

Article

# Aluminates with Fluorinated Schiff Bases: Influence of the Alkali Metal–Fluorine Interactions in Structure Stabilization

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**Abstract:** New heterometallic aluminium-alkali metal compounds have been prepared using Schiff bases with electron withdrawing substituents as ligands. The synthesis of these new species was achieved via the reaction of  $\text{AlMe}_3$  with the freshly prepared alkali-metallated ligand. The derivatives formed were characterized by NMR in solution and by single crystal X-ray diffraction in the solid state. Aluminate derivatives with lithium and sodium were prepared and a clear influence of the alkali metal in the final outcome is observed. The presence of a  $\text{Na}\cdots\text{F}$  interaction in the solid state has a stabilization effect and the species  $[\text{NaAlMe}_3\text{L}]_2$  can be isolated for the first time, which was not possible when using Schiff bases without electron withdrawing substituents as ligands.

**Keywords:** aluminium; alkali metals; Schiff bases; heterometallic compounds

## 1. Introduction

Heterometallic compounds containing main group metals have generated great interest particularly in recent years [1–5]. Within those, *-ate* species are a remarkable class of compounds formed by two metals of very different natures, an electropositive alkali metal and a less electropositive one, very often a p-block metal [6–11]. These species not only show unusual structures, they also display a wide-ranging reactivity which, on many occasions, is diverse from the one shown by the homometallic analogous [12–15]. As such, these compounds have become very popular reagents for reactions such as the activation of unreactive C–H bonds [16–18], direct orthometalation processes [19–21] or the formation of C–C and C–heteroatom bonds [22–25]. They are also active catalysts for the polymerization of polar alkenes [26–29]. More recently, their activity in catalytic processes such as the hydroboration process [30] or Meerwein-Ponndorf-Verley (MPV) reactions [31] has also been described.

The type of ligands used for these *-ate* derivatives is relatively small, especially considering the significant potential that these compounds can display. In most cases, the reported species contains N-donor connectors [32–35], being less common O-donor linkers. Ligands with O- and N- donor groups are also scarce in these compounds. In our group, we described aluminate derivatives with functionalized phenolates as bridging ligands bearing donor substituents in *ortho* positions [36–38], and more recently, with terpene oximate ligands with O- and N- donor atoms [39].

Schiff bases or the phenoxo-imino ligands are a particularly popular type of O- and N-donor ligand. Many compounds containing them have been described that have shown a remarkable catalytic activity, particularly in polymerization processes [40–43]. There are quite a few examples of aluminium

species with Schiff bases; however, no heterometallic derivatives had been reported, only recently we have published the first examples of aluminates with phenoxo-imino ligands, expanding the library of connecting ligands for *-ate* compounds [44].

The interest in phenoxo-imino ligands lies in the fact that they are very versatile and straightforward to prepare. By modifying the substituents, the electronic and steric properties of the compounds can be easily tuned [45–48]. In our previous study, we explored ligands bearing donor substituents in the iminic ring. In this work, we have extended the investigations to ligands with electron withdrawing substituents to analyse their effect on the final compounds. Interestingly, the introduction of fluorine atoms and the study of their influence on the nature of the synthesized compounds have not usually been reported for phenoxo-imino ligands [49]. As such, even though titanium compounds have been described with remarkable properties as catalysts for living ethylene polymerization [50] and Pd(II) complexes have shown to be active in hydrogenation processes [51], only 46 compounds with fluorinated phenoxo-imino ligands have been structurally characterized, mainly for titanium and aluminium [52].

In this paper, we report on the synthesis and characterization of the first examples of aluminates bearing fluorinated Schiff bases as ligands, completing the family of heterometallic aluminium-alkali metal compounds previously described by us [44]. For these species, the influence of the alkali metal is observed as well as the effect of the fluorine atoms located in the iminic ring of the ligand.

## 2. Results

The selected ligand precursor was prepared following the standard procedure for this kind of compound. In the present study, we chose the proligand HL*a* that incorporates fluorine atoms in positions 2 and 3 of the iminic ring [45,53,54].

