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Aluminium Complexes of a Phenoxyimine Ligand with a Pendant Imidazolium Moiety: Synthesis, Characterisation and Evidence for Hydrogen Bonding in Solution

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Novel alkylaluminium complexes (*phim*)$AlMe_2$ (**1**) and (*phimid*)$AlR_2^+Br^-$ [R = Me (**2**), R = *i*Bu (**3**)] bearing the Schiff base ligands 3,5-*t*Bu_2-2-(OH)C_6H_2CH=N*i*Pr (*phim*-H) and 3,5-*t*Bu_2-2-(OH)C_6H_2CH=NCH_2CH_2[CH(NCHCHN*i*Pr)]Br (*phimid*-H·Br) have been prepared and fully characterised. Complexes **1**–**3** each have a tetrahedral structure, with the aluminium atom surrounded by the oxygen and nitrogen atoms of the chelating ligand and two alkyl groups. The structures of *phimid*-H·Br and of complex **1** have been determined by X-ray diffraction studies. Investigation of the solution structures of **1**–**3** by ^{1}H NMR spectroscopy revealed that the coordinated *phimid* ligand is involved in hydrogen bonding with bromide anion. Treatment of **1** with $B(C_6F_5)_3$ led smoothly to (*phim*)Al(C_6F_5)Me (**4**) by transfer of a C_6F_5 group from $MeB(C_6F_5)_3^-$ to the initially formed coordinatively unsaturated cationic intermediate. In contrast, treatment of **2** with one equiv. of $B(C_6F_5)_3$ afforded the cationic monomethyl species (*phimid*)$AlMeBr^+MeB(C_6F_5)_3^-$ (**5**), stabilised by the coordination of the bromide anion acting as a Lewis base.

Introduction

Schiff bases have been widely employed as heterobidentate ligands in the coordination chemistry of both transition and *p*-block metal complexes.[1] Among these, aluminium-based alkyl complexes have been reported and have been shown to catalyse a variety of reactions.[2] These investigations were generally centred on the metal first-coordination sphere, with scarce attention having been paid to the influence of the second-sphere bonding interactions on the reactivity and properties of these complexes. Non-coordinating active sites may play important roles in molecular recognition and activation processes involving catalysts supported by Schiff bases. However, exploration of noncovalent interactions exhibited by this group of compounds is still an emerging area of research. In a recent paper by Lewinski et al.,[3] intra- and intermolecular noncovalent interactions such as the C–H_{imino}···O, C–H_{aryl}···O, C–H_{aliph}···O and C–H···π hydrogen bonds and π stacking of group 13 Schiff base complexes were revised, with various structural motifs being delineated and correlated to the ligand architecture and nature of the metal centre.

Moreover, the increasing interest being focused on the utilisation of ionic liquids, many of which are imidazolium salts,[4] as solvents for catalysis has prompted studies centred on the interaction between imidazolium cations and metals.[5]

We were interested in exploring the coordination behaviour of a modified phenoxyimine ligand containing a pendant imidazolium moiety. In particular we considered the salicylaldimine-functionalised imidazolium bromide ligand [3,5-*t*Bu_2-2-(OH)C_6H_2CH=NCH_2CH_2(CH{NCHCHN*i*Pr})]Br (*phimid*-H·Br), previously employed in the synthesis of N-heterocyclic carbene complexes of late transition and lanthanide metals.[6]

Here we describe the synthesis, solution properties and reactivity of novel alkylaluminium complexes bearing the *phimid*-H·Br ligand. The distinctive behaviour of these complexes is compared with that of an analogous alkylaluminium complex bearing a salicylaldimine ligand lacking the pendant imidazolium moiety: 3,5-*t*Bu_2-2-(OH)C_6H_2CH=N*i*Pr (*phim*-H).

Results and Discussion

Synthesis and Characterisation of the Ligands

The phenoxyimine ligands 3,5-*t*Bu_2-2-(OH)C_6H_2CH=N*i*Pr (*phim*-H) and [3,5-*t*Bu_2-2-(OH)C_6H_2CH=NCH_2CH_2-(CH{NCHCHN*i*Pr})]Br (*phimid*-H·Br) were prepared in high yields by modified literature procedures.[6,7] Well re-

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solved ^{1}H NMR spectra of these ligands are reported in the Supporting Information; the assignments of the protonic resonances were based on previously reported data, and in the case of *phimid*-H·Br were corroborated by long-range ^{1}H–^{1}H COSY experiments. Recrystallisation of *phimid*-H·Br from hexane/diethyl ether afforded crystals suitable for X-ray analysis.

The X-ray molecular structure of *phimid*-H·Br is shown in Figure 1, and selected geometrical parameters are given in Table 1. The crystallographically independent unit contains two ligand molecules, two bromide counterions and a water molecule. In the heteroaromatic ring, bond lengths C12A–N2A and C12A–N3A (C12B–N2B and C12B–N3B) are equivalent to each other, consistently with the resonance structures of the imidazolium ion. The H atom of the *ortho* hydroxy group points toward the lone pair of the imino N atom as the result of strong intramolecular hydrogen bonding[8] [O1A···N1A 2.611(4) Å 142.9°; O1B···N1B 2.577(5) Å 152.2°]. Each independent molecule assumes a non-elongated, bent conformation, mainly as the result of a *gauche*-type torsion angle around the C8A–C9A and C8B–C9B bond.

