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# Towards Weakly Coordinating Anions with the Extremely Electron Withdrawing Perfluoropyridinoxy Ligand –OC<sub>5</sub>F<sub>4</sub>N

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Abstract: The extreme electron withdrawing properties of the perfluoropyridinoxy ligand -OC5F4N were used for the preparation of new (weakly) coordinating borate and aluminate anions of the type  $[E(OC_5F_4N)_4]^-$  (E = B or AI). These new anions are based on the potent parent Lewis acids E(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>, which possess exceptionally high calculated fluoride ion affinities (FIAs) of 500 and 587 kJ mol for E = B and AI respectively. For aluminium, this extreme Lewis acidity dominates the chemistry and from mixtures of the neutral polymeric Lewis acid [Al(OC₅F₄N)<sub>3</sub>]<sub>n</sub>, the 5- and 6-coordinate complexes  $Al(OC_5F_4N)_3(OEt_2)_2$  (1) and  $[Al(OC_5F_4N)_2(\mu-OC_5F_4N)]_3$ (NCMe)<sub>2</sub>]<sub>2</sub> (2) were crystallized upon addition of ether or MeCN. The aluminate salts M[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] (M = Li or K) were prepared from the reaction between the alcohol 4-HO-C5F4N and either LiAlH4 or K[AlEt<sub>4</sub>] respectively. The aluminate anion [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup> remains Lewis acidic coordinating small donor molecules forming  $[Al(OC_5F_4N)_4(L)]^-$  (L = THF or NMe<sub>3</sub>) and even supports formation and structural characterisation of the aluminium dianion containing salt [Na(OEt<sub>2</sub>)<sub>2</sub>][Na][Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>5</sub>] (8). The from NaBH<sub>4</sub> and 4-HO-C5F4N accessible borate salt Na[B(OC5F4N)4] shows increased kinetic stability in comparison to the aluminium analogue.

## Introduction

Modern weakly coordinating anions (WCAs)<sup>[1,2,3]</sup> are reagents that not only support the formation, isolation and structural characterisation of reactive cations,[4] but are important components in room temperature ionic liquids,<sup>[5]</sup> electrolytes<sup>[6]</sup> and catalysis.<sup>[7]</sup> The aluminate anions [AI(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> and  $[Al(OR^{HF})_4]^-$  (where  $R^F = C(CF_3)_3$  and  $R^{HF} = C(H)(CF_3)_2$ ), as well as the related bridged analogue [(R<sup>F</sup>O)<sub>3</sub>Al-F-Al(OR<sup>F</sup>)<sub>3</sub>]<sup>-,[8]</sup> are some of the most versatile WCAs present in the literature. This is due to their simple preparation and transformation into common reagents used to introduce WCAs to a given system.<sup>[8,9,10]</sup> They also represent some the most weakly coordinating WCAs currently reported. The measured ionicities of the [Al(OR<sup>HF</sup>)<sub>4</sub>]<sup>-</sup> WCA in a series of ionic liquids has been shown to reach 100 % and this high ionicity has recently been exploited in a lithium-sulfur battery.<sup>[11]</sup> The exceptionally weak coordination of the  $[AI(OR^{F})_{4}]^{-}$  WCA is further demonstrated by the formation and structural characterization of the weakly bound complexes  $[Ag(C_2H_2)_4]^+$  [12] or  $[Ag(P_4)_2]^+$  [13] In these, complexes, the weakly bound acetylene and white phosphorus ligands are in constant competition with the counterion and

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solvent molecules for a place in the coordination sphere of the metal. It is only through the very weak coordinative strength of the  $[AI(OR^F)_4]^-$  WCA, and the use of weakly coordinating solvents that these weakly bound complexes can be prepared and characterized.

The  $[Al(OR^F)_4]^-$  WCA also shows excellent stability towards Brønsted acids, it is stable up to the level of protonated mesitylene,<sup>[14]</sup> and towards the electrophilic cations  $[CX_3]^+$  (X = Cl, Br or I)<sup>[15]</sup> and the bulky silylium ion  $[Si(C_6Me_5)_3]^+$ .<sup>[16]</sup> However, in the presence of smaller extreme electrophiles, such as *in-situ* generated "[PCl<sub>2</sub>]<sup>+</sup>" (from Ag[Al(OR<sup>F</sup>)\_4] and PCl<sub>3</sub>),<sup>[17]</sup> or smaller alkyl silylium ions  $[R_3Si]^+$ , decomposition of the anion occurs. Decomposition takes place by one of two initial pathways: (i) attack of the electrophile at the oxygen and abstraction of an intact  $-OR^F$  ligand forming the Lewis acid  $Al(OR^F)_3$  or (ii) abstraction of a peripheral fluorine atom resulting in formation of the epoxide C<sub>4</sub>F<sub>8</sub>O and the Lewis acid  $Al(OR^F)_3$  (Scheme 1).<sup>[2,3]</sup> Pathways (i) and (ii) both result in the formation of an undesired charge neutral system and the active pathway is dependent upon the relative oxo- and fluorophilicities of the given cation.

Pathway (i) - Oxophilic Cations

$$[E]^{\textcircled{e}} + [(R^{F}O)_{3}AI-OC(CF_{3})_{3}]^{\textcircled{e}} \longrightarrow E-OC(CF_{3})_{3} + AI(OR^{F})_{3}$$
Pathway (ii) - Fluorophilic Cations
$$[E]^{\textcircled{e}} + [(R^{F}O)_{3}AI-OC(CF_{3})_{3}]^{\textcircled{e}} \longrightarrow E-F + (R^{F}O)_{3}AI-OC_{4}F_{8}$$

**Scheme 1.** Initial decomposition pathways of the  $[Al(OR^F)_4]^-$  WCA in the presence of oxophilic and fluorophilic cations (E = cation;  $R^F = C(CF_3)_3$ ).

