FULL PAPER

Dalton
www.rsc.org/dalton

Synthesis of amino- and amido-aluminium derivatives and investigation of their dynamics in solution

Vincenzo Passarelli,* Giovanni Carta, Gilberto Rossetto and Pierino Zanella
ICIS–CNR, Area della Ricerca di Padova, Corso Stati Uniti 4, I–35127 Padova, Italy.
E-mail: passarel@server1.dcci.unipi.it

Received 27th November 2002, Accepted 12th February 2003
First published as an Advance Article on the web 21st February 2003

The salts $Li[Al(C_4H_8N)_4]\cdot nC_4H_8NH$ ($n = 1, 2$; C_4H_8NH = pyrrolidine) have been prepared and characterised in solution by ^1H-, ^{13}C-, ^7Li- and ^{27}Al-NMR spectroscopy. Their reaction with $AlCl_3$ (Cl/Li molar ratio = 3) affords the binary amido derivative $[Al(C_4H_8N)_3]_2$, which, on turn, is reactive towards AlX_3, yielding $[AlX_2(C_4H_8N)]_2$ (X = Cl, CH_3). The binuclear derivatives $[AlY_2(C_4H_8N)]_2$ (Y = Cl, CH_3, C_4H_8N) react with $[NH_2Et_2]Cl$ affording the amine complexes $AlY_2Cl(C_4H_8NH)_n$ (Y = CH_3, $n = 1$; Y = Cl, $n = 1, 2$). Alternatively, the *mono*chloro species $Al(CH_3)_2Cl(C_4H_8NH)$ results from the reaction of $Al(CH_3)_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)$ (CH_3/Cl molar ratio = 2). The *di*chloro-methyl derivative $Al(CH_3)Cl_2(C_4H_8NH)$ is obtained by reacting $Al(CH_3)_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)$ (Cl/CH_3 molar ratio = 2). The Lewis adducts $AlCl_3(amine)_n$ (amine = pyrrolidine, $n = 1, 2$; amine = *N*,*N*,*N*′-trimethylpropanediamine, $n = 1$) have been isolated when $AlCl_3$ was contacted with the stoichiometric amount of the amine. At variance with *N*,*N*,*N*′-trimethylpropanediamine, *N*,*N*,*N*′-trimethylethylenediamine and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine react with $AlCl_3$ yielding the salt derivatives $[AlCl_2(amine)_2][AlCl_4]$.

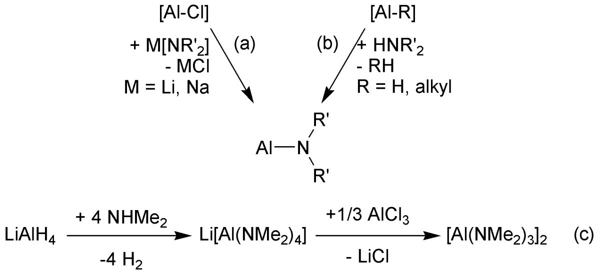
The dynamic processes of the coordinated amine ligands of $AlCl_3(amine)_n$ (amine = pyrrolidine, $n = 1, 2$; amine = *N*,*N*,*N*′-trimethylpropanediamine, $n = 1$) and $[AlCl_2(amine)_2][AlCl_4]$ (amine = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) have been investigated in solution by NMR spectroscopy.

Introduction

Amido-aluminium derivatives such as $[Al(NR_2)_3]_2$, $[HAl(NR_2)]_2$ (R = Me, Et),[1] $[AlMe_2(NH_2)]_2$[2] and $[AlMe_2(NPr_2)]_2$[3] have been successfully used as single-source precursors in the deposition of AlN *via* CVD.

In this connection, aiming at depositing thin layers of AlN *via* CVD, we have been interested in the synthesis of novel amido- and amino-aluminium derivatives, potentially usable as single source precursors.

A survey of the literature has shown[4] that two basic procedures are applicable to the synthesis of aluminium amides (Scheme 1): (a) the reaction of the alkali metal amide (lithium or sodium derivative) with the [Al–Cl] functionality; (b) the reaction of the [Al–H] or [Al–alkyl] functionalities with a secondary amine. Moreover, it has been reported[5] that the binary aluminium compound $[Al(NMe_2)_3]_2$ has been prepared by reacting the secondary amine $NHMe_2$ with $LiAlH_4$, and then the resulting lithium aluminium amide with $AlCl_3$ (Scheme 1, c).



Scheme 1

As far as amino-aluminium derivatives are concerned, it is reported[6] that amine adducts of aluminium halides or of organoaluminium compounds result from the direct interaction of the amine with the appropriate reagent, *i.e.* AlX_3 (X = Cl, Br, I, alkyl). Noteworthy, if the amine is secondary or primary, the elimination of alkane is eventually observed from compounds of general formula $AlR_3(amine)$.

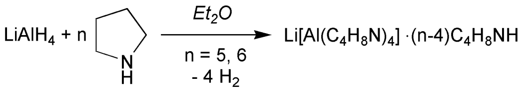
In this perspective, our study aimed at: (a) synthesising novel amido- and amino-aluminium derivatives, containing ancillary ligands such as methyl and chloride; (b) elucidating their molecular structures and dynamics in solution by multinuclear 1D and 2D NMR spectroscopy.

Results and discussion

Amido- and amino-methyl derivatives

Our synthetic investigation started with the preparation of the lithium salt $Li[Al(C_4H_8N)_4]$, potential precursor for binary amido derivatives (*vide supra*). Smith and coworkers[7] have already reported the synthesis of this compound, obtained in the form $Li[Al(C_4H_8N)_4]\cdot 2C_4H_8NH$ from a THF solution, in mixture with the THF solvento species $Li[Al(C_4H_8N)_4]\cdot 2THF$, the compound being isolated as a pure material after crystallisation from toluene. Noteworthy, the molecular structure of $Li[Al(C_4H_8N)_4]\cdot 2C_4H_8NH$ has been determined[7] showing the presence of the bimetallic core $[Li(NC_4H_8)_2Al]$, being the coordination sphere of Al completed by two pyrrolidinide groups, and that of lithium by two pyrrolidine ligands.

Interestingly, in the course of this work, the compounds $Li[Al(C_4H_8N)_4]\cdot nC_4H_8NH$ ($n = 1, 2$) have been obtained as pure materials when pyrrolidine was reacted with $LiAlH_4$ (according to the appropriate C_4H_8NH/Li molar ratio) in Et_2O, rather than THF [eqn. (1)].



(1)

At room temperature, as far as the chemical shifts are concerned, the ^1H-NMR spectra of the two compounds $Li[Al(C_4H_8N)_4]\cdot nC_4H_8NH$ ($n = 1, 2$) are similar (Table 1).

The ^{13}C-NMR spectra show the characteristic resonances of the amido groups $[C_4H_8N]^-$ ($Li[Al(C_4H_8N)_4]\cdot C_4H_8NH$: δ 50.1, $CH_2\mathit{C}H_2N$; 27.5, $\mathit{C}H_2CH_2N$; $Li[Al(C_4H_8N)_4]\cdot 2C_4H_8NH$: δ 50.6, $CH_2\mathit{C}H_2N$; 27.5, $\mathit{C}H_2CH_2N$) and those of the coordinated pyrrolidine ($Li[Al(C_4H_8N)_4]\cdot C_4H_8NH$: δ 47.0, $CH_2\mathit{C}H_2N$; 25.5, $\mathit{C}H_2CH_2N$; $Li[Al(C_4H_8N)_4]\cdot 2C_4H_8NH$: δ 47.2, $CH_2\mathit{C}H_2N$; 25.7, $\mathit{C}H_2CH_2N$). The ^{27}Al- and ^7Li-NMR

DOI: 10.1039/b211720g

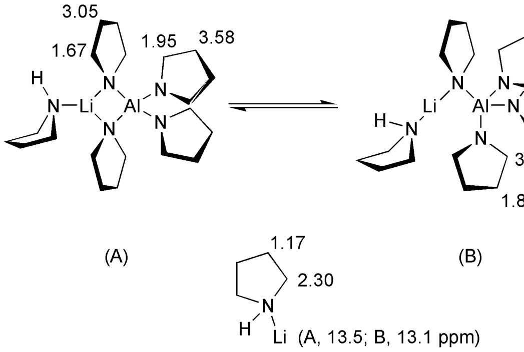
Table 1 ^1H chemical shifts (ppm) of $Li[Al(C_4H_8N)_4]\cdot nC_4H_8NH$ ($n = 1, 2$)

	$n = 1$	$n = 2$
$[C_4H_8N]^-$	3.20 (CH_2CH_2N) 1.74 (CH_2CH_2N)	3.22 (CH_2CH_2N) 1.72 (CH_2CH_2N)
C_4H_8NH	2.27 (CH_2CH_2N)	2.44 (CH_2CH_2N) 1.90 (NH)
	1.20 (CH_2CH_2N+NH)	1.31 (CH_2CH_2N)

spectra show similar chemical shifts for the two derivatives (^7Li, about 13.5 ppm; ^{27}Al, about 105 ppm).