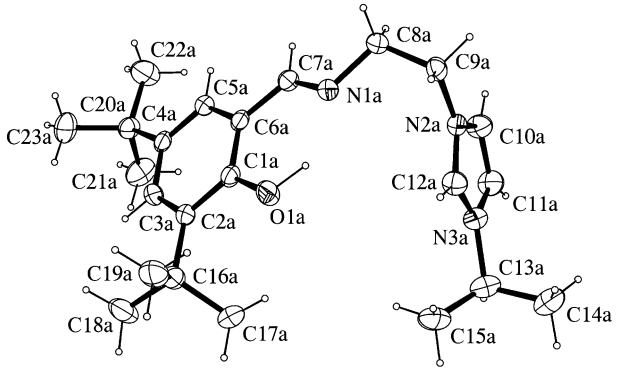


Figure 1. X-ray structure of one crystallographically independent imidazolium cation of [3,5-*t*Bu$_2$-2-(OH)C$_6$H$_2$CH=NCH$_2$CH$_2$-(CH{NCHCHN*i*Pr})]Br (*phimid*-H·Br). Displacement ellipsoids are drawn at 30% probability level.

Table 1. Selected lengths [Å], bond angles [°] and torsion angles [°] for *phimid*-H·HBr.

C7A–N1A	1.283(5)	C7B–N1B	1.282(5)
C12A–N3A	1.313(5)	C12B–N3B	1.318(5)
C12A–N2A	1.323(5)	C12B–N2B	1.322(6)
C7A–N1A–C8A	116.5(3)	C7B–N1B–C8B	119.1(4)
N1A–C8A–C9A–N2A	53.7(5)	N1B–C8B–C9B–N2B	54.3(5)

In the crystal packing (Figure 2), molecules form layers in the *ab* plane, piled up along *c*. Each layer is better described as a double layer with polar imidazolium and bromide ions on the outer regions and phenyl and *tert*-butyl groups in the inner ones. Water molecules are sandwiched between the polar surfaces of adjacent (double) layers along *c*. They are possibly involved in weak bonding[8] with bromide anions [O2···Br1$^{(i)}$ 3.354(4) Å O2–H2A···Br1$^{(i)}$ 163.6°; O2···Br2$^{(ii)}$ 3.272(4) Å O2–H2B···Br2$^{(ii)}$ 150.0°, with (i) = *x* + 1, *y* + 1, *z* and (ii) = –*x* + 1, –*y* + 1, –*z* + 1]. Bromide anions (and O atoms of water molecules) also act as hydrogen bonding acceptors with acidic H atoms of the imidazolium rings and imino H atoms as donors. Several interactions of this type that agree with cut-off rules suggested for weak hydrogen bonding[8] can be found in the packing [C11B–H11b···O2 2.263 Å 151.8°, C10A–H10a···O2$^{(i)}$ 2.727 Å 136.3°, C12A–H12a···Br2 2.930 Å 120.9°, C10B–H10b···Br2 2.944 Å 149.2°, C10A–H10a···Br1$^{(ii)}$ 2.963 Å 136.5°, with (i) = –*x* + 1, –*y* + 1, –*z* + 1 and (ii) = –*x*, –*y*, –*z* + 1]. Not unexpectedly, the closest H···Br contact is shown by H12, the most acidic H atom of the molecule.

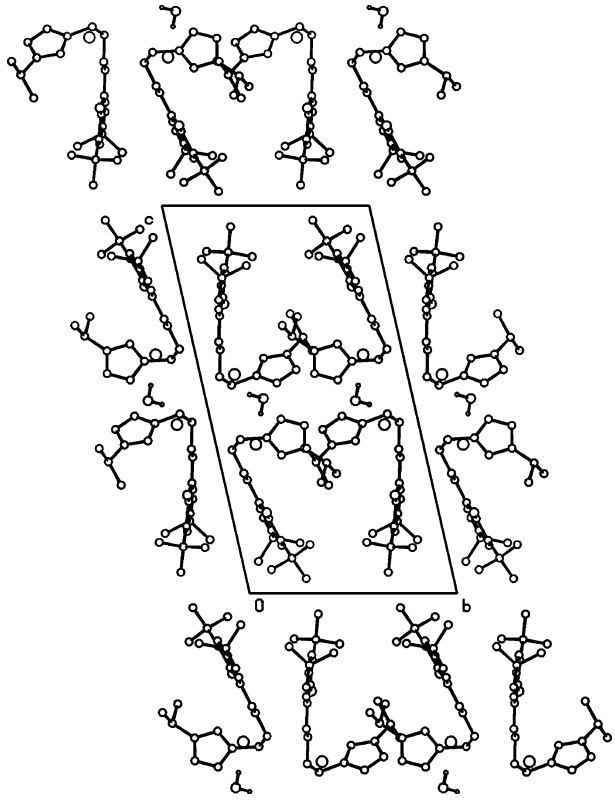


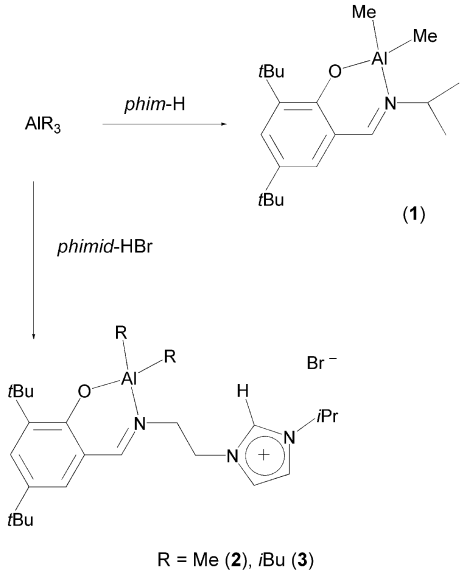
Figure 2. Crystal packing of [3,5-*t*Bu$_2$-2-(OH)C$_6$H$_2$CH=NCH$_2$-CH$_2$(CH{NCHCHN*i*Pr})]Br (*phimid*-H·Br) viewed down *a*. H atoms are shown for water molecules only.