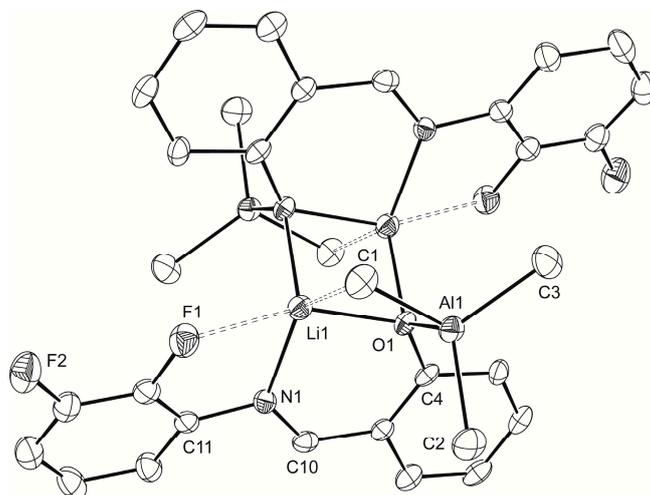
Heterometallic complexes can be obtained following different reaction pathways. In this case, the procedure employed was the formation of the alkali metal complex in situ followed by the addition of the aluminium precursor. The stoichiometric reaction between the alkali metal precursors, [Li{N(SiMe<sub>3</sub>)<sub>2</sub>}] or NaH, and the proligand gave the alkali metal homometallic compounds. The subsequent addition of a stoichiometric amount of AlMe<sub>3</sub> at low temperature led to the formation of the alkali metal aluminate complexes [MAlMe<sub>3</sub>(L*a*)] (M = Li, Na) (1–2), as shown in Scheme 1. These heterometallic complexes were characterized in the solid state by elemental analysis and by single crystal X-ray diffraction.



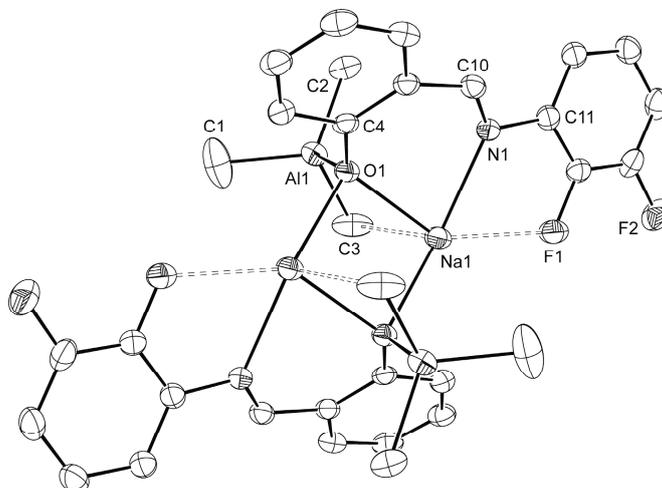
**Scheme 1.** Synthesis of the alkali metal aluminate complexes [MAlMe<sub>3</sub>L*a*]<sub>n</sub> (1–2).

The single crystal X-ray diffraction studies allowed the unequivocal characterization in the solid state of compounds 1 and 2. As shown in Figures 1 and 2, both the lithium and sodium are tetranuclear species M<sub>2</sub>Al<sub>2</sub> (M = Li, Na). The phenoxo-imino ligand acts as a bridge between the aluminium and the alkali metal through the oxygen atom. The ligand also links the alkali metals through the oxygen and a M<sub>2</sub>O<sub>2</sub> (M = Li, Na) central core is observed. Although 1 and 2 are isostructural molecules some differences in the orientation of the ligands are detected, as such, the rings from the phenoxo-imino ligand show a significantly more coplanar disposition for the lithium compound 1 (angle 16.68°) than for 2 (angle 45.18°). The Al–O distance is significantly shorter for the sodium derivative 2 (1.900(3)

Å 1 vs. 1.8621(19) Å 2), which could be related to the fact that a higher ionic component in the M-O bonding for the sodium compound can be expected, which then may provoke a stronger interaction of the aluminium and the phenoxo oxygen. Finally, the AlMe<sub>3</sub> moiety is connected to the ligand as if these compounds have been generated from the breakage of the (AlMe<sub>3</sub>)<sub>2</sub> precursor by an O-donor species, such as the metallated ligand, to form a 1:1 Lewis adduct.



