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Communications

Diazabutadiene (DAB) Complexes of Aluminum. A New Mode of Coordination for a DAB Ligand

David S. Brown, Andreas Decken,† Christopher A. Schnee, and Alan H. Cowley*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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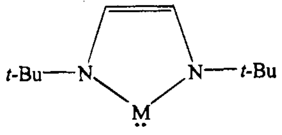
Diazabutadiene (DAB) ligands have proved to be highly effective for the stabilization of dicordinate silicon[1] and germanium[2] (**1**). Given the isoelectronic relationships between



1 (M = Si, Ge)

these group 14 atoms and AlR and GaR moieties, there is surprisingly little information available regarding analogous ring systems incorporating the heavier group 13 elements. A few DAB complexes of gallium have been reported;[3,4] however, the only DAB complex of aluminum of which we are aware is Al(t-BuDAB)$_2$.[5]

We have now prepared some t-BuDAB aluminum complexes which show a marked tendency toward dimerization. The reaction of equimolar quantities of LiN(t-Bu)CHCN(t-Bu)Li (**2**) with AlCl$_3$ in toluene solution at −78 °C afforded, after workup, a colorless crystalline solid (**3**) in 40% yield. The dimeric nature of the product was suggested by the presence of a peak at m/z = 461 in the CI mass spectrum.[6] Such a view was supported by the detection of two t-Bu and two vinylic environments of equal abundance, respectively, in the ^{1}H and ^{13}C{^{1}H} NMR spectra.[6]

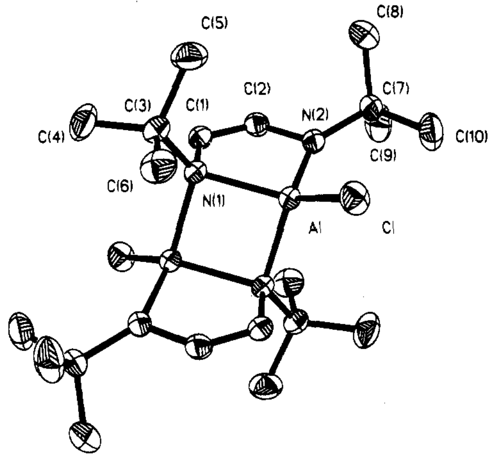
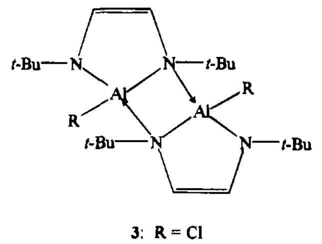
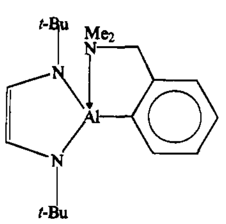


Figure 1. Structure of **3** in the crystal. The metrical parameters for **4** are shown in brackets. Selected bond distances (Å) and angles (deg): Al−N(1) 1.966(2) [Al−N(1) 1.985(2)], Al−N(2) 1.812(2) [Al−N(2) 1.849(2)], Al−N(1)′ 1.940(2) [Al−N(1)′ 1.975(2)], N(1)−C(1) 1.477(3) [N(1)−C(1) 1.465(3)], C(1)−C(2) 1.330(3) [C(1)−C(2) 1.327(3)], N(2)−C(2) 1.386(3) [N(2)−C(2) 1.383(3)], N(1)−Al−N(2) 94.55(8) [N(1)−Al−N(2) 92.50(9)], N(1)−Al−N(1)′ 87.73(7) [N(1)−Al−N(1)′ 86.83(8)], Al−N(1)−C(1) 97.73(12) [Al−N(1)−C(1) 99.64(14)], Al′−N(1)−Al 92.27(7) [Al′−N(1)−Al 93.17(8)], N(1)−C(1)−C(2) 119.0(2) [N(1)−C(1)−C(2) 119.3(2)], C(1)−C(2)−N(2) 121.8(2) [C(1)−C(2)−N(2) 121.7(2)], C(2)−N(2)−Al 103.82(14) [C(2)−N(2)−Al 105.3(2)].



3: R = Cl
4: R = Et



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Colorless crystalline **4** was produced in 38% yield using an approach virtually identical to that described for **3**. As in the case of the latter, a peak corresponding to a dimeric formulation was detected in the CI-MS (m/z 449). As expected, nonequivalence of the t-Bu groups (but not the Et groups) was evident in the ^{1}H and ^{13}C{^{1}H} NMR spectra.[6] However, for confirmation of the structure assignments for **3** and **4**, it was necessary to

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* Author to whom correspondence should be addressed.

† Current address: Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada E3B 5A6.

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appeal to X-ray crystallography.[7] Compounds **3** and **4** crystallize in the space groups $P2_1/n$ ($Z = 4$) and $P\bar{1}$ ($Z = 2$), respectively. In both cases, the crystalline state features dimers with no unusually short intermolecular interactions. As illustrated in Figure 1, the dimeric units are formed by means of donor−acceptor bonding between two pairs of nitrogen and aluminum atoms. The resulting Al_2N_2 cores are planar, and the departures from a square are modest. To our knowledge, dimerization represents a new mode of coordination for the DAB ligand system.[8,9]

With a view to obviating dimerization, **2** was treated with $ArAlBr_2$ (Ar = *o*-[(dimethylamino)methyl]phenyl)[10] in toluene solution at 25 °C. The proposed formula for the resulting colorless crystalline solid **5** (48% yield) is consistent with NMR and mass spectral data.[6] Confirmation was provided by an X-ray crystallographic study[7] that revealed a monomeric structure in which the (dimethylamino)methyl "arm" of the aryl ligand is coordinated to the aluminum atom of the AlN_2C_2 ring. The overall molecular structure is very similar to that of the analogous gallium compound.[3]