Another weak hydrogen bonding acceptor is the phenyl ring (π acceptor[8]). The packing shows a C–H···C$_g$ (C$_g$ is the centroid of the phenyl ring) interaction falling in the range of weak hydrogen bonding[8] [C14$^{(i)}$–H14f$^{(i)}$···C$_g$ 2.979 Å 173.0° with (i) = –*x* + 1, –*y* + 1, –*z* + 1].

Synthesis and Characterisation of the Complexes 1–3

Treatment of toluene solutions of anhydrous *phim*-H or *phimid*-H·Br with 1 equiv. of AlR$_3$ readily afforded the dialkylaluminium derivatives (*phim*)AlMe$_2$ (**1**) and (*phimid*)-AlR$_2^+$Br$^-$ [R = Me (**2**), R = *i*Bu (**3**)], with elimination of the corresponding alkane (Scheme 1). The reactions were fast on the NMR scale and quantitative. ^{1}H NMR monitoring of the reaction of *phimid*-H·Br in the NMR tube showed that deprotonation occurred only at the phenolic group and did not involve the imidazolium NC(H)N moiety. As a matter of fact, the signal of the NC(H)N proton

was still present, giving rise to resonances at δ = 11.12 and 11.05 ppm for **2** and **3**, respectively: only slightly shifted relative to that observed for *phimid*-H·Br. Heating of a [D_8]-toluene solution of **2** at 373 K for a few hours resulted in decomposition. Complex **1**–**3** are very soluble in halogenated and aromatic solvents; crystals of **1** suitable for X-ray analysis were grown from hexane. In the case of complex **2**, poor crystal quality and weak diffraction prevented structural analysis.



Scheme 1.

The X-ray structure of **1** is shown in Figure 3; selected geometric data are given in Table 2. The complex is monomeric, with the salicylaldiminato moiety acting as a chelating ligand through its N and O atoms. Two methyl groups complete a distorted tetrahedral coordination geometry around the Al atom. The Al–O1 [1.769(1) Å] bond length is significantly shorter than Al–N1 [1.963(2) Å]. This effect, as well as the enlargement of the Al–O1–C3 valence angle [131.8(1)°], has been observed in other salicylaldiminato Al^{III} complexes.[9] Of the bond angles around Al, the smallest is N1–Al–O1 [95.15(6)°], which is associated with the bite angle of the chelating ligand. The six-membered chelate ring is not planar, mainly because Al is a little out of the plane of the other five atoms [0.219(2) Å].

The strongest hydrogen bonding acceptor in **1** is the phenoxy oxygen atom (O1). However, the presence of the bulky *tert*-butyl group in the *ortho* position on the phenyl moiety, together with that of the two methyl groups bound to Al, make O1 largely inaccessible to close intermolecular contacts, which are indeed not found in the packing.[3] On the other hand, weak intramolecular hydrogen bonding interactions are found with O1 as acceptor and the H atoms of the adjacent *tert*-butyl group as donors (H18a···O1 2.386 Å 122.5°; H19c···O1 2.312 Å 124.8°). These interactions agree with result found by Lewinski for weak H-bonding in sterically overcrowded salicylaldiminato Al complexes.[3] The other hydrogen bonding acceptor in **1** is

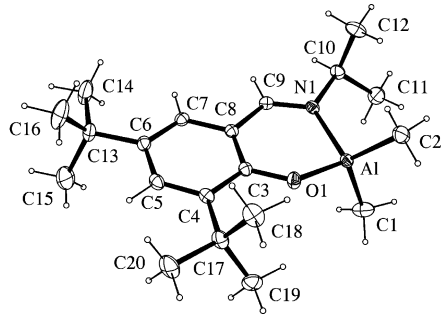


Figure 3. X-ray structure of **1**.

Table 2. Selected lengths (Å), bond angles [°] and torsion angles [°] for compound **1**.

Al–O1	1.769(1)	C2–Al–N1	110.93(8)
Al–C2	1.949(2)	C1–Al–N1	109.79(8)
Al–C1	1.955(2)	C3–O1–Al	131.8(1)
Al–N1	1.963(2)	C9–N1–C10	116.2(2)
O1–C3	1.326(2)	C9–N1–Al1	120.6(1)
N1–C9	1.291(2)	C10–N1–Al1	123.2(1)
C2–Al–C1	117.9(1)	N1–C9–C8	127.9(2)
O1–Al–N1	95.15(6)	Al–O1–C3	171.9(1)
C2–Al–N1	110.93(8)	C2–Al–N1	110.93(8)

the phenyl ring (π acceptor[8]). In this case, accessibility to intermolecular contacts is possible, but the strength as acceptor is lower than with O1. Nonetheless, the packing shows a C–H···C_g (C_g is the centroid of the phenyl ring) interaction falling in the range of weak H bonding[8] consistently with the d(H···C_g)<3.0 Å cut-off criterion suggested by Braga et al.[10] [H12b$^{(i)}$···C_g 2.92 Å 148.3° with (i) = 1.5 – x, 0.5 – y, z – 0.5].

It is worth noting that the imino H atom, the most acidic one in **1**, is not significantly involved in H bonding in the crystal packing. This, again, is presumably a consequence of the steric hindrance for intermolecular contacts around the H bonding acceptor O1.

The molecular structure of **2** in solution was determined by long-range COSY, HSQC and NOESY experiments. The NMR spectroscopic data for **1**–**3** were consistent with a tetrahedral C_s symmetric structure resulting from the κ^2-N,O coordination of the ligands to the metal centre through the phenoxy group and the imino nitrogen. In the ^{1}H NMR spectra of **1** and **2** the methyl groups bound at the aluminium centres appear as sharp singlets at –0.22 and –0.35 ppm, respectively, whereas in the ^{1}H NMR spectrum of **3** the isobutyl groups appear as an AA′MX$_3$X$_3$′ system with two multiplets centred at 2.19 ($^3J_{M,X}$ = 6.7 Hz) and 0.30 ppm ($^1J_{A,A'}$ = 14.1 Hz; $^3J_{A,M}$ = 7.1 Hz) and two doublets centred at δ = 1.14 and 0.86 ppm.