In order to improve the stability of the [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> WCA towards small extreme electrophiles, its susceptibility to decomposition pathways (i) and (ii) must be reduced. Susceptibility towards fluoride abstraction (pathway (ii)) can be significantly reduced by replacing perfluoroalkyl ligands for perfluoroaryl ligands. This has the added benefit of removing -CF3 groups, which can make obtaining high-resolution crystal structures difficult. Decomposition via abstraction of an -OR<sup>F</sup> ligand (pathway (i)) can be reduced by either increasing the steric shielding of the oxygen atoms (kinetic stability) or by increasing the Lewis acidity of the parent Lewis acid of the WCA (in this case Al( $OR^+$ )<sub>3</sub>) increasing its thermodynamic stability. The incorporation of four  $-OR^{F}$  ligands to form  $[Al(OR^{F})_{4}]^{-}$  is already approaching the upper limit of steric bulk for the formation of an homoleptic aluminate WCA.<sup>[18]</sup> Therefore, we turned our attention to the question of increasing thermodynamic stability and the formation

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of a novel WCA based on a stronger parent Lewis acid than  $Al(\text{OR}^{\text{F}})_{\scriptscriptstyle 3}.$ 

The pentafluorophenyl group has been extensively used as an electron withdrawing group for the preparation of Lewis acids (e.g.  $E(C_6F_5)_3^{[19,20]}$  and  $E(OC_6F_5)_3^{[21,22]} E = B$  or AI) and WCAs (e.g  $[B(C_6F_5)_4]^{-[19]}$  and  $[Al(OC_6F_5)_4]^{-[23]}$ ). In contrast, there are very few examples, in which a perfluoropyridine group has been used in the formation of a Lewis acid or WCA, despite DFT calculations predicting it to have even stronger electron withdrawing properties than a pentafluorophenyl group. Tyrra and co-workers reported the propionitrile coordinated gallium indium Lewis acids Ga(C<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>(NCEt) and and In(C<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>(NCEt)<sub>2</sub> formed from a redox transmetallation of AgC<sub>5</sub>F<sub>4</sub>N with metallic gallium and indium respectively.<sup>[24]</sup> Recently a study of the properties of Lewis acidic perfluoroorganotin compounds featuring a combination of -C<sub>2</sub>F<sub>5</sub> and -C<sub>5</sub>F<sub>4</sub>N ligands has been reported.<sup>[25]</sup> In addition pentafluoropyridine itself has been used as a weakly coordinating solvent and ligand for the stabilisation of reactive transition metal cations.<sup>[26]</sup> The weak coordinative strength of the pyridine-N within a (weakly) coordinating anion may also be used to slightly stabilise highly electrophilic cations.

We now report a large scale preparation for the alcohol 2,3,5,6-tetrafluoro-4-hydroxypyridine 4-HO-C<sub>5</sub>F<sub>4</sub>N, a synthetically useful reagent to introduce a perfluoropyridine group, and our efforts to prepare new aluminate and borate anions with increased thermodynamic stability towards extreme electrophiles. The extreme electron withdrawing properties of the interesting and underused perfluoropyridinoxy ligand  $-OC_5F_4N$  were used to generate anions of the type  $[E(OC_5F_4N)_4]^-$  that are based upon the extreme parent Lewis acids  $E(OC_5F_4N)_3$  (E =B or Al).

#### **Results and Discussion**

The extreme electron withdrawing properties of the perfluoropyridinoxy ligand -OC5F5N are clearly demonstrated by the high calculated fluoride ion affinities (FIAs) of the Lewis acids  $B(OC_5F_4N)_3$  (500 kJ mol<sup>-1</sup>) and  $AI(OC_5F_4N)_3$  (587 kJ mol<sup>-1</sup>; BP86/def-SV(P) with D3(BJ) dispersion).[27] Notably, both of these values are higher than the FIA of SbF<sub>5</sub> of 489 kJ mol<sup>-1</sup>, which represents the threshold for classification as a Lewis superacid. For comparison, the FIAs of some related strong Lewis acids are shown in Figure 1. The very high calculated FIAs for the B(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub> and Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub> Lewis acids mean that a WCA based upon these Lewis acids, on a thermodynamic basis, will be less susceptible to decomposition through abstraction of an intact ligand residue (decomposition pathway (i) above). Furthermore, the weak coordinative strength of the pyridine-N, on account of the perfluorination of the aromatic ring, may also stabilize smaller electrophilic cations by hemi-labile coordination, rather than coordination representing the first step in the decomposition of the WCA.



Figure 1. Comparison of FIAs of boron and aluminium based Lewis acids.

#### Preparation of the Lewis Acid [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>]<sub>n</sub>

The alcohol 2,3,5,6-tetrafluoro-4-hydroxypyridine 4-HO-C<sub>5</sub>F<sub>4</sub>N can be prepared in an efficient and scalable procedure from commercially available C<sub>5</sub>F<sub>5</sub>N and KOH in up to 50 g quantities with contamination from the 2-substituted product observed in only *ca.* 2 % (see experimental section). It is crucial that the 4-HO-C<sub>5</sub>F<sub>4</sub>N product is rigorously dried in dichloromethane solution over activated 4Å molecular sieves to remove hydrogen-bonded water. The ready preparation of 4-HO-C<sub>5</sub>F<sub>4</sub>N provides a simple and efficient entry point into this chemistry.

The dropwise addition of 3.1 equivalents of a solution of 4-HO-C<sub>5</sub>F<sub>4</sub>N in 1,2-difluorobenzene (DFB) to a solution of Et<sub>3</sub>AI in the same solvent results in immediate gas evolution and gradual formation of a colourless precipitate. This precipitate is probably an aggregated, or polymeric, form of the Lewis acid of the general formula  $[Al(OC_5F_4N)_3]_n$ , which is insoluble in weakly coordinating solvents such as fluorobenzene or dichloromethane but highly soluble in acetonitrile. Careful addition of either diethyl ether or acetonitrile to a DFB suspension of [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>]<sub>n</sub> results in dissolution and subsequent crystallization results in the coordinate aluminium isolation of the five complex  $AI(OC_5F_4N)_3(OEt_2)_2$ (1) and dimeric six coordinate  $[Al(OC_5F_4N)_2(\mu-OC_5F_4N)(NCMe)_2]_2$  (2) respectively (Scheme 2).



**Scheme 2.** Preparation of polymeric  $[Al(OC_5F_4N)_3]_n$  and donor solvent coordinated complexes  $(Py^F = 4-C_5F_4N)$ .



Figure 2. Molecular structures of  $Al(OC_5F_4N)_3(OEt_2)_2$  (1) (top) and  $[Al(OC_5F_4N)_2(\mu-OC_5F_4N)(NCMe)_2]_2$  (2) (bottom). Hydrogen atoms omitted for clarity and thermal ellipsoids were drawn at the 50 % probability level.

