

Factors affecting cation formation in group 13 alkyl halide complexes

David Atwood* and Jolin Jegier

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105, USA

The demarcation for the formation of cationic aluminium complexes is the transition between the use of chloride as a ligand ($\text{Me}_2\text{AlCl-NH}_2\text{Bu}^t$ **1**) and the relatively more polarizable bromide $\{[\text{Me}_2\text{Al}(\text{NH}_2\text{Bu}^t)_2]\text{Br}$ **2** as determined by X-ray diffractometry.

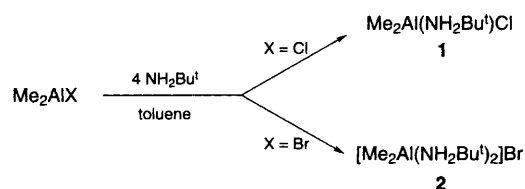
Compared to the neutral species, the charged chemistry of the group 13 elements remains relatively unexplored. Previous systematic work has focused on the use of crown ethers¹ and the salen class of ligands² in supporting cationic aluminium centres. Other structurally characterized examples which have appeared in the recent literature include those with coordinated thf,³ tetramethylethylenediamine (tmeda),⁴ acac,⁵ intramolecular stabilization⁶ and a π -stabilized complex.⁷ This sporadic interest may be attributed to a need for the further development of fundamental aluminium chemistry. However, the potential utility of aluminium cations in organic and catalytic transformations is clearly a motivating consideration.

We have begun a study towards defining what factors are important in the formation of alkyl group 13 cations of general formula $[\text{R}_2\text{M}(\text{base})_2]\text{X}$, that are not supported by chelates or macrocycles. A wide range of variables may be examined in this type of complex. Some of these include: the type of halide, X (= Cl-I), the base strength, the type of metal, M (= Al-In), and the type of ligand, R (= alkyl, alkoxy, amido, etc.).

Here we report our preliminary results on the effect of the halide in the formation of cationic aluminium complexes. Specifically, the synthesis and full characterization of $\text{Me}_2\text{Al}(\text{NH}_2\text{Bu}^t)\text{Cl}$ **1** and $[\text{Me}_2\text{Al}(\text{NH}_2\text{Bu}^t)_2]\text{Br}$ **2** are reported.

Compounds **1** and **2** are synthesized by the addition of an excess of *tert*-butylamine to the respective dimethyl aluminium halide in toluene (Scheme 1).[†] Compound **1** remained soluble after the reaction and could be isolated in quantitative yield after solvent removal under vacuum. As compound **2** was formed it began precipitating out of solution. After solvent removal *in vacuo*, **2** could be isolated in quantitative yield as a white solid. Crystalline **1** and **2** could be isolated by cooling concentrated solutions of hexane and thf (respectively) to -30°C for several days.

The molecular structures and atom numbering schemes for **1** and **2** are shown in Figs. 1 and 2, respectively.[‡] Important bond distances and angles are listed in the figure captions. The structure of **1** consists of a four-coordinate aluminium centre with bond angles deviating from ideal T_d geometry. This deviation is most obvious in the C-Al-C angle of $121.2(3)^\circ$ and the Cl-Al-N angle of $99.5(1)^\circ$. This trend is consistent with an increased p component for the bonding orbitals of the more electronegative groups and an increase in the s component for the bonding orbitals of the carbons.⁸ The bond lengths in **1** are



Scheme 1 The formation of neutral (**1**) and cationic (**2**) alkyl halide complexes

consistent with those observed in other alkyl aluminium adducts.⁹

In an analogous manner to **1**, the structure of **2** also shows a distortion from T_d geometry. For instance, the C-Al-C angle is $116.6(3)^\circ$ and the N-Al-N angle is $97.5(2)^\circ$. Despite the