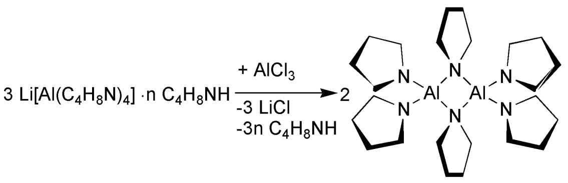
Interestingly, the ^1H- and ^7Li-NMR spectra of $Li[Al(C_4H_8N)_4]\cdot 2C_4H_8NH$ are little affected by the temperature. On the other hand, at 183 K the ^7Li-NMR spectrum of $Li[Al(C_4H_8N)_4]\cdot C_4H_8NH$ shows two lines (13.4, 13.1 ppm). Moreover, at the same temperature, the ^1H-NMR show three lines at 3.58, 3.40 and 3.05 ppm (integral ratio 1 : 2 : 1) and 1.95, 1.88 and 1.67 ppm (integral ratio 1 : 2 : 1) for the methylene protons of the amido group (CH_2CH_2N and CH_2CH_2N, respectively). Moreover, the resonance of the CH_2CH_2N and CH_2CH_2N protons of C_4H_8NH are observed at 2.30 and 1.17 ppm, respectively, as broad lines.

On this basis and keeping in mind the molecular structure of $Li[Al(C_4H_8N)_4]\cdot 2C_4H_8NH$, we propose that (a) an equilibrium exists involving two isomers (Scheme 2), namely $(C_4H_8NH)Li(C_4H_8N)_2Al(C_4H_8N)_2$ (Scheme 2, A) and $(C_4H_8NH)Li(C_4H_8N)Al(C_4H_8N)_3$ (Scheme 2, B); (b) this equilibrium slows down at 183 K; (c) a fast exchange occurs among the amido groups of the isomer B, thus making equivalent their methylene protons, even at 183 K.† The proposed assignment of the ^7Li and ^1H resonances is reported in Scheme 2.



Scheme 2

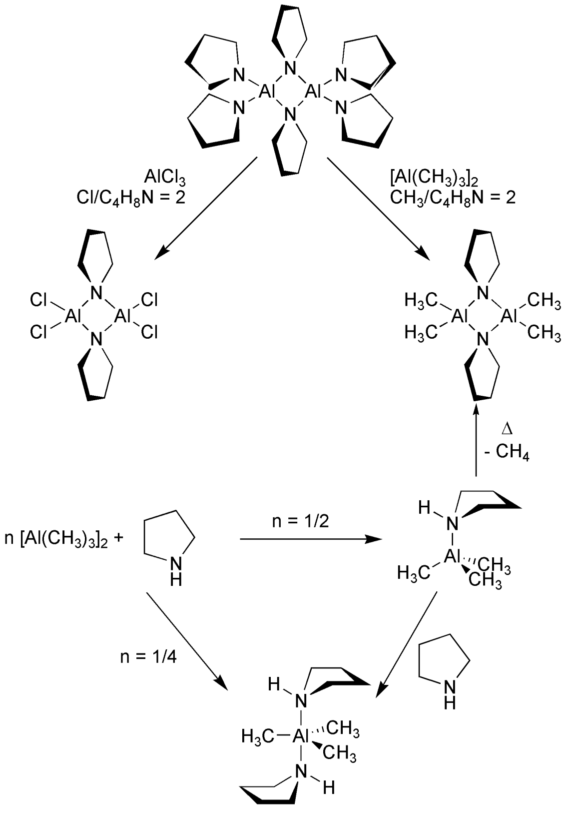
As expected, $Li[Al(C_4H_8N)_4]\cdot nC_4H_8NH$ ($n = 1, 2$) proved to be good precursors for the synthesis of $[Al(C_4H_8N)_3]_2$. As a matter of fact, $Li[Al(C_4H_8N)_4]\cdot nC_4H_8NH$ ($n = 1, 2$) reacts with $AlCl_3$ (Li/Cl molar ratio = 1) affording the above mentioned binary compound [eqn. (2)].



(2)

It is noteworthy that the synthesis of $[Al(C_4H_8N)_3]_2$ has already been described in the literature[7] starting from pyrrolidine and $AlH_3(L)_2$ (L = THF, NMe_3); moreover, the solid state molecular structure of $[Al(C_4H_8N)_3]_2$ has been determined,[7] showing the presence of the bimetallic core $[Al(C_4H_8N)_2Al]$ and of four terminal amido groups (two *per* Al). In agreement with the solid state structure, the ^1H-NMR spectrum of the compound (recorded in the course of this study as well as reported in the literature[7]) shows the characteristic resonances of the terminal and bridging pyrrolidinide ligands, respectively, at 3.21 (CH_2CH_2N) and 1.71 ppm (CH_2CH_2N), and 2.98 (CH_2CH_2N) and 1.49 ppm (CH_2CH_2N). Furthermore, four resonances are observed in the ^{13}C-NMR spectrum of the compound (terminal pyrrolidinides: δ 50.0, CH_2CH_2N; 27.2, CH_2CH_2N; bridging pyrrolidinides: δ 49.7, CH_2CH_2N; 25.4, CH_2CH_2N).

The reaction of $[Al(C_4H_8N)_3]_2$ with stoichiometric amounts of AlX_3 (X = CH_3, Cl) yields the amido derivative $[AlX_2(C_4H_8N)]_2$ (Scheme 3). The ^1H- and ^{13}C-NMR spectra of $[AlX_2(C_4H_8N)]_2$ show the characteristic resonances of the bridging pyrrolidinide ligand (^1H, X = CH_3: δ 2.62, CH_2CH_2N; 1.33, CH_2CH_2N; X = Cl: δ 2.81, CH_2CH_2N; 1.24, CH_2CH_2N; ^{13}C, X = CH_3: δ 49.7, CH_2CH_2N; 25.1, CH_2CH_2N; X = Cl: δ 50.6, CH_2CH_2N; 24.5, CH_2CH_2N). In addition the signals of the methyl groups at −0.57 and −11.9 ppm have been observed in the ^1H- and ^{13}C-NMR spectra of $[Al(CH_3)_2(C_4H_8N)]_2$, respectively. The resonances of the ^{27}Al centres in $[AlCl_2(C_4H_8N)]_2$ and $[Al(CH_3)_2(C_4H_8N)]_2$ are observed at 117.2 and 165.6 ppm, respectively.



Scheme 3

It is noteworthy that the methyl derivative $[Al(CH_3)_2(C_4H_8N)]_2$ is already known,[6b] being obtained by reacting $[Al(CH_3)_3]_2$ and pyrrolidine and then by decomposing the resulting adduct $Al(CH_3)_3(C_4H_8NH)$ (Scheme 3). Moreover, interestingly, in the course of this work, the interaction of $[Al(CH_3)_3]_2$ with pyrrolidine was re-examined showing that $Al(CH_3)_3(C_4H_8NH)$ is not the only product,[6b] the adduct $Al(CH_3)_3(C_4H_8NH)_2$ being isolated when the $[Al(CH_3)_3]_2$ is reacted with C_4H_8NH according to the Al/C_4H_8NH molar ratio 1/2 (Scheme 3), as well as by reacting $Al(CH_3)_3(C_4H_8NH)$ with C_4H_8NH (Scheme 3).

The ^1H- and ^{13}C-NMR spectra of the 1 : 2 adduct $Al(CH_3)_3(C_4H_8NH)_2$ show the resonances of the coordinated

---

† As far as the different lability of the Li–N (pyrrolidinide) bond in A and B (*i.e.* four equivalent pyrrolidinides in compound B, and two pairs of nonequivalent pyrrolidinide ligands in A) we propose that the lithium reduced coordination number in B with respect to A is responsible for the faster shift of lithium from one nitrogen to the other one and, as a consequence, of the observed equivalency of the pyrrolidinide groups in the compound B.

pyrrolidine (^{1}H: δ 2.44, CH_2CH_2N; 1.79, NH; 1.20, CH_2CH_2N; ^{13}C: δ 46.9, CH_2CH_2N; 25.5, CH_2CH_2N) and of the methyl groups (^{1}H, −0.49 ppm; ^{13}C, −9.1 ppm).

A series of ^{1}H-NMR spectra of the methyl derivatives $Al(CH_3)_3(C_4H_8NH)_n$ (n = 1, 2) was recorded at different temperatures (193–293 K): on lowering the temperature, both for $Al(CH_3)_3(C_4H_8NH)$ and $Al(CH_3)_3(C_4H_8NH)_2$, the methylene resonances shift up-field, while the methyl signals down-field. On the other hand, a different behaviour is observed for the two compounds as far as the NH resonance is concerned (Fig. 1, A): the aminic proton resonance of $Al(CH_3)_3(C_4H_8NH)$ is shifted up-field on lowering the temperature, while the same proton is shifted down-field (more drastically) in $Al(CH_3)_3(C_4H_8NH)_2$ (Fig. 1, A). Reasonably these different trends are related to the different geometries of the two compounds and to the consequently different field experienced by the aminic proton.