1 has a slightly distorted trigonal bipyramidal geometry presumably to accommodate the aryl rings, which do not adopt a propeller like geometry. The Al-O bond distances of the equatorially coordinated -OC<sub>5</sub>F<sub>4</sub>N ligands (1.736(8)-1.774(9) Å) show a wider range than those in the related  $AI(OR^{F})_{3}(OEt_{2})$ adduct (1.719(9)-1.731(8) Å). Although the Al-O bond distances for the axially coordinated diethyl ether molecules (1.972(4) and 1.980(4) Å) are longer than in Al(OR<sup>F</sup>)<sub>3</sub>(OEt<sub>2</sub>) (cf. 1.856(9) Å),<sup>[22]</sup> the coordination of two diethyl ether molecules is a clear demonstration of the increased Lewis acidity and availability of the aluminium centre. The asymmetric unit of centrosymmetric 2 is comprised of one aluminium centre coordinated by two terminal and one bridging -OC5F4N ligand in the equatorial plane and two axially coordinated acetonitrile ligands. A similar bridging coordination mode was reported for the -OC<sub>6</sub>F<sub>5</sub> ligand in the solid state structure of dimeric tetrahedral and unsolvated [Al(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub>.<sup>[22]</sup> A clear discrepancy between terminal and bridging AI-O bond distances in 2 is apparent (cf. terminal 1.792(2)/1.797(1) Å; bridging 1.918(1) Å) and all Al-O<sub>pyridoxy</sub> bond distances in 2 are longer than those in  $[Al(OC_6F_5)_3]_2$  (terminal 1.669(1)/1.686(1); bridging 1.842(1) Å) and in five coordinate monomeric 1. This presumably reflects the increased coordination number and consequent reduction in Lewis acidity present at the aluminium centre. The Al-N bond distances of 2 (2.028(2) and 2.024(2) Å) are slightly longer than that reported in  $AI(OR^{F})_{3}(NCCCI_{3})$  (cf. 1.951(3) Å)<sup>[28]</sup> but the formation of a six coordinate aluminium centre is again consistent with a high Lewis acidity being present at aluminium. In order to accommodate the bridging -OC5F4N ligands, the acetonitrile ligands show a distinct deviation form linear coordination as demonstrated by the Al-N-C angles of 167.51(11) and 168.15(11)° respectively.

The five coordinate aluminium complex Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>-(OEt<sub>2</sub>)<sub>2</sub> (**1**) retains its structure in solution and the <sup>27</sup>Al NMR spectrum shows a resonance at  $\delta_{Al}$  = 25 ppm consistent with a five coordinate aluminium centre. In contrast, the <sup>19</sup>F and <sup>27</sup>Al NMR spectra of crystalline **2** in CD<sub>3</sub>CN show multiple resonances indicating that the solid state structure is not retained in solution and a series of ligand exchange reactions can take place in solution.

Despite its insolubility in weakly coordinating solvents such as dichloromethane and DFB,  $[Al(OC_5F_4N)_3]_n$  does function as a Lewis acid and reaction with Ph<sub>3</sub>CCl in dichloromethane results in the formation of the  $[Ph_3C]^+$  cation, which is readily identified in the <sup>1</sup>H NMR spectrum. In the <sup>27</sup>Al NMR spectrum a number of resonances for anions of the type  $[Al(OC_5F_4N)_{4-n}(Cl)_n]^-$  are observed due to the facile exchange of ligands at the aluminium centre (see Figures S5-7 ESI).

#### Preparation of M[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] and [Me<sub>3</sub>NH][Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]

The simple, highly efficient, and scalable preparation of Li[Al(OR<sup>F</sup>)<sub>4</sub>] from LiAlH<sub>4</sub> and the corresponding alcohol HOR<sup>F</sup> contributes significantly to its appeal as a WCA and this simple approach formed the starting point for the synthesis of the [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup> anion. Reactions between LiAlH<sub>4</sub> and 4-HO-C<sub>5</sub>F<sub>4</sub>N in weakly coordinating solvents such as toluene or DFB do not proceed even at reflux. However, upon changing the solvent to diethyl ether the reaction proceeds at room temperature with rapid gas evolution (Scheme 3). Cooling of the filtered and concentrated reaction mixture to -28 °C resulted in the formation of colourless crystals of Li[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] (**3**) as the diethyl ether solvate (**3**·OEt<sub>2</sub>) suitable for single crystal X-ray



**Scheme 3.** Preparation of  $M[Al(OC_5F_4N)_4]$  salts (M = Li or K).

diffraction. The solid state structure of 3. OEt<sub>2</sub> (Figure 3) is polymeric with each lithium cation tetrahedrally coordinated by the nitrogen atom of four different [Al(OC<sub>5</sub>F<sub>4</sub>N]<sub>4</sub>]<sup>-</sup> anions. 3.OEt<sub>2</sub> crystallizes with one lithium cation, half of the [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup> anion and half of the OEt<sub>2</sub> solvate molecule in the asymmetric unit. The AI-O bond distances of 1.732(1) and 1.743(2) Å are towards the upper end of those reported in the [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> anion (1.714(3)-1.736(3) Å), but within the range of previously reported aluminates (1.725-1.746 Å).[10] However, they are shorter than those in the dimeric 2, presumably resulting from the reduced steric crowding at the aluminium centre. The Al-O-C bond angles measured in 3. OEt2 (137.57(11) and 146.07(11)°) are more acute than those in  $[Al(OR^{F})_{4}]^{-}$  (148.1(3)-151.7(3)°), reflecting the reduced steric demands of the -OC<sub>5</sub>F<sub>4</sub>N ligand in comparison to  $-OC(CF_3)_3$  but are within the range of those in previously reported aluminates (126.5-158.3°).[10] Interestingly,

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the diethyl ether solvate molecule is not coordinated to the lithium cation, but is incorporated within a pore created by the



Figure 3. Section of the polymeric solid state structure of Li[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]·OEt<sub>2</sub> (3·OEt<sub>2</sub>). Hydrogen atoms omitted for clarity and thermal ellipsoids were drawn at the 50% probability level.

polymeric network and is present as one molecule of diethyl ether per formula unit of Li[Al( $OC_5F_4N$ )<sub>4</sub>].