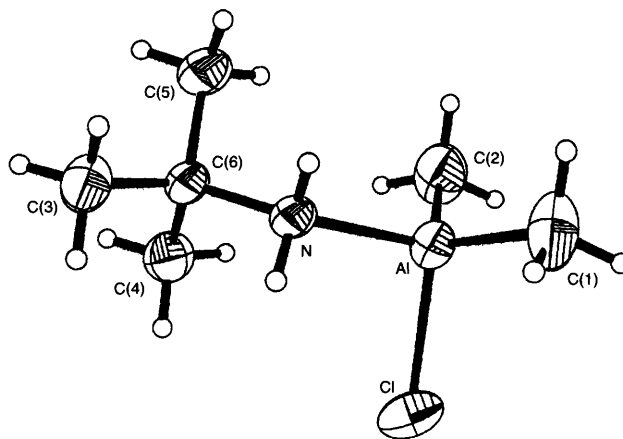


Fig. 1 Molecular structure and atom numbering scheme for **1**. Selected bond distances (Å) and angles ($^\circ$) are as follows: Al-Cl 2.204(2), Al-N 1.993(4), Al-C(1) 1.937(6), Al-C(2) 1.946(5), N-C(6) 1.519(6); Cl-Al-N 99.5(1), Cl-Al-C(1) 108.0(2), N-Al-C(1) 102.5(2), Cl-Al(1)-C(2) 108.5(2), N-Al-C(2) 114.8(2), C(1)-Al-C(2) 121.2(3).

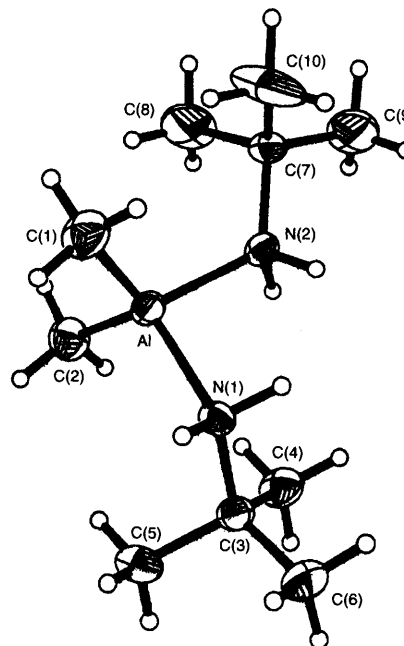


Fig. 2 Molecular structure and atom numbering scheme for **2** (only the cation is shown). Selected bond distances (Å) and angles ($^\circ$) are as follows: Al-N(1) 2.000(4), Al-N(2) 1.989(4), Al-C(1) 1.955(7), Al-C(2) 1.951(6), N(1)-C(3) 1.510(7), N(2)-C(7) 1.501(6); N(1)-Al-N(2) 97.5(2), N(1)-Al-C(1) 103.3(2), N(2)-Al-C(1) 114.7(2), N(1)-Al-C(2) 116.7(2), N(2)-Al-C(2) 106.8(2), C(1)-Al-C(2) 116.6(3), Al-N(1)-C(3) 124.2(3), Al-N(2)-C(7) 123.5(4).

cationic nature of **2**, the bond distances to the aluminium are nearly identical to that shown in neutral **1**. The Al–C and Al–N compare closely with differences of 0.002 and 0.01 Å, respectively. An interesting feature in **2** is the fact that the cationic units are connected through hydrogen bonding to the bromide anion. A unit-cell view depicting this bonding is shown in Fig. 3. The Br⋯H contacts range from a short distance of 2.48 Å to a long distance of 2.93 Å.

In complexes **1** and **2** the line between adduct and cation formation is demarcated by the use of chloride and bromide, respectively. The key difference between the two complexes lies in the fact that bromide is more polarizable than chloride and can be displaced more readily. This displacement may be envisioned to proceed either through a five-coordinate (S_N2) or a four-coordinate intermediate (S_N1). The ready formation of hydrogen bonds in the case of **2** (Fig. 3) argues in favour of this latter possibility. Additionally, the decreasing bond strength between Al–Cl and Al–Br must also be a factor.

A primary motivation for our study of cationic aluminium complexes is to determine their utility in organic synthesis and catalysis. Along these lines, we have previously reported that monocationic aluminium salen complexes oligomerize propylene oxide.² The use of **1** and **2** will be examined in a similar manner. Thus, a comparison between the effectiveness of four- and six-coordinate cations can be made.

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 30057-G3). The receipt of an NSF-CAREER award is also gratefully acknowledged.

