Aluminium-containing ring systems and N-heterocycle formation *via* nitrile insertions into Al–N bonds

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Received (in Cambridge, UK) 7th September 2000, Accepted 6th November 2000
First published as an Advance Article on the web 15th December 2000

Reactions of Me_3Al with 1,2-diaminobenzene [1,2-$(H_2N)_2C_6H_4$] or anthranilic acid, [1,2-$(H_2N)(HO_2$- C)C_6H_4], followed by treatment with acetonitrile, afford tetranuclear and hexanuclear aluminium-containing ring systems; a single crystal X-ray structure on the hexametallic product reveals the construction of quinazoline ligands arising *via* insertion of acetonitrile into Al–N bonds.

It is well over one hundred years since the trimerisation of nitriles to triazines by organometallic reagents was first noted, by Hofmann[1] using sodium, and by Frankland[2] in his studies on Et_2Zn. During the 1960s, Wade[3] and Lappert[4] did much to advance the understanding of nitrile binding and insertion reactions at main group centres; however, the potential of such reactions for synthesising useful heterocycles and interesting metal-containing ring systems has remained largely undeveloped.

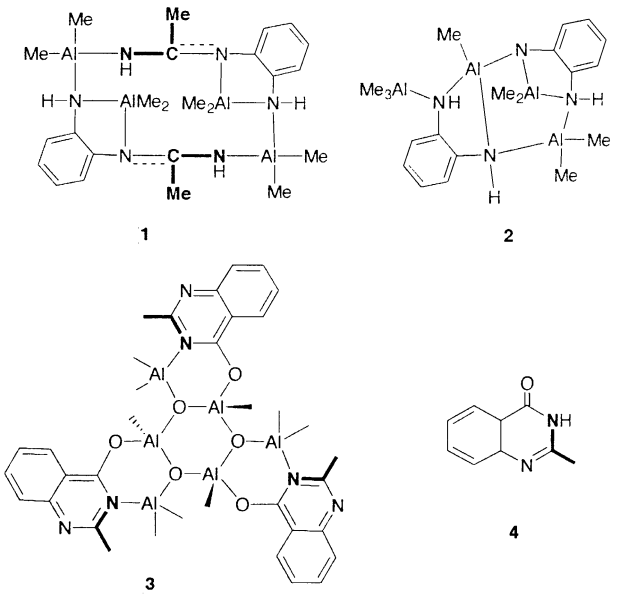
Recently, we described the synthesis of large aluminium-containing ring systems *via* treatment of Me_3Al with hydrazines;[5] these included a highly unusual octa-aluminium structural analogue of a tetrapyrrole. The key macrocycle-forming step revolves around the insertion of acetonitrile into the aluminium–nitrogen bonds of intermediate amide species. With a view to probing the generality of this approach for the synthesis of aluminium-containing macrocycles, and also to evaluate the potential of this methodology for constructing nitrogen heterocycles, we have extended the study to other classes of amine substrate. Here, we describe the reactivity of Me_3Al towards 1,2-diaminobenzene [1,2-$(H_2N)_2C_6H_4$] and anthranilic acid [1,2-$(H_2N)(HO_2C)C_6H_4$]. The former gives rise to a tetranuclear complex, the latter to an unprecedented hexanuclear species incorporating N-heterocyclic ligands.

Slow addition of a solution of Me_3Al (2 equivalents) in toluene to 1,2-$(H_2N)_2C_6H_4$, followed by a 12 h reflux, afforded a pale brown solution. After removal of the solvent under reduced pressure, the residue was dissolved in acetonitrile and heated to reflux for 2–3 min. Slow cooling of this solution, followed by standing at room temperature for 2 days, gave colourless needles of **1** in 40% yield (Scheme 1). The ^{1}H NMR spectrum‡ of **1** consists of four equal intensity singlets in the Al–methyl region (δ −0.37 to −0.75) together with a similar intensity singlet at δ 1.29 attributable to carbon-bonded methyl groups. X-Ray analysis§ reveals the product to be the C_i symmetric twelve-membered macrocyclic complex **1** comprising four aluminium atoms (two bridging and two chelating), six nitrogen atoms and two carbon atoms, The structure of this product is closely related to that obtained from the reaction of $MePhNNH_2$ with Me_3Al,[5] and is not described in further detail here.