Multinuclear NMR spectroscopy of 3 · OEt<sub>2</sub> in CD<sub>3</sub>CN shows two relatively broad resonances in the <sup>19</sup>F NMR spectrum at  $\delta_{\rm F}$  = -96.2 and -164.7 ppm, for the ortho and meta fluorine atoms respectively, and a major resonance in the <sup>27</sup>AI NMR spectrum at  $\delta_{AI}$  = 44 ppm, consistent with a four coordinate aluminium centre. This major aluminium resonance is accompanied by two smaller resonances at  $\delta_{AI}$  = 48 and 24 ppm that we attribute to a ligand exchange equilibrium aided by the donor properties of the acetonitrile solvent. Interestingly, when the same salt is characterized in diethyl ether the <sup>27</sup>AI NMR spectrum shows only a single resonance at  $\delta_{AI}$  = 45 ppm, consistent with a four coordinate aluminium centre, indicating the solvent dependence of the ligand exchange process. 3. OEt2 is insoluble in weakly coordinating solvents probably due to the polymeric structure of 3.OEt<sub>2</sub> in the solid state, which must be broken in order to obtain a solution. All efforts to remove the diethyl ether solvent molecule of 3.OEt<sub>2</sub> through the prolonged heating of a finely ground powder under vacuum (also oil diffusion and turbomolecular pumps at 10<sup>-6</sup> mbar) were unsuccessful and appreciable amounts of the diethyl ether solvate remained. In order to obtain an alkali metal salt free from donor solvents and suitable for the preparation of a range of reagents commonly used for the introduction of WCAs (e.g.  $[Ph_3C]^+$ , Ag<sup>+</sup> and [H(OEt<sub>2</sub>)<sub>2</sub>]<sup>+</sup>) alternative syntheses that didn't require the use of donor solvents were investigated.

Changing the source of aluminium from the relatively insoluble LiAlH<sub>4</sub> to the tetraalkylaluminate K[AlEt<sub>4</sub>]<sup>[29]</sup> enabled the preparation of K[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] in the weakly coordinating solvent DFB. To ensure complete alcoholysis of all aluminium-ethyl groups the reaction mixture was refluxed for 2 days. The K[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] forms as a colourless precipitate that can be characterized spectroscopically in CD<sub>3</sub>CN. A similar ligand exchange equilibrium to that observed for **3**·OEt<sub>2</sub> in CD<sub>3</sub>CN is also observed for K[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] (see ESI).

As an alternative to the direct preparation of the insoluble alkali metal salts  $M[Al(OC_5F_4N)_4]$  (M = Li or K), the preparation of a trialkylammonium salt of the type  $[Me_3NH][Al(OC_5F_4N)_4]$  was identified as a potentially soluble precursor. This would permit simple access to a range of synthetically useful reagents for the introduction of the  $[Al(OC_5F_4N)_4]^-$  anion. This approach is used in the preparation of reagents for the introduction of carborate<sup>[30]</sup> and dodecaborate<sup>[31]</sup> WCAs and so its applicability for the  $[Al(OC_5F_4N)_4]^-$  anion was also tested.

The  $[Me_3NH][Al(OC_5F_4N)_4]$  salt (4) is readily prepared from the reaction between  $Me_3N \cdot AIH_3$  and 4 equivalents of 4-HO-C<sub>5</sub>F<sub>4</sub>N in DFB, which proceeds with evolution of three equivalents of H<sub>2</sub> and the final proton being transferred to the amine. 4 has good solubility in weakly coordinating solvents such as DFB and dichloromethane and is readily purified by cooling a concentrated dichloromethane solution to -28 °C resulting in crystallization. Characterization by single crystal X-ray diffraction (see ESI Figure S32) shows the expected four coordinate aluminium centre and a hydrogen bond between the N-H bond of the ammonium cation and a nitrogen atom of the [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup> anion. Spectroscopic characterization in CD<sub>2</sub>Cl<sub>2</sub> gives a <sup>27</sup>AI NMR resonance at  $\delta_{AI}$  = 45 ppm consistent with a four coordinate aluminium centre and sharp <sup>19</sup>F NMR resonances at  $\delta_{\rm F}$  = -95.5 and -163.8 ppm. The resonance of the acidic ammonium proton is readily identified in the <sup>1</sup>H NMR spectrum at  $\delta_{\rm H}$  = 9.35 ppm.

#### Manifestations of very high Lewis acidity

The electron withdrawing properties of the -OC5F4N ligand gives rise to an anion that remains Lewis acidic and this impacts significantly on the chemistry of the  $[Al(OC_5F_4N)_4]^-$  anion. Thus, in order to test the suitability of the trialkylammonium salt 4 to function as a precursor for the preparation of further reagents commonly used to introduce WCAs, 4 was reacted with NaH in an attempt to form the corresponding Na[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] salt. The reaction proceeds through deprotonation of the ammonium cation to liberate  $H_2$  and  $Me_3N$ . The  $[Al(OC_5F_4N)_4]^-$  anion, however, remains Lewis acidic and coordinates the liberated [Na(OEt<sub>2</sub>)<sub>n</sub>]-Me₃N resulting in the formation of [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>(NMe<sub>3</sub>)]. The presence of a five coordinate aluminium species is readily identified by analysis of the crude reaction product by <sup>27</sup>AI NMR spectroscopy in CD<sub>3</sub>CN, which shows only a resonance at  $\delta_{AI}$  = 17 ppm. Further confirmation was obtained from the crystallization of [Na(OEt2)2]- $[Al(OC_5F_4N)_4(NMe_3)]$ ·OEt<sub>2</sub> (5·OEt<sub>2</sub>) from a reaction between 4 and NaH in diethyl ether and the molecular structure of 5.OEt2 is shown in Figure 4 (top).

5 ·OEt<sub>2</sub> crystallizes as a dimer, in which sodium cations are coordinated by two -OC5F4N ligands from two different the [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>(NMe<sub>3</sub>)]<sup>-</sup> anions. The tetrahedral coordination sphere at sodium is then completed by coordination of two diethyl ether solvent molecules. Solvent coordination results in the formation of discrete dimeric units, unlike the polymeric structure of Li[Al(OC5F4N)4] 3.OEt2. A further molecule of uncoordinated diethyl ether is also incorporated in the cavity generated by the dimeric units similar to that of the polymeric Li[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] 3·OEt<sub>2</sub>. The aluminium centre is five coordinate and the NMe<sub>3</sub> ligand occupies an axial position trans to a -OC5F4N ligand that binds to sodium. Interestingly, the AI-O bond distances for the equatorial ligands are identical within error (1.773(2), 1.776(2) and 1.778(2) Å) and are slightly elongated in comparison to those in  $3 \cdot OEt_2$ (cf.

