Successful extrapolation of an *f*-element synthetic method to the pseudo light lanthanoid, aluminium

Jacinta M. Bakker [a], Leonard J. Barbour [b], Glen B. Deacon [a], Peter C. Junk [a,*], Gareth O. Lloyd [a,c], Jonathan W. Steed [c]

[a] School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia
[b] Department of Chemistry, University of Stellenbosch, 7602, Matieland, South Africa
[c] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, United Kingdom

ARTICLE INFO

ABSTRACT

A redox transmetallation/ligand exchange reaction between Al metal, $Hg(C_6F_5)_2$ and 3,5-di-*tert*-butyl-pyrazole (*t*Bu$_2$pzH) in tetrahydrofuran (thf) yields [Al(*t*Bu$_2$pz)$_3$(thf)] in which the six coordinate aluminium atom has two η^2- and one η^1-*t*Bu$_2$pz ligands. By contrast an analogous reaction in 1,2-dimethoxyethane (dme) gives the organoaluminium complex [Al$_2$(*t*Bu$_2$pz)$_3$(C$_6$F$_5$)$_2$(OCH$_2$CH$_2$OCH$_3$)] in which each aluminium atom has an η^2-pyrazolate and a C$_6$F$_5$ ligand and the Al atoms are bridged by an η^1:η^1-*t*Bu$_2$pz ligand and a 2-methoxyethoxide ligand. In addition, [Al(*t*Bu$_2$pz)$_3$] was isolated from the reaction mixture in a different form from that previously reprinted.

1. Introduction

The coordination chemistry of pyrazolate anions and pyrazoles has become a mainstay of inorganic chemistry.[1] Prior to 1997 the coordination modes established for pyrazolates by crystallographic means consisted of just the simple $\mu-\eta^1$:η^1, η^1 and η^2 modes [1a,p,2]. However, post-1997, the possible modes of coordination have increased substantially to over 20, resulting in such extreme cases as $\mu-\eta^1$:η^2:η^1 (to K$^+$ and Tl$^+$) and η^5 (to Ru^{2+}) [1a,3,4a]. The synthesis of homoleptic pyrazolate complexes of d-block [4a–c], f-block [4d–f] and main group metals has also been achieved [2,3c,g]. 3,5-Di-*tert*-butylpyrazole (*t*Bu$_2$pzH) is an archetypal ligand when it comes to the coordination chemistry of the pyrazolates [1a,2,3a,c,d,g,4b–e,5]. Due to its simplicity in structure and it being the bulkiest of the simple pyrazolates, it forms many types of complexes with different metals [2,3c,4,5b]. We have previously synthesised the homoleptic [Al(*t*Bu$_2$pz)$_3$] (Compound **1**; a trigonal

crystal structure was determined.) using a metathesis method [2]. In this study, we report developments in the coordination chemistry of aluminium with *t*Bu$_2$pz through the use of a different synthetic route, namely, the redox transmetallation/ligand exchange reaction [6]. Such reactions (e.g. Scheme 1) have hitherto been used to synthesise particularly *f*-element, but also Group 2 complexes [6], derivatives of elements more electropositive than aluminium. Nevertheless, Al is a highly reactive metal and the common oxidation state is the same as that of the *f*-element complexes. It could thus be regarded as the lightest rare earth metal. Further, the well-known preparations of homoleptic aluminium alkyls and aryls from metallic aluminium and HgR$_2$ species at elevated temperatures [7] suggested that aluminium metal should participate in redox transmetallation/ligand exchange reactions.

2. Results and discussion

Carrying out the redox transmetallation/ligand exchange reaction shown in Scheme 1 using thf as the solvent resulted in a complex of formula [Al(*t*Bu$_2$pz)$_3$thf]·thf (**2**). The best yields of ca.

Al + *t*Bu$_2$pzH + Hg(C$_6$F$_5$)$_2$
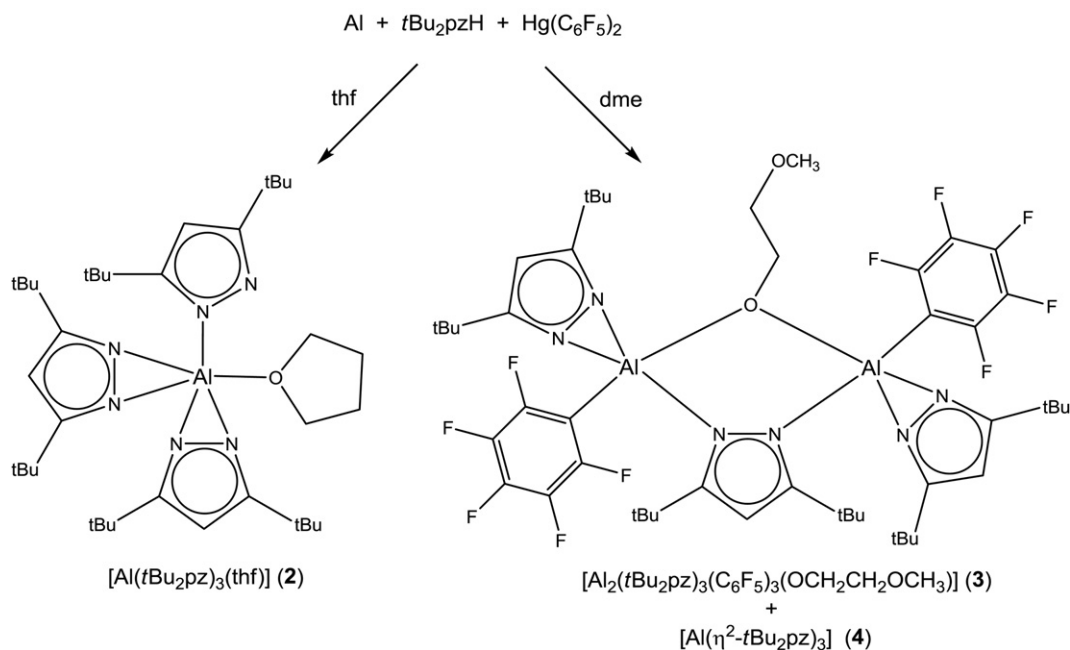
Scheme 1. Redox transmetallation/ligand exchange reaction between aluminium metal, 3,5-di-*tert*-butylpyrazole (*t*Bu$_2$pzH) and bis(pentafluorophenyl)mercury.