Hydrogen Bonding Interactions in Solution

It is well documented that the three ring protons in 1,3-dialkylimidazolium cations engage in hydrogen bonding with halide anions.[11] It is reasonable to assume that the pendant imidazolium moieties in the coordinated *phimid* li-

gands of **2** and **3** are involved in hydrogen bonding with the bromide anion, as already found in the solid structure of *phimid*-H·Br. As a matter of fact, the ^{1}H NMR resonances of the imine *H*C=N and the imidazolium protons are shifted downfield if compared with analogous literature data; the imine *H*C=N protons, for example, resonate at δ = 7.38 and 9.82 ppm in the cases of **1** and **2**, respectively. In order to probe the presence of these interactions we added a Lewis acidic compound to a solution of **2**. As expected, the addition of $AlMe_3$ to a [D_6]benzene solution of **2** caused significant upfield shifts of the resonances of the coordinated ligand, with the largest shifts being those seen for the imine *H*C=N and the imidazolium NC(*H*)N resonances (Figure 4). This behaviour can be explained by considering that the addition of $AlMe_3$ to the solution of **2** results in the replacement of Br^- with $BrAlMe_3^-$. This anion shows a lower affinity for bonding with the "acidic" hydrogen of the *phimid* ligand and generates a dissociated ion pair as shown in the following equilibrium (1):

$$Br^-[(phimid)AlMe_2]^+ + AlMe_3 \rightleftarrows [(phimid)AlMe_2]^+ + BrAlMe_3^- \quad (1)$$

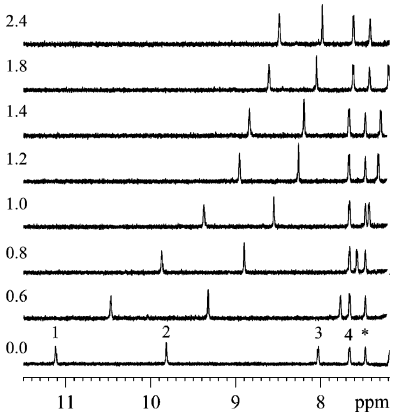


Figure 4. Expanded region of the ^{1}H NMR spectra of (*phimid*)-$AlMe_2Br$ at different $AlMe_3$/(*phimid*)$AlMe_2Br$ molar ratios. Proton resonances are labeled as in Scheme 2. The asterisk indicates the satellite peak of the deuterated solvent (C_6D_6, 298 K).

The free and hydrogen-bonded ion pairs exchange rapidly: as the $AlMe_3$/(*phimid*)$AlMe_2Br$ ratio increases, the concentration of the hydrogen-bonded complex decreases, so the population of the more shielded proton increases and the signal moves upfield. Through inspection of a plot of the chemical shifts of the resonances for **2** versus $AlMe_3$/**2** molar ratio (Figure 5) it is reliable to assume that the hydrogen-bond donor sites are the NC(*H*)N proton of the imidazolium moiety, the hydrogen atom of the imine group and H^3 of the aryl group (Scheme 2). The shifts of the other resonances are best attributed to changes in electronic distribution in the ligand.[12]

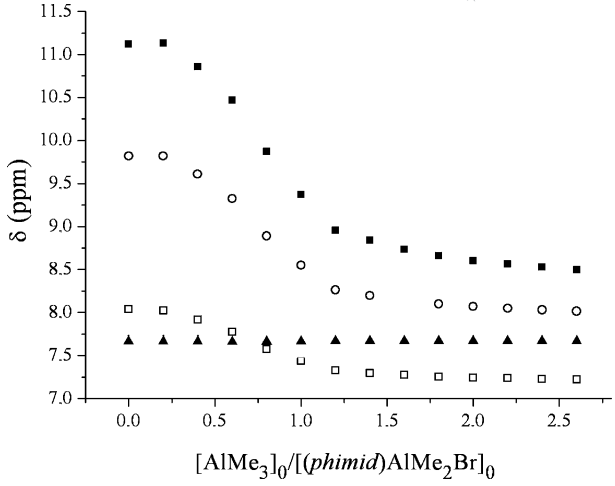
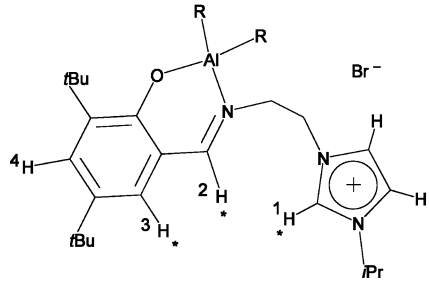


Figure 5. Plot of chemical shifts of H^1 (■), H^2 (○), H^3 (□) and H^4 (▲) (Scheme 2) for (*phimid*)$AlMe_2Br$ (**2**) versus [$AlMe_3$]$_0$/[(*phimid*)-$AlMe_2Br$]$_0$ (C_6D_6, 298 K).



Scheme 2.

The constant for equilibrium (1) (K_{eq}) was determined by standard ^{1}H NMR titrations in which the concentration of **2** was kept constant while the concentration of $AlMe_3$ was varied. A plot of the measured change in chemical shift of the NC(*H*)N proton with reference to that of **2** ($\Delta\delta$) versus [$AlMe_3$]$_0$/[**2**]$_0$ from a series of solutions containing constant [**2**]$_0$ is given in Figure 6. The titration data were analysed by nonlinear regression analysis with use of the WinEQNMR program[13] and afforded a value for K_{eq} of $3.2 \pm 0.1 \times 10^3$ M^{-1}. On repetition of the titration of **2** with the weaker Lewis acid Al*i*Bu_3, a lower value for the association constant was obtained ($K_{eq} = 1.2 \pm 0.1 \times 10^3$ M^{-1}).

