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Aluminium compounds containing bidentate ligands: chelate ring size and rigid conformation effects

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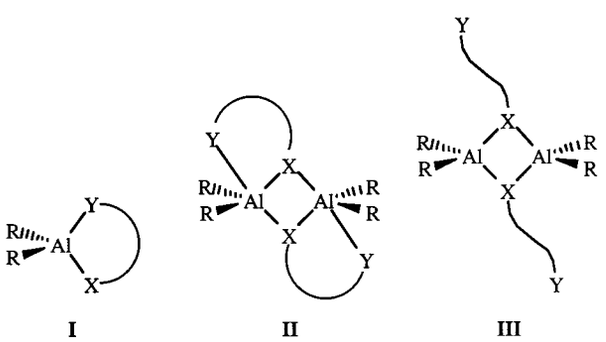
Reaction of $Al(^tBu)_3$ with 2-hydroxypyridine, 2-pyridinemethanol, 8-hydroxyquinoline and 8-quinolinemethanol, yielded $[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ **1**, $(^tBu)_2Al(OCH_2\text{-}2\text{-}C_5H_4N)$ **2**, $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3** and $(^tBu)_2Al(OCH_2\text{-}8\text{-}C_9H_6N)$ **4**, respectively. The isobutyl derivative, $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**, was prepared in an analogous manner. The molecular structures of compounds **1**, **3** and **5** have been determined by X-ray crystallography. Compounds **2**–**4** are monomeric with five (**2** and **3**) and six (**4**) membered chelate heterocyclic rings. In contrast, compound **1** and **5** exist as bridged dimers. The isobutyl groups on each of the aluminium centers in compound **5** are in an *anti* conformation both in the solid state and solution. The activation energy for the interconversion of the two *anti* enantiomers has been determined [$\Delta G^{\ddagger} = 68.5(4)$ kJ mol^{-1}]. The formation of monomeric chelate compounds for compounds **2**–**4**, rather than alkoxide bridged dimers as is found for $(^iBu)_2Al(OCH_2\text{-}2\text{-}C_5H_4N)$ and **5** is found to be due to a combination of the steric bulk of the aluminium alkyl and the rigid conformation of the pyridine and quinoline ligands.

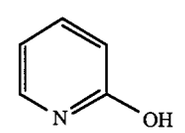
Introduction

We have recently become interested in developing an understanding of the geometric factors that control the extent of oligomerization and coordination number at the aluminium center in compounds with non-delocalized ligands containing both anionic and neutral Lewis base termini. In particular, what controls the relative stability of a monomer **I** *versus* a dimer **II**.[1] Compounds of this general type are known with a wide range of substituents, *e.g.*, X = O, S, NR′ or CH_2; Y = OR′, SR′ or NR′$_2$, where R′ = alkyl.[2] Our studies have shown that the strength of bonding at the fifth coordination site is highly dependent on steric bulk of the substituents at aluminium (R) and the neutral Lewis base donor (R′).[1] However, in the case of alkoxide-based ligands (*i.e.*, X = O) increased steric bulk does not result in the formation of a monomer (**I**); a four-coordinate dimer is formed instead (**III**).

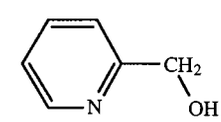


I **II** **III**

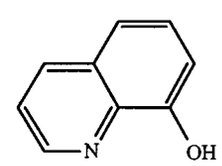
Based on these results it would appear that the Lewis base termini (Y = ether or thioether) are insufficiently basic to cleave the $Al(\mu\text{-}O)_2Al$ core of a dimeric alkoxide to give monomeric chelate compounds. We have previously observed a similar effect for aluminium aryloxides,[3] and have demonstrated that pyridine and related ligands react with oligomeric aluminium compounds to yield monomers. Thus, use of pyridine (and quinoline[4]) based ligands (**IV**–**VII**) should result in the formation of monomeric compounds given sufficient steric bulk at aluminium.



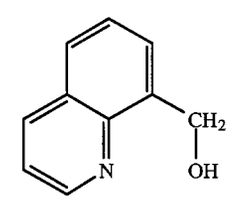
IV



V



VI



VII

Results and discussion

Reaction of $Al(^tBu)_3$ with 2-hydroxypyridine **IV**, 2-pyridinemethanol **V**, 8-hydroxyquinoline **VI** and 8-quinolinemethanol **VII**, yields $[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ **1**, $(^tBu)_2Al(OCH_2\text{-}2\text{-}C_5H_4N)$ **2**, $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3** and $(^tBu)_2Al(OCH_2\text{-}8\text{-}C_9H_6N)$ **4**, respectively. The isobutyl derivative of hydroxyquinoline **VI**, $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**, is prepared in an analogous manner. Compounds **1**–**5** have been characterized by ^1H, ^{13}C and ^{27}Al NMR spectroscopy, and MS weight (see Experimental section). The ^{27}Al NMR spectra for compounds **1**–**4** all consist of a broad resonance (δ 120–140) indicative of a four-coordinate aluminium in a $AlONC_2$ coordination environment.[5] In contrast, the ^{27}Al NMR spectrum for $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5** (δ 81) is similar to that observed for other five-coordinate compounds with AlO_2NC_2 coordination.[1,2] Compounds **3** and **5** are both yellow in color with an associated absorbance in the visible region [λ = 384 (**3**), 375 nm (**5**)], which appears to be essentially independent of the coordination about aluminium. Similar spectra have been observed for other quinoline compounds of aluminium.[6] The solid state molecular structures of compounds **1**, **3** and **5** have been determined by X-ray crystallography.