**Figure 1.** ORTEP plots for **1** showing thermal ellipsoids plots (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): C(1)-Al(1) 1.994(5), C(2)-Al(1) 1.953(6), C(3)-Al(1) 1.954(5), O(1)-Al(1) 1.902(3), C(1)⋯Li(1) 2.413(4), C(10)-N(1) 1.280(6), Li(1)-O(1) 1.982(8), Li(1)-O(1)#1 1.998(8), Li(1)-N(1) 2.007(9), Li(1)⋯F(1) 2.299(8), C(16)-F(1) 1.359(6), C(15)-F(2) 1.336(6), O(1)-Li(1)-O(1)#1 97.3(3), C(10)-N(1)-C(11) 118.5(4).



**Figure 2.** ORTEP plots for **2** showing thermal ellipsoids plots (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg.): C(3)-Al(1) 1.981(4), C(2)-Al(1) 1.965(3), C(1)-Al(1) 1.977(4), O(1)-Al(1) 1.8621(19), C(3)⋯Na(1) 2.737(6), C(10)-N(1) 1.275(3), Na(1)-O(1) 2.3254(18), Na(1)-O(1)#1 2.3657(19), Na(1)-N(1) 2.389(2), Na(1)-F(1) 2.4608(18), C(16)-F(1) 1.357(3), C(15)-F(2) 1.347(3), O(1)-Na(1)-O(1)#1 89.41(6), C(10)-N(1)-C(11) 117.3(2).

In both compounds, the alkali metal shows a pentacoordinated environment. As such, besides the oxygen atom, the iminic nitrogen atom also establishes a donor interaction with alkali metal and one of the methyl groups bonded to the aluminium interacts with the alkali metal through a M⋯Me contact. The M⋯C distances (2.413(4) Å for **1** and 2.737(6) Å for **2**) are within the shortest found in the literature [44,52]. Interestingly, the longest Al-C distance belongs to the methyl group

involved in the Me...M interaction (1.994(5) Å for **1** and 1.981(4) Å for **2**). These contacts contribute to the stabilization of the alkali metal coordination sphere. Furthermore, the *ortho* fluorine atom of the iminic ring establishes a M...F interaction (2.299(8) Å for **1** and 2.4608(18) Å for **2**) that completes the unusual pentacoordinated sphere for these metallic centres. Of particular interest is the presence of Na...F contacts since this represents a stabilizing interaction that allows the isolation of this compound. As such, for the species previously reported by us without fluorine substituents in the iminic ring, the analogous [NaAlMe<sub>3</sub>(L)] compound was not possible to detect or isolate. Compound **2** is then the first example of a sodium aluminate of stoichiometry [NaAlMe<sub>3</sub>(L)]<sub>n</sub> with phenoxo-imino ligands and one of the very few reported. The influence of Na...F interactions has been acknowledged not only in the structure but also in the reactivity of heterometallic sodium species as it has been reported for metallated reactions [55].

Finally, an interesting feature in the packing of **2**, is the presence of  $\pi$ - $\pi$  stacking interactions between the fluorinated rings, which are oriented with an anti-disposition of each other (considering the fluorine substituents), the distance between centroids is 3.62 Å, and directs the packing into chains along the *c* axis.

These species were also characterized in solution by multinuclear NMR spectroscopy (Figures 3 and 4). <sup>1</sup>H NMR spectra were recorded in C<sub>6</sub>D<sub>6</sub> and displayed the resonances for the methyl groups bound to the aluminium centre at negative values. For **1** appears at  $\delta$ -0.24 ppm and integrate for three methyl groups. These data suggest that the aluminate species show the expected [LiAlMe<sub>3</sub>(L)]<sub>n</sub> formulation also in solution. In comparison to the analogous species without the fluorine substituents, the methyl groups appear at a lower field, indicating a more acidic character, as could be expected due to the presence of these electron withdrawing groups atoms in the iminic ring [44].

