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Dialkyl aluminium amides: new reagents for the conversion of C=O into C=NR functionalities†

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A new methodology for the preparation of α-diimines and β-aminoenones has been devised and represents an alternative route to these and related nitrogenous ligands bearing highly electronegative substituents.

α-Diimines, β-diimines and β-ketoimines are assuming increasingly important roles as ligands in catalytic processes[1] and also for the stabilization of unusual bonding situations.[2] The standard method for the synthesis of such ligands involves the reaction of an α- or β-diketone with the appropriate primary amine in the presence of an acid catalyst.[3] While many of these reactions proceed in high yields, this methodology is less satisfactory for acid-sensitive carbonyls and weakly nucleophilic primary amines.[4] In order to develop catalytic systems with enhanced activity at metal centers, it has become desirable to attach highly electronegative substituents to the nitrogen atoms of these classes of ligands.[5] Since primary amines containing electron withdrawing groups are anticipated to be poor nucleophiles, we envisioned that a new synthetic methodology for converting C=O into C=NR functionalities was called for (where R may be for example, a (per)fluorinated aromatic group).

The fact that Al–O and O–H bonds are appreciably stronger than Al–N and N–H bonds suggested that primary aminoalanes would be suitable reagents for effecting the desired transformations (eqn. 1).

$$1/n[R_2AlN(H)Ar]_n \;+\; {>}C{=}O \longrightarrow [R_2AlOH] \;+\; {>}C{=}NAr \qquad (1)$$

Further support for this concept stems from the observation[6] that lithium aluminium amides will convert aldehydes and cyclic ketones into the corresponding imines. It is not known, however, whether this route is effective for aldehydes and ketones with highly electronegative substituents.

The following aminoalanes have been prepared in moderate to good yields by treatment of the appropriate primary amine with $AlMe_3$ in toluene solution: $[Me_2Al$-μ-$N(H)Ar]_2$ (Ar = *p*-fluorophenyl (**1**), 3,5-difluorophenyl (**2**), and pentafluorophenyl (**3**)).‡ The dimeric nature of **2** and **3** in the solid state was confirmed by X-ray crystallography.§ Compound **2** adopts a *cis* geometry with respect to the nitrogen substituents on the Al_2N_2 ring (Fig. 1) while in the case of **3**, the stereochemistry is *trans*. Structurally characterized examples of aluminoalane complexes have been previously reported in the literature.[7]

In two of the three α-diketone reactions studied, the use of the new aminoalane reagents results in a higher yield of the α-diimine product than that afforded by use of the primary amine methodology. Specifically, the reactions of 2,3-butanedione with **1**, **2** and **3** afford the α-diimines, ArN=CMeCMe=NAr, **4** (Ar = *p*-fluorophenyl), **5** (Ar = 3,5-difluorophenyl), and **6** (Ar = C_6F_5) in yields of 59, 22 and 15%, respectively, while the corresponding yields for the primary amine route are 70, 0.7 and 0.2%, respectively. By way of comparison, Tilset *et al.*[5a] reported that a 26% yield of ArN=CMeCMe=NAr (Ar = 3,5-$(CF_3)_2C_6H_3$) can be obtained from the reaction of 3,5-bis(trifluoromethyl)aniline with 2,3-butanedione. A further advantage of the aminoalane route is that the procedures are much cleaner for the majority of the reactions investigated, thus greatly facilitating product separation and purification. The crystalline diimines **4** and **6** possesses a *trans* molecular structure exemplified by that of **6** which is shown in Fig. 2.

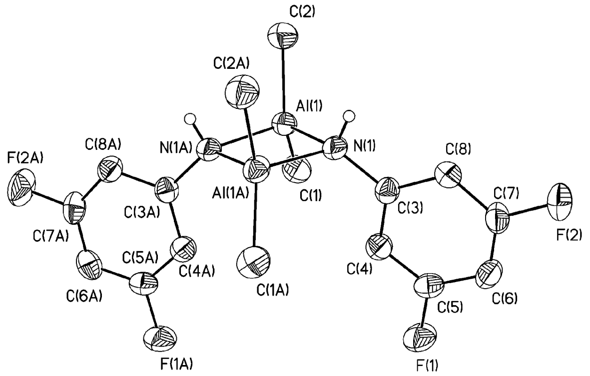

Fig. 1 Thermal ellipsoid plot (30% probability level) for **2**. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.971(2), Al(1)–N(1A) 1.989(2), Al(1)–C(1) 1.937(3), Al(1)–C(2) 1.939(3), N(1)–Al(1)–N(1A) 87.64(9), Al(1)–N(1)–Al(1A) 92.22(9), C(1)–Al(1)–C(2) 123.12(16).