1.732(2)/1.743(2) Å). The AI-O bond distance of the axially located  $-OC_5F_4N$  ligand shows even greater elongation (1.853(2) Å). The AI-N bond distance of 2.078(2) Å is longer than those reported for the four coordinate neutral complexes  $Me_{3-n}CI_nAI\cdot NMe_3$  (n = 0-3; 1.949(4)-2.045(1) Å)<sup>[32]</sup> and that of the neutral five coordinate species  $H_3AI\cdot 2NMe_3$  (2.0163(2) Å)<sup>[33]</sup> indicating that the NMe<sub>3</sub> molecule is relatively weakly bound.

Recrystallization of Li[Al(OC5F4N)4] from THF resulted in the crystallographic characterization of [Li(THF)<sub>4</sub>][Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>-(THF)]·THF (6·THF). 6·THF crystallizes with two discrete cation and anion pairs in the asymmetric unit and both anions feature a five coordinate aluminium centre in which a THF solvent molecule is bound to aluminium. The Al-O bond distances (equatorial 1.757(3)-1.785(3) Å; axial 1.818(3) and 1.833(3) Å) are marginally shorter than those of the NMe<sub>3</sub> coordinated analogue 5 OEt<sub>2</sub>. The AI-O bond distances for the coordinated THF solvent molecules are even greater (1.980(3) and 1.975(3) Å). Recently the teflate based aluminate WCA  $[Al(OTeF_5)_4]^-$  has been reported and its protonated form H[Al(OTeF<sub>5</sub>)<sub>4</sub>] shown to be a potent Brønsted acid.<sup>[34]</sup> The parent Lewis acid Al(OTeF<sub>5</sub>)<sub>3</sub> has a calculated FIA<sup>[35]</sup> of 590 kJ mol<sup>-1</sup> (cf. 587 kJ mol<sup>-1</sup> for monomeric  $Al(OC_5F_4N)_3$ ) and the  $[Al(OTeF_5)_4]^-$  WCA also remains Lewis acidic. Recrystallization of M[AI(OTeF<sub>5</sub>)<sub>4</sub>] (M = Li or Ag) from THF results in the structural characterization of  $[M(THF)_n][AI(OTeF_5)_4(THF)_2]$  (M = Li, n =4; M = Ag, n = 6), in which the aluminium centre coordinates two THF solvent molecules and is six coordinate.<sup>[36]</sup> The Al-O bond distances for the coordinated THF molecules in [Al(OTeF<sub>5</sub>)<sub>4</sub>(THF)<sub>2</sub>]<sup>-</sup> are shorter than those observed in the five coordinate 6. THF and range from 1.929(6)- 1.955(3) Å (cf. 1.980(3) and 1.975(3) Å for 6.THF).



**Figure 4.** Solid state structures of  $[Na(OEt_2)_2][Al(OC_5F_4N)_4(NMe_3)]\cdotOEt_2$ (**5**·OEt<sub>2</sub>) (top) and  $[Li(THF)_4][Al(OC_5F_4N)_4(THF)]\cdotTHF$  (**6**·THF). Hydrogen atoms and the THF solvate molecule of **6**·THF are omitted for clarity and thermal ellipsoids were drawn at the 50% probability level.

With similar calculated FIAs for Al(OTeF<sub>5</sub>)<sub>3</sub> and monomeric Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub> the coordination of two THF molecules in [Al(OTeF<sub>5</sub>)<sub>4</sub>(THF)<sub>2</sub>]<sup>-</sup> is presumably largely steric in origin and reflects the reduced primary shielding afforded by the long Te-O bond.

The combination of Lewis acidity and an accessible aluminium centre present in the  $[Al(OC_5F_4N)_4]^-$  anion also facilitates ligand exchange reactions and even supports the formation and crystallographic characterization of a dianion.

A salt metathesis reaction between 4 equivalents of Na[OC<sub>5</sub>F<sub>4</sub>N] and AICI3 in diethyl ether results in the formation of  $[Na(OEt_2)_n][Al(OC_5F_4N)_4]$  in solution. Investigation of the crude diethyl ether reaction mixture by <sup>27</sup>AI NMR spectroscopy shows a single resonance at  $\delta_{AI}$  = 41 ppm consistent with a four coordinate aluminium species with the formulation [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup>. Filtration followed by concentration and storage at ambient temperature afforded a crop of colourless crystals consisting of two different crystal types. Determination of the molecular structures of these different types of crystals by single crystal X-ray diffraction characterized one as the simple salt Na[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] OEt<sub>2</sub> (7 OEt<sub>2</sub>) (see ESI Figure S35), which has a polymeric structure similar to that of the lithium salt 3 OEt<sub>2</sub>, and the disodium salt of the related aluminium dianion [Na][Na(OEt<sub>2</sub>)<sub>2</sub>][Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>5</sub>] (8) (Scheme 4, Figure 5).

 $[Na(OEt_2)_n][Al(OC_5F_4N)_4] \qquad \longrightarrow \qquad OEt_2$  $([Na(OEt_2)_2][Na])^{2+} + Py^FO - Al^{(n)}OPy^F$  $[Al(OC_5F_4N)_5]^{2-} + OPy^FO - Al^{(n)}OPy^F$ 

**Scheme 4.** Ligand exchange reaction observed upon crystallisation of a diethyl ether solution of  $[Na(OE_{t_2})_n][Al(OC_5F_4N)_4]$  (Py<sup>F</sup> = 4-C<sub>5</sub>F<sub>4</sub>N).

The solid-state structure of **8** is polymeric and shows a five coordinate aluminium centre and two different sodium cation environments. The first features a distorted octahedral geometry, in which the sodium cation is coordinated by two diethyl ether molecules, the oxygen and *ortho*-fluorine atoms, in a chelate-type interaction, of one axial and one equatorial



**Figure 5.** Solid state structure of the disodium dianion  $[Na][Na(OEt_2)_2][Al(OC_5F_4N)_5]$  (8). Hydrogen atoms omitted for clarity and thermal ellipsoids were drawn at the 50% probability level.

 $-OC_5F_4N$  ligand of the same aluminium dianion. In contrast, the second sodium cation is *hepta*-coordinated with contacts to three different dianions. The first coordinates through the oxygen atom of an equatorial  $-OC_5F_4N$  ligand, the fluorine atom of another equatorial  $-OC_5F_4N$  ligand and a chelate-type interaction of the oxygen and *ortho*-fluorine atoms of an axial

 $-OC_5F_4N$  ligand. The second dianion coordinates through a chelate interaction of the oxygen and *ortho*-fluorine atoms and the third dianion coordinates simply through a nitrogen atom. The Al-O bond distances (equatorial 1.793(2)-1.826(2) Å; axial 1.870(2) and 1.873(3) Å) are slightly elongated from those of the monoanionic five coordinate **6** THF reflecting the increased negative charge present in the dianionic **8**.