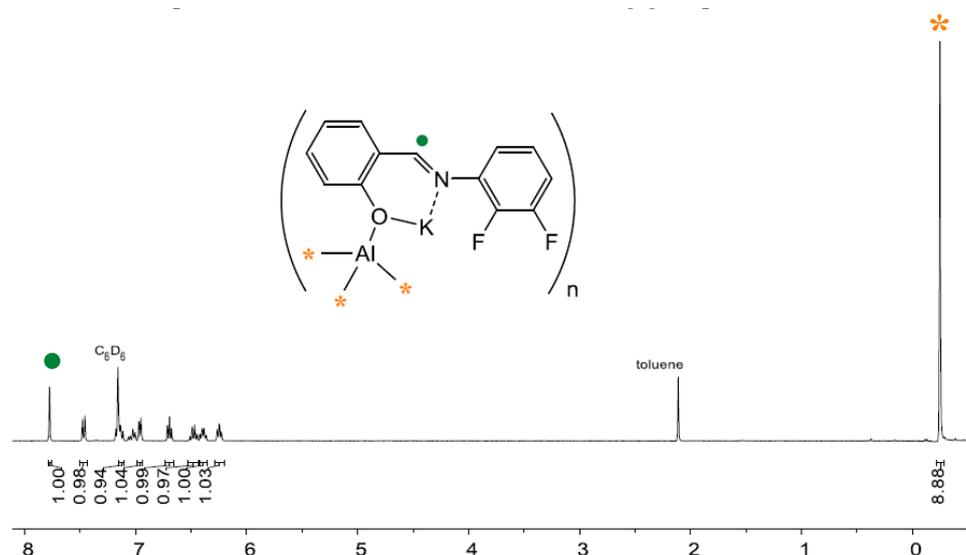
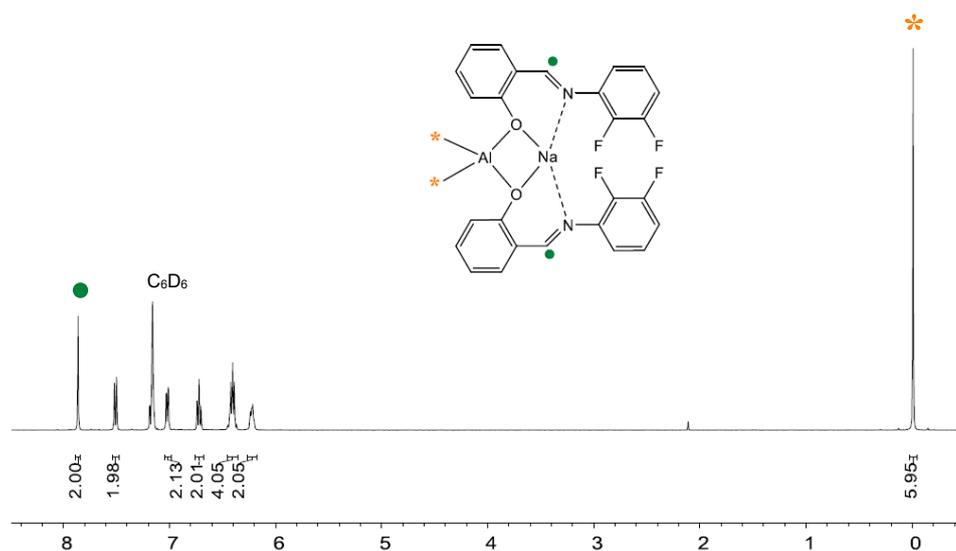


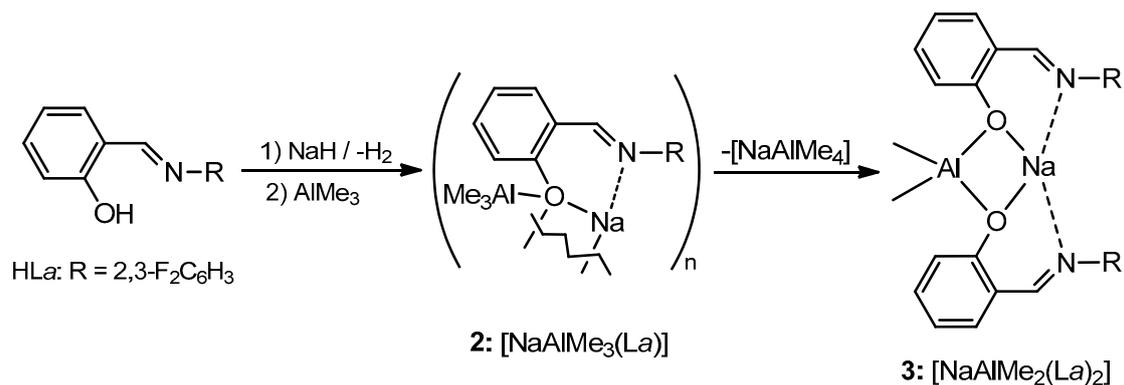
Figure 3. <sup>1</sup>H NMR spectrum of complex **1** recorded in C<sub>6</sub>D<sub>6</sub> at room temperature.