60% were achieved when the aluminium metal foil was cut into strips that were as small as possible. Elemental mercury was used for activation by surface amalgamation and the reaction was performed in a sonic bath for between 48 and 72 h. After filtration and reduction in the volume of the solution, crystals were formed over time. Single crystal X-ray diffraction confirmed the formulation (Fig. 1). Six coordinate compound **2** exhibits η^2-coordination of two *t*Bu$_2$pz ligands in the same way as for **1**. However, the η^1 thf
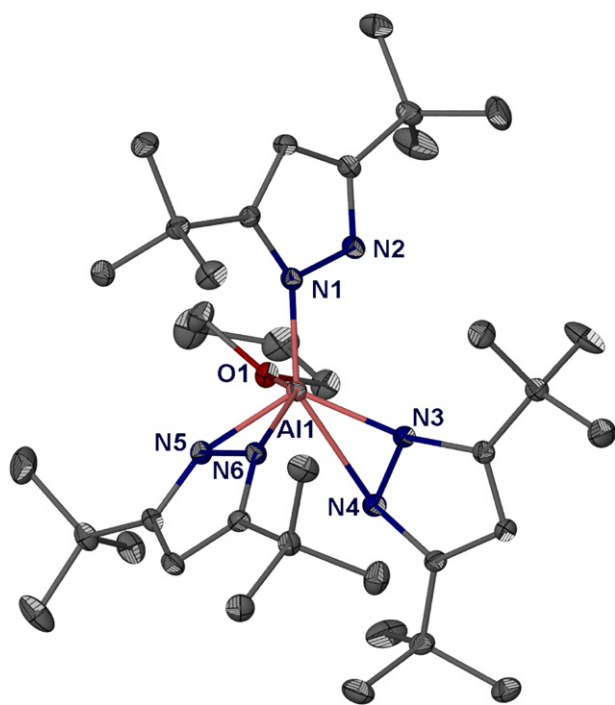
Fig. 1. Ellipsoid plot of compound **2** showing the η^2 and η^1 coordination by *t*Bu$_2$pz to Al. Hydrogen atoms and the interstitial thf have been removed for clarity. Ellipsoids are shown at 50% probability.

coordination distorts the metal environment resulting in one of the three *t*Bu$_2$pz ligands being η^1-bonded, N1–Al1 1.8770(18), N2···Al1 2.5610(18) Å. Although η^1-pyrazolate coordination is long known [1a,p], examples are relatively few, generally driven by coordination number (precious metals) [1a], or steric limitations (compound **2**), or H bonding to the free nitrogen atom [4f]. Even though two *t*Bu$_2$pz ligands are η^2-bound, they have asymmetric Al–N binding; bond lengths N3–Al1 1.8542(19); N4–Al1 2.3894 (19); N5–Al1 1.8794(18) and N6–Al 2.0304(18). Whilst the N5,6 ligand has a bite angle (Table 1) approaching that of homoleptic **1**, the more unsymmetrically coordinated N3,4 ligand has a much narrower bite angle, typical of coordination to larger metals [1a]. Additionally, each pyrazolate ring is distorted away from coplanarity with the coordination plane of the aluminium centre; (interplanar angles between plane of *t*Bu$_2$pz and N1–N2–Al1 6.07 (17)°; N3–N4–Al1 17.06(14)°; N5–N6–Al1 25.49(14)°; calculated using the MPLA function in SHELXL) [8]. *t*Bu$_2$pz coordination to four coordinate Al can be distorted to either an unsymmetrical η^2 or η^1 (η^1 or μ–η^1:η^1) due to the steric bulkiness of the ligand [5a,c,d]. In six coordinate **2** these effects are exacerbated resulting in two unsymmetrical η^2 and one unidentate ligand. The average Al–N bond length (1.99 Å) of **2** is longer than that of **1** (1.91 Å) despite the same coordination number, as thf is more bulky than half of an η^2-*t*Bu$_2$pz ligand. Complex **2** is isolated as a thf solvate from a solution in thf. The original metathesis synthesis of homoleptic **1** (trigonal system form with approximate D$_{3h}$ symmetry) was carried out in thf as well, but evaporation of the solution to dryness under vacuum removed the thf from **2** to produce the homoleptic compound before crystallisation from light petroleum [2]. The lability of thf is also evident from the mass spectrum of **2** as no signal is seen for any thf containing complex. Difficulty was experienced in obtaining a satisfactory C,H analysis (though N analysis acceptable) for this air, moisture and thermally sensitive compound but the composition was unequivocal both from the X-ray crystal structure and the ^{1}H NMR spectrum. The ^{27}Al NMR spectrum in C$_4$D$_8$O shows a broad resonance at 23.8 ppm and a narrower resonance at 67.3 ppm (Section 4). The former is indicative of a six coordinate low symmetry species and is attributed to a [Al(η^1-

Table 1
Selected bond lengths and angles for compounds **1**, **2** and one representative molecule of **4** (i = 1 − y, x − y, z; ii = 1 − x + y, 1 − x, z).

