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# Reactions of amides with organoaluminium: a useful synthetic route to aluminium diketiminates†

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The reaction of *N*-*tert*-butylbenzamide ($^t$BuNHCOPh) with 1.1 molar equivalents of $Me_3Al$ in refluxing hexane afforded a five-coordinated dimeric compound $[Me_2Al\{\eta^2\text{-}^t BuNC(Ph)(\mu\text{-}O)\}]_2$ **1**, whereas 2.2 molar equivalents yielded a monomeric compound $[Me_2Al\{\eta^2\text{-}^t BuNCPh(\mu\text{-}O)\}AlMe_3]$ **2**. Reaction of PhCONHAr with 1 molar equivalent of $Me_3Al$ in toluene at 25 °C, gave four-coordinated dimeric eight-membered ring compounds $[Me_2Al\{\mu\text{-}\eta^2\text{-}(p\text{-}XC_6H_4)NC(Ph)O\}]_2$ (X = OMe **3** or **4**). Benzanilide (PhNHCOPh) with 1.2 molar equivalents of $Me_3Al$ in refluxing toluene resulted in aluminium amidate **4** and a trace amount of an aluminium diketiminate, $[Me_2Al\{\eta^2\text{-}PhNC(Ph)C(H)C(Ph)NPh\}]$ **5**. Furthermore, $PhCONHC_6H_4X$-*p* reacts with 2 molar equivalents of $R_3Al$ in refluxing toluene affording aluminium diketiminate compounds, $[R_2Al\{\eta^2\text{-}(p\text{-}XC_6H_4)NC(Ph)C(R')C(Ph)N(p\text{-}XC_6H_4)\}]$ (R = Et, R′ = Me, X = H **6**; R = Et, R′ = Me, X = Cl **7**; R = Me, R′ = H, X = Cl **8**; R = Me, R′ = H, X = Me **9**; R = Et, R′ = Me, X = Me **10**). Thus, this process offers a readily available synthetic route to the preparation of aluminium diketiminates which is otherwise difficult with aromatic substituents.

## Introduction

The reactions between aldehydes, ketones, carboxylic acids or amidines and trialkylaluminium compounds which yield products of alkyl addition and further enolization have been extensively studied.[1] However, reports on the reactions of amides with trialkylaluminium compounds are scant, despite amidato groups being common ligands in transition metal coordination chemistry.[2] For an amidato group coordinated to aluminium there are several coordination modes possible as shown in Chart 1. The first organoaluminium amidates, $[Me_2Al(RNC(O)R')]_2$, have independently been reported by Wade[3] and Lappert and co-workers[4] as dinuclear complexes that possess an eight-membered ring with the mode VI based on spectroscopic studies. The coordination mode for $[Me_2Al(PhNC(O)Ph)]_2$ has been confirmed by Kakudo and co-workers[5] using X-ray crystallography. However, $[Me_2Al(PhNC(O)Ph)(ONMe_3)]$ is a monomer in which the amidato and $ONMe_3$ groups are both coordinated to the aluminium atom through oxygen atoms.[6] More recently, Barron and co-workers[7] reported the monomeric feature of $[(BHT)_2Al(MeNCOPh)]$ (BHT-H = 2,6-di-*tert*-butyl-4-methylphenol) according to $^{27}$Al NMR and other spectroscopic studies.

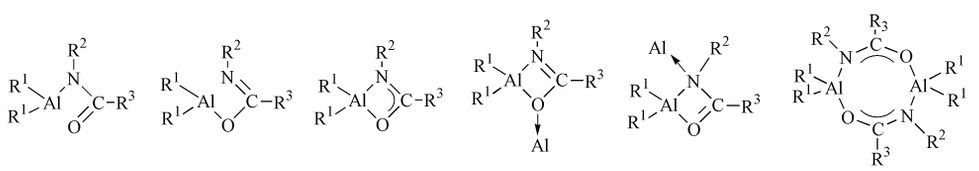
Aluminium diketiminates, which are usually prepared by reactions of diketimines with $R_3Al$, are currently interesting because they serve as precursors for cationic aluminium complexes.[8] Cationic aluminium diketiminates have demonstrated enhanced activities in olefin polymerization.[9] Several methods are available for the preparation of diketimines,[10] but their synthesis is still of interest due to their utility in the preparation of versatile compounds, such as N-heterocycles, β-aminoalcohols, and diketones.[11] In this paper we discuss the role of the Lewis basicity of amides affecting the coordination mode of the amidato ligand on aluminium and report a useful synthetic route to aluminium diketiminates *via* reactions of amides with trialkylaluminium compounds and, in turn, to diketimines.

## Results and discussion

### Syntheses and spectroscopic studies

The reaction of *N*-*tert*-butylbenzamide ($^t$BuNHCOPh) with 1.1 molar equivalents of $Me_3Al$ in refluxing hexane afforded a five-coordinated, dimeric compound $[Me_2Al\{\eta^2\text{-}^t BuNC(Ph)(\mu\text{-}O)\}]_2$ **1** which further reacted with another equivalent of $Me_3Al$ to give a monomeric product $[Me_2Al\{\eta^2\text{-}^t BuNC(Ph)(\mu\text{-}O)\}AlMe_3]$ **2** as shown in Scheme 1. Compound **2** can also be prepared directly in high yield by the reaction of PhCONHBu$^t$ with 2.2 molar equivalents of $Me_3Al$ in refluxing hexane. The yield of **1** as determined by NMR spectroscopy was above 80%, however, due to the similar solubility of **1** and **2**, the isolated yield was only 50% and the microanalysis of **1** was incorrect. In contrast, the reaction of PhCONHAr with 1 molar equivalent of $Me_3Al$ at room temperature afforded four-coordinate,

† Electronic supplementary information (ESI) available: $^1$H NMR spectra of reactions of compound **4** with $Me_3Al$, schemes showing reactions of amides with $R_3Al$. See http://www.rsc.org/suppdata/dt/b0/b009070k/



**I** **II** **III** **IV** **V** **VI**

**Chart 1** Several possible coordination modes of amidate ligands on aluminium.

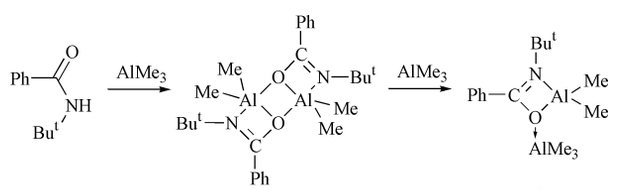
dimeric eight-membered ring aluminium compounds $[Me_2Al\{\mu\text{-}\eta^2\text{-}ArNC(Ph)O\}]_2$ (Ar = 4-MeO-$C_6H_4$ **3** or Ph **4**[3–5]) as shown in Scheme 2. All of these compounds have been characterized by spectroscopic studies as well as elemental analyses. The structures have been verified by X-ray diffraction studies of compounds **1**, **2** and **3**. It seems that the coordination modes of aluminium amidates are dependent on the amides.