It is worth noting that similar behaviour had already been observed for alkylhalogenoaluminate(III) ionic liquids. In mixtures of 1,3-dialkylimidazolium chloride with aluminium chloride the chemical shifts of the protons on the cations are highly dependent on the proportions of aluminium chloride and organic chloride salt; in particular, the NC(*H*)N proton is very sensitive, moving significantly upfield with increasing aluminium halide mole fraction.[14]

To probe the possibility of formation of bonding between hydrogen-bond donor sites in **1** and potential electron pair donors in solution, *n*Bu_4NBr was added to a [D_6]benzene solution of **1** (halide anions act as strong hydrogen bond acceptors).[8]

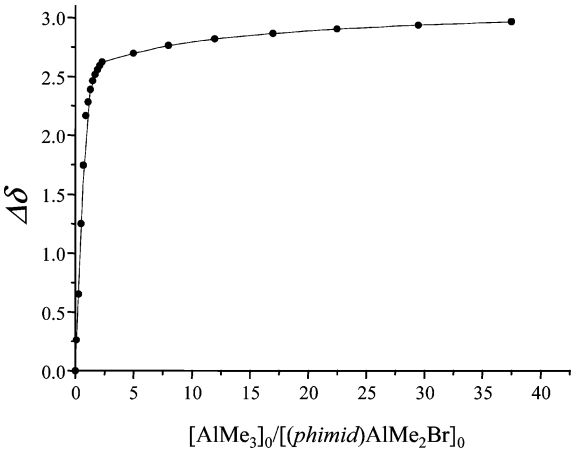


Figure 6. Plot of the measured change in chemical shift of the NC(H)N proton of (*phimid*)$AlMe_2Br$ (**2**) with reference to that of the uncomplexed **2** ($\Delta\delta$) versus $[AlMe_3]_0/[(phimid)AlMe_2Br]_0$ from a series of solutions containing constant $[\mathbf{2}]_0$. ($[\mathbf{2}]_0$ = 2.5 mM, $[AlMe_3]_0$ = 0–70 mM, C_6D_6, 298 K).

This only caused a small downfield shift of the imine *H*C=N resonance,[15] indicating the involvement of this group in labile hydrogen bonding.

Reactivity Studies: Reactions between Al Complexes 1 and 2 and $B(C_6F_5)_3$

There has been growing interest in the synthesis of cationic aluminium complexes, because the enhanced Lewis acidity of the aluminium centre should result in higher catalytic activity and may lead to new applications.[16] $B(C_6F_5)_3$ has been used successfully to generate reactive alkylaluminium cations $LnAlR^+$ from $LnAlR_2$ precursors. Treatment of dialkylaluminium complexes bearing bidentate *N*,*N*- or *N*,*O*-ligands with $B(C_6F_5)_3$ leads to unstable tricoordinate alkylaluminium cations, which react quite rapidly by abstracting a C_6F_5 group from the $MeB(C_6F_5)_3^-$ anion to form neutral $LnAlR(C_6F_5)$ products.[17] Several studies have shown that the presence of a Lewis base (L^1) can stabilise the aluminium cation through the formation of $\{LX\}Al(R)(L^1)^+$ adducts.[18] Gibson et al. showed that a pendant donor group that in the neutral aluminium complexes is weakly bonding or nonbonding becomes a normal donor group in the cationic derivatives upon treatment with $B(C_6F_5)_3$, thus stabilising these species.[19]

The addition of 1 equiv. of $B(C_6F_5)_3$ to a [D_6]benzene solution of **1** resulted in the selective and quantitative formation of (*phim*)$Al(C_6F_5)Me$ (**4**). The ^1H NMR spectrum exhibited a triplet at δ = 0.05 ppm (J_{HF} = 1.4 Hz) characteristic of an Al-Me resonance coupled to the α-fluorines of a coordinated C_6F_5 group.[17] The resonances of the *phim* fragment were generally shifted downfield with respect to the relative resonances of the precursor **1**. Two quintets in the same ^1H NMR spectrum at 1.33 and 0.96 ppm indicated the presence of $MeB(C_6F_5)_2$ and $Me_2B(C_6F_5)$ in a 4:1 molar ratio. When treatment of **1** with $B(C_6F_5)_3$ was monitored at room temperature by ^1H NMR spectroscopy, 35 mol-% conversion of the reagents was observed after 10 min, with quantitative conversion being reached in a few hours. The ^{19}F NMR spectrum revealed inter alia the presence of $MeB(C_6F_5)_3^-$, suggesting that the species **4** is formed through the transfer of a C_6F_5 group from $MeB(C_6F_5)_3^-$ by the initially formed coordinatively unsaturated cationic intermediate.

Treatment of **2** with one equiv. of $B(C_6F_5)_3$ afforded the cationic monomethyl species (*phimid*)$AlMeBr^+MeB(C_6F_5)_3^-$ (**5**). ^1H NMR monitoring of the reaction in the NMR tube showed this to be fast and quantitative in a few minutes. The ^{19}F NMR spectrum revealed only the presence of the $MeB(C_6F_5)_3^-$ anion and was unchanged over 24 h at room temperature. Complex **5** is very soluble in halogenated and aromatic solvents, but on standing it slowly decomposes to unknown species, hampering its crystallisation.

The molecular structure of **5** in solution was determined by NMR spectroscopy. In the ^1H NMR spectrum of **5** the methyl group bound at the aluminium centre appeared as a sharp singlet at –0.14 ppm and, except for protons 5 and 6 (see Scheme 2), the resonances for the *phimid* fragment were shifted to higher field with respect to the neutral complex, with the largest shifts being those for the imine *H*C=N ($\Delta\delta$ = 3.64 ppm) and the imidazolium NC(*H*)N resonances ($\Delta\delta$=2.69 ppm). The shifts of these protons were similar to those observed for **2** in the presence of $AlMe_3$ in large excess, indicating that the bromide anion is no longer involved in the hydrogen bonding with the imidazolium moiety. The inertness of **5** toward the transfer of a C_6F_5 group from $MeB(C_6F_5)_3^-$ suggests that the electrophilic aluminium centre is stabilised by coordination of the bromide anion, acting as a Lewis base.

