Structure and Bonding of the Tris(diphenylmethyleneamino)aluminium Dimer $[Al(NCPh_2)_3]_2$: Relative Strengths of Bridging and Terminal Al–X Bonds in Systems $X_2Al(\mu_2\text{-}X)_2AlX_2$

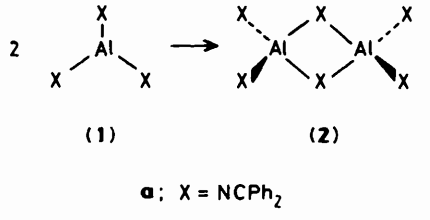
Stephen J. Bryan,[a] **William Clegg,**[b] **Ronald Snaith,**[c] **Kenneth Wade,**[a]* **and Edward H. Wong**[d]

[a] *Chemistry Department, Durham University Science Laboratories, South Road, Durham DH1 3LE, U.K.*
[b] *Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.*
[c] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[d] *Chemistry Department, University of New Hampshire, Parsons Hall, Durham, New Hampshire 03824-3598, U.S.A.*

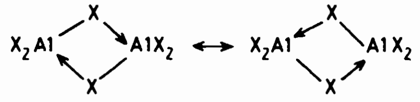
The title compound, prepared by reaction of $LiN{=}CPh_2$ with AlC_3 in 2 : 1 → 3 : 1 molar ratio, crystallises as the dimer $(Ph_2C{=}N)_2Al(\mu_2\text{-}N{=}CPh_2)_2Al(N{=}CPh_2)_2$, with Al–N distances (terminal 1.78, bridging 1.93 Å) and C=N–Al angles (terminal 148—175, bridging 130—133°) consistent with a bonding description in which each ligand functions as a source of three electrons, making the terminal Al–N bonds twice as strong as the bridging ones, an interpretation supported by molecular orbital bond index (MOBI) calculations which show this to be a general characteristic of species Al_2X_6, whether electron-precise (X=Cl, NR_2, or $N{=}CR_2$) or electron-deficient (X=Me or H).

The tendency of aluminium halides AlX_3 (**1**) (X = Cl, Br, or I) to form dimeric molecules Al_2X_6 (**2**) (Scheme 1) in nonpolar solvents is often used in inorganic chemistry textbooks[1] to illustrate the strong Lewis acidity of the monomers (**1**), and to introduce the idea that halogen atoms can bridge pairs of metal atoms by acting as sources of three electrons. Both the bridging and terminal Al–X bonds in (**2**) are normally regarded as 2-centre 2-electon (2c2e) bonds, though as the former are resonance hybrids (**3**) of 'normal' and 'dative' bonds (Scheme 2), they are understandably weaker than the terminal Al–X bonds. Here, we illustrate the generally overlooked greater strength of the terminal (as opposed to bridging) bonds by describing the crystal structure of the methyleneaminoaluminium compound $Al_2(NCPh_2)_6$ (**2a**), and by molecular orbital bond index (MOBI)[2] calculations on this and related dimers Al_2X_6, which show a consistent pattern, whether the bridging is formally electron-precise or electron-deficient.

Compound (**2a**) was prepared from $LiNCPh_2$ and $AlCl_3$ in 3 : 1 molar ratio in boiling toluene, from which it crystallised as pale orange crystals which gave satisfactory analyses for (**2a**). In the only previous study of the system, $Al(NCPh_2)_3$ was reported[3] (on the basis of cryoscopic measurements) to be monomeric in benzene, and presumed to have structure (**1a**). An *X*-ray crystallographic study† has now established that it crystallises as the dimer, (**2a**), illustrated in Figure 1. Notable features include the essentially planar, diamond-shaped $(AlN)_2$ ring with angles Al–N–Al 95° and N–Al–N 84°, and Al–N distances *ca.* 1.93 Å; the large angles C=N–Al (148—175°) by which the four (different) terminal methyleneamino ligands are attached to the metal atoms (these angles are not forced to be so large by steric constraints; nonbonded distances between the ligands are long); and the relatively short (*ca.* 1.78 Å) terminal Al–N links. Such large C=N–M angles and short N–M bonds are generally regarded as indicative of N$\rightleftharpoons$M dative π-bonding, the ligands in question functioning as sources of three electrons.[4] In classical valence



Scheme 1



(3)