However, for compound **2**, in the NMR different behaviour was observed (Figure 4). In this case, once the crystals of **2** were dissolved, the <sup>1</sup>H NMR spectrum in benzene-*d*<sub>6</sub> did not reveal the expected resonances for the characterized aluminate in the solid state. The signal of the methyl groups bound to the aluminium centre appeared at  $\delta$ -0.01 ppm, a remarkable shift compared with the lithium aluminate; moreover, this signal is consistent with three hydrogen atoms per ligand in agreement with a [NaAlMe<sub>2</sub>(La)<sub>2</sub>] (**3**) formulation (Scheme 2), a disposition already described in our previous work for the phenoxo-imino species with donor substituents [44]. In fact, for those species without the fluorine substituents, it was not possible to isolate the analogous sodium derivate, as it evolves very rapidly into the formation of compounds with the [NaAlMe<sub>2</sub>L<sub>2</sub>] formulation, via a rearrangement process that also might generate [NaAlMe<sub>4</sub>], as shown in Scheme 2. In this case, the presence of the

$\text{Na}\cdots\text{F}$  interactions seems to stabilize the structure and it was possible to isolate  $[\text{NaAlMe}_3\text{La}]$  in the solid state.

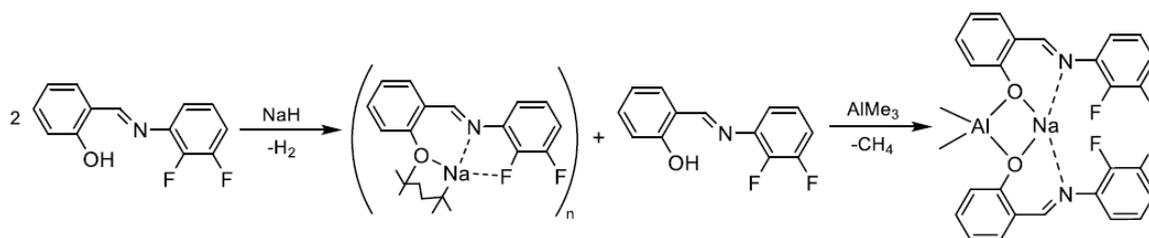


**Figure 4.**  $^1\text{H}$  NMR spectrum of complex **3** recorded in  $\text{C}_6\text{D}_6$  at room temperature.



**Scheme 2.** Proposed reaction for the formation of  $[\text{NaAlMe}_2(\text{La})_2]$  (**3**).

Taking into account these data, different reactions were carried out to understand the nature of this process. In the first place, the reaction with the correct stoichiometry (2:1:1 ratio of  $[\text{HL a}]:[\text{Na}]:[\text{Al}]$ ) to obtain the complex **3**,  $[\text{NaAlMe}_2(\text{La})_2]$ , was performed (Figure S1). In this case, after the addition of the alkali metal precursor, a mixture of the proligand and the metallated ligand was formed, and the subsequent incorporation of  $\text{AlMe}_3$  gave the aluminate complex **3**,  $[\text{NaAlMe}_2(\text{La})_2]$ , which displayed an identical  $^1\text{H}$  NMR spectrum as the one observed for the isolated crystals (Scheme 3).