Compound **1**		Compound **2**		Compound **4**	
Bond lengths (Å)	Angles (°)	Bond lengths (Å)	Angles (°)	Bond lengths (Å)	Angles (°)
Al1−N1 1.903(2)	N1−Al1−N2 43.18 (9)	Al1−N3 1.8542(19)	N3−Al1−N1 116.99(7)	Al1−N1 1.901(2)	N1−Al1−N15 115.77(9)
Al1−N2 1.911(2)	N1−Al1−N1^i 107.7 (1)	Al1−N1 1.8770(18)	N3−Al1−N5 121.24(8)	Al1−N15 1.901(2)	N1−Al1−N28 132.01(9)
	N1−Al1−N2^i 117.3 (1)	Al1−N5 1.8794(18)	N1−Al1−N5 116.20(8)	Al1−N28 1.902(2)	N15−Al1−N28 108.32(9)
	N1−Al1−N2^{ii} 131.6 (1)	Al1−O1 1.9171(16)	N3−Al1−O1 101.64(7)	Al1−N14 1.910(2)	N1−Al1−N14 107.41(9)
	N2−Al1−N2^{ii} 107.7 (1)	Al1−N6 2.0304(18)	N1−Al1−O1 93.65(8)	Al1−N27 1.913(2)	N15−Al1−N14 42.96(8)
		Al1−N4 2.3894(19)	N5−Al1−O1 98.11(7)	Al1−N2 1.920(2)	N28−Al1−N14 117.67(9)
			N3−Al1−N6 97.98(7)		N1−Al1−N27 110.06(9)
			N1−Al1−N6 108.37(8)		N15−Al1−N27 130.66(9)
			N5−Al1−N6 41.81(6)		N28−Al1−N27 43.01(8)
			O1−Al1−N6 139.51(6)		N14−Al1−N27 106.55(9)
			N3−Al1−N4 35.51(6)		N1−Al1−N2 42.85(8)
			N1−Al1−N4 149.89(7)		N15−Al1−N2 107.15(9)
			N5−Al1−N4 93.75(7)		N28−Al1−N2 107.06(9)
			O1−Al1−N4 84.61(6)		N14−Al1−N2 131.66(9)
					N27−Al1−N2 118.75(9)

tBu$_2$pz)$_3$(C$_4$D$_8$O)$_3$] complex whilst the latter is nearer the region for five coordination and the line width suggests higher symmetry [9]. A fully solvated Al(C$_4$D$_8$O)$_5^{3+}$ species is a possible explanation. In both cases the strong donor solvent either fully or partially (η^2 to η^1) displaces pyrazolate ligands. The reported ^{27}Al NMR chemical shift for highly symmetric six coordinate **1** is 0 ppm [2]. The redox transmetallation/ligand exchange reaction therefore is effective as a means to synthesise products of ligated aluminium, and should prove to have wide application. The essential role of the mercurial in the reaction is evident since direct reaction of amalgamated aluminium with TBPH in thf failed.

As thf plays an important role in the isolation of **2** and the homoleptic compound **1**, we attempted to study the effect that a change of solvent would have on the reaction product in terms of the coordination of solvent. We chose to use 1,2-dimethoxyethane (dme), so that the bidentate coordinating ability of the solvent would test if the aluminium coordination sphere could accommodate three pyrazolate ligands and two coordinated solvent oxygen atoms. However, the first compound isolated from this reaction was not a simple pyrazolate ligated complex, but had the composition [Al$_2$(tBu$_2$pz)$_3$(C$_6$F$_5$)$_2$(OCH$_2$CH$_2$OCH$_3$)]·0.5 dme (**3**) (Fig. 2, Table 2). The complex is dinuclear and contains three different ligands; the pyrazolate anion, pentafluorophenyl ligands from the postulated Al