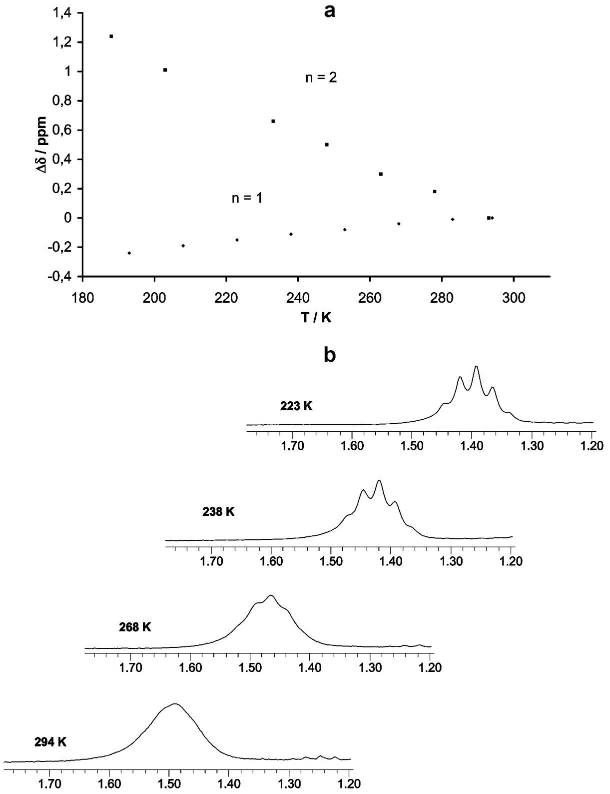
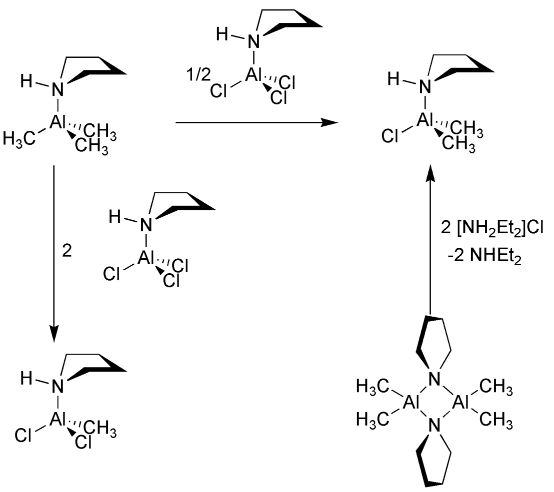


Fig. 1 (a) Variation of the chemical shift [$\Delta\delta = \delta_H(T) - \delta_H(293)$] of the aminic proton in $Al(CH_3)_3(C_4H_8NH)_n$ (n = 1, 2). (b) Signal of NH in the ^{1}H-NMR spectrum (toluene-d_8) of $Al(CH_3)_3(C_4H_8NH)$ at different temperatures.

Moreover, it is noteworthy that the resonance of the aminic proton of $Al(CH_3)_3(C_4H_8NH)$ at 223 K appears as a quintet (Fig. 1, B): reasonably, at this temperature, the exchange processes, involving the aminic proton, slow down thus allowing the vicinal coupling to the methylene protons to be observed, despite the quadrupolar effects of the ^{14}N nucleus. At variance with $Al(CH_3)_3(C_4H_8NH)$, the resonance of the aminic proton in $Al(CH_3)_3(C_4H_8NH)_2$ is observed as a broad line even at 188 K.

The reaction of $Al(CH_3)_3(C_4H_8NH)$ with $AlCl_3(C_4H_8NH)$ (*vide infra* for details about this compound) affords the methylchloro derivatives $Al(CH_3)_2Cl(C_4H_8NH)$ or $Al(CH_3)Cl_2(C_4H_8NH)$ depending on the starting $Al(CH_3)_3(C_4H_8NH)/AlCl_3(C_4H_8NH)$ molar ratio (Scheme 4).

Alternatively, $Al(CH_3)_2Cl(C_4H_8NH)$ results from the reaction of $[Al(CH_3)_2(C_4H_8N)]_2$ with $[NH_2Et_2]Cl$ (Scheme 4): reasonably, the protonation of the bridging amido groups $[C_4H_8N]$ yields the fragmentation of the dinuclear core and affords the coordinated pyrrolidine, making free a coordination site at the aluminium centre for the coordination of the chloride.



Scheme 4

The ^{1}H-NMR spectra of the two compounds $Al(CH_3)_2Cl(C_4H_8NH)$ and $Al(CH_3)Cl_2(C_4H_8NH)$ are similar showing the characteristic resonances of the coordinated pyrrolidine and methyl groups [$Al(CH_3)_2Cl(C_4H_8NH)$: δ 2.34, CH_2CH_2N; 2.15, NH; 0.96, CH_2CH_2N; −0.41, CH_3; $Al(CH_3)Cl_2(C_4H_8NH)$: δ 3.03, NH; 2.56, CH_2CH_2N; 1.15, CH_2CH_2N; −0.21, CH_3]. It is noteworthy that the number of chlorines bonded to the aluminium centre strongly affects the chemical shift of both the methyl and methylene protons. As a matter of fact, the methylene protons in $Al(CH_3)_2Cl(C_4H_8NH)$ show up-field shifted resonances with respect to $Al(CH_3)Cl_2(C_4H_8NH)$, in fair agreement with the major electronegativity of the chlorine. Moreover, a progressive down-field shift for the ^{1}H-resonance of the methyl group in $Al(CH_3)_{3-n}Cl_n(C_4H_8NH)$ is observed on increasing the number of chlorine bonded to the aluminium centre: n = 0, −0.51 ppm;‡ n = 1, −0.41 ppm; n = 2, −0.21 ppm.

The ^{13}C-NMR spectra of the two compounds are similar and show the resonances characteristic of the coordinated pyrrolidine [$Al(CH_3)_2Cl(C_4H_8NH)$: 46.5, 24.5 ppm; $Al(CH_3)Cl_2(C_4H_8NH)$: 46.8, 24.4 ppm].

Interaction of $AlCl_3$ with amines

The reaction of $AlCl_3$ with pyrrolidine (C_4H_8NH) affords $AlCl_3(C_4H_8NH)$ or $AlCl_3(C_4H_8NH)_2$ depending on the molar ratio Al/C_4H_8NH (Scheme 5). Alternative routes to $AlCl_3(C_4H_8NH)_2$ are the reaction of the binary amido derivative $[Al(C_4H_8N)_3]_2$ with stoichiometric amounts of $[NH_2Et_2]Cl$ (Scheme 5) and, obviously, the reaction of $AlCl_3(C_4H_8NH)$ with 1 mol of C_4H_8NH. On the other hand, $AlCl_3(C_4H_8NH)$ is alternatively obtained from the reaction of $[AlCl_2(C_4H_8N)]_2$ and the stoichiometric amount of $[NH_2Et_2]Cl$ (Scheme 5).

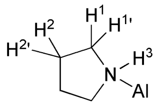
The ^{13}C-NMR spectra of the adducts $AlCl_3(C_4H_8NH)_n$ (n = 1, 2) are similar and show the resonances characteristic of the coordinated pyrrolidine (n = 1, 24.3, 47.5 ppm; n = 2, 24.9, 47.7 ppm). On the other hand, the ^{1}H-NMR spectra of the compounds are strongly affected by the temperature [as an example, the ^{1}H-NMR spectra of $AlCl_3(C_4H_8NH)_2$ recorded at different temperatures are reported in Fig. 2]. The spectra recorded at 363 K are “regular”, both $AlCl_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)_2$ showing three resonances (Table 2), assigned to the methylene protons and to the NH functionality.

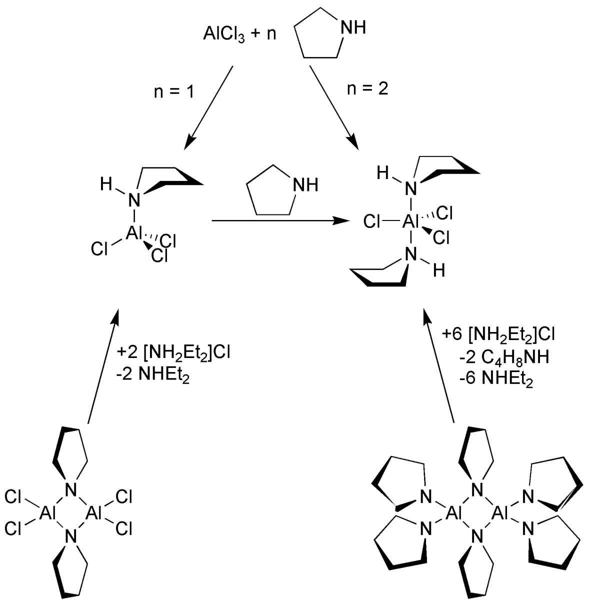
On lowering the temperature the lines at 2.58 and 1.11 ppm of $AlCl_3(C_4H_8NH)$, and at 2.88 and 1.24 ppm of $AlCl_3(C_4H_8NH)_2$ splits into two resonances (Fig. 2, Table 2) thus

---

‡ The compound $Al(CH_3)_3(C_4H_8NH)$ has been prepared by following the procedure reported in the literature[6b] and the ^{1}H-NMR spectrum has been recorded on a solution of the compound in C_6D_6, at 293 K.

