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Aluminium alkyl and aryloxide complexes of pyrazine and bipyridines: synthesis and structure†

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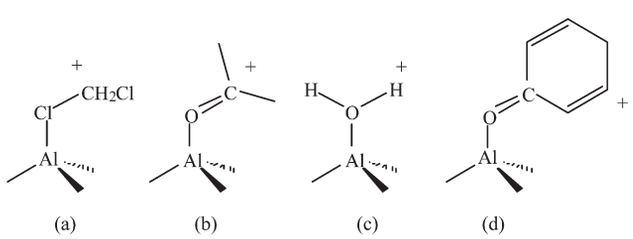
Received 13th July 2004, Accepted 22nd September 2004
First published as an Advance Article on the web 7th October 2004

The reaction of $AlMe_3$ and $[(^tBu)_2Al(\mu\text{-}OPh)]_2$ with pyrazine (pyz), 4,4′-bipyridine (4-4′-bipy), 1,2-bis(4-pyridyl)ethane (bpetha) and 1,2-bis(4-pyridyl)ethylene (bpethe) yields $(Me_3Al)_2(\mu\text{-pyz})$ (**1**), $(Me_3Al)_2(\mu\text{-}4,4'\text{-bipy})$ (**2**), $(Me_3Al)_2(\mu\text{-bpetha})$ (**3**), $(Me_3Al)_2(\mu\text{-bipethe})$ (**4**), $Al(^tBu)_2(OPh)(pyz)$ (**5**), $[(^tBu)_2Al(OPh)]_2(\mu\text{-}4,4\text{-bipy})$ (**6a**), $[(^tBu)_2Al(OPh)]_2(\mu\text{-bpetha})$ (**7a**), $[(^tBu)_2Al(OPh)]_2(\mu\text{-bipethe})$ (**8a**). Compounds **1**–**4**, **6a** and **7a** have been confirmed by X-ray crystallography. In solution compounds **1**–**4** undergo a rapid ligand-dissociation equilibrium resulting in a time-average spectrum in the ^1H NMR. In contrast, the solution equilibria for compounds **5**–**8a** are sufficiently slow such that the mono-aluminium compounds may be observed by ^1H NMR spectroscopy: $Al(^tBu)_2(OPh)(4,4\text{-bipy})$ (**6b**), $Al(^tBu)_2(OPh)(bpetha)$ (**7b**) and $Al(^tBu)_2(OPh)(bpethe)$ (**8b**). The inability to isolate $[(^tBu)_2Al(OPh)]_2(\mu\text{-pyz})$ and the relative stability of each complex is discussed with respect to the steric interactions across the bridging ligand (L) and the electronic effect on one Lewis acid–base interaction by the second Lewis acid–base interaction on the same ligand.

Introduction

Over the last decade we have been interested in the effect of Lewis acid complexation on a range of small molecules. Group 13 compounds are well known catalysts for the Friedel–Crafts reaction, in which the highly Lewis acidic center activates an alkyl or acyl halide, *via* complexation by placing a positive charge on the β-substituent (Scheme 1(a)). The increase of positive charge on the β-substituent is a general effect of the coordination of aluminium Lewis acids to organic carbonyls (Scheme 1(b))[1] and the increased acidity of coordinated water and alcohols (Scheme 1(c)).[2] Group 13 aryloxides have also been found to promote a change in regioselectivity of alkyl additions of quinonel ethers, by placing a positive charge in the γ-position of the substituent (Scheme 1(d)).[3] The presence of longer-range effects has not been as well investigated. We are interested in determining how far σ-bond donor activation extends.



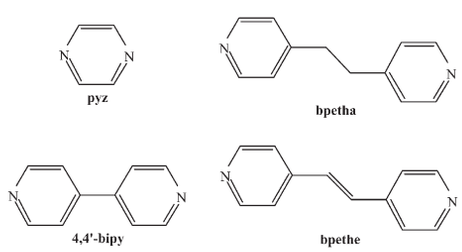
Scheme 1

Other researchers have investigated effects of multiple Lewis acid centers on the same Lewis base to enhance activity.[4] We have been interested in the result of multiple Lewis acid centers on small molecules. Part of this study has centered on the indirect activation of molecules coordinated to a weak Lewis acid (*e.g.*, Hg) by the action of a strong Lewis acid (*e.g.*, Al or Ga).[5] As an extension of this work we have been interested in the effect of binding two Lewis acid centers to different Lewis base sites on a single molecule, *i.e.*, $X_3M\text{–}L\text{–}MX_3$.

