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## Donor-free 9-aluminafluorenes: molecular structures and reactivity<sup>†</sup>

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Aluminum-doped polycyclic aromatic hydrocarbons (PAHs) are underexplored despite the broad applications of boron-containing PAHs in areas such as catalysis and optoelectronics. We disclose the donor-free, sterically unprotected 9-methyl-9-aluminafluorene (Me-AlFlu; **2**), synthesized by heating a 9,9-dimethyl-9-stannafluorene and AlMe<sub>3</sub> in hexanes. The compound is a dimer, (**2**)<sub>2</sub>, with *trans*-positioned AlMe substituents in the solid state. In solution, (**2**)<sub>2</sub> shows a dynamic *cis/trans*-interconversion rather than a monomer-dimer equilibrium (Tol-*d*<sub>8</sub>, RT). Lewis bases L cleave (**2**)<sub>2</sub> into monomeric adducts **2**·L (L = OEt<sub>2</sub>, thf, pyridine). Lewis acidic AlBr<sub>3</sub> transforms (**2**)<sub>2</sub> into a 2,2'-(Br<sub>2</sub>Al)<sub>2</sub>-1,1'-biphenyl (**3**), crystallographically characterized as dimeric (**3**)<sub>2</sub>. (**3**)<sub>2</sub> is a synthetic equivalent for the elusive free Br-AlFlu: Treatment with donor molecules furnishes Br-AlFlu·L adducts (L = OEt<sub>2</sub>, pyridine); the three-coordinate, monomeric aluminafluorene Mes<sup>\*</sup>-AlFlu was prepared from (**3**)<sub>2</sub>, Mes<sup>\*</sup>Li, and a 2,2'-dilithio-1,1'-biphenyl in quantitative yield (Mes<sup>\*</sup> = 2,4,6-(*t*Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).

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## Introduction

Doping organic  $\pi$ -electron systems with other p-block elements is an effective strategy to impart new chemical and physical properties to these species.<sup>1</sup> Specifically, the combination of a polycyclic aromatic hydrocarbon (PAH) such as fluorene with boron as a dopant to generate 9-borafluorenes (BFlus) can have a particularly pronounced effect,<sup>2,3</sup> as a conjugation barrier (*i.e.*, the CH<sub>2</sub> fragment in the carbonaceous species) is removed and a vacant B(p<sub>z</sub>) orbital is introduced instead, which can now: (i) mediate electron delocalization and bring about novel optoelectronic properties,<sup>4</sup> (ii) facilitate reduction,<sup>5,6</sup> and (iii) act as a Lewis acid to promote bond-activation reactions<sup>7</sup> or the expansion of the five-membered central borole ring.<sup>8</sup>

Compared to the extensive research on BFlus, their heavier homologues, the 9-aluminafluorenes (AlFlus),<sup>9,10</sup> are far less well explored. This is unfortunate, because AlFlus are expected to exhibit a lower degree of aryl-heteroatom double-bond character than BFlus,<sup>11</sup> leading to a greater propensity to form structurally intriguing aggregates through Al $\cdots$  $\pi$ (Ar) complexes

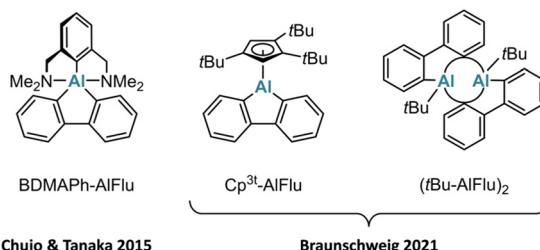
or Al-C-Al' two-electron–three-center (2e3c) bonds. Relative to open-chain arylaluminum compounds, AlFlus should possess a structurally enforced enhanced Lewis acidity due to their small endohedral C-Al-C angle. This angle (108° in a regular five-membered ring) deviates more from the ideal 120° angle of three-coordinate AlR<sub>3</sub> species than from the corresponding angles of perfectly tetrahedral (109.5°) adducts. By the same token, the behavior of Al-based Lewis acids is more diverse than that of their B-based counterparts, as Al sites, unlike B centers, can readily accommodate coordination numbers larger than four.