(C$_6$F$_5$)$_3$ precursor and a 2-methoxyethoxide anion, arising from the cleavage of dme, leading to overall five coordination. One of the three pyrazolate ligands and the methoxyethoxide ligand bridge the two metal centres. The bridging pyrazolate ligand, binds μ−η^1:η^1 to the two metals with bond lengths of Al1−N3 1.954(3) and Al2−N4 1.949 (3) and a torsion angle of ∠Al1·N3·N4·Al2 34.3(3). The five membered ring involving the bridged tBu$_2$pz and OCH$_2$CH$_2$OCH$_3$ ligands −Al1−N3−N4−Al2−O1− is not a common motif (only three rings involving −Al−N−N−Al−O− were found in the CSD [10] and all have pyrazolate ligands) [11] and is not planar (rms deviation from plane = 0.1363 Å; calculated using the MPLA function in SHELXL) [8]. The η^2 pyrazolate ligands have bond lengths of Al1−N1 1.974(3); Al1−N2 1.870(3) and Al2−N5 1.858(3); Al2−N6 2.054(3), with an average value (1.94 Å) similar to that of the μ−η^1:η^1-ligand (above), somewhat greater than that (1.90 Å) of *six* coordinate **1**, but below that (1.99 Å) of *six* coordinate **2**. These two ligands are coplanar with the Al/N coordination plane (interplanar angles of N1−N2−Al1 2.67 (15)° and N5−N6−Al2 3.37 (9)°). In addition, the chelation bite angles approach that of **1** and are similar to that of the more symmetrical η^2-tBu$_2$pz ligand of **2**. The Al−O bond lengths (Table 1) are considerably shorter than those of **2** consistent with the lower coordination number of **3**. The 2-methoxyethoxide anion is the product of the cleavage of the solvent dme and is relatively unusual, although there are precedents [12]. More usually, methoxide complexes are isolated (e.g. [6d,12g]). A 2-methoxyethoxide is
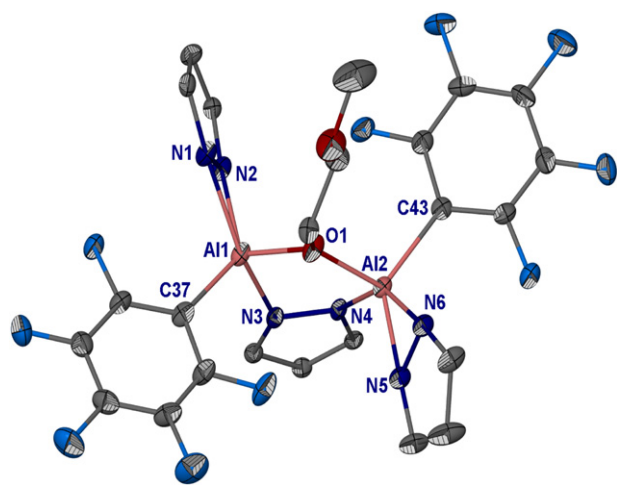
Fig. 2. Ellipsoid plot of compound **3** showing the ligation of aluminium by C$_6$F$_5$, tBu$_2$pz and a 2-methoxyethoxide anion in a bimetallic complex. Hydrogen atoms, the interstitial dme, and the t-butyl groups have been removed for clarity. Ellipsoids are shown at 30% probability.

Table 2
Selected bond lengths and angles for compound **3**

Bonds	Lengths (Å)	Angles	(°)
Al1−O1	1.821(2)	O1−Al1−N2	111.50(13)
Al1−N2	1.870(3)	O1−Al1−N3	90.71(12)
Al1−N3	1.954(3)	N2−Al1−N3	104.00(13)
Al1−N1	1.974(3)	O1−Al1−N1	100.86(12)
Al1−C37	2.008(4)	N2−Al1−N1	42.69(12)
Al2−N5	1.858(3)	N3−Al1−N1	146.68(12)
Al2−N4	1.949(3)	O1−Al1−C37	110.15(13)
Al2−C43	2.007(4)	N2−Al1−C37	127.78(14)
Al2−N6	2.054(3)	N3−Al1−C37	105.56(13)
Al2−O1	1.807(3)	N1−Al1−C37	99.60(14)
		O1−Al2−N5	111.87(13)
		O1−Al2−N4	91.46(12)
		N5−Al2−N4	105.87(13)
		O1−Al2−C43	109.04(14)
		N5−Al2−C43	125.83(14)
		N4−Al2−C43	107.01(13)
		O1−Al2−N6	99.39(12)
		N5−Al2−N6	41.59(11)
		N4−Al2−N6	147.39(13)
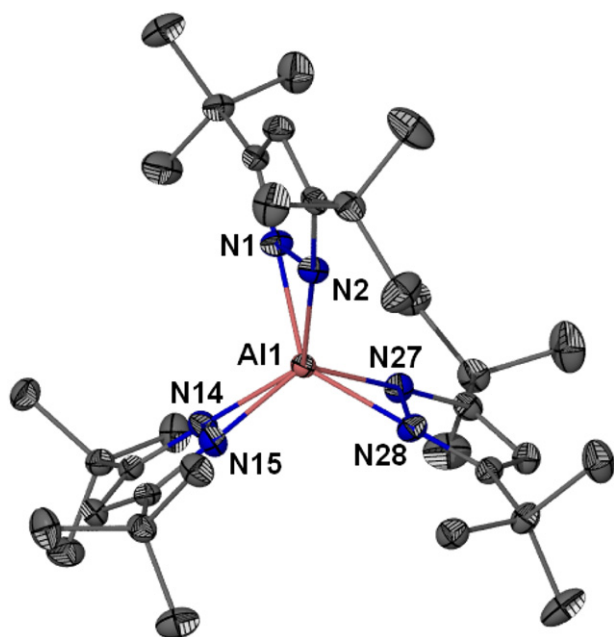
Fig. 3. One of the four unique molecules in the X-ray crystal structure of [Al(tBu$_2$pz)$_3$] (**4**).

observed in [Al(CH$_2$SiMe$_3$)$_2$(OCH$_2$CH$_2$OCH$_3$)]$_2$ [12e], but the ligand is not only bridging, it also has OCH$_3$ coordination, in contrast to **3**. The bonds between the aluminium and the C$_6$F$_5$ ligands (Al1−C37 2.008 (4) and Al2−C43 2.007(4)) match well with the average distance Al−C 1.997(52) for C$_6$F$_5$ to Al in the crystal structures observed and reported in the CSD [13]. The ^{27}Al NMR chemical shift of **3** in the non coordinating solvent C$_6$D$_6$ is near the region for five coordinate Al species and the very broad signal is consistent with a low symmetry mixed ligand complex suggesting the structural integrity is maintained in C$_6$D$_6$ [9]. The serendipitous formation of compound **3** provides evidence that the redox transmetallation/ligand exchange reaction does indeed go through an Al−C$_6$F$_5$ complex intermediate and not a mercury tBu$_2$pz complex. Compound **3** represents a small percentage of the reaction products (ca. 23%). As well as **3**, unreacted tBu$_2$pzH (ca. 40%) and the homoleptic compound [Al(tBu$_2$pz)$_3$] (**4**, ca. 37%) were found.

