_2$ (**1**), in which the B centres are coordinated in a *cis* or *trans* manner by the bridging 2-py groups (Fig. 2).[4] Although these isomers can be separated by chromatography, the only synthetically useful precursor, **1a**, is the minor product and it is unlikely that chromatography would be useful for more air-sensitive group 13 analogues of Al, Ga or In. We show here, however, that simply heating a mixture of the isomers of **1** or of the corresponding isomers of the Al counterpart $[Me_2Al(2\text{-py})]_2$ (**2**) leads to quantitative conversion into the more thermodynamically stable *trans* isomers (**1a** and **2a**). In the case of the Ga counterpart $[Me_2Ga(2\text{-py})]_2$ (**3**), only the *trans* isomer (**3a**) can be obtained in significant amounts.

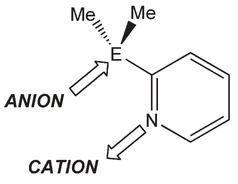
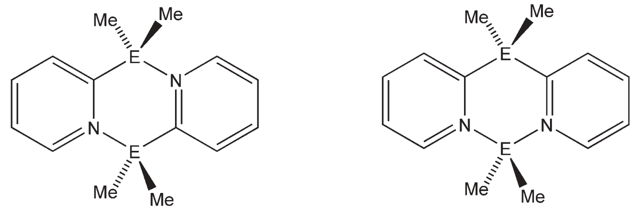


Fig. 1 The acceptor (E) and donor (N) sites for the coordination of anions and cations by a monomer unit.

The Al isomers **2** are obtained from the low-temperature reaction of Me_2AlCl with 2-Li-py (1 : 1 equiv., respectively) in 56% yield.† The presence of the two isomers **2a** and **2b** in *ca.* 50 : 50 ratio is obvious from the room-temperature ^1H NMR spectrum of isolated crystals, comprising eight multiplets in the aromatic region (δ 8.4–6.5) and three Me–Al resonances arising from the one Me environment in **2a** and the two environments in **2b** (Fig. 2b). These NMR spectroscopic observations are similar to those reported previously for the *ca.* 15 : 85 mixture of **1a** and **1b** (respectively) obtained from the reaction of Me_2BBr with 2-Li-py.[4a] Since the starting material Me_2GaCl is difficult to synthesize, the related Ga compound **3** was prepared by the *in situ* reaction of $GaCl_3$ with MeLi (1 : 2 equiv., respectively) followed by reaction with 2-Li-py (1 equiv.) (28% yield).† In contrast to the related B and Al compounds, only trace amounts of the unsymmetric isomer **3b** could be detected in the *in situ* ^1H NMR spectrum of the reaction mixture and the isolated crystalline product is exclusively **3a**.

The noticeable reduction in the amount of the *cis* isomer (**b**) as group 13 is descended is consistent with an emerging thermodynamic preference for the *trans* isomers (**a**) and with there being an accessible activation barrier between the isomers (which decreases as group 13 is descended). Subsequent semiempirical (MNDO, AM1) and DFT calculations‡ on **1**, **2** and **3** show that



E= B	**1a**	**1b**
E= Al	**2a**	**2b**
E= Ga	**3a**	**3b**

Fig. 2 *Trans* (a) and *cis* (b) isomers of **1–3**.