To this end, we have synthesized aluminium aryloxide and alkyl derivatives of pyrazine and bipyridines; the synthesis and structural characterization of the chosen compounds is reported herein. The choice of $AlMe_3$ and $(^tBu)_2Al(OPh)$ as the Lewis acids was based on our prior experience in determining the bond dissociation energies of Lewis acid–base complexes.[6] Pyridine-like compounds, as the bidentate ligands (L), were chosen because of the observation that pyridine complexes of the Group 13 metals are amongst the strongest Lewis acid–base interactions and thus should allow for the ready isolation of the desired complexes.[7]

Results and discussion

The reaction of $AlMe_3$ and $[(^tBu)_2Al(\mu\text{-}OPh)]_2$ with pyrazine (pyz), 4,4′-bipyridine (4,4′-bipy), 1,2-bis(4-pyridyl)ethane (bpetha) and 1,2-bis(4-pyridyl)ethylene (bpethe) (see Scheme 2[8]) yields the expected di-aluminium compounds: $(Me_3Al)_2(\mu\text{-pyz})$ (**1**), $(Me_3Al)_2(\mu\text{-}4,4'\text{-bipy})$ (**2**), $(Me_3Al)_2(\mu\text{-bpetha})$ (**3**), $(Me_3Al)_2(\mu\text{-bpethe})$ (**4**), $[(^tBu)_2Al(OPh)]_2(\mu\text{-}4,4\text{-bipy})$ (**6a**), $[(^tBu)_2Al(OPh)]_2(\mu\text{-bpetha})$ (**7a**) and $[(^tBu)_2Al(OPh)]_2(\mu\text{-bpethe})$ (**8a**). The compounds vary in color from white to orange-red depending on the ligand combination. In the case of pyrazine and $[(^tBu)_2Al(\mu\text{-}OPh)]_2$ the di-aluminium compound is not observed (even under conditions of excess $[(^tBu)_2Al(\mu\text{-}OPh)]_2$); only the monometallic complex, $(^tBu)_2Al(OPh)(pyz)$ (**5**), being isolated. The $AlMe_3$ complexes are all moisture sensitive, while the phenoxide derivatives can be handled in air for short periods of time. Although these ligands have been used extensively as linear linkage groups in crystal engineering, compounds **1**–**4**, **6a** and **7a** are the first



Scheme 2

† Electronic supplementary information (ESI) available: Elemental analysis and IR spectroscopy data; *ab initio* calculated structures and structural parameters of $AlMe_3(py)$ and $(^tBu)_2Al(OPh)(py)$. See http://www.rsc.org/suppdata/dt/b4/b410662h/

DOI: 10.1039/b410662h

structurally characterized aluminium bridging compounds for these ligands. To our knowledge, the only other Group 13 derivative is the ferrocene substituted boron derivative.[9]

The molecular structures of $(Me_3Al)_2$(μ-pyz) (**1**), $(Me_3Al)_2$(μ-4,4′-bipy) (**2**), $(Me_3Al)_2$(μ-bpetha) (**3**), $(Me_3Al)_2$(μ-bpethe) (**4**), $[(^tBu)_2Al(OPh)]_2$(μ-4,4-bipy) (**6a**) and $[(^tBu)_2Al(OPh)]_2$(μ-bpethe) (**7a**) as confirmed by X-ray crystallography are shown in Figs. 1–6; selected bond lengths and angles for compounds **1**–**4** are given in Table 1; those for compounds **6a** and **7a** along with the *ab initio* calculated structural parameters (see Experimental) for $Al(^tBu)_2(OPh)(py)$ are given in Table 2. The Al–C, Al–N and Al–O bond lengths are within the ranges expected.[10] The bond lengths within the ligands are within the ranges observed for the free ligands [pyrazine,[11] 4,4′-bipy,[12] 1,2-bis(4-pyridyl)ethane,[13] and 1,2-bis(4-pyridyl)ethylene[14]]. The only unusual structural parameter is the ethane bridge in compound **7a**. This shows a crystallographic disorder of the ethane bridge; similarly distorted bridges have been reported previously.[15,16]

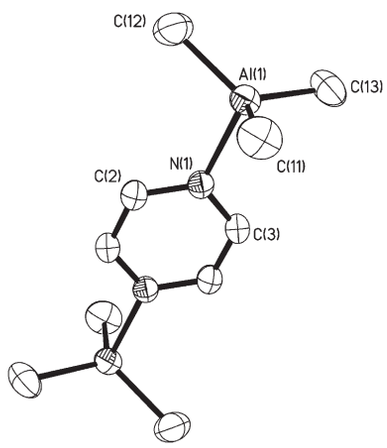


Fig. 1 Molecular structure of $(Me_3Al)_2$(μ-pyz) (**1**). Thermal ellipsoids shown at the 30% level and hydrogen atoms are omitted for clarity.

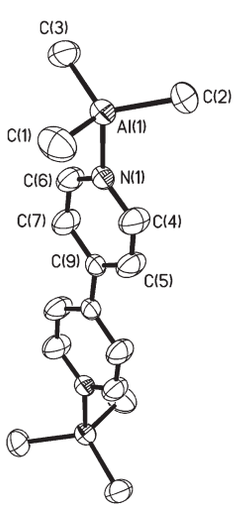


Fig. 2 Molecular structure of $(Me_3Al)_2$(μ-4,4′-bipy) (**2**). Thermal ellipsoids shown at the 30% level and hydrogen atoms are omitted for clarity.

The $AlMe_3$ moieties within the structures of compounds **1**–**4** are arranged in a staggered conformation with respect to each other (Figs. 1–4), irrespective of the identity of the bridging ligand. For compounds **2**–**4** this is the result of crystallographically imposed symmetry, but compound **1**'s conformation is not symmetry controlled (see Fig. 1). In a similar manner, compounds **6a** and **7a** adopt *anti* conformations (except for one of the independent molecules in the asymmetric unit of **7a**), without symmetry restriction (Figs. 5 and 6). Thus, the conformation around aluminium is independent of the identity of the substituents on aluminium.