Formation of the dianion **8** is presumably thermodynamically driven by the reduced solubility of **8** and its subsequent crystallization from the reaction mixture and is most likely accompanied by the formation of the previously characterized Lewis acid  $Al(OC_5F_4N)_3(OEt_2)_2$  **1**, which presumably remains in solution (Scheme 4).

#### Preparation of Na[B(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]

Although the Lewis acid  $B(OC_5F_4N)_3$  has a lower FIA than its aluminium analogue (500 vs 587 kJ mol<sup>-1</sup>) the  $[B(OC_5F_4N)_4]^-$  anion is an interesting synthetic target. The smaller size and limited coordination number of boron can be expected to provide a slight increase in kinetic stability of the borate anion in comparison to the aluminate analogue. Na[B(OC\_5F\_4N)\_4] (9) can be prepared from the reaction between NaBH<sub>4</sub> and 4 equivalents of 4-HO-C\_5F\_4N in refluxing toluene (Scheme 5).



**Scheme 5.** Preparation of  $Na[B(OC_5F_4N)_4]$  (9).

**9** can be characterized by multinuclear NMR spectroscopy in CD<sub>3</sub>CN and a sharp singlet resonance is observed in the <sup>11</sup>B{<sup>1</sup>H} and <sup>11</sup>B NMR spectra at 1.0 ppm and multiplets in the <sup>19</sup>F NMR spectrum at –96.0 and –159.6 ppm. Recrystallization from THF results in the isolation of [Na(THF)<sub>2</sub>][B(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]·THF (**10**·THF), which has been characterized by single crystal X-ray diffraction (Figure 6).



Figure 6. Solid state structure of  $[Na(THF)_2][B(OC_5F_4N)_4]$  (10·THF). Hydrogen atoms omitted for clarity and thermal ellipsoids were drawn at the 50% probability level.

The solid-state structure of **10**·THF is monomeric with a four coordinate tetrahedral boron centre. The sodium cation is bound to the anion in a manner that resembles that of the related  $[Na(THF)_2][B(OCH(CF_3)_2)_4]$ .<sup>[37]</sup> It has four Na-O interactions, two from the  $-OC_5F_4N$  ligands and two from the THF solvent molecules, and four Na-F interactions from the *ortho*-fluorine atoms of each  $-OC_5F_4N$  ligand bound to boron. The B-O distances of **10**·THF (1.451(2) and 1.485(2) Å) are similar to those reported in  $[Na(THF)_2][B(OCH(CF_3)_2)_4]$  (1.450(2)-1.487(2) Å)<sup>[37]</sup> but notably shorter than those in the related aluminate complexes above, consistent with the smaller size of boron than aluminium.

#### Comparison of [B(OC₅F₄N)₄]<sup>-</sup> and [Al(OC₅F₄N)₄]<sup>-</sup> Anions

In order to directly compare the structural parameters of the borate anion with that of the previously prepared aluminate, the  $[Me_3NH][B(OC_5F_4N)_4]$  salt (11) was prepared via a salt metathesis reaction between  $[Me_3NH]CI$  and  $Na[B(OC_5F_4N)_4]$  and characterized by single crystal X-ray diffraction. The structures of 11 and the aluminate 4 (see ESI) are essentially isostructural and so only that of 11 is displayed in Figure 7.

A tetrahedral boron (or aluminium) centre is present and as expected from the smaller size of boron the B-O bonds (1.456(2)-1.485(2) Å) of **11** are shorter than the AI-O bonds of the related aluminate (1.734(2)-1.752(2) Å) **4**. The O-C bonds in 4 (1.310(2)-1.322(2) Å), however, are shorter than those observed in the borate **11** (1.329(2)-1.337(2) Å). The E-O-C angles (E = B or AI) are notably more acute in the borate (118.30(8)-126.63(8)°) than the aluminate (134.50(14)-138.88(8)°) despite the B-O bonds being shorter than the corresponding AI-O bonds. This is consistent with a greater ionic contribution to bonding being present in the aluminate **4**.<sup>[10]</sup> Both the borate and aluminate salts also possess a hydrogen bonding interaction between the hydrogen atom of the [Me<sub>3</sub>NH]<sup>+</sup> cation and a nitrogen atom of one of the  $-OC_5F_4N$  ligands of the anion.



Figure 7. Solid state structure of  $[Me_3MH][B(OC_5F_4N)_4]$  (11). Hydrogen atoms (except N-H) are omitted for clarity and thermal ellipsoids were drawn at the 50% probability level.

#### Conclusions

The perfluoropyridinoxy ligand  $-OC_5F_4N$  has been shown to possess extreme electron withdrawing capabilities comparable to those of the  $-OTeF_5$  ligand. The aluminate anion  $[Al(OC_5F_4N)_4]$  remains Lewis acidic and coordinates THF and NMe<sub>3</sub> as testament to the extreme electron withdrawing capabilities of  $-OC_5F_4N$ . Whilst in principle an anion that remains Lewis acidic should possess increased thermodynamic

stability towards highly electrophilic cations, in the aluminate anion [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup> a combination of Lewis acidity and insufficient kinetic stability gives rise to facile ligand exchange reactions. This was demonstrated by the structural characterization of an aluminium dianion and hinders the use of the  $[Al(OC_5F_4N)_4]^-$  anion in more traditional WCA applications. This study shows that preparation of a robust new WCA requires a combination of appropriate kinetic as well as thermodynamic stability. Additionally, although the nitrogen atom of the -OC5F4N ligand is only a weak donor it coordinates to alkali metals (small cations). This results in the formation of a number of polymeric salts that are insoluble in weakly coordinating solvents typically used for the introduction of WCAs e.g. dichloromethane or DFB. In contrast the borate anion [B(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sup>-</sup> appears to show improved kinetic stability and is easily prepared in the absence of donor solvents. Its application as an anion to support the formation of reactive cations is something that is currently under investigation.

## **Experimental Section**

**General Considerations:** All reactions and manipulations were carried out under an inert argon atmosphere using standard Schlenk-line and glovebox techniques (box atmosphere kept below 1 ppm H<sub>2</sub>O/O<sub>2</sub>). Glassware has been stored in an oven at 180 °C overnight and flame dried under vacuum prior to use. Diethyl ether, MeCN, CH<sub>2</sub>Cl<sub>2</sub>, toluene and pentane were collected from a solvent purification system (SPS) and degassed by purging with argon gas before use. 1,2-difluorobenzene (DFB) and CD<sub>3</sub>CN were dried over CaH<sub>2</sub> and distilled. All solvents were stored over activated 4Å molecular sieves under argon. K[AIEt<sub>4</sub>]<sup>[29]</sup> and Me<sub>3</sub>N·AIH<sub>3</sub><sup>[38]</sup> were prepared according to literature procedures. In our experience and at our department, the high fluorine content of these complexes precludes combustion analysis due to the incomplete combustion.