The molecular structure of $[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ **1** is

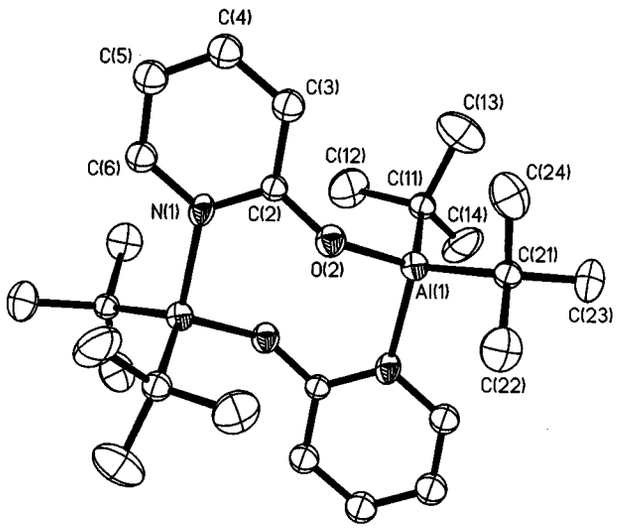
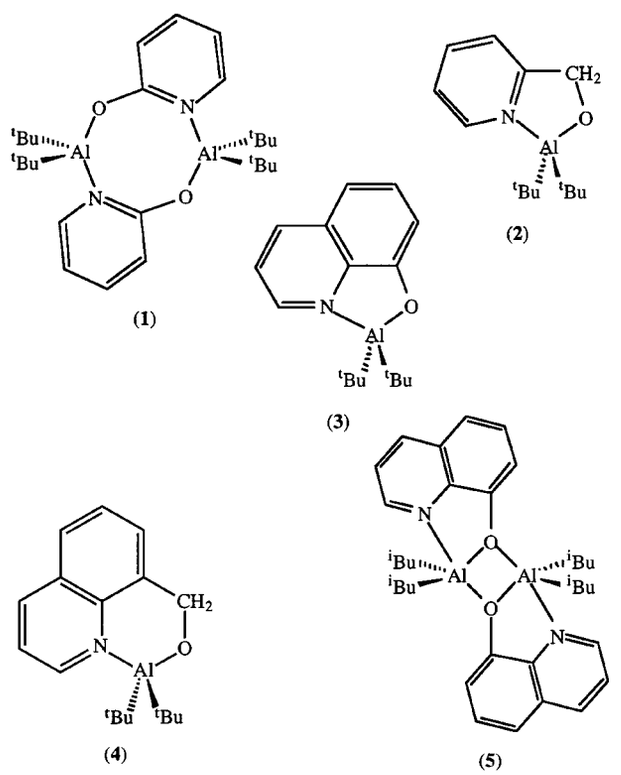


Fig. 1 Molecular structure of $[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ **1**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.



shown in Fig. 1; selected bond lengths and angles are given in Table 1. Compound **1** exists as a centrosymmetric molecule in which both the oxygen and nitrogen donor atoms of the hydroxypyridine ligands bridge the two $Al(^tBu)_2$ moieties, resulting in an eight membered $Al_2O_2C_2N_2$ cyclic core. The Al(1)–O(2) and Al(1)–N(1a) bond lengths [1.774(5) and 1.991(2) Å, respectively] are shorter than the range expected for simple Lewis acid–base complexes (2.0–2.1 Å).[7] Although the pyridine rings are stacked in the crystal lattice, the inter-ring distance (>4.5 Å) is greater than that expected for any significant electronic interaction (*i.e.*, 3.4 Å).[8]

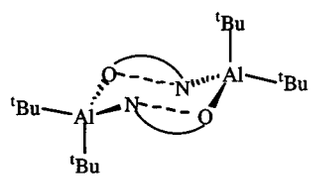
As a bridging ligand hydroxypyridine is isolobal to a carboxylate, and the structure of compound **1** is similar to those we have observed for $[R_2Al(\mu\text{-}O_2CR')]_2$. In fact, the ligand bite distance [Al(1)···Al(1a) = 4.14 Å] is within the range previously observed for alkylaluminium carboxylates [3.26–4.46 Å].[9,10] Furthermore, as with the carboxylate analogs, the eight-membered ring in $[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ adopts a chair-like conformation (**VIII**).

Table 1 Selected bond lengths (Å) and angles (°) in $[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ **1**

Al(1)–O(2)	1.774(5)	Al(1)–N(1a)	1.991(2)
Al(1)–C(11)	1.963(8)	Al(1)–C(21)	1.990(8)
O(2)–C(2)	1.296(9)		
O(2)–Al(1)–N(1a)	102.4(1)	O(2)–Al(1)–C(11)	113.3(3)
O(2)–Al(1)–C(21)	104.8(3)	C(11)–Al(1)–C(21)	120.3(3)
C(11)–Al(1)–N(1a)	106.1(2)	C(21)–Al(1)–N(1a)	108.5(2)
Al(1)–O(2)–C(2)	140.0(4)		

Table 2 Selected bond lengths (Å) and angles (°) in $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3**