It is interesting that the reaction of benzanilide (PhNHC(Ph)O) with 1.2 molar equivalents of $Me_3Al$ in refluxing toluene resulted in formation of a four-coordinate, dimeric compound $[Me_2Al\{\mu\text{-}\eta^2\text{-}PhNC(Ph)O\}]_2$ **4** and a trace amount of an aluminium diketiminate, $[Me_2Al\{\eta^2\text{-}PhNC(Ph)C(H)C(Ph)NPh\}]$ **5**. However, in the presence of 2.4 molar equivalents of $Me_3Al$, benzanilide in refluxing toluene yields 80% **5**. Compound **5** can also be prepared from the reaction of **4** with 2.2 molar equivalents of $Me_3Al$ in refluxing toluene. The formation of aluminium diketiminate **5** prompted us to further investigate similar types of reactions in order to determine (1) the reactivity of $R_3Al$ in general, (2) the source of the methine carbon atom and (3) the possible mechanism for formation of the aluminium diketiminate **5**. For this purpose, several reactions have been examined. Reactions of $PhCONHC_6H_4X\text{-}p$ with 2 molar equivalents of $R_3Al$ in refluxing toluene afforded aluminium diketiminate compounds, $[R_2Al\{\eta^2\text{-}(p\text{-}XC_6H_4)NC(Ph)C(R')C(Ph)N(p\text{-}XC_6H_4)\}]$ (R = Et, R′ = Me, X = H **6**; R = Et, R′ = Me, X = Cl **7**; R = Me, R′ = H, X = Cl **8**; R = Me, R′ = H, X = Me **9**; R = Et, R′ = Me, X = Me **10**) (Scheme 3). The yields as determined by NMR spectroscopy were above 85% for compounds **5**–**10** and the isolated yields of **5**–**7** were also good. In the case of **8**–**10** due to similar solubilities of the aluminium diketiminates and their aluminium amidate precursors, the isolated yields were low. Hydrolysis of the aluminium diketiminate **8**, followed by extraction with diethyl ether, gave the corresponding diketimine in 93% yield. This procedure offers a useful synthetic route to aluminium diketiminate derivatives containing aromatic substituents that are important precursors for the preparation of β-diketimines[12] and of cationic aluminium complexes that have potential applications as catalysts for the polymerization of ethylene.

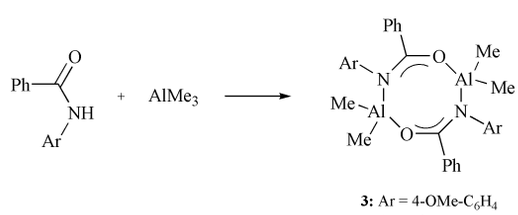
We found that in the absence of $Me_3Al$ not even a trace of compound **5** was detected on refluxing **4** in toluene for 24 h. However, in the presence of 2.2 molar equivalents of $Me_3Al$, **5** could be obtained easily in 85% yield when **4** was heated in refluxing toluene for 16 h. This suggests the possibility that the methine carbon of the diketiminate fragment is derived from the methyl group of the $Me_3Al$ present. In addition, in the reaction of **4** with 3 molar equivalents of $Et_3Al$ in refluxing toluene a mixture of **5** and **6** with a ratio of 1 : 11 was obtained as determined by $^1H$ NMR spectroscopic studies. Based on these observations, we propose that the formation of aluminium diketiminate, **5**, is initiated by the dealkylation of the aluminium amido complex leading to aluminium amidate complex **A** as illustrated in Scheme 4. **A** then dimerizes rapidly to **4** which is stable in the absence of $Me_3Al$. In the presence of an excess of $Me_3Al$ coordination of **4** with $Me_3Al$ occurs forming the intermediate **B**. Methylation of the amide and further enolization of the imine gives **C** and **D** as intermediates. Proton abstraction and intramolecular rearrangement, result in the final product **5**. The formation of **B** from **4** can be further verified by $^1H$ NMR studies of the reaction of **4** with $Me_3Al$.

### $^1H$ NMR studies of the reaction between $Me_3Al$ and compound 4

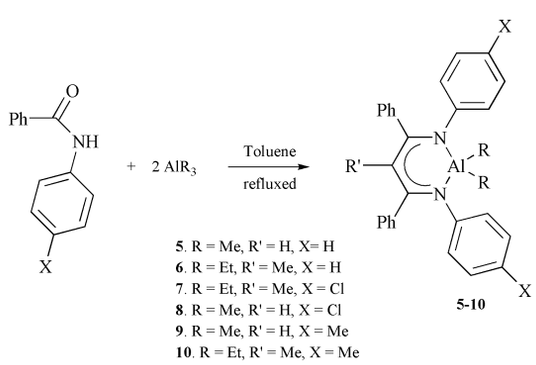
The reaction of compound **4** with 3 molar equivalents of