In 1962, Eisch *et al.* reported the formation of Ph-AlFlu through the metalative cyclization of *o*-biphenyl(diphenyl) aluminum at 200 °C. Their claim was mainly based on the analysis of hydrolysis and iodinolysis products.<sup>12,13</sup> The topic lay dormant until 2015, when Chujo and Tanaka used salt-metathesis protocols to synthesize AlFlus carrying Al-bonded phenyl rings with one or two chelating (dimethylamino)methyl substituents at their *ortho* positions (Fig. 1). Their research focused on the emission properties of the obtained four- and five-coordinate AlFlus.<sup>14,15</sup> More recently, Braunschweig *et al.* disclosed the synthesis of various aluminafluorenes R-AlFlu [R = 1,2,4-(*t*Bu)<sub>3</sub>C<sub>5</sub>H<sub>2</sub> (92%; Fig. 1), Ph<sub>2</sub>(*t*Bu)Si (44%), 2-C<sub>4</sub>H<sub>3</sub>S (79%), *t*Bu (23%; Fig. 1), Br (53%)]. The compounds were again prepared from 2,2'-dilithio-1,1'-biphenyl by salt-metathesis reactions and isolated and structurally characterized as their ether adducts – with the exception of the  $\eta^5$ -cyclopentadienide derivative, which is monomeric in the solid state, and the *t*Bu derivative, which crystallizes as a dimer.<sup>16</sup>

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic procedures, NMR spectra, X-ray crystallographic data and computational details. CCDC 2394332–2394341. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt03148b>





**Fig. 1** Known mono- and dimeric 9-aluminafluorenes featuring 2,6-bis [(dimethylamino)methyl]phenyl (BDMAFlu), 1,2,4-(tBu)<sub>3</sub>C<sub>5</sub>H<sub>2</sub> (Cp<sup>3t</sup>), and *tert*-butyl (tBu) substituents.

One aim of our study outlined herein was to develop straightforward, high-yield synthesis protocols for base-free R-AlFlus featuring (i) the small substituent R = Me to minimize steric shielding of the Al center, and (ii) the reactive substituent R = Br for late-stage derivatization. Particular emphasis was placed on the molecular structure of Me-AlFlu in non-donor solvents and in the solid state, as well as on the synthesis of the first base-free, three-coordinate, monomeric aluminafluorene, Mes\*-AlFlu (Mes\* = 2,4,6-(tBu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>). All our AlFlus were equipped with tBu groups in their 2,7-positions to enhance solubility in non-polar solvents and to facilitate NMR-spectroscopic analysis.

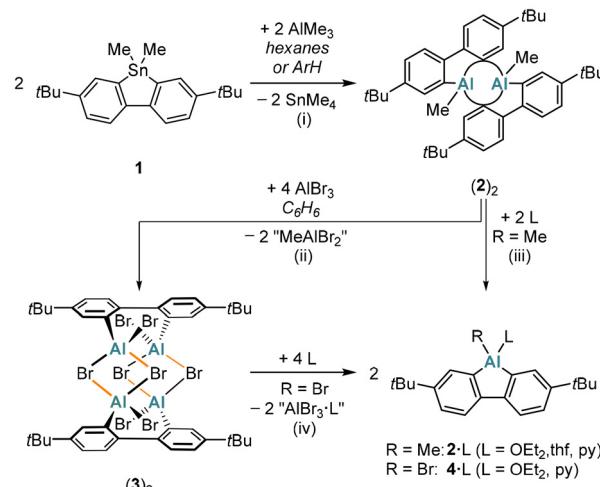
## Results and discussion

### Syntheses

The base-free Me-AlFlu (2) was synthesized by heating the 9,9-dimethyl-9-stannafluorene **1** with 1 equiv. of AlMe<sub>3</sub><sup>17</sup> in either hexanes or C<sub>6</sub>H<sub>6</sub>/toluene (Scheme 1). The only by-product formed is the volatile and relatively inert SnMe<sub>4</sub>.<sup>18,19</sup> An advantage of using hexanes as the solvent is that the dimer (2)<sub>2</sub> precipitates in pure form already upon cooling the reaction mixture to room temperature (yield: 74%); when C<sub>6</sub>H<sub>6</sub>/toluene is employed, the yield of (2)<sub>2</sub> is higher (91%), but some further workup is required. In the presence of the donor molecules Et<sub>2</sub>O, THF, or pyridine, (2)<sub>2</sub> is cleanly split into its constituting monomers to furnish the monoadducts 2-OEt<sub>2</sub>, 2-thf, or 2-py (Scheme 1).