Scheme 2

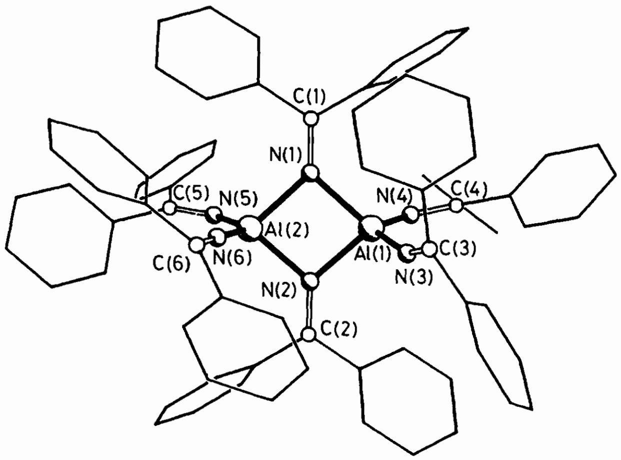


Figure 1. Molecular structure of $Al_2(NCPh_2)_6$, (**2a**). Selected bond distances (Å) and angles (°): Al(1)–N(1), 1.930(3); Al(1)–N(2), 1.934(3); Al(1)–N(3), 1.782(2); Al(1)–N(4), 1.796(3); Al(2)–N(1), 1.927(3); Al(2)–N(2), 1.921(3); Al(2)–N(5), 1.786(3); Al(2)–N(6), 1.774(3); N(1)–C(1), 1.289(4); N(2)–C(2), 1.279(4); N(3)–C(3), 1.257(4); N(4)–C(4), 1.262(4); N(5)–C(5), 1.257(4); N(6)–C(6), 1.256(4); N(1)–Al(1)–N(2), 84.0(1); N(1)–Al(2)–N(2), 84.5(1); Al(1)–N(1)–Al(2), 95.3(1); Al(1)–N(2)–Al(2), 95.4(1); Al(1)–N(1)–C(1), 131.1(2); Al(2)–N(1)–C(1), 132.6(2); Al(1)–N(2)–C(2), 133.3(2); Al(2)–N(2)–C(2), 130.5(2); Al(1)–N(3)–C(3), 155.4(3); Al(1)–N(4)–C(4), 148.1(3); Al(2)–N(5)–C(5), 148.2(3); Al(2)–N(6)–C(6), 175.1(2).

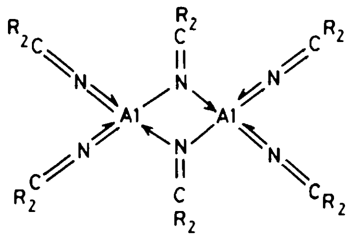
---

† *Crystal data:* $C_{78}H_{60}Al_2N_6$, $M = 1135.3$, triclinic, $a = 10.413(1)$, $b = 12.961(2)$, $c = 25.223(3)$ Å, $\alpha = 89.26(1)$, $\beta = 86.91(1)$, $\gamma = 68.70(1)°$, $U = 3166.9$ Å^3, $Z = 2$, $D_c = 1.190$ g cm^3, $F(000) = 1192$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 0.09$ mm^{-1}, space group $P\bar{1}$. $R = 0.071$ for 7365 unique reflections with $F > 4\sigma(F)$, anisotropic thermal parameters, rigid ideal hexagons for phenyl groups, and H atoms in calculated positions. Aomic co-ordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Al–X bond distances (*d*/Å) and indices (*I*) for compounds Al_2X_6.

			X		
	Cl[6]	NH_2[a]	$N{=}CH_2$[b]	Me[7]	H[8]
$d(Al\text{–}X)_t$	2.06	1.864	1.785	1.953	1.403
$I(Al\text{–}X)_t$	0.983	0.847	0.841	0.856	0.955
$d(Al\text{–}X)_\mu$	2.21	1.970	1.928	2.124	1.622
$I(Al\text{–}X)_\mu$	0.538	0.438	0.411	0.413	0.496
Ratio I_t/I_μ	1.83	1.93	2.05	2.07	1.93
$d(Al\cdots Al)$	3.40	2.832	2.850	2.606	2.478
$I(Al\cdots Al)$	0.087	0.155	0.175	0.246	0.650
Al valency	3.157	3.095	3.143	3.290	3.581
Al charge	+0.774	+0.776	+0.747	+0.617	+0.107
d-orbital occupancy	0.06	0.06	0.07	0.07	0.04

[a] Al–N distances from ref. 5. [b] Al–N distances from (**2a**).



(**4**)

bond terms, the molecule would thus be represented as shown in structure (**4**).