The foregoing X-ray crystallographic data are relevant to a discussion of the bonding in group 13 and 14 DAB complexes. West *et al.*[1] have argued for a delocalized 6-π-electron system for a silylene (**1**) while Arduengo *et al.*[11] have presented evidence for a localized structure (C═C bond plus N lone pairs) in the case of some analogous nucleophilic carbenes. Turning to **3** and **4**, if there were extensive delocalization, it would be expected that, as a consequence of the involvement of one of the nitrogen lone pairs in a donor−acceptor bond, the π-electron count of each ring system would decrease from 6 to 4 with consequent effects on the annular metrical parameters. Note, however, that the C═C and C−N (tricoordinate) bond distances in **3** (1.330(3) and 1.386(3) Å) and **4** (1.327(3) and 1.383(3) Å) are very similar to those in nucleophilic carbenes which span the ranges 1.331(2)−1.351(2) and 1.364(2)−1.375(2) Å, respectively.[11] The C═C and C−N bond distances in **6** are 1.337(2) and 1.412(2) Å, respectively. Moreover, the Al−N bond distances in **3** (1.812(2) and 1.966(2) Å) and **4** (1.849(2) and 1.985(2) Å) fall in the ranges that have been established for Al−N (tricoordinate)[12] and Al−N (tetracoordinate)[12] single bonds, as does the average Al−N (tricoordinate) bond distance in **5** (1.829(1) Å). In summary, the foregoing data point toward the view that the π-systems of DAB aluminum complexes are relatively localized.

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Supporting Information Available: Tables of crystal data, structure refinement details, bond distances, bond angles, atomic coordinates, and thermal parameters for **3**−**5** (19 pages).

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(6) Spectroscopic data for **3**: ^{1}H NMR (300.15 MHz, C_6D_6) δ 6.45 (d, 1H, $J = 6$ Hz), 4.98 (d, 1H, $J = 3$ Hz), 1.30 (s, 9H), 1.22 (s, 9H); $^{13}C\{^{1}H\}$ NMR (75.48 MHz, C_6D_6) δ 139.47, 102.31, 57.62, 52.76, 32.28, 28.06; MS (CI) 461 (M^+); HRMS calcd 460.226 086, found 460.227 290. Spectroscopic data for **4**: ^{1}H NMR (300.15 MHz, C_6D_6) δ 6.42 (d, 1H, $J = 6$ Hz), 4.74 (d, 1H, $J = 6$ Hz), 1.41 (t, 3H, $J = 7.5$ Hz), 1.23 (s, 9H), 1.22 (s, 9H) 0.69 (m, 1H), 0.44 (m, 1H); $^{13}C\{^{1}H\}$ NMR (75.48 MHz, C_6D_6) δ 138.88, 101.44, 54.97, 51.37, 31.49, 28.70, 10.26, 9.67; MS (CI) 449 (M^+); HRMS calcd 448.366 631, found 448.365 030. Spectroscopic data for **5**: ^{1}H NMR (300.15 MHz, C_6D_6) δ 7.96 (m, 1H), 7.20 (m, 2H), 6.77 (m, 1H), 6.06 (s, 2H), 3.15 (s, 2H), 1.96 (s, 6H), 1.29 (s, 18H); $^{13}C\{^{1}H\}$ NMR (75.48 MHz, C_6D_6) δ 144.19, 137.90, 128.43, 124.52, 114.86, 64.53, 50.91, 45.23, 32.51; MS (CI) 329 (M^+); HRMS calcd 329.241 165, found 329.239 37.

(7) Crystal structure data for **3**: $C_{10}H_{20}AlClN_2$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.260(1)$ Å, $b = 12.539(1)$ Å, $c = 11.094(1)$ Å, $\beta = 96.01(1)°$, $V = 1281.1(2)$ Å^3, $d_{calcd} = 1.196$ g/cm^3, Mo Kα, $\lambda = 0.710\,73$ Å; 2224 unique data collected ($\theta-2\theta$ scan technique, $4.92 \leq 2\theta \leq 49.94°$), wR2 = 10.03% ($F^2$), R1 = 4.27% ($F$). Crystal structure data for **4**: $C_{12}H_{25}AlN_2$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8.9273(9)$ Å, $b = 9.4656(7)$ Å, $c = 9.7541(6)$ Å, $\alpha = 89.872(6)°$, $\beta = 66.710(6)°$, $\gamma = 68.387(8)°$, $V = 693.86(10)$ Å^3, $d_{calcd} = 1.074$ g/cm^3, Mo Kα, $\lambda = 0.710\,73$ Å; 2439 unique data collected ($\theta-2\theta$ scan technique, $4.62 \leq 2\theta \leq 49.94°$), wR2 = 11.69% ($F^2$), R1 = 5.42% ($F$). Crystal structure data for **5**: $C_{19}H_{32}AlN_3$, triclinic, space group $P1$, $Z = 2$, $a = 9.779(2)$ Å, $b = 9.860(1)$ Å, $c = 11.126(1)$ Å, $\alpha = 100.187(4)°$, $\beta = 107.237(8)°$, $\gamma = 98.449(7)°$, $V = 985.5(2)$ Å^3, $d_{calcd} = 1.110$ g/cm^3, Mo Kα, $\lambda = 0.71073$ Å; 6830 unique data collected ($\theta-2\theta$ scan technique, $4.30 \leq 2\theta \leq 65.0°$), wR2 = 9.86% ($F^2$), R1 = 5.02% ($F$).

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