The homoleptic complex [Al(tBu$_2$pz)$_3$] (**4**) (Fig. 3) does not contain metal-bound dme solvent (Fig. 3). The isolation of this complex suggests that dme cannot replace even one tBu$_2$pz nitrogen since unidentate dme coordination is known. Analogously [YbCp$_2$F]$_3$ is isolated from dme [14a] in contrast to [YbCp$_2$F(thf)]$_2$ from thf [14b]. The crystal structure reported previously [2] of **1** (Fig. 4a) is

a homoleptic solvent free complex with Z' [15] of one. However, there are void channels (Fig 4a) that could hold disordered hexane (crystallized from light petroleum) though it was not modelled in the reported structure. The microanalysis [2] could accommodate 1/3.hexane within acceptable limits. In the new structure (**4**) there is no solvent present, and the packing is compact (Fig. 4b). Thus, the crystal structure of **1** may have contained a little disordered hexane, or these may be two crystal forms of [Al(tBu$_2$pz)$_3$]. The four crystallographically independent molecules found within the new structure **4** show a similar approximate D$_{3h}$ symmetry to **1**. However, the symmetry can be described as almost C$_3$ symmetry due to the twisting of the planes of the pyrazolate ligands. This twisting is opposite on neighbouring columns (related by P-1 symmetry) in **1** and is also evident in **4**. One of the most noticeable differences between **4** and **1** is the orientation of the two t-butyl groups on tBu$_2$pz in relation to each other. In **1** the orientation is staggered, with a torsion angle of ca. 32.5°. In **4** this is not always the case. Of the twelve examples, two are eclipsed (torsion angles of ca. 1.2° and ca. 5.6°). The other ten staggered groups have torsion angles ranging from ca. 25° to ca. 52°. The bond length range (1.868(2)−1.989(2) Å) of **4** is far wider than that of **1** (Table 1), and all bite angles are less than those of **1**, but mostly not by the three e.s.d. criterion.

3. Conclusions

We have shown that the redox transmetallation/ligand exchange reaction can be used to prepare aluminium complexes starting with simple "off the supermarket shelf" aluminium foil in reasonable yield. This one pot methodology allows for easy separation of products as the elemental mercury produced is filtered off (with the excess aluminium foil) and the pentafluorobenzene is easily evaporated leaving products and unreacted 3,5-di-$tert$-butylpyrazole. In this reaction, the putative intermediate Al(C$_6$F$_5$)$_3$ is never isolated and purified, as this compound can result in the explosive production of aluminium fluorides [16]. The complexes reported herein reveal the solvent ligand binding ability of the [Al(tBu$_2$pz)$_3$] complex. Tetrahydrofuran can coordinate but without a coordination number increase owing to an $\eta^2 \rightarrow \eta^1$-$tBu_2$pz bonding change. More sterically demanding solvents such as dme do not appear to be able to bind even if they are potential chelators. The cleavage of dme during this reaction is also interesting and formation of **3** provides evidence for an Al(C$_6$F$_5$)$_3$ intermediate. Further experiments are underway to investigate the possibilities of using the redox transmetallation/ligand exchange reaction with Al and other ligands, as well as extensions to other electropositive elements. Indeed, success has been recently achieved with the synthesis of manganese(II) aryloxides [17].
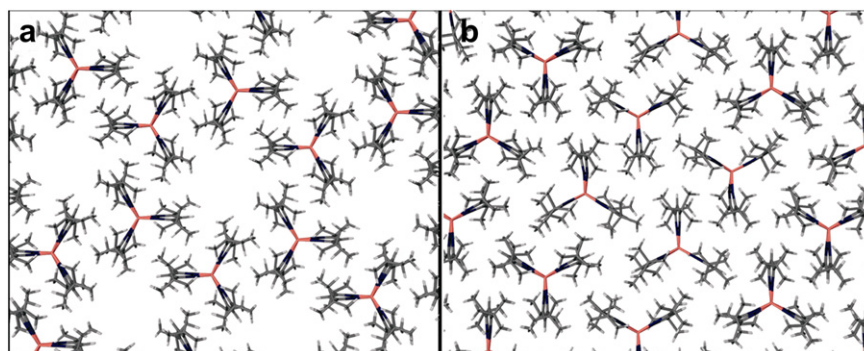

Fig. 4. (a) Figure of the homoleptic compound Al(tBu$_2$pz)$_3$ **1** channel structure. (b) High Z' structure ($Z' = 4$) of the homoleptic compound Al(tBu$_2$pz)$_3$ **4**. There are four asymmetric units. All structures shown in capped-stick representation.

4. Experimental section

The compounds described are all air- and moisture-sensitive. All manipulations were carried out under purified nitrogen using standard Schlenk techniques. Solvents (thf, dme, toluene and hexane) were dried and deoxygenated by refluxing over blue sodium benzophenone ketyl under purified nitrogen. Solvents were distilled directly into storage flasks equipped with Teflon taps and stored under nitrogen. Elemental analyses (C, H, N) were performed by The Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin, New Zealand. I.R. spectra were obtained as Nujol mulls with a Perkin Elmer 1600 FTIR instrument. The n.m.r. spectra were recorded on a Bruker AM300 spectrometer, and data were referenced to either the residual protonated solvent signals or a solution of an external standard ($Al(NO_3)_3$, 0.67 M (aq), ^{27}Al δ = 0.0). Chemicals were purchased from Aldrich and were used as received. Standard aluminium foil was used. Syntheses of 3,5-di-*tert*-butylpyrazole [18a] and bis(pentafluorophenyl)mercury [18b] have been described previously.