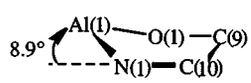
Al(1)–O(1)	1.806(4)	Al(1)–N(1)	1.979(3)
Al(1)–C(11)	1.974(6)	Al(1)–C(21)	1.937(6)
O(1)–C(9)	1.327(5)		
O(1)–Al(1)–N(1)	85.3(2)	O(1)–Al(1)–C(11)	112.2(2)
O(1)–Al(1)–C(21)	111.1(2)	N(1)–Al(1)–C(11)	106.4(2)
N(1)–Al(1)–C(21)	112.1(2)	C(11)–Al(1)–C(21)	123.2(2)
Al(1)–O(1)–C(9)	114.5(3)	Al(1)–N(1)–C(2)	132.2(3)
Al(1)–N(1)–C(10)	108.6(3)	C(2)–N(1)–C(10)	119.1(4)



VIII

Similar chair-like conformations have been observed for the gallium diphenylphosphinate compounds $[R_2Ga(\mu\text{-}O_2PPh_2)]_2$.[11] The puckering of the $Al_2O_2C_2N_2$ ring may be considered to be as a result of folding of the eight-membered ring along the two inter-ligand O···N vectors. The extent of folding (θ_{ring}) is defined as the angle between the AlON planes and the $O_2C_2N_2$ plane. We have previously demonstrated that there exists a correlation between the extent of the puckering of the $Al_2O_4C_2$ ring in aluminium carboxylates with the steric bulk of the carboxylate alkyl substituent, R.[9] However, in the absence of steric interactions, the "ideal" folding angle (θ_{ring}) should be *ca.* 130°. The fold angle in $[(^tBu)_2Al(\mu\text{-}Opy)]_2$ (127.4°) is consistent with the hydroxypyridine ligand being sterically similar to formate, $[O_2CH]^-$.

The molecular structure of $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3** is shown in Fig. 2; selected bond lengths and angles are given in Table 2. Unlike $[R_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ (R = ^{i}Bu, Et, see below), compound **3** exists as a monomer with no significant intermolecular contacts. The Al(1)–O(1) and Al(1)–N(1) bond lengths [1.806(4) and 1.979(3) Å, respectively] are typical of such interactions,[12] while the coordination about aluminium is distorted from an ideal tetrahedral geometry due to the small bite angle of the 8-quinolinol ligand [85.3(2)°]. Although the 8-quinolinol moiety is planar, the Al(1)–N(1)–C(10)–C(9)–O(1) ring is puckered (**IX**) as demonstrated by the aluminium being 0.15 Å out of the N(1)–C(10)–C(9)–O(1) plane, presumably in order to minimize the ring strain.



IX

It is interesting to note that despite the extended π system the crystal packing of compound **3** is not dominated by π···π stacking interactions. Instead, the molecules are stacked

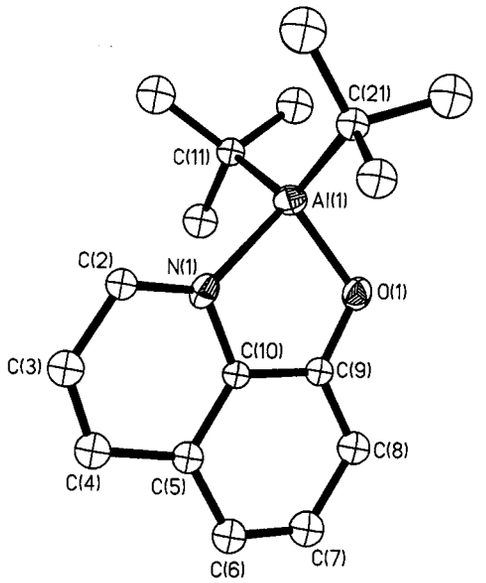


Fig. 2 Molecular structure of $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3**. Thermal ellipsoids shown at the 20% level, and hydrogen atoms are omitted for clarity.

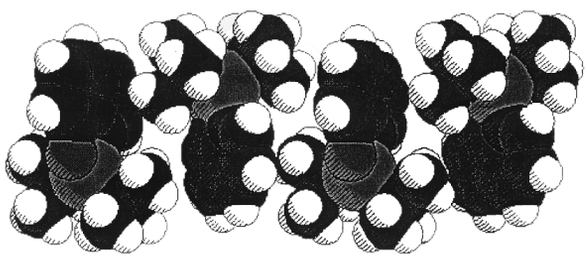


Fig. 3 A space filling representation of the "head-to-tail" molecular packing of $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3**.

Table 3 Selected bond lengths (Å) and angles (°) in $[R_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6B)]_2$ (R = Et or ^{i}Bu **5**)