Treatment of (2)<sub>2</sub> with 4 equiv. of AlBr<sub>3</sub><sup>17</sup> in C<sub>6</sub>H<sub>6</sub> results not only in quantitative AlMe/AlBr exchange but also in the incorporation of two AlBr<sub>3</sub> molecules to afford dimeric 2,2'-(Br<sub>2</sub>Al)<sub>2</sub>-1,1'-biphenyl [(3)<sub>2</sub>, 95%; Scheme 1]. Upon addition of Et<sub>2</sub>O to (3)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>, the donor adduct of Br-AlFlu, 4-OEt<sub>2</sub>, precipitates quantitatively as a colorless solid. In terms of yield, our overall synthesis cascade to 4-OEt<sub>2</sub> improves upon the published protocol<sup>16</sup> by about 40 percentage points. Although pyridine can also reconstitute the AlFlu scaffold from (3)<sub>2</sub>, it proved challenging to separate the target product 4-py from by-products such as [AlBr<sub>2</sub>(py)<sub>4</sub>][X] ([5][X]; X = Br<sup>-</sup>, AlBr<sub>4</sub><sup>-</sup>; Fig. S44 and S45†).

A particularly notable application of (3)<sub>2</sub> as a synthetic equivalent of donor-free Br-AlFlu is the preparation of Mes\*-AlFlu

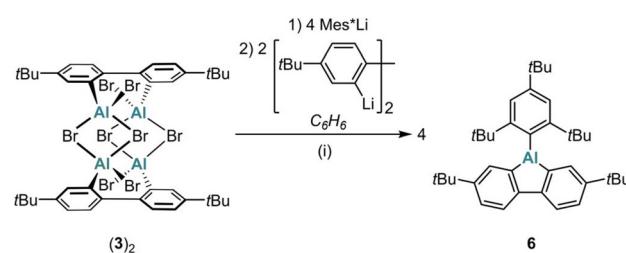


**Scheme 1** Synthesis of donor-free (2)<sub>2</sub> through Sn/Al exchange between the 9-stannafluorene **1** and AlMe<sub>3</sub> (ArH: C<sub>6</sub>H<sub>6</sub>/toluene). The addition of AlBr<sub>3</sub> to (2)<sub>2</sub> furnishes (3)<sub>2</sub>. Lewis bases (L: Et<sub>2</sub>O, THF, or pyridine), cleave (2)<sub>2</sub> or (3)<sub>2</sub> into the monomeric adducts 2-L or 4-L. (i) Hexanes, 140 °C, 3 d (74% yield) or C<sub>6</sub>H<sub>6</sub>/toluene, 120 °C, 3 d (91% yield); sealed glass ampoule. (ii) C<sub>6</sub>H<sub>6</sub>, room temperature, 1 d (95% yield). (iii) 2-OEt<sub>2</sub>: Et<sub>2</sub>O, room temperature; 2-thf: C<sub>6</sub>D<sub>6</sub>, room temperature; 2-py: C<sub>6</sub>H<sub>6</sub>, room temperature (quantitative conversions). (iv) 4-OEt<sub>2</sub>: C<sub>6</sub>H<sub>6</sub>, room temperature (quantitative conversion); 4-py: C<sub>6</sub>D<sub>6</sub>, room temperature (not isolated). Note: in (3)<sub>2</sub>, four bonds were arbitrarily chosen as formally intermolecular (highlighted in orange) to facilitate the distinction between the monomers M and M'.

(6): sequential addition of Mes\*Li (4 equiv.) and 2,2'-dilithio-4,4'-di-*tert*-butyl-1,1'-biphenyl (2 equiv.) to (3)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> gave **6** in 97% yield (Scheme 2).