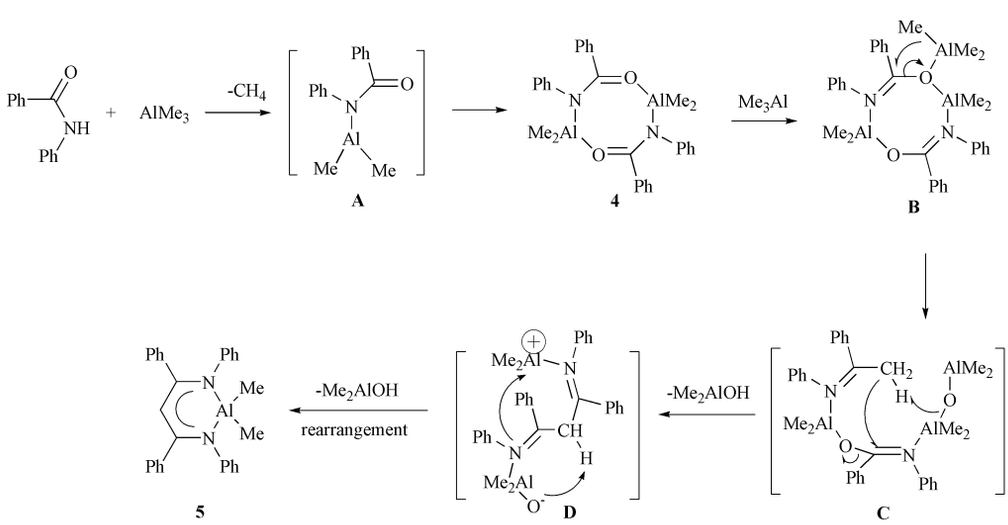

**Scheme 1**




**Scheme 2**




**Scheme 3**




**Scheme 4**

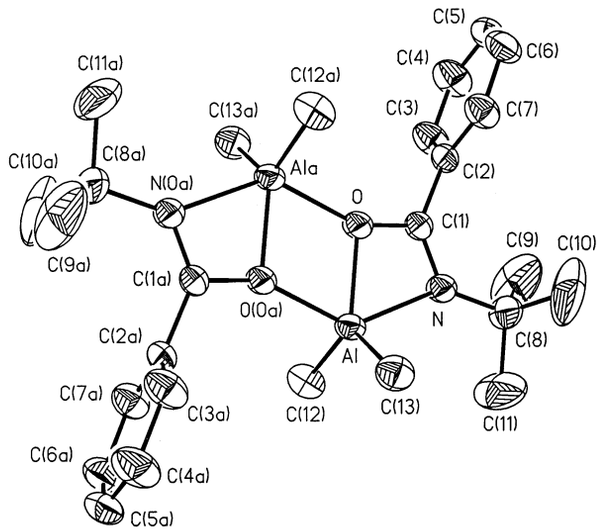



**Fig. 1** Molecular structure of compound **1**, 20% ellipsoids and all hydrogens omitted for clarity as in all cases shown.

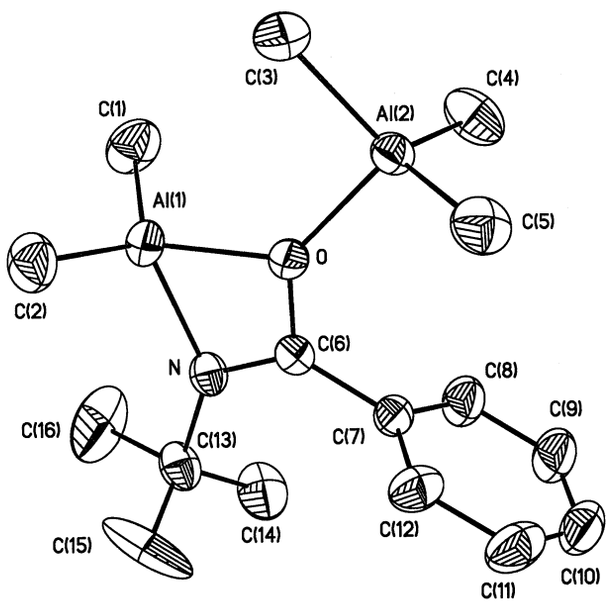



**Fig. 2** Molecular structure of compound **2**.

$Me_3Al$ in toluene-$d_8$ was monitored by $^1H$ NMR spectroscopy. Only one peak was observed in the Al–Me region at ambient temperature indicating that an equilibrium exists between the adduct **B**, **4** and $Me_3Al$.[13] When the mixture was heated to 100 °C for 5 h a resonance at $\delta$ 3.34 corresponding to the formation of an intermediate after the alkylation of **4** started to appear. This peak increased slowly as the reaction proceeded. A new peak at $\delta$ 5.40 corresponding to compound **5** appeared after 32 h and kept increasing in intensity as heating is continued. These NMR studies are consistent with our proposal that the formation of aluminium diketiminate **5** is initiated by dealkylation of aluminium amido complex **4**.

### Molecular structures of compounds 1, 2, 3, 7 and 8

The molecular structures of compounds **1** and **2** are depicted in Figs. 1 and 2 and selected bond distances and bond angles are listed in Tables 1 and 2, respectively. Complex **1** is dimeric adopting mode IV in which the *N-tert*-butylbenzamidato group acts as a chelating ligand bridging two aluminium atoms through the oxygen atom. An interesting feature is that it contains a 4,4,4-fused ring where Al, N, C(1), and O atoms are coplanar with the angle between plane AlNC(1)O and plane AlOAl(a)O(0a) being only 0.8°. The bond lengths of C(1)–N 1.276(3) and C(1)–O 1.338(3) Å indicate a localized structure with a C=N double bond and a C–O single bond. The Al–O distances within the four-membered $Al_2O_2$ chelate ring are asymmetric with bond lengths Al–O 1.910(2) and Al–O(0a) 2.002(2) Å and they are similar to normal Al–O distances in other five-coordinate aluminium alkoxides.[14] The Al–O bond in the $Al_2O_2$ core is detached by the addition of an excess of $Me_3Al$ to give monomeric complex **2**. The geometry around oxygen in **2** is distorted from trigonal planar with bond angles of Al(1)–O–C(6) 90.95(12), Al(2)–O–C(6) 136.31(14), and Al(1)–O–Al(2) 131.42(9)°. The bond lengths C(6)–N 1.279(3) and C(6)–O 1.354(3) Å in **2** are found to be similar to those in **1** indicating a localized structure with a C=N double bond and a C–O single bond character.