	$[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**	$[Et_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ [2f]
Al(1)–O(8)	1.879(4)	1.868(1), 1.863(9)
Al(1)–O(8a)	2.003(3)	2.002(9), 1.99(1)
Al(1)–N(1)	2.124(7)	2.136(9), 2.12(1)
Al(1)–C(11)	1.983(7)	1.94(1), 1.99(1)
Al(1)–C(21)	1.975(6)	1.94(1), 1.93(1)
O(8)–C(8)	1.364(8)	1.37(1), 1.36(1)
O(8)–Al(1)–N(1)	79.3(2)	79.0(4), 79.4(4)
O(8)–Al(1)–O(8a)	72.2(2)	72.4(4), 72.7(4)
O(1)–Al(1)–C(11)	114.7(2)	114.7(5), 119.5(5)
O(1)–Al(1)–C(21)	120.5(3)	120.4(5), 120.5(5)
N(1)–Al(1)–O(8a)	151.5(2)	151.2(4), 152.1(4)
N(1)–Al(1)–C(11)	96.4(3)	93.9(4), 94.3(5)
N(1)–Al(1)–C(21)	96.0(3)	97.5(5), 96.0(5)
C(11)–Al(1)–O(8a)	96.6(3)	97.0(5), 98.3(5)
C(11)–Al(1)–C(21)	124.7(3)	124.9(6), 120.0(5)
C(21)–Al(1)–O(8a)	97.2(3)	98.0(5), 99.1(5)
Al(1)–O(8)–Al(1a)	107.8(2)	107.5(4), 107.3(4)

"head-to-tail" (see Fig. 3) such that the 8-quinolinol's π system is sandwiched between the *tert*-butyl groups of adjacent molecules.

The molecular structure of $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5** is shown in Fig. 4; selected bond lengths and angles are given in Table 3 along with the corresponding values for the previously reported ethyl analog, $[Et_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$.[2f] Both compounds are dimeric being bridged by the oxygens of the chelating 8-quinolate ligands. A fifth coordination site on each aluminium is filled by interaction with the nitrogen atom of a

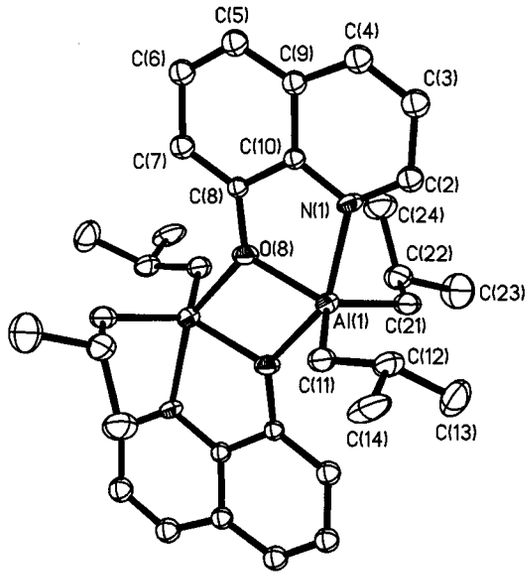


Fig. 4 Molecular structure of $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.

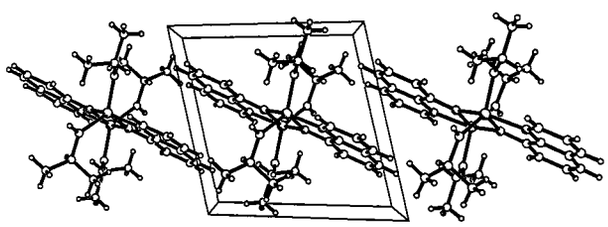


Fig. 5 Crystal packing diagram of $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**.

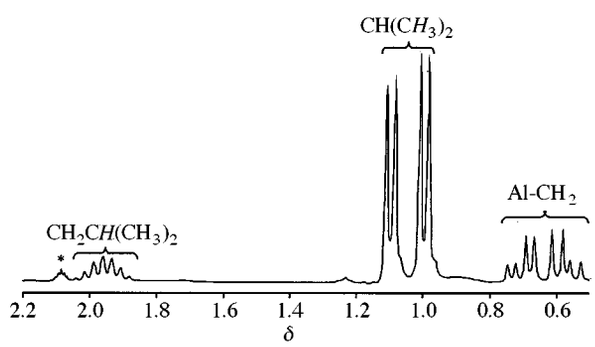


Fig. 6 Room temperature ^1H NMR spectra for $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5** showing the inequivalent isobutyl groups and anisochronous methylene (Al–CH_2) groups. Peak due to residual proton in $C_6D_5CD_3$ solvent is labelled *.

8-quinolate ligand. The Al(1)–N(1) distance [2.124(7) Å] is somewhat longer than a typical Al–N Lewis acid–base interaction, however, it is similar to that observed for $[Et_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ [2.136(9) Å] and is consistent with the axial coordination to the trigonal bipyramidal aluminium, N(1)–Al(1)–O(8a) 151.5(2)°. Despite the increased cone angle of the isobutyl as compared to an ethyl ligand, the similarity in bond lengths and angles between compound **5** and $[Et_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ is perhaps not unsurprising. The increased bulk of the isobutyl ligand occurs at the β-carbon while the van der Waals radii (*ca.* 1.7 Å) of the blade-like 8-quinolate ligands should only experience significant steric repulsion with increased substitution at the aluminium alkyl's α-carbon, *i.e.*, isopropyl and *tert*-butyl. This is clearly observed from the molecular structure of $(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3**. The aromatic rings in compound **5** are stacked in the crystal lattice (Fig. 5), with an inter-ring distance of *ca.* 3.8 Å.