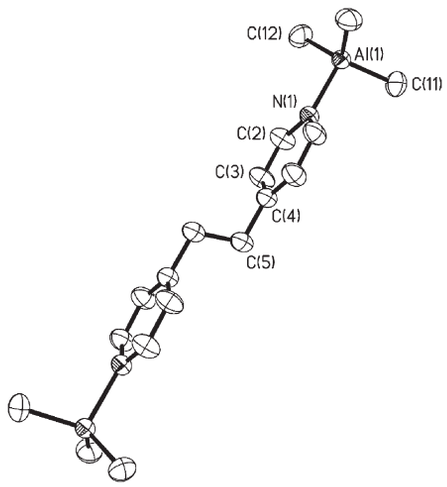


Fig. 3 Molecular structure of $(Me_3Al)_2$(μ-bpetha) (**3**). Thermal ellipsoids shown at the 30% level and hydrogen atoms are omitted for clarity.

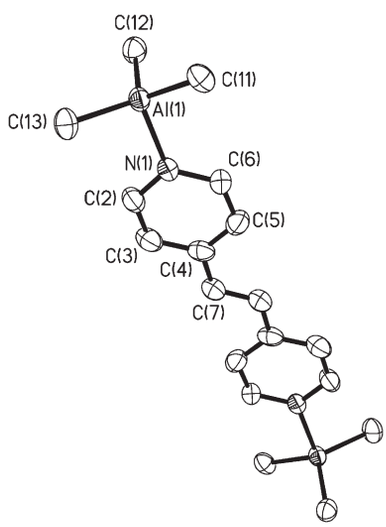


Fig. 4 Molecular structure of $(Me_3Al)_2$(μ-bpethe) (**4**). Thermal ellipsoids shown at the 30% level and hydrogen atoms are omitted for clarity.

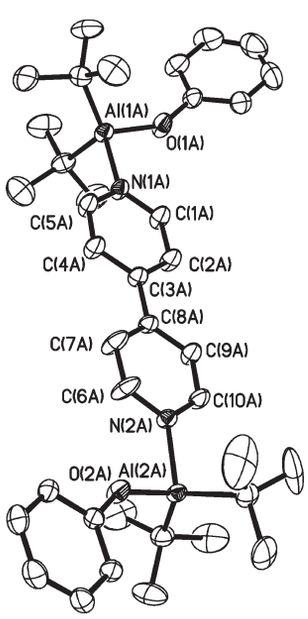


Fig. 5 Molecular structures of one of the two crystallographically independent molecules of $[(^tBu)_2Al(OPh)]_2$(μ-4,4-bipy) (**6a**). Thermal ellipsoids are shown at the 15% level and hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**–**4** as determined from X-ray crystallography in comparison with the calculated structural parameters for $AlMe_3(py)$

Compound	$(Me_3Al)_2(\mu$-pyz) (**1**)	$(Me_3Al)_2(\mu$-4,4′-bipy) (**2**)	$(Me_3Al)_2(\mu$-bpetha) (**3**)	$(Me_3Al)_2(\mu$-bpethe) (**4**)	$AlMe_3(py)$[a]
Al–N	2.073(2)	2.032(2)	2.020(2)	2.033(2)	2.115
Al–C	1.960(3)–1.963(3)	1.966(3)–1.973(3)	1.971(3), 1.972(2)	1.974(3)–1.982(3)	2.001–2.002
C–Al–N	100.2(1)–102.0(1)	100.5(1)–104.0(1)	101.9(1), 103.94(7)	101.4(1)–103.7(1)	101.14–102.46
C–Al–C	115.2(2)–118.3(2)	114.3(2)–116.4(2)	115.30(8), 114.1(2)	113.6(1)–116.5(2)	115.99–116.09

[a] Calculated structure, see Experimental section.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **6a** and **7a** as determined from X-ray crystallography in comparison with the calculated structural parameters for $(^tBu)_2Al(OPh)(py)$

	$[(^tBu)_2Al(OPh)]_2(\mu$-4,4′-bipy) (**6a**)			
	Molecule 1[a]	Molecule 2[b]	$[(^tBu)_2Al(OPh)]_2(\mu$-bpetha) (**7a**)	$(^tBu)_2Al(OPh)(py)$[c]
Al–O	1.719(5), 1.755(4)	1.732(4)	1.703(4), 1.735(3)	1.727
Al–N	2.004(5), 2.000(5)	2.005(4)	1.998(3), 2.000(3)	2.029
Al–C	1.962(7)–1.980(7)	1.997(7), 1.981(7)	1.964(5)–1.982(6)	2.008, 2.009
O–C	1.327(8), 1.348(6)	1.355(6)	1.300(6), 1.334(5)	1.348
O–Al–C	110.0(3)–114.3(3)	112.0(3), 112.2(3)	108.3(2)–113.8(2)	112.7
C–Al–C	122.3(3), 123.1(3)	122.9(4)	121.3(2), 121.4(3)	121.4
C–Al–N	102.3(3)–107.7(3)	103.5(2), 105.9(3)	103.9(2)–108.5(2)	104.1, 106.3
O–Al–N	95.6(2), 94.8(2)	96.1(2)	96.2(2), 102.6(2)	95.9
C–O–Al	147.9(5), 141.4(4)	138.9(4)	162.4(4), 146.5(3)	159.1

[a] Whole molecule in asymmetric unit. [b] Half of a centrosymmetric molecule in asymmetric unit. [c] Calculated structure, see Experimental section.