**NMR Spectroscopy:** NMR samples were prepared under an inert argon atmosphere in flame dried NMR tubes fitted with a J Young's reseatable valve. <sup>1</sup>H, <sup>19</sup>F and <sup>27</sup>Al NMR spectra were acquired either on a Bruker Biospin Avance II+ 400 MHz WB a Bruker Avance 200 MHz or a Bruker Avance III HD 300 MHz spectrometer. <sup>1</sup>H NMR spectra are reported relative to SiMe<sub>4</sub> and samples in OEt<sub>2</sub> were referenced to the CH<sub>3</sub> resonance at  $\delta$  = 1.12 ppm. Data analysis was performed using Bruker TOPSPIN 3.5 software. All relevant spectra can be found in the ESI.

**Single crystal X-ray diffraction:** Single crystal X-ray diffraction data were collected using a Bruker SMART APEX2 Quazar CCD area detector diffractometer. Crystals were selected under perfluoropolyether oil, mounted on 0.1 to 0.3 mm diameter CryoLoops and quench-cooled using an Oxford Cryosystems open flow N<sub>2</sub> cooling device. Data were collected at 100 K using monochromated Cu K<sub>a</sub> radiation Mo K<sub>a</sub> radiation ( $\lambda = 0.71073$  Å). The structures were solved with SHELXT<sup>[39]</sup> and refined with SHELXL<sup>[39]</sup> and SHELXLe.<sup>[40]</sup> Disordering of fragments was done with the help of the implemented DSR tool.<sup>[41]</sup> All structures have been deposited in the CCDC and details can be found in the ESI for CCDC 1868393-1868402. Graphical representations have been prepared using Mercury.

**Computational Details:** All calculations were performed using the TURBOMOLE 7.1 program package using the BP86 functional with the def-SV(P) basis set using D3(BJ) dispersion corrections.<sup>[42]</sup> Vibrational frequencies were calculated using the AOFORCE module and checked for imaginary vibrational frequencies.<sup>[43]</sup> FIA calculations were performed using Me<sub>3</sub>Si-F as an anchor point as described in the literature.<sup>[27]</sup>

**Preparation of 4-HO-C**<sub>5</sub>**F**<sub>4</sub>**N**: A mixture of C<sub>5</sub>**F**<sub>5</sub>**N** (100.0 g, 0.59 mol) and KOH (86.0 g, 1.53 mol) in H<sub>2</sub>O (320 mL) was heated to 70 °C for 66 h. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL) and the aqueous phase acidified with dilute aqueous HCl and extracted with diethyl ether (3 x 90 mL). The organic phases were combined and the solvent removed in-vacuo to yield a pale orange solid. This solid was then sublimed at 90 °C under vacuum (*ca.* 1 x 10<sup>-2</sup> mbar) to yield 4-HO-C<sub>5</sub>F<sub>4</sub>N as a colourless solid. 4-HO-C5<sub>5</sub>F<sub>4</sub>N must be dried in CH<sub>2</sub>Cl<sub>2</sub> solution over activated 4Å molecular sieves before further use. Yield 78.8 g, 79 %. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 298 K): δ 6.98 (br s, 1H, OH). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>, 298 K): δ -90.5 (m, o-ArC-*F*), -163.1 (m, *m*-ArC-*F*).

**Preparation of [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>3</sub>]**<sub>n</sub>: A solution of 4-HO-C<sub>5</sub>F<sub>4</sub>N (2.000 g, 12.0 mmol) in DFB (7 mL) was added dropwise to a stirred solution of Et<sub>3</sub>Al (0.441 mg, 3.9 mmol) in DFB (5 mL) and gas evolution was observed. During the addition, a colourless precipitate formed and the reaction mixture was stirred for 15 h. The solid was then isolated by filtration, washed with DFB (3 x 5 mL) and dried under vacuum. Crude yield 1.723 g, 85 %. Careful addition of OEt<sub>2</sub> or MeCN to a suspension of [Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]<sub>n</sub> in DFB results in dissolution and **1** or **2** respectively being obtained upon crystallisation. Spectroscopic data for **1**. <sup>19</sup>F NMR (377 MHz, OEt<sub>2</sub>, 298 K):  $\delta$  –93.5 (m, o-ArC-F), –164.1 (m, m-ArC-F). <sup>27</sup>Al NMR (104 MHz, OEt<sub>2</sub>, 298 K)  $\delta$  25 (br s). **2** does not retain the solid state structure in solution.

**Preparation of Li[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]·OEt<sub>2</sub>:** To a stirred -30 °C solution of LiAlH<sub>4</sub> (0.113 g, 3.0 mmol) in diethyl ether (20 mL) a solution of 4-HO-C<sub>5</sub>F<sub>4</sub>N (2.000 g, 12.0 mmol) was added dropwise and immediate effervescence observed. The reaction mixture was stirred at -30 °C for 1 h and then warmed to room temperature and stirred for a further 4 h. After filtration the reaction mixture was concentrated and storage at -30 °C resulted in the formation of colourless crystals which were isolated and dried under vacuum. Yield 1.625 g, 70 %. <sup>19</sup>F NMR (282 MHz, OEt<sub>2</sub>, 298 K): δ -95.9 (s, *o*-ArC-*F*), -164.7 (s, *m*-ArC-*F*). <sup>27</sup>Al NMR (78 MHz, OEt<sub>2</sub>, 298 K): δ 45. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 298 K): δ 3.42 (q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 1.12 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN, 298 K): δ -96.2 (s, *o*-ArC-*F*), -164.7 (s, *m*-ArC-*F*). <sup>27</sup>Al NMR (78 MHz, CD<sub>3</sub>CN, 298 K): δ 44 (major resonance), 47, 24 (minor resonances). Only a single resonance is observed when characterised in diethyl ether (see above).