**Table 1** Selected bond lengths (Å) and angles (°) for compound **1**

| | | | |
|---|---|---|---|
| Al–O | 1.9096(17) | Al–C(13) | 1.947(3) |
| Al–C(12) | 1.955(3) | Al–O(0a) | 2.0019(18) |
| Al–N | 2.157(2) | Al–C(1) | 2.484(2) |
| O–C(1) | 1.338(3) | O–Al(a) | 2.0019(18) |
| N–C(1) | 1.276(3) | N–C(8) | 1.475(3) |
| | | | |
| O–Al–C(13) | 119.13(11) | O–Al–C(12) | 117.26(12) |
| C(13)–Al–C(12) | 123.51(13) | O–Al–O(0a) | 72.75(7) |
| C(13)–Al–O(0a) | 99.62(11) | C(12)–Al–O(0a) | 99.50(11) |
| O–Al–N | 63.14(7) | C(13)–Al–N | 100.79(11) |
| C(12)–Al–N | 101.03(11) | O(0a)–Al–N | 135.89(7) |
| O–Al–C(1) | 32.23(8) | C(13)–Al–C(1) | 113.04(10) |
| C(12)–Al–C(1) | 112.27(11) | O(0a)–Al–C(1) | 104.98(7) |
| N–Al–C(1) | 30.91(7) | C(1)–O–Al | 98.22(14) |
| C(1)–O–Al(a) | 154.52(15) | Al–O–Al(a) | 107.25(7) |
| C(1)–N–C(8) | 128.8(2) | C(1)–N–Al | 88.83(14) |
| C(8)–N–Al | 142.29(16) | N–C(1)–O | 109.81(19) |
| N–C(1)–C(2) | 133.4(2) | O–C(1)–C(2) | 116.8(2) |

**Table 2** Selected bond lengths (Å) and angles (°) for compound **2**

| | | | |
|---|---|---|---|
| Al(1)–C(1) | 1.915(4) | Al(1)–O | 1.9172(16) |
| Al(1)–C(2) | 1.931(3) | Al(1)–N | 1.949(2) |
| Al(2)–O | 1.9366(16) | Al(2)–C(4) | 1.950(3) |
| Al(2)–C(5) | 1.950(3) | Al(2)–C(3) | 1.973(3) |
| O–C(6) | 1.354(3) | N–C(6) | 1.279(3) |
| N–C(13) | 1.498(3) | C(6)–C(7) | 1.476(3) |
| | | | |
| C(1)–Al(1)–O | 114.10(16) | C(1)–Al(1)–C(2) | 122.98(19) |
| O–Al(1)–C(2) | 112.11(13) | C(1)–Al(1)–N | 114.84(15) |
| O–Al(1)–N | 67.63(7) | C(2)–Al(1)–N | 112.39(13) |
| C(1)–Al(1)–C(6) | 120.09(16) | C(2)–Al(1)–C(6) | 116.94(14) |
| O–Al(2)–C(4) | 104.76(13) | O–Al(2)–C(5) | 107.78(11) |
| C(4)–Al(2)–C(5) | 115.49(18) | O–Al(2)–C(3) | 97.14(12) |
| C(4)–Al(2)–C(3) | 116.05(19) | C(5)–Al(2)–C(3) | 113.13(18) |
| C(6)–O–Al(1) | 90.95(12) | C(6)–O–Al(2) | 136.31(14) |
| Al(1)–O–Al(2) | 131.42(9) | C(6)–N–C(13) | 128.6(2) |
| C(6)–N–Al(1) | 91.83(14) | C(13)–N–Al(1) | 139.39(16) |
| N–C(6)–O | 109.58(19) | N–C(6)–C(7) | 132.5(2) |
| O–C(6)–C(7) | 117.90(18) | | |

The molecular structure of compound **3** is depicted in Fig. 3 and selected bond lengths and angles are listed in Table 3. Complex **3** crystallizes in a dimeric form and is composed of a centrosymmetrical eight-membered ring (mode VI). The bridging NCO group coordinates to two aluminium atoms through both nitrogen and oxygen atoms. The aluminium atom has a distorted tetrahedral coordination consisting of two methyl carbons, nitrogen and oxygen atoms. The bond lengths C(1)–N 1.307(2) and C(1)–O(1) 1.300(2) Å indicate a delocalized structure within the OCN group. N, C(1), O(1), C(2), and C(8) are coplanar with deviations of only 0.012 Å. The bond distances Al–O(1) 1.818(1), Al–N(0a) 1.965(1), Al–C(15) 1.950(2), and Al–C(16) 1.959(2) Å in **3** are all similar to those of its analog $[Me_2Al(\mu\text{-}\eta^2\text{-PhNCOPh})]_2$.[4] Based on the crystal structures of **1, 2, 3** and $[Me_2Al(\mu\text{-}\eta^2\text{-PhNCOPh})]_2$, it seems that the coordination mode of the amidato ligand on aluminium is

**Table 3** Selected bond lengths (Å) and angles (°) for compound **3**

| | | | |
|---|---|---|---|
| Al–O(1) | 1.8177(10) | Al–C(15) | 1.9503(17) |
| Al–C(16) | 1.9587(17) | Al–N(0a) | 1.9650(11) |
| O(1)–C(1) | 1.2997(15) | N–C(1) | 1.3073(18) |
| N–Al(0a) | 1.9650(11) | | |
| | | | |
| O(1)–Al–C(15) | 108.67(6) | O(1)–Al–C(16) | 109.23(7) |
| C(15)–Al–C(16) | 116.45(9) | O(1)–Al–N(0a) | 102.72(5) |
| C(15)–Al–N(0a) | 111.98(7) | C(16)–Al–N(0a) | 106.90(6) |
| C(1)–O(1)–Al | 127.83(8) | C(11)–O(2)–C(14) | 118.45(15) |
| C(1)–N–C(8) | 122.44(11) | C(1)–N–Al(a) | 118.25(9) |
| C(8)–N–Al(a) | 118.97(8) | O(1)–C(1)–N | 117.14(11) |
| O(1)–C(1)–C(2) | 116.25(11) | N–C(1)–C(2) | 126.56(11) |