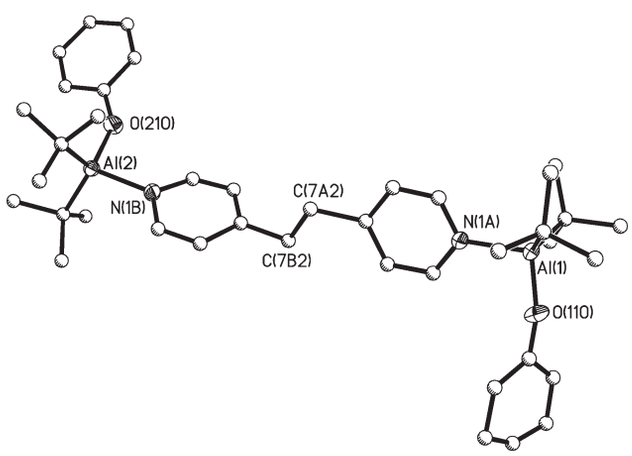


Fig. 6 Molecular structure of $[(^tBu)_2Al(OPh)]_2(\mu$-bpetha) (**7a**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted and carbon atoms shown as shaded spheres for clarity.

In a similar manner, as may be seen from Figs. 2 and 5, the 4,4-bipy rings in compounds **2** and **6a** are coplanar (as are the rings in compound **4**, see Fig. 4), suggesting that the substituents on the aluminium appear to have little effect on the geometry of the ligand. However, the bridging bpetha ligands in compounds **3** and **7a** adopt different geometries, possibly as a result of the lack of conjugation between the ligand rings allowing for more flexible packing of the terminal $AlR_{3-x}(OR)_x$ groups (see Figs. 3 and 6). In both compounds the two pyridine rings adopt *anti* conformations about the central C_2 unit, rather than a *gauche* conformation.[15] However, while the rings in compound **3** are coplanar (although not with the C_2H_4 unit) in a manner that has been observed previously,[17] the bpetha ligand in compound **7a** adopts a twist geometry reminiscent of the orientations reported for the bis(4-pyridyl)propane ligand.[16,18]

While we do not have directly analogous monomeric derivatives for comparison, it is worth noting that the *ab initio* calculated structure of $Al(^tBu)_2(OPh)(py)$ faithfully reproduces the structural features of compounds **6a** and **7a**, in particular the Al–N distances, the terminal phenoxide Al–O distances and Al–O–C angles (Table 2). A similar comparison may be made between the observed X-ray structure data for compounds **1**–**4** and the calculated structural parameters for $AlMe_3(py)$, see Table 1. This suggests that the presence of the second Lewis acid center (in the di-aluminium derivatives) does not alter the structural aspects of the other Lewis acid–base interaction. However, ^1H and ^{13}C NMR spectroscopic measurements suggest that there is an effect of one Lewis acid on the second within the same molecule.

The solution ^1H and ^{13}C NMR spectra of compounds **1**–**4** show a single set of resonances due to the ligand and $AlMe_3$ groups. The chemical shifts are temperature-dependant consistent with the presence of solution equilibria typical of such Group 13 Lewis acid–base complexes. An indication of the extent of dissociation may be obtained from the ^{13}C NMR signal of the Al–CH_3 group. We have shown that the ^{13}C NMR shift of the aluminium methyl group in $AlMe_3L$ is controlled by the steric bulk of the ligand (L) and as a consequence the equilibrium constant (K_{eq} in eqn. (1)).[19]

$$AlMe_3L \overset{K_{eq}}{\rightleftharpoons} AlMe_3 + L \quad (1)$$

For a series of compounds with identical steric bulk of L, the ^{13}C NMR shift of the aluminium methyl group will be determined by the position of the equilibrium (eqn. (1)).[20] Thus for the series of compounds **1**–**4** the ^{13}C NMR shift is going to be identical for the complex. However, due to the equilibrium (eqn. (1)) the actual observed ^{13}C NMR shift will be a time average between uncomplexed $AlMe_3$ and $AlMe_3(L)$. The value for K_{eq} can be calculated if the shifts of the free and complexed $AlMe_3$ are known. Unfortunately, since the equilibrium is sufficiently facile even at low temperature we can only compare relative shifts as a measure of relative K_{eq} values. However, from the ^{13}C NMR shifts of the methyl groups (see Experimental section) it may be concluded that at the same temperatures and concentrations, the order of the extent of ligand dissociation follows the trend **1** (pyz) > **2** (4.4′-bipy) > **3** (bpetha) ≈ **4** (bpethe), *i.e.*, K_1 is larger for compound **1** than compound **4**. Thus the BDE for the second Al–N bond is less in compound **1** than in compound **4**. We can conclude that the greater the σ-bond distance between the two nitrogen (or aluminium) atoms the less the deactivation of one Al–N bond by the other Al–N interaction. The similarity of compounds **3** and **4** confirms that there is no effect of unsaturation but rather σ-bond distance is

the important parameter in determining the communication between remote Lewis acid centers (see below).

