

An unusual imine (N=C) alkylaluminum reaction

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Addition of 3 equiv. of AlMe_3 to a heptadentate Schiff-base ligand made from salicylaldehyde and bis(2-aminoethyl)ethylenediamine (H_3L^1) results in an unusual alkylaluminumation of one of the imine bonds; addition of 2 equiv. of $\text{B}(\text{OMe})_3$ or AlMe_3 to one of these ligands leads to the formation of bimetallic derivatives containing four- and five-coordinate metals, respectively.

In the course of our explorations of group 13 Schiff-base chelate complexes we have discovered an unusual imine (N=C) alkylaluminumation reaction. Schiff-base ligands (and the salen class, in particular) form a wide range of complexes with transition¹ and main-group metals.² One of the reasons why these ligands are so useful is because they do not undergo further reactions after coordinating a metal. In fact, transition-metal complexes of the reduced form of the salen ligand (the salan class)³ are difficult to isolate because they dehydrogenate back to the Schiff-base derivative when exposed to air.⁴

In turning our attention to ligands possessing multiple (more than four) binding sites we examined those derived from the condensation of 3 equiv. of salicylaldehyde (with H or Bu^t at the 2,4-positions, or Cl at the 4-position, of the aryl ring) with bis(2-aminoethyl)ethylenediamine. The resulting ligands are denoted H_3L^1 , H_3L^2 and H_3L^3 , respectively. We had intended to prepare neutral bi- and tri-metallic derivatives of these ligands for potential catalytic applications. Previously reported group 13 complexes with this⁵ and related systems⁶ have focused on charged compounds useful in medicinal applications.

In the present work, two neutral bimetallic derivatives, $(\text{HL}^2)[\text{B}(\text{OMe})_2]_2$ **1** and $\text{L}^1\text{AlMe}(\text{AlMe}_2)$ **2**, could be prepared in good yields using the appropriate stoichiometry (Scheme 1).[†] The X-ray data for **1** was such that a full solution could not be obtained. However, the overall morphology of the molecule is

clear (Fig. 1). The formation of **1** follows similar reactions for bimetallic salen derivatives.⁷ This is not the case for **2** for which the ²⁷Al NMR data indicates that only five-coordinate aluminum is present (δ 65.40). In the ¹H NMR there are two Al–Me shifts in a 1 : 2 ratio. This data can tentatively be attributed to the structure shown in Scheme 1. Surprisingly, in reactions with 3 equiv. of the aluminium reagent, one of the N=C bonds undergoes an unusual alkylaluminumation reaction in the formation of trimetallic derivative **3** (Scheme 1, Fig. 2).

In the structure[‡] one portion of the molecule coordinates an AlMe_2 unit by an oxygen and imine nitrogen, forming a six-

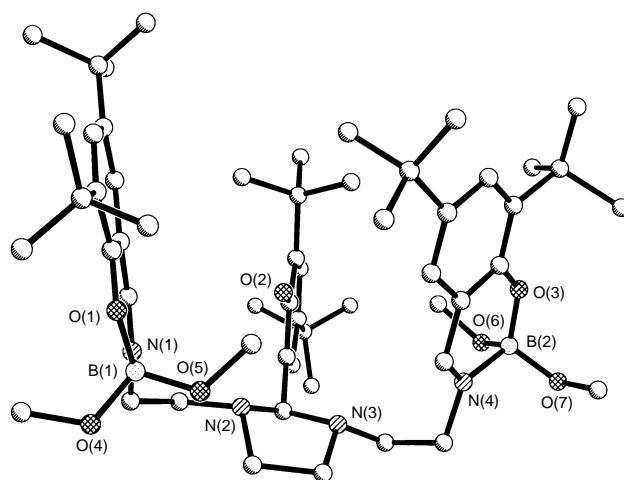
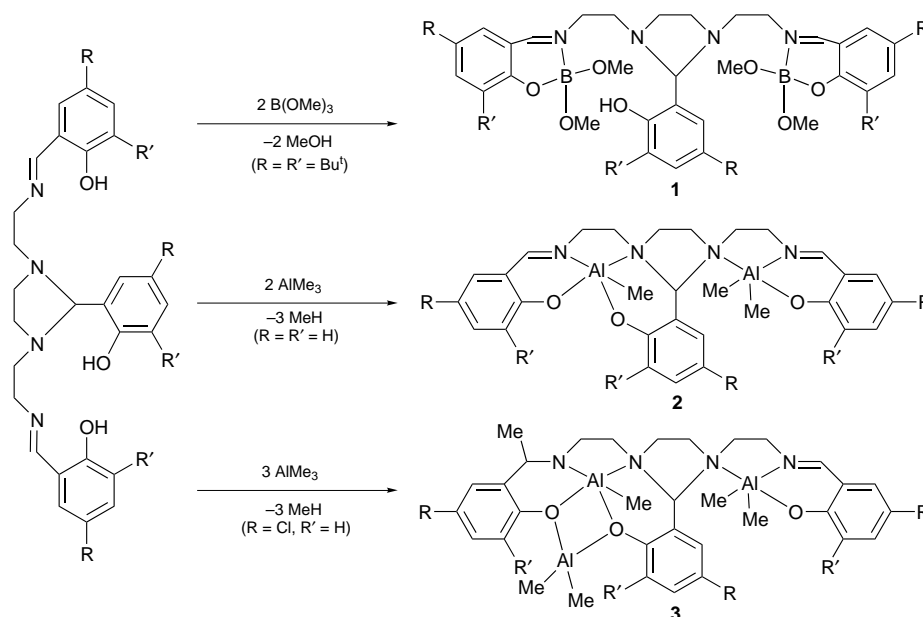