In the absence of acetonitrile, the 2 : 1 reaction of Me_3Al and 1,2-$(H_2N)_2C_6H_4$ (in toluene) has been shown to afford the asymmetric complex $[(Me_2Al)_2AlMe(C_6H_4(NH)_2)_2]\cdot AlMe_3$ **2**.[6] This, or a closely related derivative, is the likely precursor to **1**. Formation of the 12-membered ring product is brought about by insertion of two acetonitrile molecules into the Al–N bonds, in a related manner to that postulated for the reaction of hydrazines with Me_3Al/MeCN.[5]

Similar treatment of anthranilic acid, [1,2-(NH_2)-$(HO_2C)C_6H_4$] (twice sublimed) with 2 equivalents of a toluene solution of Me_3Al affords, after work-up in acetonitrile, large yellow prisms for which the ^{1}H NMR spectrum possesses nine distinct singlets in the Al–methyl region. The X-ray analysis§ of the product revealed the chiral trimeric hexanuclear complex $[(Me_2AlL)(MeAl)(\mu_3\text{-}O)(\mu\text{-}O)]\}_3$ **3** (L = quinazoline) shown in Fig. 1. The central Al_3O_3 ring has a twisted boat conformation, whereas the three attached Al_2O_2CN rings each have a folded envelope geometry. All six aluminium atoms exhibit marked departures from ideal tetrahedral geometry with angles in the range 100.9(2)–124.4(3)°. Although not possessing strict C_3 symmetry [the methyls on Al(2) and Al(4) are 'up', whilst that on Al(6) is 'down'], the pattern of bonding throughout the structure is essentially three-fold symmetric. It is interesting to note that whilst all of the Al–O bond lengths within the central Al_3O_3 ring and also those to O(2), O(4) and O(6) are all essentially the same [1.770(4)–1.794(4) Å], those to Al(1), Al(3) and Al(5) are all significantly longer [1.811(4)–1.827(4) Å]. As **3** is not the product of a chiral synthesis, the presence in the crystals of molecules of only one chirality is a consequence of spontaneous resolution upon crystallisation.

Whereas the formation of **1** can be rationalised in terms of acetonitrile insertion into the aluminium–nitrogen bonds of **2**, the carboxylic acid group of anthranilic acid contributes oxygen atoms to the Al_3O_3 core around which the quinazoline ligands are clustered. The reaction reproducibly affords **3** in *ca.* 45% yield; its hydrolysis then readily releases the 2-methyl-4(3*H*)-quinazolinone heterocycle **4** (identified by comparison of NMR data with those of an authentic sample) in excellent yield. We



Scheme 1 Compounds **1**–**4** (inserted molecules of acetonitrile are shown in bold).

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DOI: 10.1039/b007810g

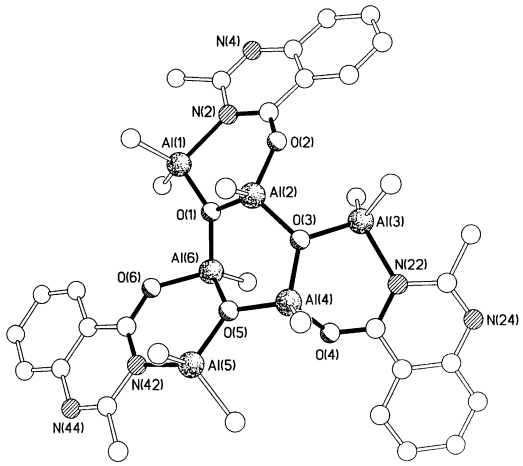

Fig. 1 The molecular structure of **3**. Selected bond lengths (Å); Al(1)–O(1) 1.811(4), Al(1)–N(2) 2.021(5), Al(2)–O(1) 1.785(4), Al(2)–O(3) 1.788(4), Al(2)–O(2) 1.779(4), Al(3)–O(3) 1.827(4), Al(3)–N(22) 2.034(5), Al(4)–O(3) 1.770(4), Al(4)–O(4) 1.783(5), Al(4)–O(5) 1.785(4), Al(5)–O(5) 1.825(4), Al(5)–N(42) 2.015, Al(6)–O(1) 1.784(4), Al(6)–O(5) 1.794(4), Al(6)–O(6) 1.785(5).