Table 2 Selection of ^{1}H-NMR data (toluene-d$_8$) of $AlCl_3(C_4H_8NH)_n$ (n = 1, 2)

Structure	Position	$AlCl_3(C_4H_8NH)$			$AlCl_3(C_4H_8NH)_2$		
		δ_H			δ_H		
		223 K	363 K	$T_{coalescence}$ /K	223 K	363 K	$T_{coalescence}$ /K
	H^1, $H^{1'}$	2.34, 2.08	2.58	313	3.00, 2.82	2.88	313
	H^2, $H^{2'}$	0.88, 0.68	1.11	318	1.22, 0.86	1.24	310
	H^3	5.24	2.80	–	2.68	3.51	–



Scheme 5

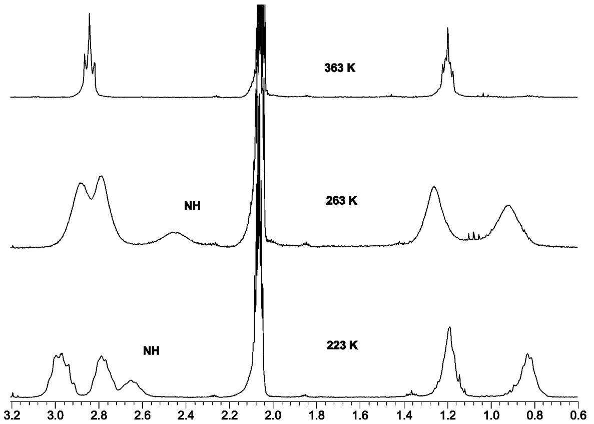
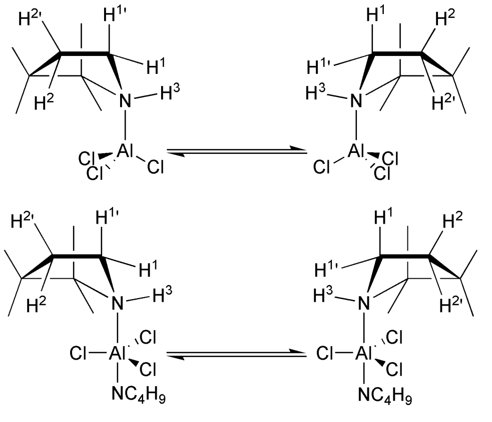


Fig. 2 ^{1}H-NMR spectra of $AlCl_3(C_4H_8NH)_2$ at different temperatures (the resonance at about 2.1 ppm is due to the residual protons of toluene-d$_8$).

indicating that a dynamic process is slowing down and that, as a consequence, each proton in the methylene groups experiments a different chemical environment.

As a matter of fact, the coordination of the pyrrolidine to the metal centre makes chemically different the two faces of the pyrrolidine, *i.e.* the geminal methylene protons experiment different chemical environments depending on whether they "look" at the metal centre or not. On the basis of the NMR data, the two faces of the coordinated pyrrolidine are not interconverting at 223 K, the resonances of geminal protons coalescing above 310 K (Table 2).

This picture is fairly confirmed by the proton COSY spectra recorded at 223 K on toluene-d$_8$ solutions of both $AlCl_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)_2$. The geminal coupling between the inequivalent methylene protons (both $CH_2C\mathit{H}_2N$ and $C\mathit{H}_2CH_2N$) yields the crosspeaks between the resonances at 2.08 and 2.34 ppm, and 0.88 and 0.68 ppm for the 1 : 1 adduct, and between the resonances at 1.22 and 0.86 ppm, and 3.00 and 2.82 ppm for the 1 : 2 adduct. Moreover the crosspeaks between the resonances at both 2.34 and 2.08 ppm and those at 0.88 and 0.68 ppm for $AlCl_3(C_4H_8NH)$ and between the resonances at both 3.00 and 2.82 ppm and those at 1.22 and 0.86 ppm for the $AlCl_3(C_4H_8NH)_2$ are indicative of the vicinal coupling between the methylene protons $CH_2C\mathit{H}_2N$ and $C\mathit{H}_2CH_2N$. The proposed dynamic processes involving the coordinated pyrrolidine of both $AlCl_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)_2$ are reported in Scheme 6.



Scheme 6

Finally the ^{27}Al-NMR spectra of $AlCl_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)_2$ show resonances at 113.0 and 62.9 ppm, respectively, thus confirming the proposed coordination number 4 for $AlCl_3(C_4H_8NH)$, and 5 for $AlCl_3(C_4H_8NH)_2$.§

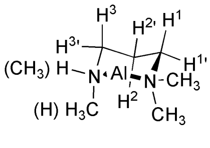
The reaction of $AlCl_3$ with *N*,*N*,*N'*-trimethylpropanediamine ($C_6H_{16}N_2$, TMPDA) affords the Lewis adduct $AlCl_3(C_6H_{16}N_2)$ [eqn. (3)] as a sticky colourless material.

The ^{1}H-NMR spectrum of $AlCl_3(C_6H_{16}N_2)$ is strongly affected by the temperature (Fig. 3). As a matter of fact, the ^{1}H-NMR spectrum at 363 K shows two singlets of the methyl groups at 2.39 and 2.00 ppm, for the $NH(CH_3)$ and $N(CH_3)_2$ functionalities, respectively.

---

§ It is reported that the chemical shift of ^{27}Al is sensitive to the coordination number,[8,9] *i.e.* on increasing the coordination number of the aluminium centre, the ^{27}Al-NMR resonance shifts up-field. Interestingly, in the laboratories where this work has been carried out, the Lewis adducts $AlCl_3(NH^iPr_2)$ and $AlCl_3(NHMeBu)_2$ have been synthesised and crystallographically characterised in the solid state:[10] $AlCl_3(NH^iPr_2)$ contains the metal centre tetrahedrally coordinated by three chlorines and the nitrogen of the amine; on the other hand, the aluminium centre in $AlCl_3(NHMeBu)_2$ is pentacoordinated (trigonal bypiramid coordination polyhedron) to three chlorines (equatorial) and two nitrogen atoms (apical). The ^{27}Al-NMR spectra of these compounds have been recorded at room temperature and resonances at 105.8 and 64.0 ppm have been observed for $AlCl_3(NHPr_2)$ and $AlCl_3(NHMeBu)_2$, respectively.

Table 3 Selection of ^{1}H-NMR data (toluene-d$_8$) of AlCl$_3$(*N*,*N*,*N*′-trimethylpropanediamine)[a]

		δ_H	
Structure	Position	363 K	213 K
	N*H*	4.78 [br]	5.75 [br]
	N(C*H*$_3$)$_2$	2.00 [s]	1.92 [s]
	NH(C*H*$_3$)	2.38 [s]	2.41 [s], 2.43 [s]
	H^3, H$^{3\prime}$	2.92 [t]	3.70 (H^3) [t], 2.35 (H$^{3\prime}$) [d]
	H^1, H$^{1\prime}$	2.16 [t]	2.52 (H^1) [t], 1.77 (H$^{1\prime}$) [d]
	H^2, H$^{2\prime}$	1.28 [qn]	1.23 (H^2) [qr], 0.59 (H$^{2\prime}$) [d]

[a] br: broad; s, singlet; d, doublet; t, triplet; qr, quartet; qn, quintet.

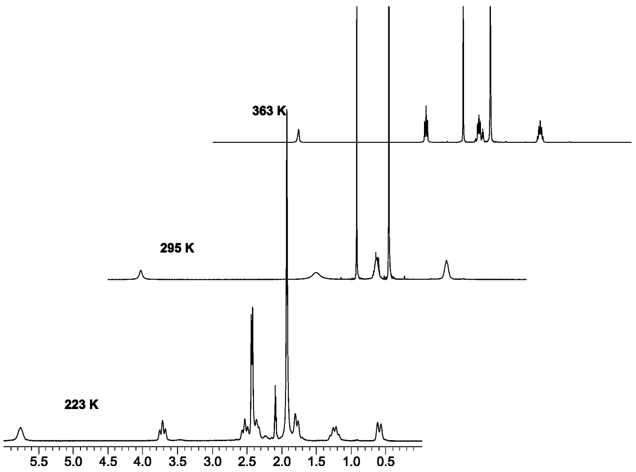
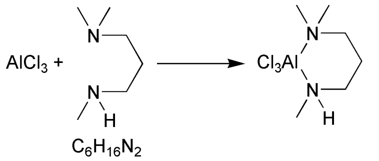


Fig. 3 ^{1}H-NMR spectra of AlCl$_3$(*N*,*N*,*N*′-trimethylpropanediamine) at different temperatures (the resonance at about 2.1 ppm is due to the residual protons of toluene-d$_8$).