Fig. 1 Preliminary structure of **1** demonstrating the overall morphology of the molecule



Scheme 1 General syntheses of group 13 compounds with H_3L^n ($n = 1-3$)

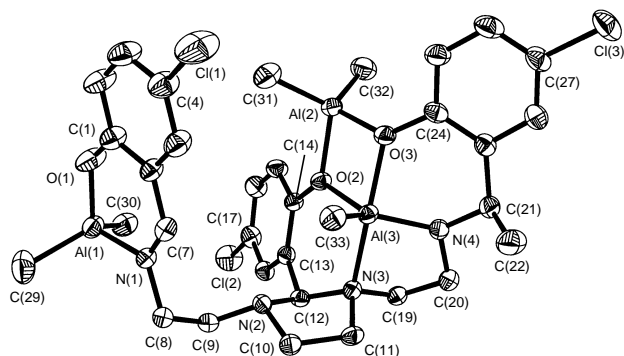


Fig. 2 Molecular structure and atom numbering scheme for **3**. Selected bond distances (Å) and angles (°): Al(1)–O(1) 1.769(3), Al(1)–C(30) 1.945(5), Al(1)–C(29) 1.947(5), Al(1)–N(1) 1.961(3), Al(2)–O(3) 1.816(3), Al(2)–O(2) 1.884(3), Al(2)–C(31) 1.935(5), Al(2)–C(32) 1.943(5), Al(3)–N(4) 1.822(3), Al(3)–O(2) 1.912(3), Al(3)–O(3) 1.944(3), Al(3)–C(33) 1.966(4), Al(3)–N(3) 2.091(3), N(4)–C(21) 1.459(5), C(21)–C(22) 1.524(6); O(1)–Al(1)–C(30) 110.6(2), O(1)–Al(1)–C(29) 112.2(2), C(30)–Al(1)–C(29) 119.1(2), O(1)–Al(1)–N(1) 95.77(14), C(30)–Al(1)–N(1) 110.5(2), C(29)–Al(1)–N(1) 106.1(2), O(3)–Al(2)–O(2) 79.95(11), O(3)–Al(2)–C(31) 115.9(2), O(2)–Al(2)–C(31) 108.8(2), O(3)–Al(2)–C(32) 110.6(2), O(2)–Al(2)–C(32) 116.9(2), C(31)–Al(2)–C(32) 118.7(2), N(4)–Al(3)–O(2) 120.37(13), N(4)–Al(3)–O(3) 90.82(13), O(2)–Al(3)–O(3) 76.15(11), N(4)–Al(3)–C(33) 127.4(2), O(2)–Al(3)–C(33) 111.6(2), O(3)–Al(3)–C(33) 93.9(2), N(4)–Al(3)–N(3) 83.96(13), O(2)–Al(3)–N(3) 89.82(11), O(3)–Al(3)–N(3) 159.98(12), C(33)–Al(3)–N(3) 104.7(2), Al(2)–O(2)–Al(3) 100.78(12), Al(2)–O(3)–Al(3) 102.05(13), N(4)–C(21)–C(22) 112.0(3), N(4)–C(21)–C(23) 113.6(3), C(22)–C(21)–C(23) 110.3(3).

membered ring. This is a familiar coordination mode for Schiff-base ligands. The second portion of the molecule contains two aluminium atoms linked by bridging oxygens. The terminal AlMe₂ group adopts a geometry that is structurally similar to the other AlMe₂ group. The central, five-coordinate aluminium atom is in a distorted trigonal-bipyramidal geometry. The equatorial bond distances are systematically shorter than the axial distances. This is exemplified in the distances for axial, Al(3)–N(3) [2.091(3) Å] compared to equatorial, Al(3)–N(4) [1.822(3) Å] atoms. The oxygens follow a similar trend [Al(3)–O(2) 1.912(3), Al(3)–O(3) 1.944(3) Å]. Closely related to **3** is the trimetallic complex (salan)AlMe(AlMe₂)₂ [salan = *N,N'*-bis(*o*-hydroxybenzyl)-1,2-diaminoethane].⁸ It also contains four- and five-coordinate (trigonal bipyramidal) aluminiums bridged by oxygen atoms. In this complex the axial atoms are oxygen and form an angle of 163.0(1)° at distances of 1.982(3) and 1.959(3) Å. The differences in the N=C and N–C(Me) linkages are reflected in the N–C bond distances of 1.290(5) and 1.459(5) Å, respectively. Furthermore, the imine group appears as a singlet in the ¹H NMR (δ 7.94) while the amine NCH(Me) appears as a multiplet (δ 4.14).