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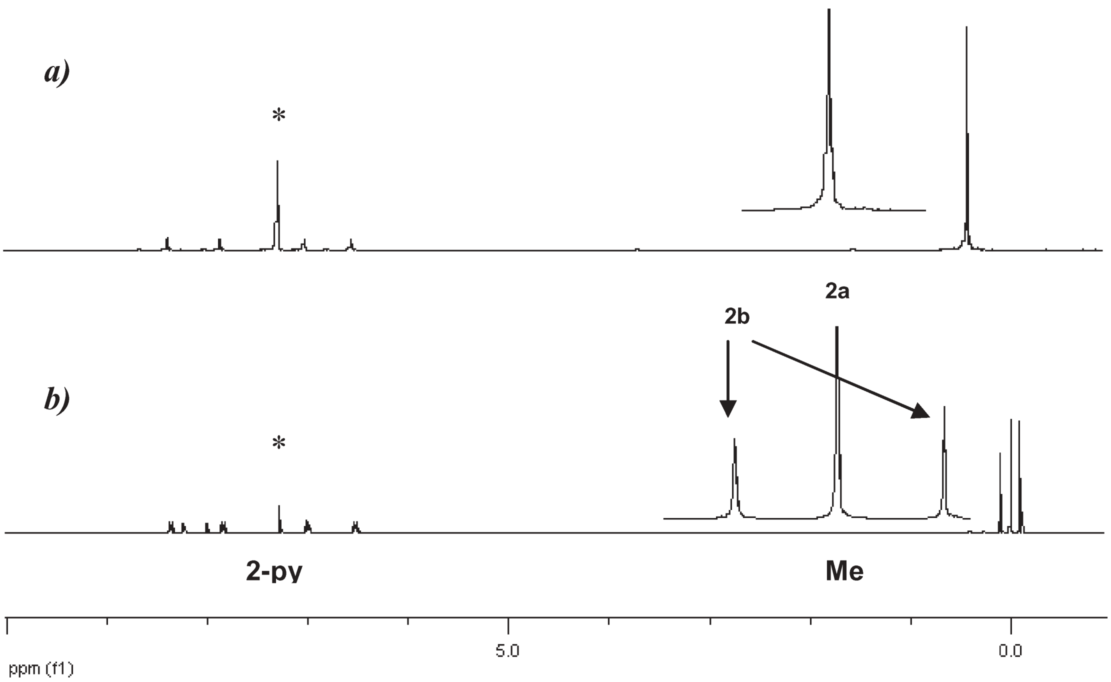

Fig. 3 The ^{1}H NMR spectrum of **2** in toluene before (b) and after (a) heating. The inserts show expansions of the Me-region of the spectrum (* denotes solvent peaks).

although the *trans* isomers **a** are more stable than the *cis* isomers **b**, in each case there is only a small difference in energy between the two (*e.g.*, DFT $\Delta E = 20.4$ kJ mol^{-1} in the case of **1a** and **1b**, $\Delta E = 4.6$ kJ mol^{-1} in the case of **3a** and **3b**). Heating a mixture of the isomers of **1** or **2** at reflux for *ca.* 30 min in toluene results in quantitative conversion into **1a** and **2a** (respectively), as shown by a combination of ^{1}H and ^{11}B NMR spectroscopy. For example, the ^{1}H NMR spectrum of **2** before and after reflux is shown in Fig. 3. Thus, regioselective access to the synthetically useful symmetric isomers is possible without the need for time-consuming chromatography or fractional crystallisation.

The X-ray structures of **2** and **3a**§ are very similar to each other (both compounds being isomorphous). Both compounds are dimers consisting of boat-shaped $E_2(CN)_2$ ring units (Fig. 4). The presence of a planar $B_2(CN)_2$ ring in the structurally-characterised boron isomer **1b**[4a] and in the symmetrical-isomer of [Et_2B(2-py-4Me)]$_2$[5] presumably stems from the lower strain in this ring, as compared to **2** and **3a** in which much larger Al and Ga centres are accommodated. The shallow boat-shaped conformations of **2** and **3a** are more similar to that found in [Me_2B(2-py)$_2BPh_2$] than in the distinctly distorted Ni(II) complex [Ni{Me_2B(2-py)$_2$}$_2$].[4b] At first sight, molecules of **2** and **3a** *appear* to exhibit similar disorder in which the each of the pyridyl ring atoms is inverted about a centre of symmetry mid-way between the two Al and Ga atoms. This disorder results in the bridging pyridyl-C and -N atoms having 50 : 50 N and C occupancy. However, as shown by the ^{1}H NMR studies mentioned above, the nature of the disorder of **2** and **3a** must in fact be quite different. In **2**, the pyridyl ring site disorder probably arises largely from the superimposition of both **2a** and **2b** whereas in **3a** this disorder effectively results from the superimposition of the two boat-shaped enantiomers (*i.e.*, Ga–NC–Ga–NC and Ga–CN–Ga–CN). Nonetheless, the outcome of this disorder is to render discussion of the core E–C and E–N bond lengths and core bond angles meaningless.