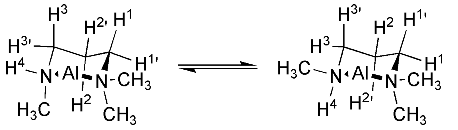


(3)

Moreover, a broad line is observed for the aminic proton at 4.76 ppm. The resonances of the methylene groups are observed at 2.92 [C*H*$_2$NH(CH$_3$)], 2.16 [C*H*$_2$N(CH$_3$)$_2$] and 1.28 ppm (CH$_2$C*H*$_2$CH$_2$). In addition, due to the ^{1}H–^{1}H vicinal coupling, the resonances at 2.92 and 2.16 ppm are triplets ($^3J_{HH}$ = 5.9 Hz) and that at 1.28 is a quintet ($^3J_{HH}$ = 5.9 Hz).

On lowering the temperature up to the room temperature, the ^{1}H-NMR spectrum changes, the amininc proton resonance shifting up-field and the methylene resonances appearing as three unresolved broad lines at 2.99, 2.12 and 1.12 ppm (Fig. 3).

Noteworthily at 213 K, each methylene resonance splits into two signals (Table 3), thus indicating that the inversion of the six-membered ring [AlN$_2$C$_3$] (Scheme 7) is slowing down and, as a consequence, each methylene proton experiments a different chemical environment, in dependence of the orientation with respect to the ring (axial or equatorial) (Table 3). Moreover, the observed structure of each signal suggests that spin–spin coupling occurs between geminal and vicinal (axial–axial) protons, the estimated coupling constants being about 12 Hz.



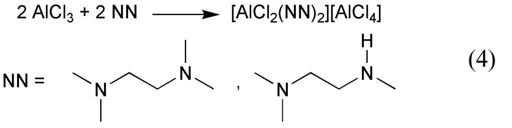
Scheme 7

Interestingly, the singlet of the methyl group in the NH(CH$_3$)$_2$ functionality splits into two lines (2.41 and 2.43 ppm, at 213 K) reasonably due to the two possible orientations of the methyl with respect to the molecular plane, *i.e.* in the plane or perpendicular to it (Scheme 7).

Due to the geminal coupling between the methylene protons, the proton COSY spectrum, recorded at 213 K, shows cross-peaks between the resonances at 1.23 and 0.59 ppm, 2.52 and 1.77 ppm, and 3.70 and 2.35 ppm. Moreover the crosspeaks between the resonances at 1.23 and 2.52 ppm, and 1.23 and 3.70 ppm indicate the ^{1}H–^{1}H vicinal axial–axial coupling.

Five lines are observed in the ^{13}C{^{1}H}-NMR spectrum (ppm 59.4, CH$_2$; 51.8, CH$_2$; 45.1, CH$_3$; 34.2, CH$_3$; 21.3, CH$_2$), and the ^{27}Al-NMR spectrum show a resonance at 73.9 ppm, thus confirming the proposed coordination number 5.§

At variance with TMPDA, AlCl$_3$ reacts with *N*,*N*,*N*′-trimethylethylenediamine (TRMEDA) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) affording the salts [AlCl$_2$(amine)$_2$][AlCl$_4$] [eqn. (4)].

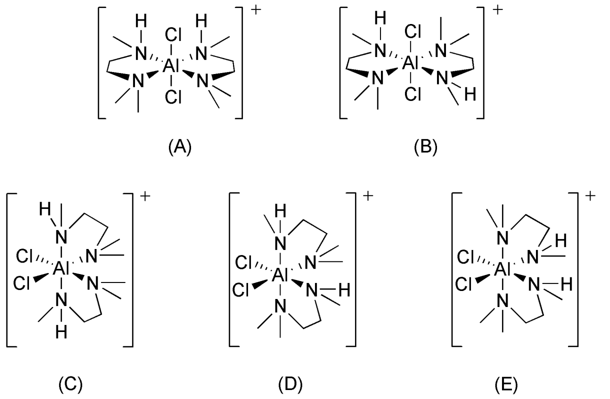


$$2\ AlCl_3 + 2\ NN \longrightarrow [AlCl_2(NN)_2][AlCl_4]$$

(4)

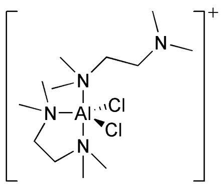
The ^{27}Al-NMR spectra of the compounds show the signal of the [AlCl$_4$]$^-$ anion (about 100 ppm), moreover a resonance is observed at 27.4 ([AlCl$_2$(TRMEDA)$_2$][AlCl$_4$]) and 63.2 ppm ([AlCl$_2$(TMEDA)$_2$][AlCl$_4$]), due to the cation [AlCl$_2$(amine)$_2$]$^+$, thus suggesting that the aluminium centre has different coordination numbers in the two cations, reasonably five in [AlCl$_2$(TMEDA)$_2$]$^+$, and six in [AlCl$_2$(TRMEDA)$_2$]$^+$.§

As far as [AlCl$_2$(TRMEDA)$_2$][AlCl$_4$] is concerned, a cluster of signal is observed in the ^{1}H-NMR spectrum (*cf.* Experimental), and, on the other hand, the ^{13}C{^{1}H}-NMR spectrum shows ten lines (*cf.* Experimental). If an octahedral arrangement of the donor atoms around the metal centre is assumed, five structures for the cation [AlCl$_2$(TRMEDA)$_2$]$^+$ are postulatable (Scheme 8).



Scheme 8

Table 4 Selection of ^1H-NMR data (THF-d_8, 183 K) with the proposed structure of the cation $[AlCl_2(N,N,N',N'\text{-tetramethylethylenediamine})_2]^+$ and the assignment

Structure	Position	δ_H
	$C\mathit{H}_2N(CH_3)_2$	2.90
	$N(C\mathit{H}_3)_2$	2.71
	$C\mathit{H}_2N(CH_3)_2Al$	2.66
	$AlN(C\mathit{H}_3)_2$	2.40

The structure D should account for the ^{13}C-NMR spectrum, indicating ten inequivalent carbon atoms, but it cannot be excluded that a mixture of two or more isomers is present. Therefore, no decisive conclusions has been drawn about the solution structure of the cation $[AlCl_2(TRMEDA)_2]^+$. On the other hand, many attempts have been carried out to grow single crystals suitable for a diffractometric measurement, but unfortunately they were unsuccessful.

The ^1H-NMR spectrum of the cation $[AlCl_2(TMEDA)_2]^+$ is strongly affected by the temperature. As a matter of fact, at 293 K, two lines have been observed at 2.64 (CH_2) and 2.39 (CH_3) ppm (Fig. 4). On the other hand, at 183 K (Fig. 4), four lines have been observed whose assignment is reported in Table 4, together with the proposed structure of the cation $[AlCl_2(TMEDA)_2]^+$.

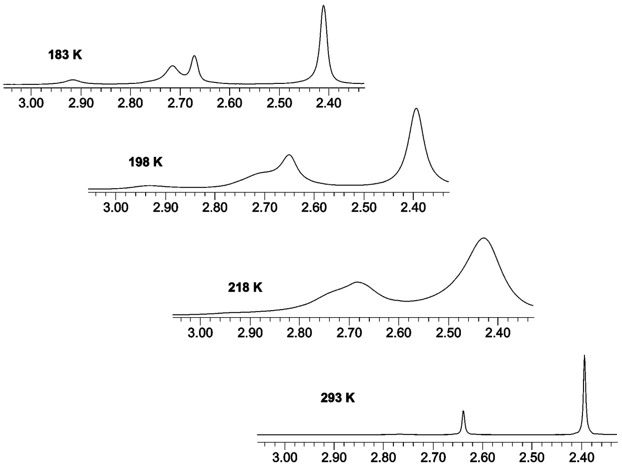
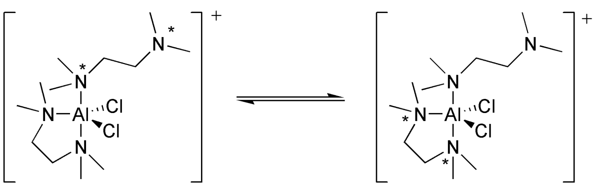


Fig. 4 ^1H-NMR spectra (THF-d_8) of $[AlCl_2(N,N,N',N'\text{-tetramethylethylenediamine})_2]^+$ in $[AlCl_2(N,N,N',N'\text{-tetramethylethylenediamine})_2][AlCl_4]$ at different temperatures.

It is noteworthy that the variation of the ^1H-NMR spectra as a function of the temperature (Fig. 4) indicates the exchange between the mono- and bi-dentate amines (Scheme 9).