The methyl group of $MeB(C_6F_5)_3^-$ in the ^1H NMR spectrum of **5** appeared at δ = 1.16 ppm, indicating that the anion is not substantially coordinated to the aluminium centre. This was further confirmed by the small chemical shift difference ($\Delta\delta$ = 2.8 ppm) between the *m*- and *p*-fluorine ^{19}F NMR resonances.[20]

Conclusions

New alkylaluminium complexes **2** and **3** bearing a modified phenoxyimine ligand with a pendant imidazolium moiety (*phimid*-H·Br) are reported. The coordination behaviour of these compounds was investigated and compared with that of an analogous novel alkylaluminium complex (**1**) incorporating a salycilaldimine ligand lacking the pendant imidazolium portion (*phim*-H). The structural features of both these types of complexes were considered with regard to the hydrogen bond interactions.

The ability of **1** to engage in intermolecular hydrogen bonding was detected by ^1H NMR solution experiments conducted in the presence of a source of halide anions such as nBu_4NBr: in this case, **1** is able to enter into a labile hydrogen bond with bromide anion through the imine proton.

More significantly, treatment of **2** and **3** with a Lewis acid such as $AlMe_3$ in solution, monitored by ^1H NMR spectroscopy, gave evidence of strong involvement of the NC(*H*)N proton of the imidazolium moiety, the hydrogen atom of the imine group and H^3 of the aryl group in hydrogen bonding interactions with bromide anion. The presence of an imidazolium tail thus strengthens the hydrogen donor sites on the skeleton of the salicylaldimine ligand. The manifestation of these hydrogen interactions implies that the imidazolium pendant moiety of the coordinated ligand is forced to assume a bent conformation to allow the hydrogen bond donor sites to surround the bromide anion.

Reactivity studies of Al complexes **1** and **2** with $B(C_6F_5)_3$, with the goal of generating monoalkyl cationic species as potential active catalysts from the corresponding neutral dialkyl precursors, revealed different behaviour. Because of the instability of the initially formed tricoordinate alkylaluminium cation, complex **1** afforded the neutral (*phim*)Al(C_6F_5)Me product through the abstraction of a C_6F_5 group from the $MeB(C_6F_5)_3^-$ counterion.

In contrast, the presence of the imidazolium bromide moiety as a pendant arm in **2** allowed the formation of a cationic monomethyl species (*phimid*)$AlMeBr^+MeB(C_6F_5)_3^-$ in which the bromine was no longer involved in the hydrogen bonding with the imidazolium moiety.

The influence of the noncovalent interactions observed in the second coordination spheres of **2** and **3** on their catalytic abilities in ring-opening polymerisation of cyclic esters is currently under investigation.

Experimental Section

General: All experiments were performed under nitrogen by standard Schlenk-type techniques or in a glove-box (type MBRAUN). Toluene and hexane were distilled from sodium/benzophenone. C_6D_6 and C_7D_8 were degassed under N_2 flow and stored over activated molecular sieves (4 Å) in a glove-box prior to use. NMR spectra were recorded on Bruker AM 300 and Bruker AVANCE 400 instruments operating at 300 MHz and 400 MHz for ^1H, respectively. The ^1H and ^{13}C chemical shifts are referenced to $SiMe_4$ with use of the residual protio impurities of the deuterated solvents as external references. ^{11}B and ^{19}F chemical shifts are reported versus $BF_3(OEt_2)$ and $CFCl_3$, respectively. Elemental analyses were performed with a Perkin–Elmer 240-C instrument. $AlMe_3$ and Al(*i*Bu)$_3$ (Aldrich) were checked for purity by ^1H NMR and used as received. $B(C_6F_5)_3$ was purchased from Boulder Scientific and used as received. 3,5-*t*Bu$_2$-2-(OH)C_6H_2CH=N*i*Pr (*phim*-H) and [3,5-*t*Bu$_2$-2-(OH)C_6H_2CH=NCH$_2$CH$_2$(CH{NCHCHN*i*Pr})]Br (*phimid*-H·Br) were synthesised by modified literature procedures.[6,7] All other chemicals were obtained commercially and used as received unless stated otherwise.

Synthesis of (*phim*)$AlMe_2$ (1): A solution of $AlMe_3$ (1.09 mmol) in hexane (5.0 mL, 0.218 M) was added at room temperature to a solution of (*phim*-H) (0.300 g 1.09 mmol) in hexane (20 mL, 0.0545 M). Evolution of methane was observed. The resulting yellow solution was stirred for one hour. The solution was filtered and cooled to –30 °C, affording a crystalline, yellow solid (0.22 g, 61%). Single crystals suitable for X-ray analysis were grown from a saturated hexane solution at –30 °C. Spectroscopic data for (*phim*)$AlMe_2$ (**1**): ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.68 (d, 1 H, Ph–*H*), 7.38 (s, 1 H, C*H*=N), 6.79 (d, 1 H, Ph–*H*), 2.99 [m, 1 H, C*H*(CH$_3$)$_2$], 1.60 [s, 9 H, C(C*H*$_3$)$_3$], 1.33 [s, 9 H, C(C*H*$_3$)$_3$], 0.95 [d, 6 H, CH(C*H*$_3$)$_2$], –0.22 [s, 6 H, Al(C*H*$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR spectroscopic data (100 MHz, C_6D_6, 25 °C): –7.2, 23.5, 29.9, 31.9, 34.5, 35.9, 60.2, 119.3, 129.3, 131.9, 139.1, 141.2, 162.4, 170.3 ppm. $C_{20}H_{34}AlNO$ (331.53): calcd. C 72.46, H 10.36, N 4.23; found C 72.95, H 10.94, N 4.83.