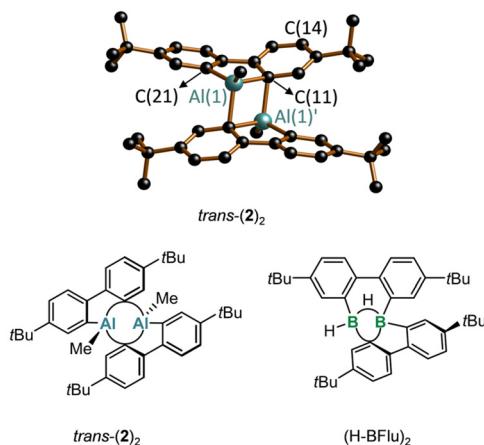
### Solid-state structures

In the solid state, Me-AlFlu forms centrosymmetric dimers, with the Al-bonded Me substituents adopting a *trans*-configuration (*trans*-(2)<sub>2</sub>; Fig. 2).<sup>20</sup> The individual monomers, M and M', are linked by two Al...C interactions, resulting in two Al(1) ...Al(1)' bridging aryl rings (Ar<sub>b</sub>) and two terminal rings (Ar<sub>t</sub>), with bridging [C(11)] and terminal [C(21)] *ipso*-C atoms. The position of Ar<sub>b</sub> is asymmetric between Al(1) and Al(1)', as indicated by the differing angles Al(1)-C(11)...C(14) = 153.13(17)° and Al(1)'-C(11)...C(14) = 128.38(16)°. The fact that the



**Scheme 2** Synthesis of Mes\*-AlFlu (**6**) using (3)<sub>2</sub> as a synthetic equivalent of the elusive Br-AlFlu. (i) C<sub>6</sub>H<sub>6</sub>, room temperature, 1 d (97% yield).

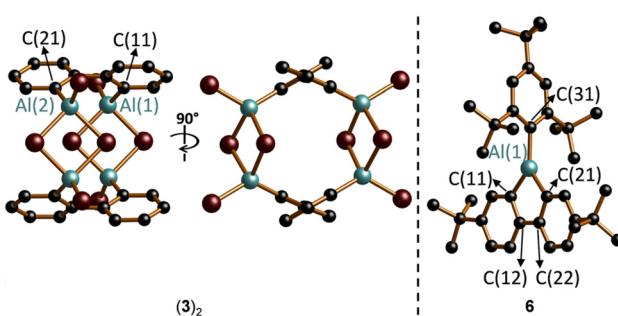




**Fig. 2** Top: molecular structure of  $trans\text{-}(2)_2$  in the solid state; H atoms omitted for clarity (C: black, Al: turquoise). Bottom: structural formulae of  $trans\text{-}(2)_2$  and of the comparable 9-borafluorene dimer  $(H\text{-BF}_2)_2$ .

Al(1)'-C(11)-C(14) angle is significantly closer to  $90^\circ$  than the Al(1)-C(11)-C(14) angle can still be viewed as a remnant of the initial intermolecular Al- $\cdots\pi$ (Ar) complex when the two hetero-fluorene units first encountered each other. Correspondingly, the 'intermonomer' Al(1)'-C(11) bond (2.148(3) Å) is longer by 0.055 Å than the 'intramonomer' Al(1)-C(11) bond (2.093(3) Å; cf. Al(1)-C(21) = 1.971(3) Å). The range of C-C bond lengths in Ar<sub>b</sub> (1.382(5)-1.427(5) Å) is close to that in Ar<sub>t</sub> (1.389(5)-1.409(5) Å), indicating that the bridging mode does not lead to a systematic bond-length alternation. However, the two C-C bonds involving the bridging C(11) atom are slightly longer than the other four (1.409(4) and 1.427(5) Å vs. 1.382(5)-1.401(5) Å). Finally, we note that  $trans\text{-}(2)_2$  has very similar structural parameters to Braunschweig's  $(t\text{Bu-AlFlu})_2$ ,<sup>16</sup> while the comparable 9-borafluorene dimer  $(H\text{-BF}_2)_2$  shows one B-( $\mu$ -H)-B two-electron-three-center bond and one B- $\cdots$ B'-bridging aryl ring (the three other rings remain terminally bonded).<sup>21</sup>

X-ray crystallography reveals that the compound  $(3)_2$  no longer contains the 9-aluminafluorene motif but instead forms a centrosymmetric 2,2'-(Br<sub>2</sub>Al)<sub>2</sub>-1,1'-biphenyl dimer (Fig. 3).