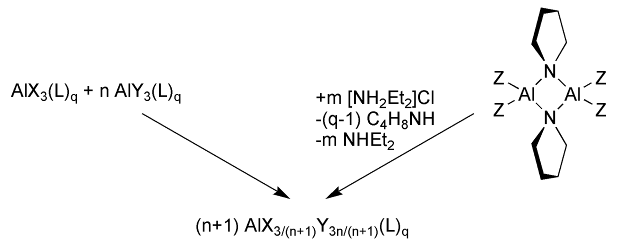


Scheme 9

Reason suggests that the different reactivities of *N*,*N*,*N'*-trimethylpropanediamine, *N*,*N*,*N'*-trimethylethylenediamine and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine towards $AlCl_3$ are due to the different steric hindrances. As a matter of fact, the presence of two methyl groups on each nitrogen in *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) prevents the chelation of the mono-dentate coordinated amine. On the other hand, two *N*,*N*,*N'*-trimethylethylenediamines coordinate bidentatedly to the aluminium centre in $[AlCl_2(amine)_2]^+$, thanks to the reduced steric hindrance of H with respect to CH_3. Similarly, as far as *N*,*N*,*N'*-trimethylpropanediamine is concerned, the presence of three methylene units connecting the two amine ends enlarges the bite angle of the bidentate ligand with respect to *N*,*N*,*N'*-trimethylethylenediamine, thus preventing the coordination of a further amine molecule and, as a consequence, the splitting of the $[AlCl_3]$ moiety.

Conclusions

The ligand exchange reactions between $[Al(C_4H_8N)_3]_2$ and AlX_3 (X = Cl, CH_3) or $Al(CH_3)_3(C_4H_8NH)$ and $AlCl_3(C_4H_8NH)$ are a valuable tool for the synthesis of novel aluminium derivatives (Scheme 10).



X = C_4H_8N; Y = Cl, CH_3; n = 2, q = 0
X = Cl; Y = CH_3; L = C_4H_8NH; n = 0.5, 2; q = 1
Z = Cl; m = 2; X = Cl, n = 0; q = 1; L = C_4H_8NH
Z = CH_3; m = 2; X = Cl; Y = CH_3; n = 2; q = 1; L = C_4H_8NH
Z = C_4H_8N; m = 6; X = Cl, n = 0; q = 2; L = C_4H_8NH

Scheme 10

On the other hand, the protonation reaction of amido derivatives is an alternative route affording chloro- or methyl-chloro-derivatives (Scheme 10).

The course of the reaction of $AlCl_3$ with aliphatic amines strongly depends on the nature of the amine. The monodentate amine pyrrolidine affords the 1 : 1 or the 1 : 2 adducts $AlCl_3(C_4H_8NH)_n$ (n = 1, 2). In a similar way, the Lewis adduct $AlCl_3$(amine) is obtained when the bidentate amine *N*,*N*,*N'*-trimethylpropanediamine is reacted with $AlCl_3$. On the other hand, the reaction of *N*,*N*,*N'*-trimethylethylenediamine or *N*,*N*,*N'*,*N'*-tetramethylethyenediamine with $AlCl_3$ proceeds through the splitting of $AlCl_3$ yielding the salt $[AlCl_2(amine)_2][AlCl_4]$.

As far as the adducts $AlCl_3(amine)_n$ (amine = pyrrolidine, n = 1, 2; amine = *N*,*N*,*N'*-trimethylpropanediamine, n = 1) and the salt $[AlCl_2(amine)_2][AlCl_4]$ (amine = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) are concerned, variable temperature NMR investigations indicate the presence of dynamic processes involving the coordinated amine ligands, *i.e.* (a) the inversion of the six-membered ring $[AlN_2C_3]$ of $AlCl_3(TMPDA)$; (b) the exchange between the mono- and bidentate amines in $[AlCl_2(amine)_2]^+$ (amine = *N*,*N*,*N'*,*N'*- tetramethylethylenediamine); (c) the inversion of the coordinated pyrrolidine in $AlCl_3(C_4H_8NH)_n$ (n = 1, 2).

Experimental

All operations were carried out in a glove-box, under an atmosphere of dinitrogen. Elemental analyses (C, H, N) were performed using a Fisons Instruments analyser (Mod. EA 1108); the chlorine content of the samples was determined by potentiometric titration using a standard solution of silver nitrate (Aldrich). NMR spectra were recorded with a BRUKER AMX 300 spectrometer (300 MHz for ^1H). ^1H- and

^{13}C-NMR spectra are referred to TMS; ^{27}Al-NMR spectra are referred to $[Al(H_2O)_6]^{3+}$ in H_2O. ^{7}Li-NMR spectra are referred to a 0.1 M solution of LiCl in D_2O. Multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

Aluminium chloride ($AlCl_3$, Fluka) was sublimed at 363 K, 5×10^{-3} atm and stored under dinitrogen. Lithium aluminium hydride ($LiAlH_4$, Aldrich) was used dissolved in Et_2O (a known quantity of the commercial product was contacted with Et_2O for 3 h; the undissolved solid was filtered off, dried *in vacuo* and weighed, thus allowing the calculation of the title of the ethereal solution). $Al(CH_3)_3(C_4H_8NH)$ was prepared according to the procedure reported in the literature.[6b] Pyrrolidine (C_4H_8NH, Aldrich) was refluxed over BaO for 12 h, then distilled and stored under dinitrogen. *N*,*N*,*N*′-trimethylethylenediamine ($C_5H_{14}N_2$, Aldrich), *N*,*N*,*N*′-trimethylpropanediamine ($C_6H_{16}N_2$, Aldrich) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine ($C_6H_{16}N_2$, Aldrich) were stored over molecular sieves (4A) under an atmosphere of dinitrogen. Aluminium trimethyl ($[Al(CH_3)_3]_2$, Fluka, purum and 11.2% w/w solution in toluene) and diethylamine hydrochloride ($[NH_2Et_2]Cl$, Fluka) were used as received.

Synthesis of $LiAl(C_4H_8N)_4 \cdot nC_4H_8NH$ (n = 1, 2)

Only the procedure for $n = 1$ is reported in detail, the synthesis of $LiAl(C_4H_8N)_4 \cdot 2C_4H_8NH$ being similar except for the $C_4H_8NH/LiAlH_4$ molar ratio (5, $n = 1$; 6, $n = 2$).

A solution of pyrrolidine, C_4H_8NH, (4.92 g, 69.2 mmol) in 50 ml of Et_2O was added dropwise (about 1 h) to a solution of $LiAlH_4$ (520 mg, 13.7 mmol) in 130 ml of Et_2O. Gas evolution was observed during the addition and in the following 2 h. After 6 h stirring, the solvent was removed *in vacuo* until a suspension of a colourless solid resulted (about 10 ml of residual solvent). The suspension was filtered, the solid dried *in vacuo* and finally identified as $LiAl(C_4H_8N)_4 \cdot C_4H_8NH$ (4.75 g, 90% yield). Found: C, 62.1; H, 10.5; N, 18.2. $C_{20}H_{41}AlLiN_5$ requires C, 62.3; H, 10.7; N, 18.2%. δ_{H} (toluene-d_8, 293 K): 3.20 (br, 16H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 2.27 (br, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{NH}$), 1.74 (br, 16H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.20 (br, 5H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2NH}+\mathrm{N}\mathit{H}$). δ_{C} (C_6D_6, 298K): 50.1 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$), 47.0 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2NH}$), 27.5 ($\mathit{C}\mathrm{H_2CH_2N}$), 25.5 ($\mathit{C}\mathrm{H_2CH_2NH}$). δ_{Li} (toluene-d_8, 293 K): 13.5. δ_{Al} (C_6D_6, 293 K): 105.2.

$LiAl(C_4H_8N)_4 \cdot 2C_4H_8NH$ (80% yield). Found: C, 63.0; H, 11.2; N, 18.7. $C_{24}H_{50}AlLiN_6$ requires C, 63.1; H, 11.0; N, 18.4%. δ_{H} (toluene-d_8, 293 K): 3.22 (br, 16H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 2.44 (br, 8H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{NH}$), 1.90 (br, 2H, $\mathrm{N}\mathit{H}$), 1.72 (br, 16H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.31 (br, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2NH}$). δ_{C} (C_6D_6, 293 K): 50.6 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$, t, $^1J_{\mathrm{CH}} = 131.1$ Hz), 47.2 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2NH}$, t, $^1J_{\mathrm{CH}} = 124.8$ Hz), 27.5 ($\mathit{C}\mathrm{H_2CH_2N}$, t, $^1J_{\mathrm{CH}} = 129.0$ Hz), 25.7 ($\mathit{C}\mathrm{H_2CH_2NH}$, t, $^1J_{\mathrm{CH}} = 131.8$ Hz). δ_{Li} (toluene-d_8, 293 K): 13.4. δ_{Al} (C_6D_6, 293 K): 104.9.

Synthesis of $[Al(C_4H_8N)_3]_2$

Only the procedure starting from $LiAl(C_4H_8N)_4 \cdot C_4H_8NH$ is described in detail, that one from $LiAl(C_4H_8N)_4 \cdot 2C_4H_8NH$ being similar.