Synthesis of (*phimid*)$AlMe_2Br$ (2): A solution of $AlMe_3$ (0.71 mmol) in toluene (5.0 mL, 0.142 M) was added at room temperature to a suspension of *phimid*-H·Br (0.320 g, 0.71 mmol) in toluene (40 mL). Evolution of methane was observed. The resulting pale yellow solution was stirred for one hour. The solution was concentrated and cooled to –30 °C, affording a yellow solid (0.190 g, 59%). Spectroscopic data for (*phimid*)$AlMe_2Br$: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 11.12 (s, 1 H, NC*H*N), 9.82 (s, 1 H, C*H*=N), 8.04 (d, 1 H, Ph–*H*), 7.66 (d, 1 H, Ph–*H*), 6.26 (s, 1 H, NC*H*), 5.57 (s, 1 H, NC*H*), 4.66 (m, 2 H, NC*H*$_2$), 4.38 [m, 1 H, C*H*(CH$_3$)$_2$], 4.32 (m, 2 H, NC*H*$_2$), 1.58 [s, 9 H, C(C*H*$_3$)$_3$], 1.37 [s, 9 H, C(C*H*$_3$)$_3$], 1.08 [d, 6 H, CH(C*H*$_3$)$_2$], –0.35 [s, 6 H, Al(C*H*$_3$)$_2$] ppm. Selected $^{13}C\{^1H\}$ NMR spectroscopic data (100 MHz, C_6D_6, 25 °C): δ = –8.4, 22.6, 29.9, 31.8, 49.5, 53.7, 55.8, 119.4, 123.0, 130.7, 133.7, 135.2, 176.2 ppm. $C_{25}H_{41}AlBrN_3O$ (506.58): calcd. C 59.27, H 8.17, N 8.30; found C 59.83, H 8.74, N 8.12.

Synthesis of (*phimid*)$AlMe_2Br$ (2; NMR Tube Reaction): In a glove-box, $AlMe_3$ (1.3 μL, 0.013 mmol) dissolved in C_6D_6 (0.3 mL) was added to a suspension of *phim*-H·Br (6 mg, 0.013 mmol) in C_6D_6 (0.3 mL) at room temperature. The resulting pale yellow solution was transferred to a NMR tube (10 mm o.d.) and analysed.

^1H NMR Titration: The ^1H NMR titration was performed by addition of increasing amounts of $AlMe_3$ to a [D_6]benzene solution of **2** (2.50 mM, 0.6 mL). During titration the concentration of $AlMe_3$ was varied over the 0.25–56.0 mM range. The appearance of a singlet at δ = 0.01 ppm was attributed to the $BrAlMe_3^-$ anion. The chemical shift of the imidazolium proton at δ = 11.12 ppm was followed and plotted against the concentration of $AlMe_3$ added. The titration data were analysed by nonlinear regression analysis with use of the WinEQNMR program.[13]

Synthesis of (*phimid*)Al*i*Bu_2Br (3): A solution of Al*i*Bu_3 (1.00 mmol) in toluene (5.0 mL, 0.20 M) was added at room temperature to a suspension of *phimid*-H·Br (0.450 g, 1.00 mmol) in toluene (40 mL). Evolution of isobutene was observed. The resulting pale yellow solution was stirred for one hour. The solution was concentrated and cooled to –30 °C, affording a yellow solid (0.28 g, 47%). Spectroscopic data for (*phimid*)Al*i*Bu_2Br: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 11.05 (s, 1 H, NC*H*N), 9.81 (s, 1 H, C*H*=N), 8.04 (d, 1 H, Ph–*H*), 7.68 (s, 1 H, Ph–*H*), 6.42 (s, 1 H, NC*H*), 5.68 (s, 1 H, NC*H*), 4.81 (m, 2 H, NC*H*$_2$), 4.41 [m, 1 H, C*H*(CH$_3$)$_2$], 4.36 (m, 2 H, NC*H*$_2$), 2.19 [m, 2 H, AlCH$_2$C*H*(CH$_3$)$_2$], 1.61 [s, 9 H, C(C*H*$_3$)$_3$], 1.35 [s, 9 H, C(C*H*$_3$)$_3$], 1.26 [d, 6 H, CH(C*H*$_3$)$_2$], 1.14 [d, 3 H, AlCH$_2$CH(C*H*$_3$)$_2$], 0.86 [m, 3 H, AlCH$_2$CH(C*H*$_3$)$_2$], 0.30 [m, 4 H, AlC*H*$_2$CH(CH$_3$)$_2$] ppm. $C_{31}H_{53}AlBrN_3O$ (590.76): calcd. C 63.02, H 9.06, N 7.11; found C 63.54, H 9.72, N 7.47.