In contrast to that observed for the $AlMe_3$ complexes in solution, the ^1H NMR spectrum of compound **5** shows peaks associated with free pyrazine and $[(^tBu)_2Al(\mu\text{-}OPh)]_2$. In a similar manner, solution NMR for compounds **6a**–**8a** show multiple sets of resonances associated with the 2 : 1 complexes (*i.e.*, **6a**–**8a**), the 1 : 1 complexes [*i.e.*, $Al(^tBu)_2(OPh)(L)$] (**6b**–**8b**), the free ligand and $[(^tBu)_2Al(\mu\text{-}OPh)]_2$. For example, the solution ^1H and ^{13}C NMR spectra of compound **6a** dissolved in $CDCl_3$ shows four sets of resonances (Fig. 7), the first can be assigned to the Lewis acid–base complex (**6a**), while the other two are consistent with uncoordinated 4,4-bipy and the dimeric species $[(^tBu)_2Al(\mu\text{-}OPh)]_2$. The fourth set of resonances is assigned to the formation of the new complex, $(^tBu)_2Al(OPh)(4,4\text{-bipy})$ (**6b**). Variable-temperature NMR confirms that equilibria are present, although the presence of the multiple sets of resonances (as opposed to a time average signal) indicates that the reaction is slow on the NMR time scale (10^{-5} s). Based upon the ^1H NMR spectra {and the lack of observation of $[(^tBu)_2Al(OPh)]_2(\mu\text{-pyz})$} the relative order for the K_1 (*cf.*, Scheme 3) to be **1** (pyz) ≪ **2** (4.4′-bipy) < **3** (bpetha) ≈ **4** (bpethe), *i.e.*, the extent of ligand dissociation is greater for **1** than compound **4**. Both of these trends are consistent with a σ induction effect of the first Lewis acid on the second Lewis base (nitrogen) site.

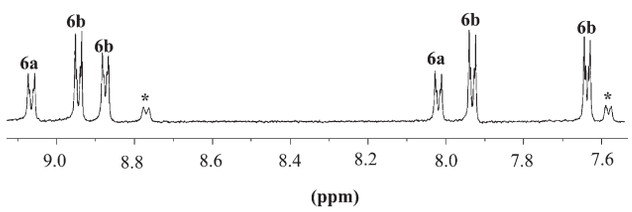
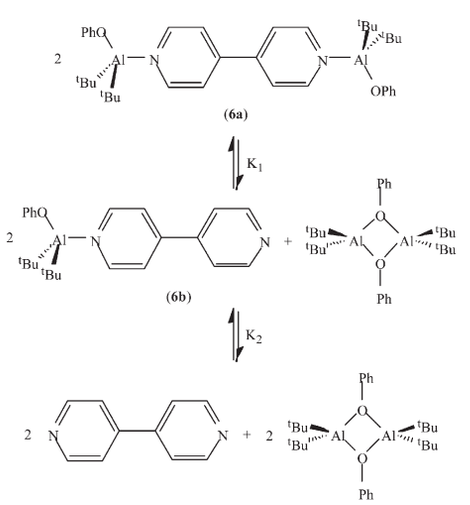


Fig. 7 ^1H NMR spectra of the 4,4′-bipy resonances, showing the presence of $[(^tBu)_2Al(OPh)]_2(\mu\text{-}4,4'\text{-bipy})$ (**6a**), $(^tBu)_2Al(OPh)(4,4'\text{-bipy})$ (**6b**) and uncoordinated 4,4′-bipy (*).



Scheme 3

The concentration dependence of the equilibria is confirmed from the UV-visible spectra. For example, compound **6a** is bright orange, but when the sample is dilute enough to see absorptions in the UV/visible, the spectra of shows two peaks at 271 and 278 nm which are due to uncoordinated 4,4-bipy in solution.

Experimental

All reactions were performed under an inert atmosphere of purified nitrogen using standard inert-atmosphere techniques. Solvents were distilled and degassed prior to use. $CDCl_3$ was dried by storage over activated 4 Å Linde molecular sieves. Pyrazine, 4,4′-bipyridyl, 1,2-bis(4-pyridyl)ethane and *trans*-1,2-bis(4-pyridyl)ethylene were purchased from Sigma–Aldrich and used as received. $[(^tBu)_2Al(\mu\text{-}OPh)]_2$ was prepared as previously reported.[21] Solution NMR spectra were recorded on a Bruker Avance 400 and 500 spectrometer using either $CDCl_3$ or C_6D_6 as internal locks. Proton and carbon spectra were collected using a 5 mm broadband probe. Chemical shifts are relative to TMS (^1H and ^{13}C). All spectra are reported at 298 K unless otherwise stated. Melting points were determined in sealed capillaries and are uncorrected. IR spectra were recorded on a Thermo Nicolet FTIR spectrometer. IR samples were analyzed using a diamond cell ATR. Elemental analysis was performed by Prevalere Life Sciences, Inc., Whitesboro, NY.