A solution of $AlCl_3$ (375, 2.81 mmol) in Et_2O/THF (5/10 ml) was added to a solution of $LiAl(C_4H_8N)_4 \cdot C_4H_8NH$ (3.25 g, 8.43 mmol) in THF (50 ml). The mixture was stirred for 6 h, then the solvent was removed *in vacuo* and the solid suspended in toluene (30 ml). The suspension was stirred for 1 h, then the solid was filtered off and dried (colourless, 340 mg). The solution was evaporated yielding a colourless residue which was dried *in vacuo* and identified as $[Al(C_4H_8N)_3]_2$ (2.50 mg, 94% yield). Found: C, 61.0; H, 10.0; N, 17.4. $C_{12}H_{24}AlN_3$ requires C, 60.7; H, 10.2; N, 17.7%. δ_{H} (C_6D_6, 293 K): 3.21 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$); 2.98 (m, 1H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$); 1.71 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$); 1.49 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$). δ_{C} (C_6D_6, 293 K): 50.0 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$); 49.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$); 27.2 ($\mathit{C}\mathrm{H_2CH_2N}$); 25.4 ($\mathit{C}\mathrm{H_2CH_2N}$). δ_{Al} (C_6D_6, 293 K): 105.9.

Synthesis of $[AlX_2(C_4H_8N)]_2$ (X = Cl, CH_3)

X = Cl. A suspension of $AlCl_3$ (520 mg, 3.90 mmol) in toluene (15 ml) was treated with $[Al(C_4H_8N)_3]_2$ (462 mg, 1.95 mmol of aluminium). $AlCl_3$ promptly dissolved and after 3 h stirring the solution was evaporated yielding a colourless residue which was washed with pentane, dried *in vacuo* and identified as $[AlCl_2(C_4H_8N)]_2$ (765 mg, 78% yield). Found: C, 28.5; H, 4.8; Cl, 42.0; N, 8.0. $C_4H_8AlCl_2N$ requires C, 28.6; H, 4.8; Cl, 42.2; N, 8.3%. δ_{H} (C_6D_6, 293 K): 2.81 (br, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 1.24 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$). δ_{C} (C_6D_6, 293 K): 50.6 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$, t, $^1J_{\mathrm{CH}} = 141.8$ Hz), 24.5 ($\mathit{C}\mathrm{H_2CH_2N}$, $^1J_{\mathrm{CH}} = 133.2$ Hz). δ_{Al} (C_6D_6, 293 K): 117.2.

X = CH_3. A 11.2% w/w toluene solution of $[Al(CH_3)_3]_2$ (2.86 g of solution, 4.44 mmol of aluminium) was added to a solution of $[Al(C_4H_8N)_3]_2$ (528 mg, 2.22 mmol of aluminium) in toluene (20 ml). After 3 h stirring, the solution was evaporated yielding a colourless residue which was dried *in vacuo* and identified as $[Al(CH_3)_2(C_4H_8N)]_2$ (650 mg, 77% yield). Found: C, 56.5; H, 10.8; N, 11.4. $C_6H_{14}AlN$ requires C, 56.7; H, 11.1; N, 11.0%. δ_{H} (C_6D_6, 293 K): 2.62 (4H, m, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 1.33 (4H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), −0.57 (6H, s, $\mathrm{C}\mathit{H}_3$). δ_{C} (C_6D_6, 293 K): 49.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$, t, $^1J_{\mathrm{CH}} = 138.7$ Hz), 25.1 ($\mathit{C}\mathrm{H_2CH_2N}$, t, $^1J_{\mathrm{CH}} = 132.1$ Hz), −11.9 ($\mathit{C}\mathrm{H_3}$). δ_{Al} (C_6D_6, 293 K): 165.6.

Synthesis of $Al(CH_3)_3(C_4H_8NH)_2$

The aluminium derivative $Al(CH_3)_3(C_4H_8NH)$ (350 mg, 2.44 mmol) was contacted with C_4H_8NH (175 mg, 2.46 mmol). The liquid material obtained was stirred for 2 h and finally identified as $Al(CH_3)_3(C_4H_8NH)_2$. Found: C, 61.3; H, 12.8; N, 13.0. $C_{11}H_{27}AlN_2$ requires C, 61.6; H, 12.7; N, 13.1%. δ_{H} (C_6D_6, 293 K): 2.44 (m, 8H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 1.79 (br, 2H, $\mathrm{N}\mathit{H}$), 1.20 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), −0.49 (s, 9H, $\mathrm{C}\mathit{H}_3$). δ_{C} (toluene-d_8, 293 K): 46.9 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$), 25.5 ($\mathit{C}\mathrm{H_2CH_2N}$), −9.1 ($\mathit{C}\mathrm{H_3}$).

Synthesis of $Al(CH_3)_2Cl(C_4H_8NH)$

Reaction of $[Al(CH_3)_2(C_4H_8N)]_2$ with $[NH_2Et_2]Cl$. A suspension of $[NH_2Et_2]Cl$ (700 mg, 6.39 mmol) in THF (30 ml) was treated with $[Al(CH_3)_2(C_4H_8N)]_2$ (820 mg, 6.45 mmol of aluminium): a colourless solution promptly resulted. After 2 h stirring, the solvent was removed *in vacuo* yielding a colourless solid which was identified as $Al(CH_3)_2Cl(C_4H_8NH)$ (1.00 g, 95% yield). Found: C, 43.8; H, 9.1; Cl, 21.5; N, 8.8. $C_6H_{15}AlClN$ requires C, 44.0; H, 9.2; Cl, 21.7; N, 8.6%. δ_{H} (C_6D_6, 293 K): 2.34 (m, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$); 2.15 (br, 1H, $\mathrm{N}\mathit{H}$); 0.96 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$); −0.41 (s, 6H, $\mathrm{C}\mathit{H}_3$). δ_{C} (C_6D_6, 293 K): 46.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$, t, $^1J_{\mathrm{CH}} = 142.3$ Hz); 24.5 ($\mathit{C}\mathrm{H_2CH_2N}$, t, $^1J_{\mathrm{CH}} = 133.4$ Hz); −9.2 ($\mathit{C}\mathrm{H_3}$, q, $^1J_{\mathrm{CH}} = 61.0$ Hz). δ_{Al} (C_6D_6, 293 K): 158.6.

Reaction of $AlCl_3(C_4H_8NH)$ with $Al(CH_3)_3(C_4H_8NH)$. A solution of $Al(CH_3)_3(C_4H_8NH)$ (282 mg, 1.97 mmol) in toluene (20 ml) was treated with $AlCl_3(C_4H_8NH)$ (200 mg, 0.98 mmol). After 3 h stirring at 333 K, the solution was evaporated and the residue identified (spectroscopically and analytically) as $Al(CH_3)_2Cl(C_4H_8NH)$ (463 mg, 96% yield).

Synthesis of $Al(CH_3)Cl_2(C_4H_8NH)$

A solution of $Al(CH_3)_3(C_4H_8NH)$ (200 mg, 1.40 mmol) in toluene (20 ml) was treated with $AlCl_3(C_4H_8NH)$ (572 mg, 2.80 mmol). After 3 h stirring at 333 K, the solution was evaporated and the residue identified as $Al(CH_3)Cl_2(C_4H_8NH)$ (710 mg, 92% yield). Found: C, 32.5; H, 6.2; Cl, 38.8; N, 7.6. $C_5H_{12}AlCl_2N$ requires C, 32.6; H, 6.6; Cl, 38.5; N, 7.6%. δ_{H} (C_6D_6, 293 K): 3.03 (br, 1H, $\mathrm{N}\mathit{H}$), 2.56 (br, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 1.15 (br, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), −0.21 (s, 3H, $\mathrm{C}\mathit{H}_3$). δ_{C} (C_6D_6, 293 K): 46.8 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2N}$), 24.4 ($\mathit{C}\mathrm{H_2CH_2N}$).

Synthesis of $AlCl_3(C_4H_8NH)_n$ ($n = 1, 2$)

Reaction of $AlCl_3$ with C_4H_8NH. Only the procedure for $n = 1$ is reported in detail, the other being similar except for the $AlCl_3/C_4H_8NH$ molar ratio (1, $n = 1$; 0.5, $n = 2$). A suspension of $AlCl_3$ (1.32 g, 9.90 mmol) in toluene (30 ml) was treated with C_4H_8NH (700 mg, 9.84 mmol): the solid promptly dissolved. After 12 h stirring, the solution was evaporated until a suspension resulted (about 10 ml of residual solvent). The solid was filtered off, dried *in vacuo* and identified as $AlCl_3(C_4H_8NH)$ (1.70 g, 84% yield). Found: C, 23.2; H, 4.5; Cl, 52.2; N, 6.9. $C_4H_9AlCl_3N$ requires C, 23.5; H, 4.4; Cl, 52.0; N, 6.8%. δ_H (toluene-d_8, 293 K): 5.49 (br, 1H), 2.45 (br, 1H), 2.25 (br, 1H), 1.06 (br, 1H), 0.82 (br, 1H) (see Results and discussion for the assignment). δ_C (toluene-d_8, 293 K): 47.5 ($CH_2\mathit{C}H_2N$), 24.3 ($\mathit{C}H_2CH_2N$). δ_{Al} (toluene-d_8, 293 K): 113.0.