**Table 4** Selected bond lengths (Å) and angles (°) for compound **7**

| | | | |
|---|---|---|---|
| Al–N(1) | 1.918(4) | Al–N(2) | 1.928(4) |
| Al–C(29) | 1.890(7) | Al–C(31) | 1.969(8) |
| N(1)–C(1) | 1.344(5) | N(1)–C(4) | 1.446(5) |
| N(2)–C(3) | 1.335(5) | N(2)–C(23) | 1.438(5) |
| C(1)–C(2) | 1.403(5) | C(1)–C(10) | 1.498(5) |
| C(2)–C(3) | 1.396(5) | C(2)–C(16) | 1.523(5) |
| | | | |
| C(29)–Al–N(1) | 113.6(3) | C(29)–Al–N(2) | 112.0(3) |
| N(1)–Al–N(2) | 91.57(15) | C(29)–Al–C(31) | 112.8(4) |
| N(1)–Al–C(31) | 112.0(3) | N(2)–Al–C(31) | 113.2(3) |
| C(1)–N(1)–C(4) | 119.6(3) | C(1)–N(1)–Al | 122.3(3) |
| C(4)–N(1)–Al | 117.6(3) | C(3)–N(2)–C(23) | 120.0(3) |
| C(3)–N(2)–Al | 122.5(3) | C(23)–N(2)–Al | 116.9(3) |
| N(1)–C(1)–C(2) | 123.3(4) | N(1)–C(1)–C(10) | 117.5(3) |
| C(2)–C(1)–C(10) | 119.1(3) | C(3)–C(2)–C(1) | 124.1(3) |
| C(3)–C(2)–C(16) | 118.0(3) | C(1)–C(2)–C(16) | 117.9(4) |
| N(2)–C(3)–C(2) | 123.8(4) | N(2)–C(3)–C(17) | 118.2(4) |
| C(2)–C(3)–C(17) | 118.0(3) | C(9)–C(4)–C(5) | 118.8(4) |

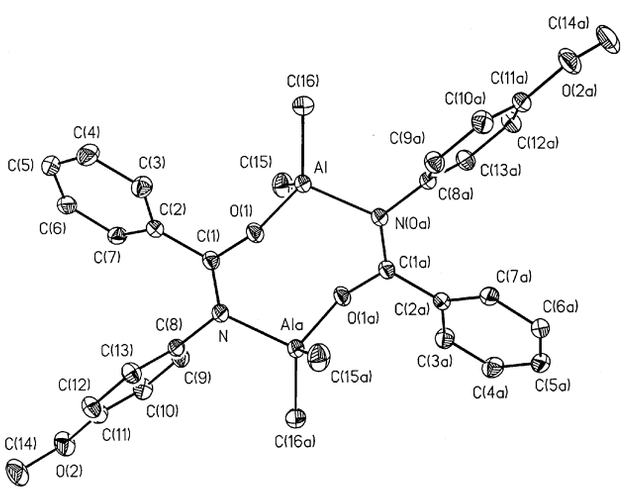



**Fig. 3** Molecular structure of compound **3**.

highly dependent on the basicity of the amide and the steric hindrance of the substituent on nitrogen. The more acidic and less steric hindered amides such as benzanilide tend to form eight-membered ring complexes. In contrast less acidic and more sterically hindered amides, such as *N*-*tert*-butylbenzamide, prefer to have four-membered rings.[15] Further studies of the Lewis acidity and steric effect of amides on the coordination modes of amidato ligands on aluminium are in progress.

The molecular structures of compounds **7** and **8** are shown in Fig. 4 and bond lengths and angles are listed in Tables 4 and 5, respectively. The geometry around aluminium in **7** is distorted from tetrahedral with the bond distance Al–N(1) at 1.918(4), Al–N(2) at 1.928(4), Al–C(29) at 1.890(7), and Al–C(31) at 1.969(8) Å. The AlNCCCN backbone of the aluminium diketiminate is essentially planar. Similar bond lengths of C(1)–N(1) 1.344(5), C(3)–N(2) 1.335(5), C(1)–C(2) 1.403(5), and C(2)–C(3) 1.396(5) Å present further evidence for a delocalized structure within the diketiminato ligand which has also been observed in other aluminium diketiminates.[16] Compound **8** differs from **7** by replacing the methyl groups on aluminium with ethyl as well as a proton at the 2 position instead of methyl on the diketiminate group. The geometry around Al in **8** is nearly identical to that for **7** with bond distances Al–N(1) 1.927(2), Al–N(2) 1.917(2), Al–C(28) 1.951(2), and Al–C(29) 1.961(2) Å, respectively.

**Table 5** Selected bond lengths (Å) and angles (°) for compound **8**

| | | | |
|---|---|---|---|
| Al–N(2) | 1.9170(15) | Al–N(1) | 1.9266(15) |
| Al–C(28) | 1.951(2) | Al–C(29) | 1.961(2) |
| Cl(1)–C(7) | 1.7418(18) | Cl(2)–C(25) | 1.740(2) |
| N(1)–C(1) | 1.335(2) | N(1)–C(4) | 1.440(2) |
| N(2)–C(3) | 1.343(2) | N(2)–C(22) | 1.436(2) |
| C(1)–C(2) | 1.402(2) | C(1)–C(10) | 1.493(2) |
| C(2)–C(3) | 1.392(2) | | |
| | | | |
| N(2)–Al–N(1) | 94.94(6) | N(2)–Al–C(28) | 111.72(9) |
| N(1)–Al–C(28) | 109.64(8) | N(2)–Al–C(29) | 108.63(8) |
| N(1)–Al–C(29) | 111.51(8) | C(28)–Al–C(29) | 118.01(9) |
| C(1)–N(1)–C(4) | 119.73(14) | C(1)–N(1)–Al | 123.54(12) |
| C(4)–N(1)–Al | 116.72(10) | C(3)–N(2)–C(22) | 119.80(14) |
| C(3)–N(2)–Al | 122.48(12) | C(22)–N(2)–Al | 117.70(11) |
| N(1)–C(1)–C(2) | 122.25(15) | N(1)–C(1)–C(10) | 121.82(15) |
| C(2)–C(1)–C(10) | 115.85(15) | C(3)–C(2)–C(1) | 128.26(16) |
| N(2)–C(3)–C(2) | 122.73(15) | N(2)–C(3)–C(16) | 120.70(15) |