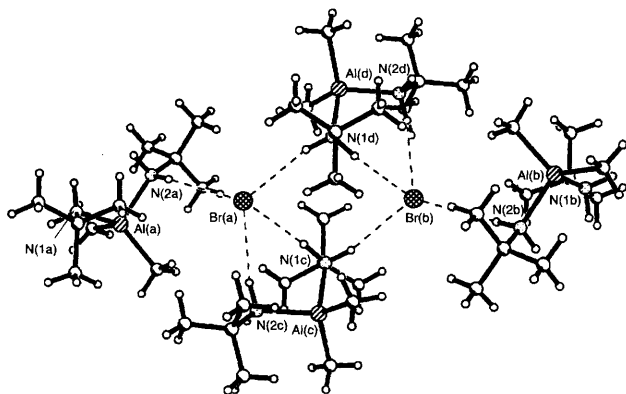


Fig. 3 View of the hydrogen bonding in **2**

Footnotes

† Full experimental details are given in supplementary material available from the authors. Only spectroscopic and physical data are given here. **1**: Mp 61–63 °C. ¹H NMR (C_6D_6): δ –0.27 (s, 6 H, $AlCH_3$), 0.66 [s, 9 H, $C(CH_3)_3$], 2.47 (br s, 2 H, NH_2). IR, ν/cm^{-1} : 3240s, 3207s, 3130m, 2976s, 2945m, 2879m, 1579s, 1475m, 1402s, 1377s, 1302s, 1197s, 898w, 696s (br). Anal. Calc.: C, 43.51; H, 10.35. Found: C, 43.19; H, 10.27%. **2**: Mp 148–151 °C. ¹H NMR [2H_8]thf: δ –0.60 (s, 6 H, $AlCH_3$), 1.26 [s, 18 H, $C(CH_3)_3$], 4.16 (br s, 4 H, NH_2). IR, ν/cm^{-1} : 3053s (br), 2995m, 1581s, 1481m, 1400s, 1375s, 1311s, 1192s, 1097w, 893m, 752s, 705s, 673m. Anal. Calc.: C, 42.41; H, 9.96. Found: C, 41.98; H, 9.82%.

‡ Crystallographic data: $Me_2Al(NH_2Bu^t)Cl$ **1**: triclinic, space group $P\bar{1}$; $a = 10.292(1)$, $b = 8.990(3)$, $c = 10.393(3)$ Å, $\alpha = 71.97(1)$, $\beta = 80.25(3)$, $\gamma = 81.97(3)^\circ$, $U = 547.0(4)$ Å³, $Z = 2$, 1032 observed reflections ($F > 4.0\sigma F$); $R = 0.052$, $R_w = 0.0511$.

$[Me_2Al(NH_2Bu^t)_2]Br$ **2**: monoclinic, space group $P2_1/c$; $a = 9.099(1)$, $b = 17.255(2)$ Å, $\beta = 104.81(1)^\circ$, $U = 1562.1(3)$ Å³, $Z = 4$, 1464 observed reflections ($F > 4.0\sigma F$); $R = 0.0387$, $R_w = 0.0395$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/94.

References

- H. G. Richey Jr. and G. L. BergStresser, *Organometallics*, 1988, **7**, 1459; M. F. Self, W. T. Pennington, J. A. Laske and G. H. Robinson, *Organometallics*, 1991, **10**, 36; J. L. Atwood, in *Coordination Chemistry of Aluminum*, ed. G. H. Robinson, VCH Inc., New York, 1993, p. 197.
- D. A. Atwood, J. A. Jegier and D. Rutherford, *J. Am. Chem. Soc.*, 1995, **117**, 6779; M. G. Davidson, C. Lambert, I. Lopez-Solera, P. R. Raithby and R. Saith, *Inorg. Chem.*, 1995, **34**, 3765; D. A. Atwood, J. A. Jegier and D. Rutherford, *Inorg. Chem.*, 1996, **35**, 63.
- S. Y. Knjazhansky, I. Y. Nomerotsky, B. M. Bulychev, V. K. Belsky and G. L. Soloveichik, *Organometallics*, 1994, **13**, 2075.
- W. Uhl, J. Wagner, D. Fenske and G. Baum, *Z. Anorg. Allg. Chem.*, 1992, **612**, 25.
- J. Lewinski, S. Pasynkiewicz and J. Lipkowski, *Inorg. Chim. Acta*, 1990, **178**, 113.
- L. M. Engelhardt, U. Kynast, C. L. Raston and A. H. White, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 681.
- C. Dohmeier, H. Schnockel, C. Robl, U. Schneider and R. Ahlrichs, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1655.
- This is 'Bent's Rule' in operation: H. A. Bent, *J. Chem. Educ.*, 1960, **37**; 616; *Chem. Rev.*, 1961, **61**, 275.
- A. Haaland, in *Coordination Chemistry of Aluminum*, ed. G. H. Robinson, VCH Inc., New York, 1993, p. 1.

Received, 5th February 1996; Com. 6/00837B