$AlCl_3(C_4H_8NH)_2$ (78% yield). Found: C, 34.8; H, 6.6; Cl, 38.7; N, 10.1. $C_8H_{18}AlCl_3N_2$ requires C, 34.9; H, 6.6; Cl, 38.6; N, 10.2%. δ_H (toluene-d_8, 293 K): 2.90 (br, 1H), 2.83 (br, 1H), 2.49 (br, 1H), 1.29 (br, 1H), 0.97 (br, 1H) (see Results and discussion for the assignment). δ_C (toluene-d_8, 293 K): 47.7 ($CH_2\mathit{C}H_2N$), 24.9 ($\mathit{C}H_2CH_2N$). δ_{Al} (toluene-d_8, 293 K): 62.9.

Reaction of $[AlCl_2(C_4H_8N)]_2$ with $[NH_2Et_2]Cl$. A suspension of $[NH_2Et_2]Cl$ (900 mg, 8.21 mmol) in THF (20 ml) was treated with $[AlCl_2(C_4H_8N)]_2$ (1.38 g, 8.21 mmol of aluminium). The resulting solution was stirred for 4.5 h and then the solvent was removed *in vacuo*. The solid was washed with pentane, dried *in vacuo* and identified (analytically and spectroscopically) as $AlCl_3(C_4H_8NH)$ (1.50 g, 89% yield).

Reaction of $[Al(C_4H_8N)_3]_2$ with $[NH_2Et_2]Cl$. A suspension of $[NH_2Et_2]Cl$ (1.30 g, 11.9 mmol) in THF (20 ml) was treated with $[Al(C_4H_8N)_3]_2$ (920 mg, 3.88 mmol of aluminium). The resulting solution was stirred for 6 h, and then the solvent was removed. The solid was washed with pentane, dried *in vacuo* and identified (analytically and spectroscopically) as $AlCl_3(C_4H_8NH)_2$ (900 mg, 84% yield).

Reaction of $AlCl_3$ with bidentate amines

***N,N,N'*-Trimethylethylenediamine ($C_5H_{14}N_2$).** A solution of $C_5H_{14}N_2$ (1.19 g, 11.6 mmol) in toluene (10 ml) was added dropwise to a suspension of $AlCl_3$ (1.50 g, 11.2 mmol) in toluene (20 ml). After 12 h stirring a colourless suspension resulted; the solid was filtered off, washed with pentane, dried *in vacuo* and finally identified as $[AlCl_2(C_5H_{14}N_2)_2][AlCl_4]$ (1.88 g, 71% yield). Found: C, 25.4; H, 6.1; Cl, 45.5; N, 11.7. $C_5H_{14}AlCl_3N_2$ requires C, 25.5; H, 6.0; Cl, 45.2; N, 11.9%. δ_H (THF-d_8, 293 K): 4.9–4.4, 3.6–3.2, 3.2–2.0 (see Results and discussion). δ_C (THF-d_8, 293 K): 55.0 (CH_2, t, $^1J_{CH}$ = 137.3 Hz), 54.5 (CH_2, t, $^1J_{CH}$ = 136.0 Hz), 45.9 (CH_3, q, $^1J_{CH}$ = 141.6 Hz), 45.6 (CH_3, q, $^1J_{CH}$ = 146.7 Hz), 45.0 (CH_3, q, $^1J_{CH}$ = 143.0 Hz), 44.1 (CH_3, q, $^1J_{CH}$ = 151.0 Hz), 43.1 (CH_2, t, $^1J_{CH}$ = 142.1 Hz), 42.6 (CH_2, t, $^1J_{CH}$ = 135.8 Hz), 33.9 (CH_3, q, $^1J_{CH}$ = 137.3 Hz), 33.8 (CH_3, q, $^1J_{CH}$ = 137.3 Hz). δ_{Al} (THF-d_8, 293 K): 99.8, 27.4.

***N,N,N',N'*-Tetramethylethylenediamine ($C_6H_{16}N_2$).** A solution of $C_6H_{16}N_2$ (850 mg, 7.31 mmol) in toluene (10 ml) was added dropwise to a suspension of $AlCl_3$ (970 g, 7.27 mmol) in toluene (20 ml). After 12 h stirring, a colourless suspension resulted; the solid was filtered off, washed with pentane, dried *in vacuo* and finally identified as $[AlCl_2(C_6H_{16}N_2)_2][AlCl_4]$ (1.38 g, 77% yield). Found: C, 28.5; H, 6.5; Cl, 42.7; N, 11.3. $C_6H_{16}AlCl_3N_2$ requires C, 28.9; H, 6.5; Cl, 42.6; N, 11.2%. δ_H (THF-d_8, 293 K): 2.60 (br, 1H, CH_2), 2.37 (br, 3H, CH_3). δ_C (THF-d_8, 293 K): 57.4 (CH_2), 46.4 (CH_3). δ_{Al} (THF-d_8, 293 K): 100.0, 63.2.

***N,N,N'*-Trimethylpropanediamine ($C_6H_{16}N_2$).** A solution of $C_6H_{16}N_2$ (620 mg, 5.33 mmol) in toluene (10 ml) was added dropwise to a suspension of $AlCl_3$ (700 mg, 5.25 mmol) in toluene (20 ml). After 3 h stirring, the colourless solution was evaporated and the residue washed with pentane, dried *in vacuo* and finally identified as $AlCl_3(C_6H_{16}N_2)$ (1.16 g, 85% yield). Found: C, 29.1; H, 6.7; Cl, 42.3; N, 11.2. $C_6H_{16}AlCl_3N_2$ requires C, 28.9; H, 6.5; Cl, 42.6; N, 11.2%. δ_H (C_6D_6, 293 K): 5.77 (br, 1H, $N\mathit{H}$), 1.97 (br, 2H, $C\mathit{H}_2NHCH_3$), 2.41 (s, 3H, $NHC\mathit{H}_3$), 2.08 (br, 2H, $C\mathit{H}_2N(CH_3)_2$), 1.90 (s, 6H, $N(C\mathit{H}_3)_2$), 1.04 (br, 2H, $CH_2C\mathit{H}_2CH_2$). δ_C (C_6D_6, 293 K): 59.4 ($\mathit{C}H_2N(CH_3)_2$, t, $^1J_{CH}$ = 137.2 Hz), 51.8 ($\mathit{C}H_2NHCH_3$, t, $^1J_{CH}$ = 145.0 Hz), 45.1 ($CH_2N(\mathit{C}H_3)_2$, q, $^1J_{CH}$ = 133.9 Hz), 34.2 ($CH_2NH\mathit{C}H_3$, q, $^1J_{CH}$ = 143.6 Hz), 21.3 ($CH_2\mathit{C}H_2CH_2$, t, $^1J_{CH}$ = 124.8 Hz). δ_{Al} (C_6D_6, 293 K): 73.9.

Acknowledgements

VP is indebted to Dr. Sergio Tamburini (ICIS-CNR, Padova) for support in acquiring and discussing 2D-NMR spectra. Insightful comments and helpful discussions with Prof. Fausto Calderazzo and Prof. Guido Pampaloni (Università di Pisa) are kindly acknowledged.

References

1 Y. Takahashi, K. Yamashita, S. Motojima and K. Singiyama, *Surf. Sci.*, 1979, **86**, 238.
2 L. V. Interrante, W. Lee, M. McConnel, N. Lewis and E. Hall, *J. Electrochem. Soc.*, 1989, **136**, 472.
3 D. C. Bradley, D. M. Frigo and E. A. D. White, *Eur. Pat.*, 0 331 448, 1989.
4 D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259 and refs therein.
5 J. K. Ruff, *J. Am. Chem. Soc.*, 1961, **83**, 2835.
6 (*a*) M. J. Taylor, Aluminum and Gallium, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, 3 105; and refs therein; (*b*) C. J. Thomas, L. K. Krannich and C. L. Watkins, *Polyhedron*, 1993, **12**, 389; (*c*) L. M. Engelhardt, P. C. Junk, Colin, L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 3297; (*d*) D. C. Bradley, G. Coumbarides, I. S. Harding, G. E. Hawkes, I. A. Maia and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1999, 3553; (*e*) E. S. Bento, D. C. Bradley, G. E. Hawkes, I. A. Maia and K. D. Sales, *Magn. Reson. Chem.*, 2000, **38**, 331.
7 M. M. Andrianarison, M. C. Ellerby, I. B. Gorrel, P. B. Hitchcock, J. D. Smith and D. R. Stanley, *J. Chem Soc., Dalton Trans.*, 1996, 211.
8 R. Benn, A. Rufinska, H. Lehmkuhl, E. Janssen and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 779.
9 *NMR and the periodic table*, ed. R. K. Harris and B. E. Mann, Academic Press, London, 1978.
10 M. Belogourova, F. Benetollo and P. Zanella, unpublished results.