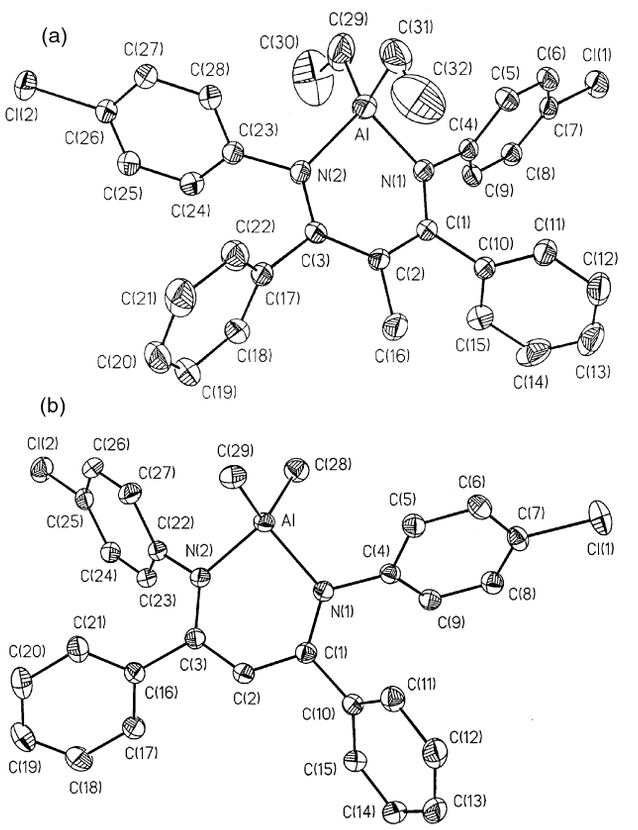



**Fig. 4** Molecular structures of (a) $[Et_2Al\{\eta^2\text{-}(p\text{-}ClC_6H_4)NC(Ph)C(Me)C(Ph)N(p\text{-}ClC_6H_4)\}]$ **7** and (b) $[Me_2Al\{\eta^2\text{-}(p\text{-}ClC_6H_4)NC(Ph)C(H)C(Ph)N(p\text{-}ClC_6H_4)\}]$ **8**.

In conclusion, we have developed a useful synthetic route to the preparation of aluminium diketiminate derivatives by reactions of amides with trialkylaluminium. Aluminium diketiminates are useful precursors for many applications. They can easily be converted into diketimines and their derivatives that also represent useful precursors for further synthetic purposes.

## Experimental

### General

All experiments were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least 24 hours over sodium–benzophenone (toluene, hexane), or phosphorus pentaoxide ($CH_2Cl_2$) and freshly distilled prior to use. Deuteriated solvents were dried over molecular sieves. $Me_3Al$ (2.0 M in toluene) and $Et_3Al$ (1.9 M in toluene) were purchased and used without further treatment. Benzanilide was recrystallized prior to use. *N-tert*-Butylbenzamide, $PhCONHC_6H_4OMe$-*p*, $PhCONHC_6H_4Cl$-*p*, and $PhCONHC_6H_4Me$-*p* were prepared according to the literature method.[17] Melting points were determined with a Buchi 535 digital melting point apparatus. $^1H$ and $^{13}C$ NMR spectra were recorded on a VXR-200 (200 MHz) or a VXR-300 (300 MHz) spectrometer with chemical shifts given in ppm from internal TMS. The temperatures for the VT NMR studies were calibrated with the methanol peaks. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer.

### Preparations

**$[Me_2Al(\mu\text{-}\eta^2\text{-}Bu^tNCOPh)]_2$ 1.** To a rapidly stirred solution of *N-tert*-butylbenzamide (0.71 g, 4.0 mmol) in hexane (10 ml) was added $Me_3Al$ (2.2 ml, 4.4 mmol). The reaction mixture was heated to reflux for 24 h and the volatile materials were removed under vacuum giving white solids. The residue was taken up in toluene (30 ml) and the insoluble material removed by filtration. The filtrate was allowed to concentrate to *ca*. 15 ml and colorless crystals were obtained at −20 °C after 12 h. Yield: 0.47 g (50%). $^1H$ NMR ($CDCl_3$): $\delta$ 7.45–7.38 (m, 5H, Ph), 1.10 (s, 9H, $Bu^t$), −0.86 (s, 6H, $AlCH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 167.10 (C=N), 133.80, 129.82, 128.06, 127.26 (Ph), 52.89 (C-N), 31.11 ($C(CH_3)_3$) and −10.8 ($AlCH_3$). mp 113–115 °C.

**$[Me_2Al\{Bu^tNCOPh)\}AlMe_3]$ 2.** Following the same procedures as above but with 2.2 molar equivalents of $Me_3Al$, colorless crystals of **2** were obtained. Yield: 1.0 g (82%). Calc. for $C_{16}H_{29}Al_2NO$: C, 62.93; H, 9.57; N, 4.59%. Found: C, 62.50; H, 9.36; N, 4.86%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.62–7.36 (m, 5H, Ph), 1.19 (s, 9H, $Bu^t$), −0.45 (s, 6H, $AlMe_2$) and −0.86 (s, 9H, $AlMe_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 172.68 (C=N), 131.46, 129.57, 128.38, 127.42 (Ph), 54.43 (C–N), 30.69 ($C(CH_3)_3$), −8.06 ($AlMe_3$) and −10.27 ($AlMe_2$). mp 86–90 °C.