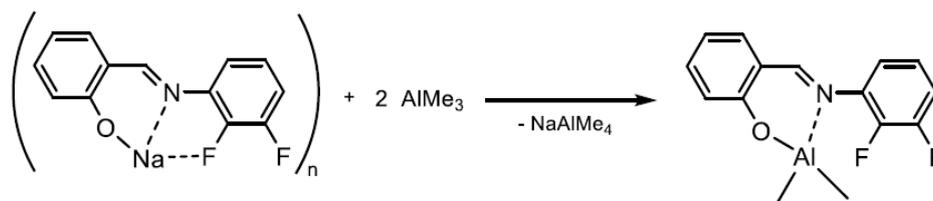


**Scheme 3.** Synthesis of  $[\text{NaAlMe}_2(\text{La})_2]$  (**3**).

Besides, to support the proposal where the reaction pathway follows a ligand rearrangement with the formation of sodium tetramethylaluminate,  $[\text{NaAlMe}_4]$ , the stoichiometric reaction (1:1:1 of

[HL*a*]:[Na]:[Al]) was monitored in a valved NMR tube. In this reaction, a signal at  $\delta$ -0.40 ppm was detected that can be attributed to the tetramethylaluminate species [NaAlMe<sub>4</sub>] in agreement with the mechanism proposed (Figure S2). We had already observed this behaviour in the formation of [NaAlMe<sub>2</sub>(L)<sub>2</sub>] aluminates with phenoxo-imino ligands containing donor substituents [44].

Finally, to have clear evidence regarding the formation of [NaAlMe<sub>4</sub>], the reaction between the alkali metal compound [Na*La*] with two equivalents of trimethylaluminium (AlMe<sub>3</sub>) was performed (Scheme 4) [56]. In this reaction, the aluminium derivative [AlMe<sub>2</sub>(*La*)] was clearly identified, which proves the possibility of ligand rearrangements in these systems. Confirming this, a signal at  $\delta$ -0.40 ppm attributable to [NaAlMe<sub>4</sub>] could also be detected (Figure S3).



**Scheme 4.** Metathesis reaction between the sodium complex and AlMe<sub>3</sub>.

### 3. Materials and Methods

#### 3.1. General Procedures

All manipulations were performed under an inert atmosphere using Schlenk-line techniques ( $O_2 < 3$  ppm) and a glove box ( $O_2 < 0.6$  ppm) MBraun MB-20G (MBraun, Garching, Germany). Solvents were purified using an MBraun Solvent Purification System (MBraun, Garching, Germany). Deuterated solvents were degassed and stored in the glove box in the presence of molecular sieves (4 Å). Fluoroaniline compounds were purchased from Fluorochem (Fluorochem, Derbyshire, UK) and used as received. 2-hydroxybenzaldehyde and metallic precursors were purchased from Sigma-Aldrich (Merck, Darmstadt, Germany). NMR spectra were recorded with a Bruker 400 Ultrashield (Bruker, Karlsruhe, Germany) (<sup>1</sup>H 400 MHz, <sup>13</sup>C 101 MHz) at room temperature. All chemical shifts were determined using the residual signal of solvents and were reported versus SiMe<sub>4</sub>. The assignment of the signal was carried out from 1D (<sup>1</sup>H, <sup>19</sup>F{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H}) and 2D (<sup>1</sup>H-<sup>13</sup>C HSQC) NMR experiments. Elemental analyses were performed with a PerkinElmer 2400 CHNS/O analyzer Series II (PerkinElmer, Ohio, OH, USA) and were the average of at least two independent measurements.

#### 3.2. Synthesis of Complex [LiAlMe<sub>3</sub>(O-2-(2,3-C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>N=CH)C<sub>6</sub>H<sub>4</sub>)], [LiAlMe<sub>3</sub>*La*] (**1**)