In a typical experiment, a large excess of Al foil (cut into small strips, 0.500 g, 18.5 mmol) was combined with tBu_2pzH (0.911 g, 5.06 mmol), $Hg(C_6F_5)_2$ (1.38 g, 2.58 mmol) and 2 drops of elemental mercury in a Schlenk flask. These starting materials were dried under vacuum for ca. 3 h prior to the addition of thf (compound **2**) or dme (compound **3**) (50 ml). The reaction vessel was placed in a sonic bath for 48−72 h. After this time, the precipitated mercury and excess aluminium were left to settle to the bottom of the reaction mixture. The reaction solution was separated through a filter cannula, concentrated to crystallisation and stored at ambient temperature or cooled to 5 °C until single crystals of the product deposited (**2** or **3**). The filtrate following isolation of **3** was evaporated until precipitation began. After heating to dissolve this precipitate, and standing at room temperature overnight, crystals of **4** deposited. The mother liquor was removed by cannula leaving **4** (37%), and evaporated to dryness leaving unreacted 3,5-di-tert-butylpyrazole (40%).

Analytical data: Compound **2**: ^1H n.m.r. (C_4D_8O) 1.15, s, 54H, (tBu); 5.91, s, 3H, (-CH-) ^{27}Al n.m.r. (C_4D_8O) δ ($W_{1/2}$ Hz) 23.8 (1800) and 67.3 (130). I.r. absorption: 2955s; 2924s; 2845s; 1511m; 1462s; 1375s; 1309w; 1257s; 1232w; 1204w; 1075s; 992w; 960w; 915w; 796w; 723s. Mass Spectrum: m/z 564.4 (46%, $Al(tBu_2pz)_3^+$), 385.3 (100%, M-tBu_2pz^+). Elemental analysis: Calculated for $C_{41}H_{73}AlN_6O_2$ (709.08): C 69.5%, H 10.4%, N 11.9% Observed: C 67.0%, H 9.7%, N 12.0%. Compound **3**: ^1H n.m.r. (C_6D_6) 1.22, s, 54H, (tBu); 3.12, m, 8H, (−O−CH_2−); 3.33, m, 9H (−CH_3); 5.98, s, 3H, (−CH−) ^{27}Al n.m.r. (C_6D_6) δ ($W_{1/2}$ Hz) 77.9 (4600). ^{19}F n.m.r. ((C_6D_6)) −119.7, m, 4F, F2,6; −154.4, m, 2F, F4; − 162.5, m, 4F, F3,5. I.r. absorption: 2934s; 2848s; 1635m; 1507m; 1456s; 1380m; 1365m; 1303w; 1268w; 1252w; 1227w; 1205w; 1125w; 1069m; 962m; 804m; 799m; 722w; 666w. Mass Spectrum: m/z 821.3 (18%, M-tBu_2pzH^+), 225.1 (100%, [$Al(C_6F_5)OMe$]$^+$). No molecular ion peak was seen. Elemental analysis: Calculated for $C_{48}H_{64}Al_2F_{10}N_6O_2$ (1000.99 − loss of dme of solvation): C 57.6%, H 6.4%, N 8.4% Observed: C 57.4%, H 7.5%, N 8.4%.

Attempted reaction of amalgamated aluminium with TBPH: A large excess of oven dried Al foil (cut into small strips, 0.14 g, 5.10 mmol) was combined with dried TBPH (0.911 g, 5.06 mmol), and two drops of elemental mercury and thf (30 ml) were added. After sonication for 3d the reaction solution was passed through a filter cannula and concentrated to dryness. IR (strong NH band) and ^1H NMR (1:1 ratio of amine and backbone proton signals) spectra indicated the resulting powder was TBPH.

5. X-ray structure determinations

Intensity data were collected using an Enraf-Nonius KAPPA CCD at 123 K with Mo-Kα radiation (λ = 0.7170 Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fibre which was mounted on the diffractometer. Reflections were measured using psi and omega scans and were reduced to unique reflections, with $F_o > 2\sigma(F_o)$ being considered observed. Data were initially processed and corrected for absorption using the programs DENZO [19] and SORTAV [20]. The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2, with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97 [21] and SHELXL-97 [22] through the graphical interface X-Seed [23], which was also used to generate the figures.

Crystal data for **2**: $C_{41}H_{73}AlN_6O_2$, M = 709.03, colourless rectangular prism, 0.39 × 0.36 × 0.31 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.934(7), b = 19.011(10), c = 19.148(12) Å, β = 101.095(15)°, V = 4263(4) Å^3, Z = 4, D_c = 1.105 g/cm^3, F_{000} = 1560, $2\theta_{max}$ = 53.0°, 31846 reflections collected, 8799 unique (R_{int} = 0.0467). Final $GooF$ = 1.029, $R1$ = 0.0548, $wR2$ = 0.1237, R indices based on 6473 reflections with $I > 2\sigma(I)$ (refinement on F^2), 497 parameters, 34 restraints. Lp and absorption corrections applied, μ = 0.087 mm^{-1}.

Crystal data for **3.0.5dme**: $C_{50}H_{69}Al_2F_{10}N_6O_3$, M = 1046.07, colourless block, 0.40 × 0.38 × 0.25 mm^3, triclinic, space group P-1 (No. 2), a = 10.618(2), b = 12.964(3), c = 20.759(4) Å, α = 73.27(3), β = 76.49(3), γ = 87.32(3)°, V = 2660.1(9) Å^3, Z = 2, D_c = 1.306 g/cm^3, F_{000} = 1102, $2\theta_{max}$ = 52.0°, 32,892 reflections collected, 10,390 unique (R_{int} = 0.0796). Final $GooF$ = 1.036, $R1$ = 0.0697, $wR2$ = 0.1778, R indices based on 5682 reflections with $I > 2\sigma(I)$ (refinement on F^2), 695 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.136 mm^{-1}.