The aminoalanes **1**, **2** and **3** also react with 2,4-pentanedione to afford the β-aminoenones O=CMeCH=C(Me)N(H)Ar, **7** (Ar = *p*-fluorophenyl), **8** (Ar = 3,5-difluorophenyl) and **9** (Ar = C_6F_5) in yields of 68, 57 and 52%, respectively. The yields of **7**, **8** and **9** obtained *via* the conventional approach are somewhat inferior (54, 14 and 11%, respectively). Compounds **7**–**9** adopt the β-aminoenone structure in the solid state rather than the β-ketoimine tautomeric alternative and the C=O and C–N(H)Ar functionalities are arranged in a *syn* fashion (Fig. 3). Such a

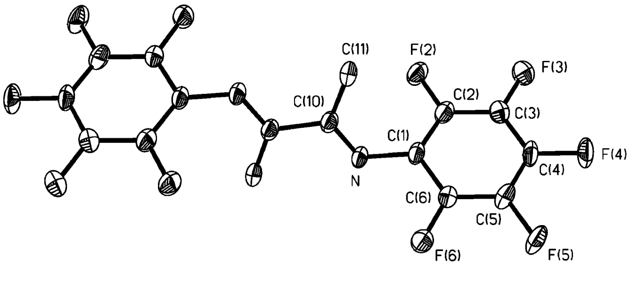

Fig. 2 Thermal ellipsoid plot (30% probability level) for **6**. Selected bond distances (Å) and angles (°): N(1)–C(10) 1.293(4), C(10)–C(10A) 1.494(5), C(10)–C(11) 1.487(5), N(1)–C(1) 1.408(4), C(10A)–C(10)–C(11) 118.8(3), C(10A)–C(10)–N(1) 114.8(3), C(11)–C(10)–N(1) 126.4(3).

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† Electronic supplementary information (ESI) available: HRMS, ^1H and ^{19}F NMR data for **1**–**9**. See http://www.rsc.org/suppdata/cc/b2/b203693b/

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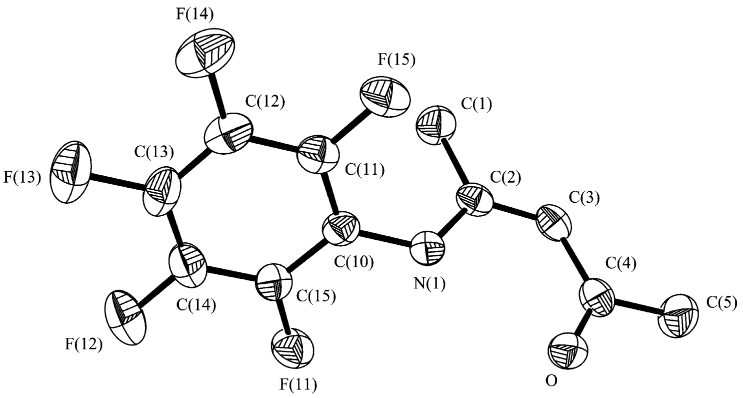

Fig. 3 Thermal ellipsoid plot (30% probability level) for **9**. Selected bond distances (Å) and angles (°): N(1)–C(10) 1.411(4), N(1)–C(2) 1.349(4), C(2)–C(3) 1.374(4), C(3)–C(4) 1.427(5), C(4)–C(5) 1.506(5), C(4)–O 1.240(4), C(10)–N(1)–C(2) 125.2(3), N(1)–C(2)–C(1) 117.7(3), C(1)–C(2)–C(3) 121.6(3), N(1)–C(2)–C(3) 120.7(3), C(3)–C(4)–O 121.9(3), C(3)–C(4)–C(5) 119.2(3), C(5)–C(4)–O 118.9(3).

structure assignment is consistent with the pattern of bond distances in the NC_3O skeleton (Fig. 3 caption) and the detection of N–H resonances at δ (ppm, C_6D_6) 12.8 (**7**), 12.7 (**8**) and 12.5 (**9**) in the ^1H NMR spectra. The coordination chemistry of these new and related nitrogenous ligands bearing highly electronegative substituents is under active investigation.