note that the formation of N-heterocycles by this methodology is related to the intramolecular Ritter reaction[7–9] in which nitrilium salts, generated in the presence of Friedel–Crafts reagents, react with a second nitrile molecule to give quinazoline ring systems.[9]

Future studies will focus on further exploiting nitrile insertions into aluminium (and gallium) bonds to access unusual inorganic ring systems and nitrogen heterocycle products.

The EPSRC and the Leverhulme Trust (for a Research Fellowship to C. R.) are thanked for financial support. Professor Charles Rees is thanked for helpful discussions.

Notes and References

‡ Satisfactory microanalyses have been obtained.

For **1**: ^{1}H NMR (400 MHz, C_6D_6, 298 K), δ −0.75, −0.48, −0.42, −0.37 (4 × s, 8 × 3H, AlMe), 1.29 (s, 2 × 3H, CMe), 6.36–7.27 (3 × m, 8H, aryl H), NH not seen. ^{13}C NMR (100.6 MHz, C_6D_6, 298 K), δ −12.24, −12.81 (br, AlMe), −8.91 (br, AlMe), −5.99 (br, AlMe). IR: ν(N–H) 3247 cm^{-1}.

For **3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ −0.87, −0.82, −0.59, −0.47, −0.46, −0.45, −0.24, −0.23, −0.22 (9 × s, each 3H, AlMe), 2.79 (s, 3H, Me-quin), 2.88 (s, 3H, Me-quin), 2.89 (s, 3H, Me-quin), 7.61 (m, 3H, quinH), 7.82 (m, 3H, quinH), 7.92 (m, 3H, quinH), 8.35 (m, 3H, quinH). ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K), δ −12.24, −11.56 (2 × m, 3 × AlMe), −7.22, −6.79, −6.45, −5.43, −5.10, −4.57 (6 × s, 3 × $AlMe_2$), 25.53, 25.82, 25.93 (3 × s, Me-quin), 117.15 (m, 3 × aryl C), 125.28–127.61 (overlapping m, 9 × aryl C), 136.33 (m, 3 × aryl C), 150.98 (m, 3 × aryl C), 158.45 (m, 3 × aryl C), 169.31 (m, 3 × aryl C). EI-MS: *m*/*z*: 807 (M^+ − Me). IR: $\nu(\mu_3\text{-O})Al_3$ 800 cm^{-1}.

§ *Crystal data*: For **1**: $C_{24}H_{42}N_6Al_4$, M = 522.6, orthorhombic, space group *Pbca* (no. 61), a = 8.717(1), b = 16.868(1), c = 20.416(2) Å, V = 3002.0(4) Å^3, Z = 4 (the complex has crystallographic C_i symmetry), D_c = 1.156 g cm^{-3}, μ(Cu-Kα) = 16.1 cm^{-1}, F(000) = 1120, T = 183 K; clear prisms, 0.27 × 0.23 × 0.13 mm, Siemens P4/RA diffractometer, ω-scans, 2182 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give R_1 = 0.069, wR_2 = 0.173 for 1479 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta < 120°$] and 162 parameters.

For **3**: $C_{36}H_{48}N_6O_6Al_6$, M = 822.7, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.152(1), b = 16.054(1), c = 22.310(1) Å, V = 4352.3(6) Å^3, Z = 4, D_c = 1.256 g cm^{-3}, μ(Cu-Kα) = 17.9 cm^{-1}, F(000) = 1728, T = 173 K; yellow rhombs, 0.50 × 0.23 × 0.23 mm, Siemens P4/RA diffractometer, ω-scans, 4017 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give R_1 = 0.055, wR_2 = 0.133 for 3483 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta < 128°$] and 488 parameters. The absolute structure of **3** was determined by use of the Flack parameter which refined to a value of −0.07(7).

CCDC 182/1855. See http://www.rsc.org/suppdata/cc/b0/b007810g/ for crystallographic files in .cif format.

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