At room temperature, a mixture of H*La* (0.700 g, 3.00 mmol) and [Li{N(SiMe<sub>3</sub>)<sub>2</sub>}] (0.518 g, 3.60 mmol) in toluene (30 mL) was stirred for one night. The resultant solution was cooled to  $-78$  °C, and AlMe<sub>3</sub>, 2 M in toluene (1.50 mL, 3.00 mmol) was added dropwise. Then, the reaction was warmed to room temperature, and it was concentrated to 10 mL and stored at  $-20$  °C. After a few days, crystals were obtained. Yield: 0.251 g, 27%. The single crystal used for the for X-ray diffraction analysis were obtained from a NMR tube. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 295 K):  $\delta$  7.78 (s, 1H, HC=N), 7.47 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.15 (m, 1H, ArH), 6.96 (m, 1H, ArH), 6.69 (m, 1H, ArH), 6.47 (m, 1H, ArH), 6.39 (m, 1H, ArH), 6.23 (m, 1H, ArH),  $-0.24$  [s, 9H, Al(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 101 MHz, 295 K):  $\delta$  164.1 (C=N), 161.9 (C-O), multiplets from 151.9 to 144.5 (C-F, hardly assignable due to complicated <sup>13</sup>C-<sup>19</sup>F coupling), 136.5, 136.0, 124.8, 122.3, 122.1, 118.7, 115.1, 114.9, 112.1 (Ar-C),  $-8.14$  [Al(CH<sub>3</sub>)<sub>3</sub>]. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 376 MHz, 295 K):  $\delta$   $-136.7$  (d, 1F, *o*-F),  $-154.8$  (d, 1F, *m*-F). Anal. Calcd for C<sub>16</sub>H<sub>17</sub>AlF<sub>2</sub>LiNO (311.24 g/mol): C 61.75, H 5.51, N 4.50. Found: C 61.62, H 5.21, N 4.96.

### 3.3. Synthesis of Complex $[NaAlMe_3\{(O-2-(2,3-C_6H_3F_2N=CH)C_6H_4)\}]$ , $[NaAlMe_3(La)]$ (**2**)

The same method as that for **1** was used but with **HLa** (0.560 g, 2.40 mmol), NaH (0.057 g, 2.40 mmol) and  $AlMe_3$ , 2 M in toluene (1.20 mL, 2.40 mmol). Yield: 0.221 g, 27%. Anal. Calcd for  $C_{16}H_{17}AlF_2NaNO$  (327.28 g/mol): C 58.72, H 5.24, N 4.28. Found: C 59.31, H 5.18, N 4.54.

### 3.4. Synthesis of Complex $[NaAlMe_2\{(O-2-(2,3-C_6H_3F_2N=CH)C_6H_4)\}_2]$ , $[NaAlMe_2(La)_2]$ (**3**)

At room temperature, a mixture of **HLa** (0.560 g, 2.40 mmol) and NaH (0.029 g, 1.20 mmol) in toluene (20 mL) was stirred few hours. This solution was cooled to  $-78^\circ C$ , and  $AlMe_3$ , 2 M in toluene (0.60 mL, 1.20 mmol) was added dropwise. Then, the mixture was warmed to room temperature, and reacted one night. After, the solution was dried under vacuum and the resultant solid was washed with n-hexane twice to give a yellow powder. Yield: 0.503 g, 77%.  $^1H$  NMR ( $C_6D_6$ , 400 MHz, 295 K):  $\delta$  7.86 (s, 2H, HC=N), 7.51 (d, 2H,  $C_6H_4$ ), 7.19 (bs, 2H, ArH), 7.02 (m, 2H,  $C_6H_4$ ), 6.72 (m, 2H, ArH), 6.42–6.21 (m, 6H, ArH),  $-0.01$  [s, 6H,  $Al(CH_3)$ ].  $^{13}C$  NMR ( $C_6D_6$ , 101 MHz, 295 K):  $\delta$  168.3 (C-O), 162.4 (C=N), multiplets from 152.0 to 143.3 (C-F, hardly assignable due to complicated  $^{13}C$ - $^{19}F$  coupling), 142.0, 137.6, 134.8, 133.3, 124.6, 123.5, 122.5, 118.3, 115.0, 114.1 (Ar-C),  $-8.18$  [ $Al(CH_3)$ ].  $^{19}F$  NMR ( $C_6D_6$ , 376 MHz, 295 K):  $\delta$   $-137.9$  (d, 1F, *o*-F),  $-157.1$  (d, 1F, *m*-F). Anal. Calcd for  $C_{28}H_{22}AlF_4N_2NaO_2$  (544.46 g/mol): C 61.77, H 4.07, N 5.15. Found: C 61.47, H 4.18, N 5.40.