In summary, the aminoalane method represents a useful alternative methodology for the conversion of C=O into C=NR functionalities. Complementarity between the amine and aminoalane routes is nicely illustrated by the fact that the reaction of 2,4-pentanedione with $(C_6F_5)_2NH$ and *p*-toluene sulfonic acid in refluxing toluene results in the corresponding β-diketimine[8] while the reaction of 2,4-pentanedione with **3** affords β-aminoalane **9**.

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Notes and references

‡ *Synthetic procedures*: note that standard Schlenk-line and glovebox techniques were used when appropriate.

(a) *Aminoalane complexes **1**–**3***. A toluene solution of the appropriate primary amine was added dropwise to an equimolar quantity of $AlMe_3$ in toluene solution. Following the cessation of gas evolution, the reaction mixture was stirred for an additional 1.0 h at ambient temperature. Colorless crystals of **1**, **2** and **3** were obtained upon storage of resulting solutions overnight at −30 °C in yields of 45, 28, and 27%, respectively.

(b) *α-Diimines **4**–**6** and β-aminoenones **7**–**9***. The α-diimines **4**–**6** were prepared by addition of a toluene solution of the aminoalane complex **1**, **2** or **3** to an equimolar quantity of 2,3-butanedione in toluene solution. In each case, the resulting solution was treated with methanol and DI water, followed by extraction with $CHCl_3$. After drying over $MgSO_4$, the organic layer was filtered through a frit fitted with a pad of alumina. Colorless crystals of **4** and **5** were obtained by storage of the saturated 2 : 1 pentane–Et_2O solutions overnight at −30 °C. The β-aminoenones **7**–**9** were prepared by addition of a toluene solution of **1**, **2** or **3** to a toluene solution of 2,4-pentanedione. (The use of either 1 : 1 or 2 : 1 mole ratios of aminoalane : diketone produced the same result.) In the case of **9**, the stirred reaction mixture was refluxed for 45 h, while for **7** and **8** the reaction mixture was stirred for 90 h at ambient temperature. Crystals of **8** and **9** were grown in the same manner as **4** and **5**, while crystals of **7** were grown as described for **6**.

§ *Crystal data* for **2**: $C_{16}H_{20}Al_2F_4N_2$, monoclinic, space group $C2/c$, a = 14.241(5), b = 7.324(2), c = 18.512(7) Å, β = 106.376(6)°, V = 1852.7(11) Å^3, Z = 4, D_c = 1.328 g cm^{-3}, μ(Mo-Kα) = 0.194 mm^{-1}. *Crystal data* for **6**: $C_{16}H_6F_{10}N_2$, triclinic, space group $P1$, a = 6.3833(13), b = 7.7232(15), c = 8.2726(17) Å, α = 91.79(3), β = 107.64(3), γ = 103.10(3)°, Z = 1, D_c = 1.837 g cm^{-3}, μ(Mo-Kα) = 0.197 mm^{-1}. *Crystal data* for **9**: $C_{11}H_7F_5NO$, monoclinic, space group $P2_1/c$, a = 10.830(5), b = 8.734(5), c = 11.608(5) Å, β = 90.433(3)°, V = 1098.0(9) Å^3, Z = 4, D_c = 1.604 g cm^{-3}, μ(Mo-Kα) = 0.161 mm^{-1}. All three structures were solved by direct methods and refined to R_1 values of 0.0914, 0.0596, and 0.0723 for **2**, **6** and **9**, respectively. CCDC reference numbers 184628–184630. See http://www.rsc.org/suppdata/cc/b2/b203693b/ for crystallographic data in CIF or other electronic format.

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