In summary, the current study has revealed an unprecedented quantitative rearrangement between isomers of [Me_2E(2-py)]$_2$. This now provides access to a range of more detailed chemical

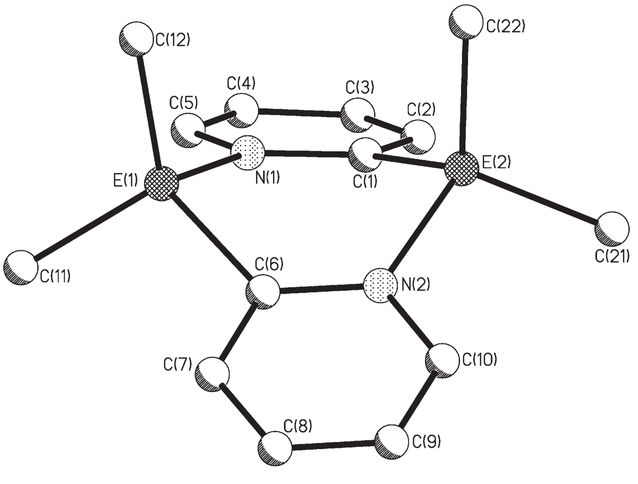

Fig. 4 Structures of the thermodynamically preferred isomers **2a** and **3a**. H-atoms and disordering of the pyridyl rings have been omitted for clarity. Selected bond lengths (Å) and angles (°); E = Al (**2**), Al(1)–C(Me) range 1.957(3)–1.971(3), Al(1)–N/C range 1.983(2)–2.003(2), Al(1)···Al(2) 3.514(3), C(py)–Al–N(py) mean 103.8, C(Me)–Al–C(Me) mean 114.8, Al···Al–C(Me) mean 95.0, Al···Al–C(Me) mean 150.1, puckering of Al(CN)$_2$Al ring about Al···Al 42.4: E = Ga (**3a**), Ga(1)–C(Me) range 1.973(7)–1.992(6), Ga(1)–N/C range 2.019(5)–2.027(5), Ga(1)···Ga(2) 3.547(6), C(py)–Ga–N(py) mean 103.1, C(Me)–Ga–C(Me) mean 116.8, Ga···Ga–C(12,22) mean 94.0, Ga···Ga–C(11,21) mean 149.2, puckering of Ga(CN)$_2$Ga ring about Ga···Ga 43.4.

studies on the pure *trans* isomers, which had previously only been obtainable in small quantities. Indeed, we have recently realised one of the goals of these studies by showing using *in situ* ^{1}H NMR spectroscopy that addition of various (amide and alkoxide) nucleophiles to pure **2a** and **3a** does indeed result in the selective formation of new functionalised anions (as outlined in eqn (1)). These studies and theoretical investigations of the mechanism of the new pyridyl 'ring-flipping' reaction will be the subject of a future full paper.

Notes and references

† *Synthesis of* **2a/b**; a solution of Me_2AlCl (1.0 mol dm^{-3} in hexanes, 39.5 ml, 39.5 mmol) was added drop-wise to a thf (100 ml) solution of 2-Li-py (39.5 mmol) at −78 °C. The solution was allowed to warm slowly to room temperature and stirred overnight. The solvent of the resulting brown solution was removed *in vacuo* and the crude product was dissolved in toluene (50 ml). The mixture was filtered and the filtrate was then brought to reflux for 2 h. After reflux, the solution was concentrated until a precipitate formed. The product was dissolved with gentle heating and stored at −30 °C overnight to give a crystalline product. The solvent was removed *via* cannula and the product was washed with hexane (20 ml). The white crystalline product was dried *in vacuo* and isolated. Yield 2.98 g, 56%. ^{1}H NMR (+25 °C, 500.2 MHz, D_6-benzene), **2a**, δ = 8.36 (dt, 3H, C(6)–H py), 7.84 (dt, 3H, C(3)–H py), 6.99 (mult., C(5)–H py), 6.51 (td, 3H, C(4)–H), 0.01 (s, 6H, Me); **2b**, δ = 8.23 (dt, 3H, C(6)–H py), 7.99 (dt, 3H, C(3)–H py), 6.99 (dt, 3H, C(5)–H py), 6.51 (dt, 3H, C(4)–H py), 0.11 (s, Me_2Al), −0.10 (s, Me_2Al). Elemental analysis, found C 59.8, H 7.4, N 10.0; calcd., C 62.2, H 7.3, N 10.0%.