To probe the bonding in (**2**), we carried out MOBI calculations on the model compound $Al_2(N{=}CH_2)_6$, with metal, nitrogen, and carbon atom positions as in (**2**), and hydrogen atoms replacing the phenyl groups at suitable distances (1.07 Å) along the C–phenyl bonds. The results (Table 1) show the terminal Al–N bonds to have bond indices (0.84) twice those of the bridging Al–N bonds (0.41). Calculations on the model compound $Al_2(NH_2)_6$, with atomic co-ordinates derived similarly from those of $Al_2(NMe_2)_6$[5] (which contains planar terminal Me_2N–Al units), afforded similar metal–nitrogen bond indices. Indeed, when the calculations were extended to include Al_2Cl_6,[6] Al_2Me_6,[7] and Al_2H_6 (using the atomic co-ordinates calculated by Baird),[8] it was apparent that, whether the species Al_2X_6 were formally electron-precise (X = Cl, NH_2, or $N{=}CH_2$) or electron-deficient (X = Me or H) the bond indices of the terminal Al–X bonds were roughly twice those of the bridging bonds (I_t/I_μ ranged from 1.83 to 2.07). Since bond indices correspond to covalent bond orders,[2] and correlate well with bond enthalpies,[9] these results imply that the terminal Al–X bonds in compounds Al_2X_6 are roughly twice as strong as the bridging bonds, whether the systems are formally electron-deficient or -precise. This indicates a greater strength for the terminal bonds, particular those in the electron-precise systems, than previously estimated,[10] the difference arising because the capacity of terminal ligands with lone pair electrons (halogen, NR_2, $N{=}CR_2$, *etc.*) to indulge in dative π-bonding had been underestimated in earlier work.

Interestingly, despite the formal electron count of twelve electrons in the valence shell of each metal atom in (**2a**) [and, by implication, in Al_2Cl_6, $Al_2(NH_2)_6$, and related 'electron-precise' systems], the d-orbital occupancy is invariably <0.1 (Table 1). The metal valencies and charges, as expected, reflect the electronegativities of the substituents X. Metal–metal bonding interactions were strongest, as expected,[11] in the electron-deficient systems.

The pattern found here for compounds Al_2X_6 is expected to hold for other categories of bridged compound, whether formally electron-deficient or -precise. In particular, strengthening of the terminal bonds is expected where opportunities for dative π-bonding exist, *i.e.* wherever the ligand atom has one or more lone pairs of electrons. Calculations on beryllium systems $XBe(\mu_2\text{-}X)_2BeX$ support this view.[12] We have also carried out EHMO calculations on these aluminium and beryllium systems, and find that they afford (very small) Mulliken overlap populations for the terminal and bridging Al–X and Be–X bonds that are broadly supportive of the pattern found for the bond indices in Table 1, though giving terminal: bridging ratios generally higher for the systems with hydrogen or alkyl bridges than for bridged halides, amides, or imides. However, since these same EHMO calculations, even with charge iteration, afford high atomic charges, and require due allowance to be made for bond polarities, the bond indices in Table 1 are believed to provide a more direct guide to bond orders and strengths. These and other calculations will be reported in a full account of this work.

We thank Brian Hall for assistance with experimental work, the S.E.R.C. and Durham University Fellowship Foundation for financial support, and Professor P. G. Perkins for the MOBI program.

Received, 7th April 1987; Com. 456

References

1 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', Pergamon, Oxford, 1984, p. 264; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley, Chichester, 1980, p. 331; A. G. Sharpe, 'Inorganic Chemistry,' Longman, London, 1981, p. 273; J. E. Huheey, 'Inorganic Chemistry,' 3rd edn., Harper and Row, London, 1983, p. 206.

2 D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc. Dalton Trans.*, 1973, 627.

3 R. Snaith, C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc. (A)*, 1970, 2635.

4 G. J. Bullen and K. Wade, *Chem. Commun.*, 1971, 1122; N. W. Alcock and M. Pierce-Butler, *J. Chem. Soc., Dalton Trans.*, 1975, 2469; J. B. Farmer, H. M. M. Shearer, J. D. Sowerby, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1976, 160; J. R. Jennings, R. Snaith, M. M. Mahmoud, S. C. Wallwork, S. J. Bryan, J. Halfpenny, E. A. Petch, and K. Wade, *J. Organomet. Chem.*, 1983, **249**, C1; W. Clegg, S. J. Bryan, and K. Wade, *Acta Crystallogr., Sect. C*, 1984, **40**, 2082.

5 K. Ouzounis, H. Riffel, H. Hess, U. Kohler, and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1983, **504**, 67.

6 K. J. Palmer and N. Elliott, *J. Am. Chem. Soc.*, 1938, **60**, 1852.

7 J. C. Huffman and W. E. Streib, *Chem. Commun.*, 1971, 911.

8 N. C. Baird, *Can. J. Chem.*, 1985, **63**, 71.

9 D. Laurie and P. G. Perkins, *Inorg. Chim. Acta,* 1982, **63**, 53; C. E. Housecroft, R. Snaith, K. Moss, R. E. Mulvey, M. E. O'Neill, and K. Wade, *Polyhedron*, 1985, **4**, 1875; R. E. Mulvey, M. E. O'Neill, K. Wade, and R. Snaith, *Polyhedron*, 1986, **5**, 1437.

10 K. Wade, *J. Chem. Educ.*, 1972, **49**, 502.

11 R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, 1973, **50**, 53.

12 B. Hall, J. B. Farmer, H. M. M. Shearer, J. D. Sowerby, and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1979, 102.