Crystal data for **4**: $C_{33}H_{57}N_6Al_1$, M = 564.83, colourless prism, 0.45 × 0.21 × 0.18 mm^3, triclinic, space group P-1 (No. 2), a = 10.4999 (5), b = 19.4670(10), c = 33.9263(18) Å, α = 91.127(3), β = 92.024 (2), γ = 97.265(2)°, V = 6872.6(6) Å^3, Z = 8, D_c = 1.092 g/cm^3, F_{000} = 2480, $2\theta_{max}$ = 55.0°, 142,018 reflections collected, 31,492 unique (R_{int} = 0.0448). Final $GooF$ = 1.107, $R1$ = 0.0781, $wR2$ = 0.1757, R indices based on 24,910 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1442 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.089 mm^{-1}.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-745488 for **2**, CCDC-745489 for **3** and CCDC-745490 for **4**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email for inquiry: fileserv@ccdc.cam.ac.uk; email for deposition: deposit@ccdc.cam.ac.uk).

References

[1] (a) M.A. Halcrow, Dalton Trans. (2009) 2059;
(b) A.Y. O'Brien, J. Hitzbleck, A. Torvisco, G.B. Deacon, K. Ruhlandt-Senge, Eur. J. Inorg. Chem. (2008) 172;
(c) S. Nieto, J. Perez, L. Riera, V. Riera, D. Miguel, Chem. Eur. J. 12 (2006) 2244;
(d) S. Trofimenko, Chem. Rev. 72 (1972) 497;

(e) M.A. Omary, O. Elbjeirami, C.S.P. Gamage, K.M. Sherman, H.V.R. Dias, Inorg. Chem. 48 (2009) 1784;

(f) I. Saeed, S. Katao, K. Nomura, Inorg. Chem. 48 (2009) 5011;

(g) R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151;

(h) F. Mani, Coord. Chem. Rev. 120 (1992) 325;

(i) T.A. Kaden, Coord. Chem. Rev. 192 (1999) 371;

(j) M.D. Ward, J.A. McCleverty, J.C. Jeffery, Coord. Chem. Rev. 222 (2001) 251;

(k) K.R. Gust, J.E. Knox, M.J. Heeg, H.B. Schlegel, C.H. Winter, Eur. J. Inorg. Chem. (2002) 2327;

(l) K.R. Gust, J.E. Knox, M.J. Heeg, H.B. Schlegel, C.H. Winter, Angew Chem. Int. Ed. 41 (2002) 1591;

(m) S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115;

(n) A.W. Addison, P.J. Burke, J. Heterocycl. Chem. 18 (1981) 803;

(o) T. Basu, H.A. Sparkes, M.K. Bhunia, R. Mondal, Cryst. Growth Des. 9 (2009) 3488;

(p) J.E. Cosgriff, G.B. Deacon, Angew Chem. Int. Ed. 37 (1998) 286;

(q) D. Pfeiffer, M.J. Heeg, C.H. Winter, Angew Chem. Int. Ed. 37 (1998) 2517.

[2] G.B. Deacon, E.E. Delbridge, C.M. Forsyth, P.C. Junk, B.W. Skelton, A.H. White, Aust. J. Chem. 52 (1999) 733.

[3] (a) C. Yelamos, M.J. Heeg, C.H. Winter, Inorg. Chem. 37 (1998) 3892;

(b) G.B. Deacon, E.E. Delbridge, C.M. Forsyth, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (2000) 745;

(c) S. Beaini, G.B. Deacon, A.P. Erven, P.C. Junk, D.R. Turner, Chem. Asian J. 2 (2007) 539;

(d) J.R. Perera, M.J. Heeg, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 121 (1999) 4536;

(e) S. Beaini, G.B. Deacon, E.E. Delbridge, P.C. Junk, B.W. Skelton, A.H. White, Eur. J. Inorg. Chem. (2008) 4586;

(f) N.C. Mösch-Zanetti, R. Kratzner, C. Lehmann, T.R. Schneider, I. Uson, Eur. J. Inorg. Chem. (2000) 13;

(g) J. Hitzbleck, G.B. Deacon, K. Ruhlandt-Senge, Angew Chem. Int. Ed. 43 (2004) 5218.

[4] (a) I.A. Guzei, A.G. Baboul, G.P.A. Yap, A.L. Rheingold, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 119 (1997) 3387 Typical examples: *d* block:;

(b) I.A. Guzei, G.P.A. Yap, C.H. Winter, Inorg. Chem. 36 (1997) 1738;

(c) O.M. El-Kadri, M.J. Heeg, C.H. Winter, Inorg. Chem. 45 (2006) 5278 *f*-block;

(d) G.B. Deacon, A. Gitlits, B.W. Skelton, A.H. White, Chem. Commun. (1999) 1213;

(e) G.B. Deacon, A. Gitlits, P.W. Roesky, M.R. Burgstein, K.C. Lim, B.W. Skelton, A.H. White, Chem. Eur. J. 7 (2001) 127;

(f) G.B. Deacon, C.M. Forsyth, A. Gitlits, R. Harika, P.C. Junk, B.W. Skelton, A.H. White, Angew Chem. Int. Ed. 41 (2002) 3249.