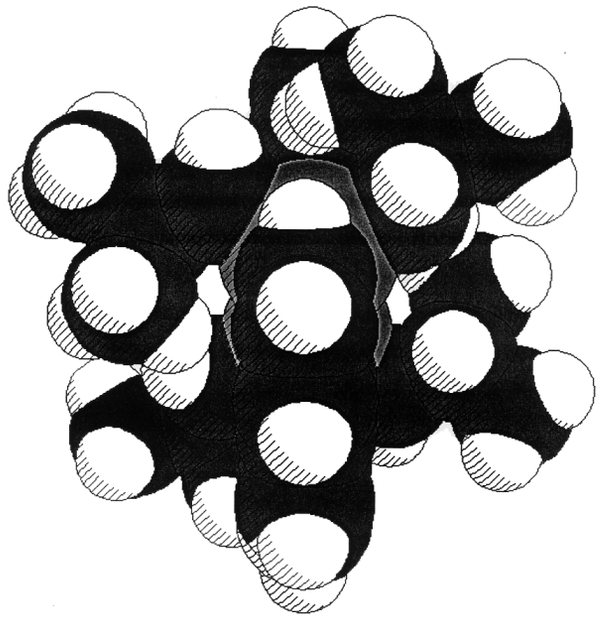
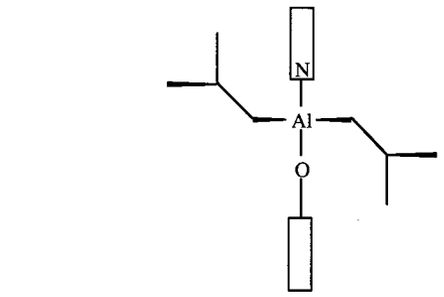


Fig. 7 Space filling diagram of $[(^{i}Bu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**, showing the *anti* arrangement of the isobutyl groups.

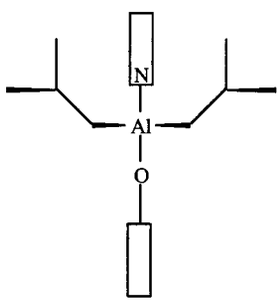
The room temperature solution ^1H NMR of compound **5** (Fig. 6) shows the presence of inequivalent isobutyl groups, but only a single set of resonances for the quinoline ligand. The presence of anisochronous methylene (Al–CH_2) groups indicates that there is hindered rotation about the Al–C bonds. Dzugan and Goedken previously observed a similar inequivalence of the ethyl groups in the ^1H NMR spectrum of $[Et_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$.[2f] Their explanation for this inequivalence involved the dissociation of the quinoline's nitrogen from the axial site on the aluminium and re-coordination in an equatorial manner. However, such a reorganization of the aluminium coordination sphere would require the "bite angle" of the quinoline to change from 79.3(2) to 114–120°, clearly an unfavorable geometry. Furthermore, as is discussed below, the dissociation of the quinoline nitrogen is disfavored due to significant geometric strain. Based upon the solid state structure we proposed an alternative explanation for the observed inequivalence of the isobutyl (and ethyl) groups in $[R_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$.

As is seen from Fig. 4, the isobutyl groups on each aluminium center are positioned *anti* with respect to each other (*i.e.*, **X**). This orientation allows for minimization of steric interactions between the quinoline and the isobutyl groups (Fig. 7), as compared to either of the two possible *syn* arrangements (**XI** and **XII**). In the *syn* isomers the isobutyl groups are either both next to the nitrogen containing ring (**XI**) or closer to the all-carbon ring and have a small inter isobutyl distance (**XII**).

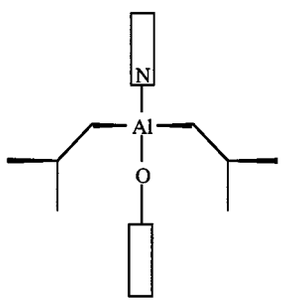
In the *anti* conformation the isobutyl groups would be magnetically inequivalent, *i.e.*, one isobutyl [C(21)–C(24) in Fig. 4] is close to the nitrogen containing ring, while the other [C(11)–C(14) in Fig. 4] is closer to the all-carbon ring, thus explaining the observed room temperature ^1H NMR spectrum. In addition, the presence of a single set of resonances for the quinoline ligand indicates that the molecular structure of compound **5** retains its C_2 symmetry, *i.e.*, the *anti* isomer. Although the dimeric molecule of $[R_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ has a center of symmetry, each of the aluminium centers are chiral, thus enantiomeric forms of the *anti* isomer are possible. If we assume that the *anti* form is the only stable conformation, then the two enantiomers may be interconverted [eqn. (1)]. The anisochronous nature of the methylene groups (see Fig. 6) indicates that at room temperature this exchange does not occur or is slow on the NMR time scale, however, at higher temperatures such an exchange could occur. This is indeed observed. Heating



X

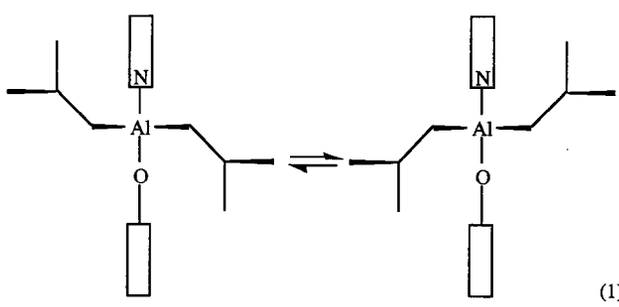


XI



XII

a NMR sample causes the coalescence of the signals due to the inequivalent isobutyl groups. The activation energy for this process has been determined from the ^1H NMR data [$\Delta G^{\ddagger}$ = 68.5(4) kJ mol^{-1}]. Given the discussion below on the geometric strain of dissociating the quinoline ligand, it is unlikely that the process in eqn. (1) involves cleavage of the Al–N bond, but



(1)

involves rotation about the Al–C bond. The value measured, therefore, is rather large for such a process, probably due to the presence of C–H · · · ring interactions.