**$[Me_2Al(\mu\text{-}\eta^2\text{-}(4\text{-}MeO\text{-}C_6H_4)NCOPh)]_2$ 3.** To a rapidly stirred solution of $PhCONHC_6H_4OMe$-*p* (0.91 g, 4.0 mmol) in hexane (30 ml) was added $Me_3Al$ (2.1 ml, 4.2 mmol). The reaction mixture was stirred at 25 °C for 16 h and the volatile materials were removed under vacuum to give a white solid. The residue was extracted by toluene (30 ml) and allowed to concentrate to *ca*. 15 ml. Colorless crystals were obtained at room temperature after 12 h. Yield: 1.10 g (50%). Calc. for $C_{16}H_{18}AlNO_2$: C, 66.41; H, 6.69; N, 5.16%. Found: C, 65.93; H, 6.23; N, 5.68%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.37–6.51 (m, 8H, Ph), 3.75 (s, 3H, $OCH_3$) and −0.91 (s, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 174.81 (C=N), 157.58, 135.60, 134.18, 130.62, 129.45, 127.85, 114.05 (Ph), 55.08 ($OCH_3$) and −10.41 ($CH_3$). IR (KBr, $cm^{-1}$, 1500–1700 $cm^{-1}$): 1656(s), 1591(s) and 1533 (s). mp 129–131 °C (decomp.).

**Thermal reaction of benzanilide with $Me_3Al$.** To a rapidly stirred solution of benzanilide (0.79 g, 4.0 mmol) in toluene (30 ml) was added $Me_3Al$ (2.4 ml, 4.8 mmol). The reaction mixture was refluxed for 24 h during which it changed from colorless to yellow. The volatile materials were removed under vacuum and the residue was extracted with hot hexane (75 ml). The extract was then concentrated to *ca*. 25 ml and allowed to cool to room temperature giving $[Me_2Al\{\mu\text{-}\eta^2\text{-}PhNC(Ph)O\}]_2$ **4** (71%). The residue was redissolved in toluene (10 ml) followed by cooling to −20 °C yielding yellow crystals of $[Me_2Al\{\eta^2\text{-}PhNC(Ph)C(H)C(Ph)NPh\}]$ **5** (5%). Compound **4** (Calc. for $C_{15}H_{16}AlNO$: C, 71.13; H, 6.37; N, 5.53%. Found: C, 70.90; H, 5.93; N, 5.89%): $^1H$ NMR ($CDCl_3$) $\delta$ 7.35–6.97 (m, 10H, Ph) and −0.89 (s, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$ 174.58 (C=N), 142.66, 133.96, 130.62, 129.35, 128.77, 127.72, 126.53, 125.94 (Ph) and −10.8($CH_3$); IR (KBr, $cm^{-1}$, 1500–1700 $cm^{-1}$) 1656(s), 1591(s) and 1533 (s). mp 103–105 °C.

**$[Me_2Al\{\eta^2\text{-}PhNC(Ph)C(H)C(Ph)NPh\}]$ 5.** To a rapidly stirred solution of compound **4** (2.02 g, 4.0 mmol) in toluene (10 ml) was added $Me_3Al$ (4.2 ml, 8.4 mmol). The reaction mixture was then refluxed for 16 h and the volatile materials were removed under vacuum. The residue was extracted by hot hexane (75 ml) and the filtrate allowed to concentrate to *ca*. 25 ml. Greenish yellow crystals were obtained overnight at room temperature. Yield: 1.46 g (85%). Calc. for $C_{29}H_{27}AlN_2$: C, 80.91; H, 6.32; N, 6.51%. Found: C, 80.73; H, 6.21; N, 6.91%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.26–6.91 (m, 10H, Ph), 5.28 (s, 1H, CH), 4.63 and −0.81 (s, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 168.8 (C=N), 142.01, 139.37, 128.87, 128.35, 128.28 (Ph), 101.63 (C=C) and −8.87 ($CH_3$). IR (KBr, $cm^{-1}$, 1500–1700 $cm^{-1}$): 1655(s) and 1591(s). mp 126–128 °C.

**General procedures for compounds 6–10.** To a rapidly stirred solution of benzanilide (0.79 g, 4.0 mmol) in toluene (10 ml) was added $Et_3Al$ (4.2 ml, 8.0 mmol). The reaction mixture was refluxed for 16 h and the volatile materials were removed under vacuum. The residue was extracted with hot hexane (25 ml) and the extract allowed to concentrate to *ca*. 10 ml. Greenish yellow crystals were obtained at room temperature overnight.

*Compound* ***6.*** Yield: 1.72 g (67%). Calc. for $C_{32}H_{33}AlN_2$: C, 81.83; H, 7.10; N, 6.25%. Found: C, 81.33; H, 7.04; N, 5.93%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.36–6.91 (m, 10H, Ph), 1.34 (s, 1H, CH), 0.81 (t, 3H, $CH_3$) and −0.20 (q, 2H, $CH_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 171.03 (C=N), 146.42, 138.66, 129.40, 128.03, 127.79, 126.49, 124.18 (Ph), 100.99 ($CCH_3$), 20.60 ($CCH_3$), 9.33 ($CH_2CH_3$) and 0.77 ($CH_2CH_3$). IR (KBr, $cm^{-1}$, 1500–1700 $cm^{-1}$): 1655 (s), 1595 (s) and 1536 (s). mp 128.5–130.5 °C.

*Compound* ***7.*** Yield: 1.72 g (86%). Calc. for $C_{32}H_{31}AlCl_2N_2$: C, 70.98; H, 5.77; N, 5.17%. Found: C, 70.51; H, 5.60; N, 5.62%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.26–6.78(m, 18H, Ph), 1.32 (s, 1H, CH), 0.80 (t, 3H, $CH_3$) and −0.22 (q, 2H, $CH_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 171.33 (C=N), 144.95, 138.19, 130.17, 129.78, 129.26, 128.25, 128.10, 127.57 (Ph), 20.60 ($CCH_3$), 9.31 ($CH_2CH_3$) and 0.61 ($CH_2CH_3$). mp: 160–162 °C.