### 3.5. Single-crystal X-Ray Structure Determination for $(1 \cdot 2C_6D_6)$ and **2** (Table 1)

Data collection was performed at 200(2) K, with the crystals covered with perfluorinated ether oil. Single crystals of **1c** were mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Multiscan [57] absorption correction procedures were applied to the data. The structure was solved using the WINGX package [58], by direct methods (SHELXS-97) and refined using full-matrix least-squares against  $F^2$  (SHELXL-97) [59,60]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for the carbon atoms involved in the interaction with the alkali metal in **2** (C3), and for the iminic carbon in **1** (C10), those atoms were found in the Fourier map and refined freely. For **1** disordered solvent molecules were present in the asymmetric unit: two molecules of benzene per molecule of **1**. No chemical sense could be made of the disorder solvent molecule, so a squeeze procedure [61,62] was applied to remove its contribution from the structure factors. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1878166( $1 \cdot 2C_6D_6$ ) and CCDC-1878167(**2**).

**Table 1.** Crystallographic data for 1·2C<sub>6</sub>D<sub>6</sub>, and 2.

	[LiAlMe <sub>3</sub> La]·2C <sub>6</sub> D <sub>6</sub>	[NaAlMe <sub>3</sub> La]
Empirical formula	C <sub>32</sub> H <sub>34</sub> Al <sub>2</sub> Li <sub>2</sub> F <sub>4</sub> N <sub>2</sub> O <sub>2</sub> ·2C <sub>6</sub> D <sub>6</sub>	C <sub>32</sub> H <sub>34</sub> Al <sub>2</sub> Na <sub>2</sub> F <sub>4</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	790.59	654.55
Colour, shape	Yellow/block	Yellow/block
Crystal size (mm)	0.45 × 0.42 × 0.27	0.49 × 0.48 × 0.45
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1
a (Å)	11.699(3)	8.5668(8)
b (Å)	16.669(6)	10.2749(8)
c (Å)	10.7558(17)	11.1625(8)
α (°)	90	111.026(6)
β (°)	90.35(2)	91.093(5)
γ (°)	90	112.001(6)
V (Å <sup>3</sup> )	2097.5(9)	836.87(13)
Z	2	1
ρ <sub>calcd.</sub> (mg m <sup>-3</sup> )	1.233	1.299
F <sub>000</sub>	816	340
μ (mm <sup>-1</sup> )	0.125	0.166
θ Range (°)	3.001 to 27.518	3.063 to 27.498
Reflns. Collected	16768	7166
Indep. Reflns./R(int)	4744/0.2050	3829/0.0734
Data/restraints/param	4744/147/203	3829/0/215
R <sub>1</sub> /wR <sub>2</sub> (I > 2σ(I)) <sup>a</sup>	0.0982/0.2357	0.0498/0.1165
R <sub>1</sub> /wR <sub>2</sub> (all data) <sup>a</sup>	0.1892/0.2927	0.1230/0.1505
GOF	0.873	0.918
Max/min Δρ (e.Å <sup>-3</sup> )	0.524 and -0.931	0.238 and -0.473

$$^a R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|; wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}; GOF = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}.$$

#### 4. Conclusions

For the first time, the synthesis of alkali metal aluminates [MAlMe<sub>3</sub>(La)] (M = Li (**1**), Na (**2**)) has been achieved with fluorinated Schiff bases as ligands. The presence of the fluorine substituents in the ligands facilitates the isolation of the aluminate [NaAlMe<sub>3</sub>(La)] (**2**) in the solid state thanks to the presence of a stabilizing Na···F interaction, in contrast with the behaviour observed in analogous compounds without fluorine substituents in the iminic ring. Although the lithium derivative **1** maintains its structure when dissolved, the sodium compound **2** in the solution evolves rapidly into the formation of [MAlMe<sub>3</sub>(La)]<sub>2</sub>. The mechanism for this transformation is based on interchange reactions via a ligand rearrangement with the formation of the [MAlMe<sub>4</sub>] species, which can be detected by NMR techniques, in a similar way as observed previously for the aluminates without fluorine substituents. Studies of the reactivity of these species towards small molecules are ongoing.

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**Sample Availability:** Samples of the compounds 1–3 are available from the authors.



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