Monomer *versus* dimer: rigid conformation effects

We have previously shown that for dimeric aluminium compounds with non-delocalized ligands containing both anionic and neutral Lewis base termini (**II**, where X = O, S, NR′ or CH_2; Y = OR′, SR′ or NR′$_2$), that an increase in the steric bulk of the aluminium alkyl substituents (R) results in dissociation of the neutral Lewis base, *i.e.*, **III**. Why then in the case of the pyridine and quinoline derived ligands are monomeric compounds (*cf.*, **I**) formed?

The simplest explanation of the monomeric nature of compounds **2**–**4** would be that the increased basicity of the pyridine and quinoline derived ligands cleaves the Al_2O_2 core. However, while pyridine ($pK_b \approx 9$) is more basic than Et_2O ($pK_b = 17.6$) it is actually less basic than trimethylamine ($pK_b = 4.21$) or ammonia ($pK_b = 4.76$). Thus, based on a basicity argument, compounds of the type $[(R)_2Al\{\mu\text{-}O(CH_2)_nNMe_2\}]_2$ would be expected to be monomeric, which they are not.[1] Therefore, basicity cannot be the reason for compounds **2**–**4** being monomeric and other factors need to be considered. An alternative explanation could involve the shape of the pyridine and quinoline

derived ligands. Both classes of ligand are "blade-like", which allows them to fit between other substituents. In this regard they should have lower steric bulk than a tertiary amine derivative and again on these grounds $[(R)_2Al\{\mu\text{-}O(CH_2)_nNMe_2\}]_2$ would also be expected to be monomeric. Therefore, the shape cannot be the controlling difference. A more consistent explanation with the observations described is as follows.

As an example, consider the structure of $[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5** shown in Fig. 4. If the steric bulk of the aluminium alkyl groups is increased such that inter-ligand repulsion is increased, then the Al–N bond will lengthen (weaken), and eventually dissociate. In order for this to happen, one of two things would have to occur. First, the O(8)–C(8)–C(10) angle would have to increase significantly, or second, the quinoline ligand would have to rotate about the O(8)–C(8) axis. Clearly, the former is limited by the rigid geometry about the sp^2 carbon, C(8). A consideration of a space filling model of compound **5** suggests the latter possibility to be equally disfavored. Thus, the quinoline's nitrogen cannot readily dissociate from the aluminium. However, formation of a monomeric compound (*i.e.*, compound **3**) does allow for relief of all inter-ligand steric hindrance. Similar rationalization may be used for compounds **2** and **4**. Thus, we propose that the formation of monomeric structure for compounds **2**–**4** is associated with the rigid conformation of the pyridine and quinoline ligands.

In conclusion, the stability of monomeric *versus* dimeric structures in this system depends upon a combination of factors: the steric bulk at the aluminium, the rigidity of the ligand, and the ring size formed by chelating ligation.

Experimental

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000–400 cm^{-1}) were obtained using a Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates unless otherwise stated. NMR spectra were obtained on Bruker AM-250 and AM-300 spectrometers using (unless otherwise stated) C_6D_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C), and external $[Al(H_2O)_6]^{3+}$ (^{27}Al). The synthesis of $Al(^tBu)_3$ was performed according to a literature method.[13] 2-Hydroxypyridine, 2-pyridinemethanol, 8-hydroxyquinoline and 8-quinolinemethanol were obtained from Aldrich and were used without further purification. 8-Quinolinol was prepared from the reduction of 8-quinolinecarboxylic acid by lithium aluminium hydride.[14]

Synthesis

$(^tBu)_2Al(O\text{-}2\text{-}C_5H_4N)$ 1. $Al(^tBu)_3$ (3.16 g, 15.96 mmol) was dissolved in hexane (50 mL) and cooled to −78 °C. 2-Hydroxypyridine (1.52 g, 15.9 mmol) was added dropwise and upon completion, the mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was then filtered and the solid product was recrystallized in toluene. Yield: *ca*. 60%. Mp 205–207 °C. MS (EI, %): *m*/*z* 413 ($2M^+ - {}^tBu$, 60), 357 ($2M^+ - {}^tBu - H_2C{=}CMe_2$, 10), 235 ($M^+$, 8), 178 ($M^+ - {}^tBu$, 30), 121 ($M^+ - 2\ {}^tBu$, 10), 77 ($C_5H_4N$, 100), 57 ($^tBu$, 20). IR ($cm^{-1}$): 2824w, 1622m, 1507m, 1447w, 1261m, 1094s, 1023s, 800s, 651m, 478m, 406m. ^1H NMR (C_6D_6): δ 8.18 [1 H, d, J(H–H) = 5.0, 6-CH], 7.12 [1 H, dd, J(H–H) = 5.0, 4-CH], 7.35 [1 H, d, J(H–H) = 7.0, 3-CH], 6.55 [1 H, dd, J(H–H) = 7.0 Hz, 5-CH], 1.59 [18 H, s, $C(CH_3)$]. ^{13}C NMR (C_6D_6): δ 169.6 (OC), 145.9 (6-CH), 140.7 (4-CH), 121.5 (5-CH), 117.0 (3-CH), 34.3 [$C(CH_3)_3$]. ^{27}Al NMR (C_7H_8/C_6D_6): δ 129 ($w_{\frac{1}{2}}$ = 4176 Hz).