*Compound* ***8.*** Yield: 0.48 g (22%). Calc. for $C_{29}H_{25}AlCl_2N_2$: C, 69.75; H, 5.05; N, 5.61%. Found: C, 69.19; H, 5.18; N, 5.99%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.30–6.81(m, 18H, Ph), 5.30 (s, 1H, CH) and −0.83 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 169.25 (C=N), 144.68, 138.91, 130.17, 128.90, 128.85, 128.64, 128.00, 127.44 (Ph), 102.23 (CH) and −9.18 ($CH_3$). mp 157–159 °C.

*Compound* ***9.*** Yield: 0.21 g (23%). Calc. for $C_{31}H_{31}AlN_2$: C, 81.19; H, 6.81; N, 6.11%. Found: C, 81.80; H, 7.13; N, 5.50%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.27–6.77 (m, 18H, Ph), 5.21 (s, 1H, CH), 2.20 (s, 6H, $CH_3$) and −0.82 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 168.77 (C=N), 143.50, 139.70, 133.9, 129.04, 128.97, 128.30, 127.71, 126.08 (Ph), 101.46 (CH), 20.86 (CH) and −9.10 ($AlCH_3$).

*Compound* ***10.*** Yield: 0.25 g (25%). Calc. for $C_{34}H_{37}AlN_2$: C, 81.57; H, 7.45; N, 5.60%. Found: C, 81.80; H, 7.13; N, 5.50%. $^1H$ NMR ($CDCl_3$), $\delta$ 7.19–6.73 (m, 10H, Ph), 2.15 (s 6H, $CH_3$), 1.30 (s, 1H, $CH_3$), 0.81 (t, 3H, $CH_3$) and −0.23 (q, 2H, $CH_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.84 (C=N), 143.80, 138.91, 133.46, 129.38, 128.63, 127.78, 127.60, 126.18 (Ph), 100.60 ($CCH_3$),

**Table 6** Crystallographic data for compounds **1**, **2**, **3**, **7** and **8**

| | **1** | **2** | **3** | **7** | **8** |
|---|---|---|---|---|---|
| Chemical formula | $C_{13}H_{20}AlNO$ | $C_{16}H_{29}Al_2NO$ | $C_{16}H_{18}AlNO_2$ | $C_{32}H_{31}AlCl_2N_2$ | $C_{29}H_{25}AlCl_2N_2$ |
| $M$ | 233.3 | 305.4 | 283.3 | 541.5 | 499.4 |
| Space group | $C2/c$ | $Pbca$ | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Monoclinic | Monoclinic |
| $a$/Å | 22.798(3) | 14.576(1) | 10.102(1) | 9.8996(7) | 7.3864(5) |
| $b$/Å | 11.009(2) | 13.431(1) | 9.746(1) | 25.165(2) | 20.746(1) |
| $c$/Å | 12.582(2) | 21.021(2) | 16.249(1) | 12.537(1) | 17.518(1) |
| $\beta$/° | 112.38(2) | — | 104.01(2) | 94.80(1) | 98.09(1) |
| $V$/Å$^3$ | 2920.1(7) | 4115.4(5) | 1552.2(2) | 3112.3(11) | 2657.7(3) |
| $Z$ | 8 | 8 | 4 | 4 | 4 |
| $T$/K | 293 | 293 | 293 | 293 | 293 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.121 | 0.137 | 0.131 | 0.259 | 0.297 |
| No. observed reflections [$F > 4\sigma(F)$] | 2875 | 4050 | 3034 | 6131 | 5226 |
| No. parameters | 145 | 262 | 181 | 334 | 307 |
| $R1$ | 0.0582 | 0.0546 | 0.0366 | 0.0771 | 0.0420 |
| $wR2$ | 0.1904 | 0.1920 | 0.1281 | 0.2182 | 0.1407 |

20.84 ($CHCH_3$), 20.60 ($CH_3$), 9.37 ($CH_2CH_3$) and 0.84 ($CH_2CH_3$).

### Hydrolysis of aluminium diketiminate

Compound **8** (0.20 g, 0.4 mmol) was suspended in water (30 ml) and stirred at room temperature for 16 h. The mixture was then extracted with diethyl ether (10 ml) twice. The extract was then dried under vacuum to give a colorless solid. Yield: 0.16 g (93%). Calc. for $C_{27}H_{20}Cl_2N_2$: C, 73.14; H, 4.55; N, 6.32%. Found: C, 73.09; H, 4.82; N, 6.90%. $^1$H NMR ($CDCl_3$): $\delta$ 7.29 (m, 12H, Ph), 7.06 (d, $J$ = 7.8, Ph), 6.65 (d, $J$ = 8.8 Hz, Ph) and 5.39 (s, 1H, CH). $^{13}$C NMR ($CDCl_3$): $\delta$ 161.37 (C=N), 143.94, 137.59, 128.76, 128.57, 128.35, 128.25, 127.92, 123.47 (Ph) and 102.48 (CH).

### Thermal reaction of compound 4 with $Et_3Al$

To a rapidly stirred solution of compound **4** (1.52 g, 3.0 mmol) in toluene (10 ml) was added $Et_3Al$ (4.3 ml, 8.0 mmol). The reaction mixture was then refluxed for 16 h and the volatile materials were removed under vacuum. The residue was extracted by hot hexane (50 ml) and the extract allowed to concentrate to *ca*. 25 ml. Greenish yellow crystals were obtained overnight at room temperature. $^1$H NMR spectroscopic study of the residue showed that it is a mixture of **5** and **6** with a molar ratio 1 : 11.

### X-Ray crystallographic studies

Suitable crystals of compound **1**, **2**, **3**, **7** and **8** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Absorption corrections were made based on symmetry equivalent reflections using the SADABS program.[18] The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structures were solved by direct methods using a SHELXTL package.[19] All non-H atoms were located from successive Fourier maps and hydrogen atoms refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data are listed in Table 6. In compound **2** the *tert*-butyl group on the nitrogen atom is disordered. There are two positions for each carbon atom attached to the carbon attached to the nitrogen atom. The final value for the site occupancy of the two *tert*-butyl groups is 60/40.

CCDC reference numbers 139979, 139980 and 152733–152735.

See http://www.rsc.org/suppdata/dt/b0/b009070k/ for crystallographic data in CIF or other electronic format.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