The use of group 13 reagents in the reduction of alkynes, alkenes and carbonyl substituents is a well known, yet still expanding area of chemistry.⁹ Alkylaluminum reactions generally require the intermediacy of a group 4 catalyst.¹⁰ The catalyst acts to activate the substrate in a manner that is still being defined. That an aluminium species is being produced in **3** that can alkylate carbon–nitrogen multiple bonds in the absence of a metal catalyst is an intriguing prospect. Based upon the fact that a compound containing two five-coordinate aluminium atoms can be isolated (**2**), the third equivalent of AlMe₃ presumably effects the alkylation in **3**. The coordination of the first two AlR_n units makes the imine linkage vulnerable to this addition. This type of reaction bears some resemblance to the alkylation of nitriles in which the first step is the formation of an organoaluminium–nitrile adduct.¹¹ Whether the formation

of **3** is through an intra- or intermolecular alkylation remains to be determined.

This work was supported by the National Science Foundation (Grant 9452892) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 31901-AC3). Partial support was provided by Union Carbide. The receipt of an NSF-CAREER (CHE-9625376) award is also gratefully acknowledged.

Footnotes

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† Full experimental details will be published in due course. Only a partial list of data is given here. **1**: mp 182–184 °C. ¹H NMR (CDCl₃): δ 1.13–1.41 (m, 54 H, CCH₃), 2.85 (s, 6 H, OCH₃), 3.16 (s, 6 H, OCH₃) 2.72, 2.93, 3.35, 3.50 (m, 12 H, NCH₂), 3.81 (s, 1H, NCHN), 6.84 (d, 1 H, Ph H), 7.06 (d, 2 H, Ph H), 7.17 (d, 1 H, Ph H), 7.51 (d, 2 H, Ph H), 8.07 (s, 2 H, N=CH). Analysis. Calc: C, 70.34; H, 9.38. Found: C, 69.95; H, 9.28%. **2**: mp > 260 °C. ¹H NMR (CDCl₃): δ –0.92 to –0.73 (m, 9 H, AlCH₃), 2.46–3.02, 3.28–3.71 (m, 12 H, NCH₂), 3.86 (s, 1 H, NCHN), 6.63–7.41 (m, 12H, Ph H), 8.14 (s, 1 H, N=CH), 8.21 (s, 1 H, N=CH). ²⁷Al (CDCl₃): δ 65.40. Analysis. Calc: C, 65.00; H, 6.49. Found: C, 65.13; H, 6.24%. **3**·1.5C₆H₅Me: mp > 260 °C. ¹H NMR (CDCl₃): δ –0.99 to –0.53 (m, 15 H, AlCH₃), 1.38 (d, 3 H, CCH₃), 2.35 (s, 3 H, PhCH₃), 2.73–2.77, 3.08, 3.48 (m, 12 H, NCH₂), 3.53 (s, 1 H, NCHN), 4.14 (m, 1H, NCH₂CH₃), 7.11 (m, 9 H, Ph H), 7.94 (s, 1 H, N=CH). ²⁷Al (CDCl₃): δ 54.50, 163.95. Analysis Calc. for **3**·C₆H₅Me: C, 58.46; H, 6.08. Found: C, 58.15; H, 6.26%.

‡ Crystallographic data: **1**, monoclinic, *P*₂/c, *a* = 15.4330(14), *b* = 20.6409(19), *c* = 22.7704(20) Å, β = 98.779(2)°, *U* = 7168.5(5) Å³, *Z* = 4, 2670 observed [*I* > 4.0 σ (*I*)], *R*₁ = 0.1932, *wR*₂ = 0.5439. **3**·1.5C₆H₅Me, monoclinic, *P*₂₁/n, *a* = 11.8994(6), *b* = 31.498(2), *c* = 13.7396(7) Å, β = 115.006(1)°, *U* = 4667.0(4) Å³, *Z* = 4, 6024 observed [*I* > 2.0 σ (*I*)], *R*₁ = 0.0620, *wR*₂ = 0.1218. CCDC 182/515.

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Received in Columbia, MO, USA; 19th February 1997; 7/01185G