Synthesis of **3a**; a solution of $GaCl_3$ (0.881 g, 5.0 mmol) in thf (25 ml) was reacted with MeLi (1.6 M in Et_2O, 6.25 ml, 10.0 mmol) at −78 °C. The reaction was warmed to room temperature and stirred for 1 h. The solution of Me_2GaCl produced was then added drop-wise to 2-Li-py (5.0 mmol) in thf (20 ml) at −78 °C. The reaction was slowly warmed to room temperature and stirred overnight. The solvent of the resulting orange solution was removed *in vacuo* and the crude product was dissolved in toluene (20 ml). The mixture was filtered through celite and the volume of the filtrate was reduced, before being stored at −30 °C to afford white crystals of **3**. The solvent was removed *via* cannula and the product dried *in vacuo*. Yield 0.250 mg, 28%. ^{1}H NMR (+25 °C, 500.2 MHz, D_6-benzene), δ = 8.33 (dt, 3H, C(6)–H py), 7.64 (dt, 3H, C(3)–H py), 6.97 (td, C(5)–H py), 6.52 (td, 3H, C(4)–H), 0.28 (s, 6H, Me) (only traces of **3b** were found in the ^{1}H NMR spectrum of the mother liquor). Elemental analysis, found C 47.3, H 5.7, N 7.9; calcd., C 47.3, H 5.7, N 7.1%.

‡ DFT calculations (LSDA/pBP86/DN*) were carried out within Spartan Pro.[6] This approach utilises a perturbative Becke–Perdew (pBP86) procedure[7] within the local spin density approximation LSDA. Instead of Gaussian basis sets, Spartan Pro utilises atomic solutions supplemented with d-type functions for heavy atoms, including numerical polarisation (DN*). It is generally considered that the pBP86 method compares most closely to the Gaussian B88-P86 method, whilst the DN* basis set is close to 6-311 + G*. Comparisons of DFT methods can be found in the literature.[8]

§ Crystal data for **2** and **3a**; data were collected on a Nonius KappaCCD diffractometer at 180(2) K. The structures were solved by direct methods and refined by full-matrix least squares on F^2.[9] **2**: $C_{14}H_{20}Al_2N_2$, M = 270.28, monoclinic, space group $C2/c$, Z = 8, a = 14.027(3), b = 16.564(3), c = 14.656(3) Å, β = 112.26(3)°, V = 3151.5(11) Å^3, μ(Mo-Kα) = 0.170 mm^{-1}, ρcalc = 1.139 Mg m^{-3}. Of a total of 12 895 reflections collected, 3605 were unique (Rint = 0.048). Final $R1$ = 0.049 [$I > 2\sigma(I)$] and $wR2$ = 0.140 (all data).[9] **3a**: $C_{28}H_{40}Ga_4N_4$, M = 355.76, monoclinic, space group $C2/c$, Z = 8, a = 14.016(3), b = 16.479(3), c = 14.743(3) Å, β = 112.21(3)°, V = 3152.4(11) Å^3, μ(Mo-Kα) = 3.404 mm^{-1}, ρcalc = 1.499 Mg m^{-3}. Of a total of 9210 reflections collected, 1553 were unique (Rint = 0.063).[9] Final $R1$ = 0.046 [$I > 2\sigma(I)$] and $wR2$ = 0.123 (all data). CCDC 621854 and 621855. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613748b

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