$(^tBu)_2Al(OCH_2\text{-}2\text{-}C_5H_4N)$ 2. Prepared in an analogous manner to compound **1** using $Al(^tBu)_3$ (5.44 g, 27.5 mmol) and 2-pyridylmethanol (3.00 g, 27.5 mmol). Yield: 55%. Mp 143–145 °C. ICP Analysis (calc.): Al, 11.7 ± 0.02 (10.8%). MS (EI, %): *m*/*z* 192 ($M^+ - {}^tBu$, 35), 135 ($M^+ - 2{}^tBu$, 28), 57 (^tBu, 100). IR (cm^{-1}): 1609w, 1574w, 1260m, 1087s, 1059s, 1020s, 927s, 800s, 679w, 636w. ^1H NMR (C_6D_6): δ 7.97 [1 H, d, J(H–H) = 5.0, 6-CH], 6.68 [1 H, m, dd, J(H–H) = 7.5, 5-CH], 6.30 [1 H, dd, J(H–H) = 5.0, 4-CH], 6.26 [1 H, d, J(H–H) = 7.5 Hz, 3-CH], 5.07 (2 H, s, OCH_2), 1.29 [18 H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 145.6 (6-CH), 139.2 (4-CH), 122.5 (5-CH), 120.7 (3-CH), 67.7 (OCH_2), 32.2 [$C(CH_3)_3$]. ^{27}Al NMR (C_7H_8/C_6D_6): δ 124 ($w_{\frac{1}{2}}$ = 5836 Hz).

$(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ 3. Prepared in an analogous manner to compound **1** using $Al(^tBu)_3$ (5.44 g, 27.5 mmol) and 8-hydroxyquinoline (3.98 g, 27.5 mmol). Yellow crystals resulted after placing the reaction mixture in the freezer (−25 °C). Yield: 50%. Mp 89–91 °C. MS (EI, %): *m*/*z* 285 (M^+, 20), 228 ($M^+ - {}^tBu$, 35), 171 ($M^+ - 2{}^tBu$, 50), 57 (^tBu, 20). IR (cm^{-1}): 2965m, 2827m, 1261s, 1094s, 1019s, 802s. ^1H NMR (C_6D_6): δ 7.77 [1 H, d, J(H–H) = 5.0, 2-CH], 7.39 [1 H, d, J(H–H) = 10.0, 7-CH], 7.17 [1 H, dd, J(H–H) = 5.0, 3-CH], 6.65 [1 H, dd, J(H–H) = 10.0, J(H–H) = 5.0, 6-CH], 6.47 [1 H, d, J(H–H) = 5.0, 4-CH], 6.44 [1 H, d, J(H–H) = 5.0 Hz, 5-CH], 1.18 [18 H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 159.9 (OC), 143.9 (2-CH), 140.8 (4-CH), 132.1 (5-CH), 121.6 (3-CH), 114.8 (7-CH), 113.5 (6-CH), 33.3 [$C(CH_3)_3$], 30.3 [$C(CH_3)_3$]. ^{27}Al NMR (C_7H_8/C_6D_6): δ 138 ($w_{\frac{1}{2}}$ = 4638 Hz). UV/VIS (λ/nm, 8.77×10^{-4} M, $CHCl_3$): 384 (ε = 2264 L mol^{-1} cm^{-1}).

$(^tBu)_2Al(OCH_2\text{-}8\text{-}C_9H_6N)$ 4. Prepared in an analogous manner to compound **1** using $Al(^tBu)_3$ (5.44 g, 27.5 mmol) and 8-quinolinemethanol (4.37 g, 27.5 mmol). Yield; 30%. Mp 118–120 °C. MS (EI, %): *m*/*z* 299 (M^+, 5), 242 ($M^+ - {}^tBu$, 100), 185 ($M^+ - 2{}^tBu$, 20), 57 (^tBu, 20). IR (cm^{-1}): 1592w, 1508w, 1456w, 1262m, 1088s, 1022s, 799s, 677w, 648w, 591w. ^1H NMR (C_6D_6): δ 8.43 [1 H, d, J(H–H) = 5.0, 2-CH], 7.34 [1 H, d, J(H–H) = 10.0, 7-CH], 6.99 (1 H, m, 4-CH), 6.97 (1 H, m, 6-CH), 6.92 (1 H, m, 5-CH), 6.47 [1 H, dd, J(H–H) = 7.5, J(H–H) = 5.0 Hz, 3-CH], 5.52 (2 H, s, OCH_2), 1.30 [18 H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 147.7 (2-CH), 142.4 (4-CH), 130.0 (5-CH), 127.1 (6-CH), 120.2 (3-CH), 103.0 (7-CH), 67.3 (CH_2O), 32.5 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$]. ^{27}Al NMR (C_7H_8/C_6D_6): δ 132 ($w_{\frac{1}{2}}$ = 2720 Hz).