Generation of (*phim*)Al(C_6F_5)Me (4): In a glove-box, equimolar amounts of (*phim*)$AlMe_2$ (**1**, 7 mg, 0.021 mmol) and $B(C_6F_5)_3$ (11 mg, 0.021 mmol) were placed in a sample vial and dissolved in C_6D_6 (0.7 mL). The resulting pale yellow solution was transferred to a NMR tube (10 mm o.d.) and analysed at 25 °C. Spectroscopic data for (*phim*)Al(C_6F_5)Me: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.72 (d, 1 H, Ph–*H*), 7.47 (s, 1 H, C*H*=N), 6.85 (d, 1 H, Ph–*H*),

3.02 [m, 1 H, C*H*$(CH_3)_2$], 1.53 [s, 9 H, C(CH_3)$_3$], 1.29 [s, 9 H, C(CH_3)$_3$], 0.82 [dd, 6 H, CH(CH_3)$_2$], 0.05 [s, 3 H, Al(CH_3)] ppm. ^{19}F NMR (376 MHz, C_6D_6, 25 °C): δ = –122.3 (q, 2 F, *o*-C_6F_5), –154.3 (t, 1 F, *p*-C_6F_5), –161.6 (m, 2 F, *o*-C_6F_5) ppm. Spectroscopic data for [MeB(C_6F_5)$_2$]: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.33 (t, 3 H, B–CH_3) ppm. ^{19}F NMR (376 MHz, C_6D_6, 25 °C): δ = –130.2 (m, 4 F, *o*-C_6F_5), –147.3 (m, 2 F, *p*-C_6F_5), –162.2 (m, 4 F, *m*-C_6F_5) ppm. ^{11}B NMR (–25.19 MHz, C_6D_6, 25 °C): δ = 71.5 [s, 1B, Me*B*(C_6F_5)$_2$] ppm. Spectroscopic data for [Me_2B(C_6F_5)] δ = 0.96 (t, 3 H, B-CH_3) ppm. ^{19}F NMR (376 MHz, C_6D_6, 25 °C): δ = –131.3 (d, 2 F, *o*-C_6F_5), –151.7 (m, 1 F, *p*-C_6F_5), –162.8 (m, 2 F, *m*-C_6F_5) ppm. ^{11}B NMR (–25.19 MHz, C_6D_6, 25 °C): δ = 80.4 [s, 1B, Me_2*B*(C_6F_5)] ppm.

Generation of (*phimid*)AlMeBr$^+$MeB(C_6F_5)$_3^-$ (5): In a glove-box, equimolar amounts of (*phimid*)AlMe_2Br (**2**, 11 mg, 0.021 mmol) and B(C_6F_5)$_3$ (11 mg, 0.021 mmol) were placed in a sample vial and dissolved in C_6D_6 (0.7 mL). The resulting yellow solution was transferred to a NMR tube (10 mm o.d.) and analysed at 25 °C. Spectroscopic data for (*phimid*)AlMeBr$^+$: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.70 (d, 1 H, Ph–*H*), 7.48 (s, 1 H, NC*H*N), 7.13 (s, 1 H, C*H*=N), 6.79 (d, 1 H, Ph–*H*), 6.46 (s, 1 H, NC*H*), 6.06 (s, 1 H, NC*H*), 4.04 [m, 1 H, C*H*$(CH_3)_2$], 3.36 (m, 2 H, NCH_2), 2.98 (m, 2 H, NCH_2), 1.47 [s, 9 H, C(CH_3)$_3$], 1.21 [s, 9 H, C(CH_3)$_3$], 0.51 [dd, 6 H, CH(CH_3)$_2$], –0.14 [s, 3 H, Al(CH_3)$_2$] ppm. Spectroscopic data for [MeB(C_6F_5)$_3$]$^-$: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.16 (BCH_3) ppm. ^{19}F NMR (376 MHz, C_6D_6, 25 °C): δ = –132.5. (d, 2 F, *o*-C_6F_5), –163.9 (t, 2 F, *m*-C_6F_5), –166.8 (t, 1 F, *p*-C_6F_5) ppm. ^{11}B NMR (–25.19 MHz, C_6D_6, 25 °C): δ = –14.7 [s, 1B, Me*B*(C_6F_5)$_3^-$] ppm.

Crystal Structure Determinations: Data collection was performed at low temperature (–100 °C) for (*phim*)AlMe_2 (**1**) and at 20 °C for (*phimid*-H·Br) on a Bruker–Nonius kappa CCD diffractometer (graphite monochromated Mo-K_α radiation, phi scans + omega scans to fill the asymmetric unit). Cell parameters were obtained from a least-squares fit of the θ angles of 188 reflections in the range $3.460° \le \theta \le 21.129°$ for complex **1** and of 98 reflections in the range $3.919° \le \theta \le 18.044°$ for (*phimid*-H·Br). A semiempirical absorption correction (multiscan, SADABS[21]) was applied in both cases. Both structures were solved by direct methods and anisotropically refined by the full-matrix, least-squares method on F^2 against all independent measured reflections (SIR97[22] and SHELX-97[23] programs). H atoms were placed in calculated positions or located by difference Fourier map and riding on carrier atoms. Max. residual electronic density was 0.306 (–0.348) e Å^{-3} for complex **1** and 0.340 (–0.659) e Å^{-3} for (*phimid*-H·Br). Some crystal and collection data are reported in Table 3.

Table 3. Crystal, collection and refinement data.

	(*phim*)AlMe_2	*phimid*-H·Br
Chemical formula	$C_{20}H_{34}NOAl$	($C_{23}H_{36}N_3O$) Br·1/2 H_2O
Formula weight	331.46	459.47
T [K]	173	293
Crystal system	orthorhombic	triclinic
Space group	*Pbcn*	$P\bar{1}$
a [Å]	25.018(4)	10.347(1)
b [Å]	14.638(4)	11.830(2)
c [Å]	11.902(4)	21.585(4)
α [°]	90	101.85(1)
β [°]	90	91.36(2)
γ [°]	90	106.81(2)
V [Å^3]	4359(2)	2465.5(7)
Z, d_{calc} [g cm^{-3}]	8, 1.010	4, 1.238
μ [mm^{-1}]	0.098	1.687
Theta range	3.26°–27.50°	2.27°–27.50°
Data/parameters	4966/218	10350/526
R_1 [$I > 2\sigma(I)$]	0.0548	0.0591
wR_2 (all data)	0.1308	0.1479

CCDC-689736 (for **1**) and -689737 (for *phimid*-H·Br) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): NMR spectra and 2D NMR experiments for **1**–**5**.

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