$(Me_3Al)_2(\mu\text{-pyz})$ (1)

$AlMe_3$ (0.50 mL, 5.2 mmol) was injected into a cooled (−78 °C) solution of pyrazine (0.209 g, 2.61 mmol) in hexane (50 mL). The solution was allowed to warm to room temperature, and was stirred for an additional 1.5 h. All volatiles were then removed *in vacuo* leaving a yellow powder. Yield: 0.56 g, 96%. Mp: 90 °C (decomp.). ^1H NMR ($CDCl_3$): δ 9.01 (4H, s, NC*H*), −0.72 (18H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.38 (N*C*), −8.45 (*C*H_3).

$(Me_3Al)_2(\mu\text{-}4,4'\text{-bipy})$ (2)

The compound was prepared by a method analogous to that for compound **1** using $AlMe_3$ (0.50 mL, 5.2 mmol) and 4,4′-bipyridyl (0.407 g, 2.61 mmol). All volatiles were removed *in vacuo* leaving an off-white powder. X-Ray quality crystals were obtained through slow evaporation of a $CDCl_3$ solution. Yield: 0.77 g, 98%. Mp: 135 °C (decomp.). ^1H NMR ($CDCl_3$): δ 8.84 [4H, dd, J(H–H) = 3.3 Hz, J(H–H) = 6.6 Hz, NC*H*], 7.84 [4H, dd, J(H–H) = 3.3 Hz, J(H–H) = 6.6 Hz, C*H*], −0.75 (18H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.6 (N*C*), 147.7 (C-*ipso*), 123.4 (NC*C*), −8.5 (*C*H_3).

$(Me_3Al)_2(\mu\text{-bpetha})$ (3)

The compound was prepared by a method analogous to that for compound **1** using $AlMe_3$ (0.50 mL, 5.2 mmol) and 1,2-bis(4-pyridyl)ethane (0.480 g, 2.61 mmol). All volatiles were removed *in vacuo* leaving a white powder. Yield: 0.83 g, 97%. Mp: 138 °C (decomp.). ^1H NMR ($CDCl_3$): δ 8.56 [4H, dd, J(H–H) = 3.4 Hz, J(H–H) = 6.5 Hz, NC*H*], 7.42 [4H, dd, J(H–H) = 3.4 Hz, J(H–H) = 6.5 Hz, NCC*H*], 3.14 (4H, s, CH_2) −0.80 (18H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.8 (C-*ipso*), 147.5 (N*C*), 125.2 (NC*C*), 35.2 (*C*H_2), −8.6 (*C*H_3).

$(Me_3Al)_2(\mu\text{-bpethe})$ (4)

The compound was prepared by a method analogous to that for compound **1** using $AlMe_3$ (0.50 mL, 5.2 mmol) and 1,2-bis(4-pyridyl)ethylene (0.475 g, 2.61 mmol). All volatiles were removed in vacuum leaving a pale-yellow powder. Yield: 0.817 g, 96%. Mp: 155 °C (decomp.). ^1H NMR ($CDCl_3$): δ 8.66 [4H, dd, J(H–H) = 2.8 Hz, J(H–H) = 5.3 Hz, NC*H*], 7.70 [4H, dd, J(H–H) = 2.8 Hz, J(H–H) = 5.3 Hz, NCC*H*], 7.40 (2H, s, C*H*), −0.77 (18H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.0 (N*C*), 146.5 (C-*ipso*), 131.9 (NC*C*), 122.9 (*C*H), −8.6 (*C*H_3).

$Al(^tBu)_2(OPh)(pyz)$ (5)

$[(^tBu)_2Al(\mu\text{-}OPh)]_2$ (0.500 g, 1.07 mmol) and pyrazine (0.085 g, 1.07 mmol) were dissolved in hexane (70 mL). The solution was stirred for 1.5 h yielding a bright yellow solution. All volatiles were removed *in vacuo* yielding a yellow powder. Yield: 0.604 g, 90%. Mp: 93 °C (decomp.). ^1H NMR (C_6D_6): δ 8.05 [2H, dd, J(H–H) = 1.5 Hz, J(H–H) = 4.5 Hz, NC*H*], 7.85 [2H, dd, J(H–H) = 1.5 Hz, J(H–H) = 4.5 Hz, NC*H*], 7.30 (2H, m, *o*-C*H*), 7.15 (2H, m, *p*-C*H*), 6.93 (1H, m, *p*-C*H*), 0.30 [18H, s, C(CH_3)$_3$].