$[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ 5. Prepared in an analogous manner to compound **1** using $HAl(^iBu)_2$ (2.94 g, 20.7 mmol) and 8-hydroxyquinoline (3.00 g, 20.7 mmol). Yellow crystals resulted after placing the mixture in the freezer (−25 °C). Yield: 70%. Mp 89–91 °C. MS (EI, %): *m*/*z* 285 (M^+, 5), 228 ($M^+ - {}^iBu$, 100), 172 ($M^+ - 2{}^iBu$, 90), 57 (^iBu, 7). IR (cm^{-1}): 2960m, 1255s, 1096s, 1019s, 804s, 743w, 691w, 661w. ^1H NMR (C_6D_6): δ 8.70 [1 H, d, J(H–H) = 4.5, 2-CH], 7.50 [1 H, d, J(H–H) = 7.8, 7-CH], 7.26 [1 H, dd, J(H–H) = 4.5, 3-CH], 6.82 [1 H, dd, J(H–H) = 7.8, 6-CH], 6.66 [1 H, d, J(H–H) = 4.5, 4-CH], 6.64 [1 H, d, J(H–H) = 4.5, 5-CH], 2.04 [1 H, sept, J(H–H) = 6.3, CH], 2.02 [1 H, sept, J(H–H) = 6.7, CH], 1.16 [6 H, d, J(H–H) = 6.5, CH_3], 1.06 [6 H, d, J(H–H) = 6.3, CH_3], 0.78 [2 H, d, J(H–H) = 6.1, Al–CH_2], 0.69 [2 H, d, J(H–H) = 6.1 Hz, Al–CH_2]. ^{13}C NMR (C_6D_6): δ 160.0 (OC), 144.9 (2-CH), 138.8 (4-CH), 129.9 (5-CH), 121.9 (3-CH), 114.5 (7-CH), 113.0 (6-CH), 29.7 [$CH(CH_3)_2$], 28.8 [$CH(CH_3)_2$], 27.2 [$CH(CH_3)_2$], 1.75 (Al–CH_2). ^{27}Al NMR (C_7H_8/C_6D_6): δ 81 ($w_{\frac{1}{2}}$ = 7500 Hz). UV/VIS (λ/nm 3.51×10^{-4} M, $CHCl_3$): 375 (ε = 2330 L mol^{-1} cm^{-1}).

Crystallographic studies

Crystals of compounds **1**, **3** and **5** were sealed in glass capillaries under argon and mounted on the goniometer of a Enraf-Nonius CAD-4 automated diffractometer using Mo-Kα radiation with a graphite monochromator. Data collection and

Table 4 Summary of X-ray diffraction data

Compound	$[(^tBu)_2Al(\mu\text{-}O\text{-}2\text{-}C_5H_4N)]_2$ **1**	$(^tBu)_2Al(O\text{-}8\text{-}C_9H_6N)$ **3**	$[(^iBu)_2Al(\mu\text{-}O\text{-}8\text{-}C_9H_6N)]_2$ **5**
Formula	$C_{26}H_{44}Al_2N_2O_2$	$C_{17}H_{24}AlNO$	$C_{34}H_{48}Al_2N_2O_2$
M	470.62	285.37	570.74
Crystal size/mm	0.07 × 0.09 × 0.42	0.14 × 0.17 × 0.42	0.09 × 0.09 × 0.31
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	7.986(2)	10.763(2)	9.288(1)
b/Å	9.187(1)	12.579(1)	9.854(2)
c/Å	11.620(1)	13.443(1)	10.288(1)
α/°	111.889(9)		68.46(1)
β/°	96.13(1)	105.15(1)	85.58(1)
γ/°	107.78(1)		76.67(2)
U/Å^3	729.4(2)	1756.8(4)	852.2(4)
Z	1	4	1
D_c/g cm^{-3}	1.071	1.079	1.112
μ/cm^{-1}	1.17	1.07	1.11
T/K	298	298	298
2θ Range/°	3.0–44.0	2.0–44.0	3.0–44.0
No. reflections collected	1793	2415	2090
No. individual reflections	1793	2286	2090
No. observed reflections	867 ($\|F_o\| > 6.0\sigma\|F_o\|$)	638 ($\|F_o\| > 6.0\sigma\|F_o\|$)	1012 ($\|F_o\| > 6.0\sigma\|F_o\|$)
Weighting scheme (w^{-1})	0.04 ($\|F_o\|)^2 + \sigma(\|F_o\|)^2$	0.04 ($\|F_o\|)^2 + \sigma(\|F_o\|)^2$	0.04 ($\|F_o\|)^2 + \sigma(\|F_o\|)^2$
R	0.0576	0.0326	0.0589
R_w	0.0609	0.0401	0.0608
Largest difference peak/e Å^{-3}	0.26	0.10	0.35

cell determinations were perfomed in a manner previously described,[15] using the θ–2θ scan technique. Pertinent details are given in Table 4. The structures were solved by direct methods, SHELX 86 (**3** and **5**)[16] and SIR (**1**).[17] The models were refined using full-matrix least-squares techniques. Due to the weak scattering of the crystals, all atoms could not be refined with anisotropic parameters. The Al, O and N atoms in all three structures and the *tert*-butyl groups in **1** and **5** were refined in this fashion. Hydrogen atoms were included and constrained to 'ride' upon the appropriate atoms [d(C–H) = 0.95 Å, U(H) = 1.3 B_{eq}(C)]. All computations other than those specified were performed using MOLEN.[18] A summary of cell parameters, data collection, and structure solution is given in Table 4. Scattering factors were taken from ref. 19.

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