[5] (a) Z.K. Yu, J.E. Knox, A.V. Korolov, M.J. Heeg, H.B. Schlegel, C.H. Winter, Eur. J. Inorg. Chem. (2005) 330;

(b) G.B. Deacon, E.E. Delbridge, D.J. Evans, R. Harika, P.C. Junk, B.W. Skelton, A.H. White, Chem. Eur. J. 10 (2004) 1193;

(c) W.J. Zheng, N.C. Mosch-Zanetti, T. Blunck, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, Organometallics 20 (2001) 3299;

(d) W.J. Zheng, H.W. Roesky, M. Noltemeyer, Organometallics 20 (2001) 1033.

[6] (a) G.B. Deacon, G.D. Fallon, C.M. Forsyth, S.C. Harris, P.C. Junk, B.W. Skelton, A.H. White, Dalton Trans. (2006) 802;

(b) M.L. Cole, P.C. Junk, New J. Chem. 29 (2005) 135;

(c) G.B. Deacon, C.M. Forsyth, S. Nickel, J. Organomet. Chem. 647 (2002) 50 and references therein;

(d) G.B. Deacon, P.C. Junk, G.J. Moxey, M. Guino, K. Ruhlandt-Senge, Dalton Trans. (2009) 4878.

[7] (a) J.J. Eisch, Aluminium. in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 1. Pergamon, Oxford, 1982 Chapter 6;

(b) S. Dagorne, D.A. Atwood, Chem. Rev. 108 (2008) 4037;

(c) J. Alcantara-Garcia, V. Jancik, J. Barroso, S. Hidalgo-Bonilla, R. Cea-Olivares, R.A. Toscano, M. Moya-Cabrera, Inorg. Chem. 48 (2009) 5874.

[8] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112.

[9] (a) H. Haraguchi, S. Fujiwara, J. Phys. Chem. 73 (1969) 3467;

(b) R. Benn, A. Rufinska, Angew Chem. Int. Ed. Engl. 25 (1986) 861.

[10] CSD, version 1.11; May 2009 update, Cambridge Crystallographic Data Centre.

[11] (a) Z.K. Yu, J.M. Wittbrodt, A.B. Xia, M.J. Heeg, H.B. Schlegel, C.H. Winter, Organometallics 20 (2001) 4301;

(b) W.J. Zheng, N.C. Mosch-Zanetti, H.W. Roesky, M. Noltemeyer, M. Hewitt, H.G. Schmidt, T.R. Schneider, Angew Chem. Int. Ed. 39 (2000) 4276.

[12] (a) W. Uhl, Coord. Chem. Rev. 163 (1997) 1;

(b) W.K. Wong, L. Zhang, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1999) 3053;

(c) W. Uhl, A. Vester, D. Fenske, G. Baum, J. Organomet. Chem. 464 (1994) 23;

(d) A. Ecker, R. Koppe, C. Uffing, H. Schnöckel, Z. Anorg. Allg. Chem. 624 (1998) 817;

(e) M. Westerhausen, C. Birg, H. Nöth, J. Knizek, T. Seifert, Eur. J. Inorg. Chem. (1999) 2209;

(f) D. Britnell, M.G.B. Drew, G.W.A. Fowles, D.A. Rice, Inorg. Nucl. Chem. Lett. 9 (1973) 415;

(g) G.B. Deacon, P.C. Junk, G.J. Moxey, Z. Anorg. Allg. Chem. 634 (2008) 2789.

[13] CCDC Vista. Cambridge Crystallographic Data Centre, Cambridge, United Kingdom, 1994.

[14] (a) G.B. Deacon, D. Stellfeldt, G. Meyer, Eur. J. Inorg. Chem. (2000) 1061;

(b) G.B. Deacon, S.C. Harris, G. Meyer, D. Stellfeldt, D.L. Wilkinson, G. Zelesny, J. Organomet. Chem. 552 (1998) 165.

[15] (a) J.W. Steed, CrystEngComm (2003) 169;

(b) K.M. Anderson, M.R. Probert, C.N. Whiteley, A.M. Rowland, A.E. Goeta, J.W. Steed, Cryst. Growth. Des. 9 (2009) 1082;

(c) K.M. Anderson, A.E. Goeta, J.W. Steed, Cryst. Growth Des. 8 (2008) 2517;

(d) K.M. Anderson, J.W. Steed, CrystEngComm 9 (2007) 328;

(e) G.R. Desiraju, CrystEngComm 9 (2007) 91.

[16] T. Belgardt, J. Storre, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, Inorg. Chem. 34 (1995) 3821.

[17] G.B. Deacon, L.Y. Goh, W.R. Jackson, B.W. Skelton, W. Chen, A.H. White, Z. Anorg. Allg. Chem. 636 (2010) 1478.

[18] (a) J. Elguero, E. Gonzales, R. Jacquier, Bull. Soc. Chim. Fr. (1968) 707;

(b) G.B. Deacon, J.E. Cosgriff, E.T. Laurenz, C.M. Forsyth, D.L. Wilkinson, in: W.A. Hermann, F.T. Edelmann (Eds.), Synthetic Methods in Organometallic and Inorganic Chemistry (Hermann/Brauer), vol. 6, Thieme, NewYork, 1997, pp. 48–51.

[19] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.

[20] R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33.

[21] G.M. Sheldrick, SHELXS-97 Program for Crystal Structure Solution. University of Göttingen, Germany, 1997.

[22] G.M. Sheldrick, SHELXL-97 Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997.

[23] L.J. Barbour, Supramol. Chem. 1 (2001) 189.