$[(^tBu)_2Al(OPh)]_2(\mu$-4,4-bipy) (6a)

A 100 mL round bottom flask was charged with $[(^tBu)_2Al(\mu$-OPh)$]_2$ (0.25 g, 0.53 mmol) and 4,4-bipy (0.16 g, 1.06 mmol). After 5 minutes, the reactants changed color from white to orange. CH_2Cl_2 (30 mL) was added to the reaction mixture, giving a bright orange solution that was stirred for 18 h and cooled to −30 °C. After 20 days, all solvent was removed and the resulting orange oil was dissolved degassed toluene (15 mL). This was cooled to −30 °C for two days giving bright orange crystals suitable for single crystal X-ray analysis. Yield: 0.326 g, 98%. ^{1}H NMR ($CDCl_3$): δ 9.07 [2H, dd, J(H–H) = 3.6 Hz, J(H–H) = 6.6 Hz, 2-C*H*], 8.02 [2H, dd, J(H–H) = 3.6 Hz, J(H–H) = 6.6 Hz, 3-C*H*], 7.21 (5H, m, C*H*), 0.95 [18H, s, C(CH_3)$_3$]. ^{13}C CPMAS: δ 165.4 (O*C*), 152.1 (2-*C*H), 133.7 (3-*C*H), 125.6 (4-*C*H) 125.4 (OC*C*H), 35.8 [C(*C*H$_3$)$_3$]. ^{27}Al MAS NMR: δ 52.2, 27.0, 5.8 ($W_{1/2}$ = 6760 Hz).

$[(^tBu)_2Al(OPh)$(4,4-bipy)] (6b)

^{1}H NMR ($CDCl_3$): δ 8.95 [2H, dd, J(H–H) = 3.5 Hz, J(H–H) = 6.7 Hz, 2-C*H*], 8.88 [2H, dd, J(H–H) = 2.9 Hz, J(H–H) = 6.1 Hz, 7-C*H*], 7.94 [2H, dd, J(H–H) = 3.5 Hz, J(H–H) = 6.7 Hz, 3-C*H*], 7.64 [2H, dd, J(H–H) = 2.9 Hz, J(H–H) = 6.1 Hz, 6-C*H*], 6.86 (2H, m, OC*H*), 6.85 (2H, m, *m*-C*H*), 6.77 (1H, m, *p*-C*H*), 0.96 [18H, s, C(CH_3)$_3$].

$[(^tBu)_2Al(OPh)]_2(\mu$-bpetha) (7a)

$[(^tBu)_2Al(\mu$-OPh$)]_2$ (0.500 g, 1.07 mmol) and 1,2-bis(4-pyridyl)-ethane (0.200 g, 1.07 mmol) were dissolved in hexane (70 mL). The solution was stirred for 1.5 h, during which time a precipitant was observed. The supernatant was decanted and the precipitant dried *in vacuo* leaving a white solid. The solid was dissolved in toluene and kept at −30 °C for 10 days giving X-ray quality crystals. Yield: 0.68 g, 96%. Mp: 125 °C. ^{1}H NMR ($CDCl_3$): δ 8.75 [4H, dd, J(H–H) = 2.8 Hz, J(H–H) = 5.3 Hz, N–C*H*], 7.50 [4H, dd, J(H–H) = 2.8 Hz, J(H–H) = 5.3 Hz, NCC*H*], 7.18 (2H, m, *o*-C*H*), 6.82 (2H, m, *m*-C*H*), 6.76 (1H, m, *p*-C*H*) 3.23 (4H, s, CH_2) 0.90 [18H, s, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.3 (O*C*), 154.6 (C-*ipso*), 147.7 (N*C*), 129.3 (*o*-*C*H), 125.3 (NC*C*H), 119.7 (*m*-*C*H), 117.6 (*p*-*C*H), 35.2 (*C*H$_2$), 30.4 [C(*C*H$_3$)$_3$], 14.9 [*C*(CH$_3$)$_3$].

$(^tBu)_2Al(OPh)$(bpetha) (7b)

^{1}H NMR ($CDCl_3$): δ 8.68 [2 H, dd, J(H–H) = 3.5 Hz, J(H–H) = 6.6 Hz, N–C*H*], 8.53 [2H, m, J(H–H) = 5.8 Hz, N–C*H*], 7.42 [2 H, m, J(H–H) = 6.6 Hz, NCC*H*], 7.18 (2H, m, *o*-C*H*), 6.81 (2H, m, *m*-C*H*), 6.77 (1H, m, *p*-C*H*), 3.12 (2 H, m, CH_2), 3.03 (2 H, m, CH_2), 0.89 [18H, s, C(CH_3)$_3$].

$[(^tBu)_2Al(OPh)]_2(\mu$-bpethe) (8a)

The compound was prepared by a method analogous to that for compound **7** using $[(^tBu)_2Al(\mu$-OPh$)]_2$ (0.500 g, 1.07 mmol) and 1,2-bis(4-pyridyl)ethylene (0.195 g, 1.07 mmol). The supernatant was decanted and the precipitant dried in vacuum leaving a red–orange solid. Yield: 0.683 g, 98%. Mp: 135 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.86 [4H, dd, J(H–H) = 3.7 Hz, J(H–H) = 6.7 Hz, N–C*H*], 7.81 [4H, dd, J(H–H) = 3.7 Hz, J(H–H) = 6.7 Hz, N–C–C*H*], 7.48 (2H, s, C*H*), 7.20 (2H, m, *o*-C*H*), 6.83 (2H, m, *m*-C*H*), 6.77 (1H, m, *p*-C*H*), 0.93 [18H, s, (CH_3)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.3 (O*C*), 148.1 (N*C*), 147.2 (C-*ipso*), 132.4 (*C*H), 129.3 (*o*-*C*H), 123.1 (NC*C*H), 119.7 (*m*-*C*H), 117.7 (*p*-*C*H), 30.4 [C(*C*H$_3$)$_3$], 15.1 [*C*(CH$_3$)$_3$].