**Preparation of K[AI(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]:** A solution of 4-HO-C<sub>5</sub>F<sub>4</sub>N (0.378 g, 2.2 mmol) in DFB (15 mL) was added dropwise to a solution of K[AIEt<sub>4</sub>] (0.100 g, 0.5 mmol) in DFB (7 mL) and immediate gas evolution was observed. Once the rate of gas evolution had reduced the reaction mixture was refluxed for 2 days and a colourless precipitate formed. After cooling to room temperature the precipitate was isolated by filtration and washed with DFB (3 x 7 mL) and dried under vacuum. Yield 0.325 g, 81 %.<sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN, 298 K): δ -96.1 (s, *o*-ArC-*F*), -164.7 (s, *m*-ArC-*F*). <sup>27</sup>Al NMR (78 MHz, CD<sub>3</sub>CN, 298 K): δ 44 (major resonance), 48, 24 (minor resonances). K[AI(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>] is not soluble in diethyl ether so was characterised in MeCN.

**Preparation of [Me<sub>3</sub>NH][Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]:** To a stirred –30 °C solution of Me<sub>3</sub>NAIH<sub>3</sub> (0.183 g, 2.1 mmol) in DFB (10 mL) a solution of 4-HO-C<sub>5</sub>F<sub>4</sub>N (1.304 g, 7.8 mmol) in DFB (20 mL) was added dropwise and gas evolution was observed. After stirring for 14 h, whilst slowly attaining room temperature, the reaction mixture was filtered and the solvent removed in-vacuo. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL) and the resulting mixture concentrated. Storage at –28 °C afforded colourless crystals of [Me<sub>3</sub>NH][Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]. Yield 1.075 g, 74 %. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 9.35 (br s, 1H, NH), 3.07 (s, 9H, N(CH<sub>3</sub>)<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ –95.5 (s, o-ArC-F), –163.8 (m, m-ArC-F). <sup>27</sup>Al NMR (78 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 45.

**Preparation of Na[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>(NMe<sub>3</sub>)]·(0.6·OEt<sub>2</sub>):** A suspension of  $[Me_3NH][Al(OC_5F_4N)_4]$  ( 1.040 g, 1.4 mmol) in diethyl ether (25 mL) was transferred onto a rapidly stirred suspension of NaH (0.034 g, 1.4 mmol)

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in diethyl ether (10 mL) and stirred at room temperature for 14 h. The resulting suspension was stored at -28 °C and in addition to a powder colourless crystals of Na(OEt<sub>2</sub>)[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>(NMe<sub>3</sub>)] also formed. The solid was isolated and dried under vacuum to yield Na[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>(NMe<sub>3</sub>)]·(0.6OEt<sub>2</sub>). Yield 0.720 g, 68 %, (ca. 80 % purity). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  3.41 (q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 2.60 (s, 9H, N(CH<sub>3</sub>)<sub>3</sub>), 1.12 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  –99.8 (br s, o-ArC-F), –165.4 (br s, m-ArC-F). <sup>27</sup>Al NMR (78 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  17.

**Preparation of NaOC**<sub>5</sub>F<sub>4</sub>N: To a stirred suspension of NaH (0.273 g, 11.4 mmol) in diethyl ether (10 mL) was slowly added a solution of HO-C<sub>5</sub>F<sub>4</sub>N (2.000 g, 11.9 mmol) in diethyl ether (15 mL) and gas evolution observed. The reaction mixture was stirred for 14 h and the solid isolated by filtration and washed with diethyl ether (2 x 10 mL). The solid obtained was then dried under vacuum at 80 °C. Yield 1.900 g, 88 %. <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN, 298 K): δ –102.7 (s, o-ArC-F), –173.9 (m, m-ArC-F).

**Preparation of a Na<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>5</sub>] and Na[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]OEt<sub>2</sub> Mixture: To a stirred -78 °C slurry of NaOC<sub>5</sub>F<sub>4</sub>N (0.946 g, 5 mmol) in diethyl ether (20 mL), was added a solution of AlCl<sub>3</sub> (0.162 g, 1.2 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 14 h, whilst slowly attaining room temperature. After filtration, the solvent was removed in-vacuo and the residue extracted into diethyl ether (3 x 10 mL) and concentrated. Storage at room temperature afforded a mixture of colourless crystals of Na<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>5</sub>] and Na[Al(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]·OEt<sub>2</sub>. Yield 0.201 g. Crude NMR before crystallisation. <sup>19</sup>F NMR (376 MHz, OEt<sub>2</sub>, 298 K): δ –95.9 (br s, o-ArC-F), –164.7 (m, m-ArC-F). <sup>27</sup>Al NMR (104 MHz, OEt<sub>2</sub>, 298 K): δ 41.** 

**Preparation of Na[B(OC**<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]: A round bottomed flask fitted with a reflux condenser was charged with NaBH<sub>4</sub> (0.107 g, 2.9 mmol) and 4-HO-C<sub>5</sub>F<sub>4</sub>N (2.000 g, 12.0 mmol). Toluene (50 mL) was added and the resulting suspension refluxed for 5 days. After cooling to room temperature the solid isolated by filtration and washed with toluene (3 x 10 mL) and dried under vacuum. Yield 1.200 g, 60 %. Recrystallization from THF resulted in the formation of [Na(THF)<sub>2</sub>][B(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]·THF. <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  –96.0 (s, o-ArC-F), –159.6 (m, m-ArC-F). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  1.0.

**Preparation of [Me<sub>3</sub>NH][B(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]:** To a suspension of NaBH<sub>4</sub> (0.115 g, 3.0 mmol) in THF (7 mL), a solution of 4-HO-C<sub>5</sub>F<sub>4</sub>N (2.09 g, 12.5 mmol) in THF (10 mL) was added dropwise and gas evolution observed. Once gas evolution had ceased toluene (20 mL) was added and the reaction mixture refluxed for 3 days. After cooling to room temperature the crude reaction mixture was transferred onto [Me<sub>3</sub>NH]Cl (0.290 g, 3.0 mmol) and stirred for 14 h. The reaction mixture was filtered and the solvent removed in-vacuo to yield a white solid, which was extracted into diethyl ether (2 x 10 mL). Concentration of this solution and storage at room temperature resulted in the formation of colourless crystals of [Me<sub>3</sub>NH][B(OC<sub>5</sub>F<sub>4</sub>N)<sub>4</sub>]. Yield 1.220 g, 55 %. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 298 K): δ 6.92 (br s, 1H, NH), 2.80 (s, 9H, N(CH<sub>3</sub>)<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN, 298 K): δ -96.0 (s, o-ArC-F), -159.6 (m, m-ArC-F). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CD<sub>3</sub>CN, 298 K): δ 1.0.

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