$(^tBu)_2Al(OPh)$(bpethe) (8b)

^{1}H NMR ($CDCl_3$): δ 8.80 [2 H, dd, J(H–H) = 1.3 Hz, J(H–H) = 6.6 Hz, N–C*H*], 8.73 [2H, dd, J(H–H) = 2.2 Hz, J(H–H) = 4.4 Hz, 7-C*H*], 7.77 [2 H, dd, J(H–H) = 3.2 Hz, J(H–H) =

Table 3 Summary of X-ray diffraction data

Compound	$(Me_3Al)_2$(pyz) (**1**)	$(Me_3Al)_2(\mu$-4,4′-bipy) (**2**)	$(Me_3Al)_2(\mu$-bpetha) (**3**)	$(Me_3Al)_2(\mu$-bpethe) (**4**)	$[(^tBu)_2Al(OPh)]_2(\mu$-4,4′-bipy) (**6a**)	$[(^tBu)_2Al(OPh)]_2(\mu$-bpetha) (**7a**)
Empirical formula	$C_{10}H_{22}Al_2N_2$	$C_{16}H_{26}Al_2N_2$	$C_{18}H_{30}Al_2N_2$	$C_{18}H_{28}Al_2N_2$	$C_{38}H_{54}Al_2N_2O_2$	$C_{40}H_{58}Al_2N_2O_2$
M	224.26	300.25	328.40	326.38	624.79	652.87
Space group	$P\bar{1}$	$P2_1/n$	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	6.474(1)	6.852(1)	15.685(3)	6.4011(6)	8.978(2)	15.005(3)
b/Å	7.163(1)	8.876(2)	10.732(2)	7.3288(7)	14.490(3)	18.916(4)
c/Å	8.313(2)	16.565(3)	6.536(1)	11.199(1)	23.729(5)	15.520(3)
α/°	82.28(3)			97.76(1)	77.02(3)	
β/°	89.50(3)	100.56(3)	103.38(3)	92.51(1)	84.27(3)	110.19(3)
γ/°	81.10(3)			102.63(1)	83.07(3)	
V/Å^3	377.4(1)	990.5(3)	1070.4(4)	506.48(8)	2978.0(10)	4134(1)
Z	1	2	2	1	3	4
D_c/g cm^{-3}	0.987	1.007	1.019	1.070	1.045	1.049
μ_c/mm^{-1}	0.17	0.14	0.14	0.14	0.10	0.10
No. collected	4492	4116	6559	6292	13,656	17990
No. indep.	1796	1423	1396	2428	8,558	5964
No. obsd. ($\|F_o\| > 4.0\sigma\|F_o\|$)	1277	1157	1144	1952	3389	3113
Weighting scheme parameters	SHELXTL 0.0853, 0.0564	SHELXTL 0.0693, 0.2218	SHELXTL 0.1045, 0.1868	SHELXTL 0.1167, 0.1867	SHELXTL 0.1, 0	SHELXTL 0.1007 2.5803
R^a	0.0469	0.0433	0.0467	0.0752	0.0819	0.0635
$R_w{}^a$	0.1299	0.1228	0.0573	0.2167	0.1845	0.1643

^{a} $R = \Sigma|F_o - F_c|/\Sigma F_o$; $R_w = \{\Sigma[\{w(F_o^2 - F_c^2)^2\}/\{w(F_o^2)^2\}]\}^{1/2}$.

6.6 Hz, NCC*H*], 7.49 (2H, s, C*H*), 7.20 (2H, m, *o*-C*H*), 6.84 (2H, m, *m*-C*H*), 6.77 (1H, m, *p*-C*H*), 0.94 [18H, s, C(CH_3)$_3$].

Crystallographic studies

Single crystal diffraction data for compounds **1**–**4**, **6a** and **7a** were collected at ambient temperature on a Bruker CCD SMART system, equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. The structures were solved using the direct methods program XS[22] and difference Fourier maps and refined by using full-matrix least squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions and allowed to ride on the attached carbon atoms [*d*(C–H) = 0.95 Å]. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 3).

CCDC reference numbers 244715–244720.

See http://www.rsc.org/suppdata/dt/b4/b410662h/ for crystallographic data in CIF or other electronic format.

Computational methods

Density functional calculations on $AlMe_3$(py) and Al(^{t}Bu)$_2$(OPh)(py) were carried out using a Gaussian-98 suite.[23] Complete geometry optimizations were performed at B3LYP[24] level using the 6–31G** basis set for C and H and Stuttgart RLC ECP basis set for Al. Vibrational frequencies were then evaluated to verify the existence of the true potential minimum and to determine zero-point energies. Molecular mechanics calculations were performed using Spartan (02 Windows) running on a PC. The final structures are optimized using molecular mechanics method MMFF94.

Acknowledgements

Financial support for this work is provided by the ACS-PRF and NSF (CHE-0243575). The Bruker CCD Smart System Diffractometer of the Texas Center for Crystallography at Rice University was funded by the Robert A. Welch Foundation and the Bruker Avance 200 NMR spectrometer was purchased with funds from ONR Grant N00014-96-1-1146.

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