**Fig. 3** Left: molecular structure of  $(3)_2$  in the solid state, viewed from two different perspectives; tBu-groups in the 2,7-positions of the biphenyl backbones and H atoms omitted for clarity. Right: molecular structure of **6** in the solid state; H atoms omitted for clarity (C: black, Al: turquoise, Br: brown).

The two Br<sub>2</sub>Al substituents in each monomer adopt an approximate *s-trans* configuration with a torsion angle Al(1)-C(11)-C(21)-Al(2) of 129.55(19)° [Al(1)-C(11) = 1.945(5) Å, Al(2)-C(21) = 1.956(4) Å]. Four Br atoms occupy bridging positions between Al centers of different monomers, assembling the cage-like structure of  $(3)_2$ . The underlying structural feature, a four-membered R(Br)Al-( $\mu$ -Br)<sub>2</sub>-Al(Br)R ring, is common not only for aluminum tribromide (R = Br) but also for numerous dibromo(organo)alanes.<sup>22</sup>

The 2,4,6-(tBu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-substituted Mes\*-AlFlu (**6**) exists as a monomeric species with a three-coordinate Al center in the crystal lattice (Fig. 3). The sum of C-Al-C angles is  $360^\circ$ , confirming a trigonal-planar ligand environment, although the endocyclic C(11)-Al(1)-C(21) bond angle is nearly rectangular (91.79(6)°). All three Al-C bonds are of equal length, regardless of whether they are endo- or exocyclic, or whether the respective *ipso*-C(p<sub>z</sub>) orbital is positioned parallel or orthogonal to the vacant Al(p<sub>z</sub>) orbital [Al(1)-C(11)/C(21)/C(31) = 1.9611(14)/1.9516(14)/1.9606(13) Å]. Within the five-membered AlC<sub>4</sub> core, the length of the central C(12)-C(22) bond (1.5024(19) Å) approaches that of a typical C-C single bond (1.54 Å),<sup>23</sup> while the benzannulated bonds are significantly shorter [C(11)-C(12)/C(21)-C(22) = 1.4208(18)/1.4134(18) Å]. The other ten C-C bonds within the biphenyl fragment fall within a narrow range of 1.389(2)-1.4041(19) Å, closely matching the corresponding bonds in C<sub>6</sub>H<sub>6</sub> (1.39 Å).<sup>24</sup> Taken together, this analysis of bond lengths suggests that the AlFlu moiety of **6** preserves two largely unperturbed Clar sextets within its two C<sub>6</sub>H<sub>3</sub> fragments, with no indication of a delocalized (antiaromatic)  $\pi$ -system, nor any significant Al(1)=C(11)/C(21) double-bond character in the AlC<sub>4</sub> heterocycle.

The donor adducts 2-OEt<sub>2</sub>, 2-py, and 4-py were subjected to X-ray analysis to confirm that  $(2)_2$  and  $(3)_2$  can indeed serve as precursors of Me-AlFlu and Br-AlFlu, respectively (Fig. S40, S41, S43†). Furthermore, compared to donor-free **6**, the C-C bond lengths within the C<sub>6</sub>H<sub>3</sub>-C<sub>6</sub>H<sub>3</sub> units of 2-py and 4-py were found to differ by no more than  $3\sigma$  (and much less for most bonds).<sup>25</sup> This observation again suggests that the vacant Al(p<sub>z</sub>) orbital exerts no significant electron-withdrawing mesomeric effect on the  $\pi$ -electron system.

### NMR analysis

At room temperature, **2** gives severely broadened <sup>1</sup>H NMR signals, providing limited diagnostic value (Tol-d<sub>8</sub>; Fig. 4 and S7†). At 70 °C, two sharp resonances are detectable in the aliphatic region of the spectrum (integral ratio 3H : 18H); the aromatic region contains one broad feature and two doublets with coupling constants of about 8.2 Hz (Fig. 4 and S6†). At -30 °C, the <sup>1</sup>H NMR spectrum of **2** is characterized by two well-resolved sets of signals attributable to two different but closely similar components (Fig. 4 and S8†); the same is true for the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Fig. S9†). The proton-integral values of the two sets indicate a minor-to-major component ratio of approximately 0.12 : 1 (Fig. S8†). Focusing on the major component, the <sup>1</sup>H NMR spectrum reveals one singlet at -0.67 ppm (6H), and two additional singlets at 1.47 and

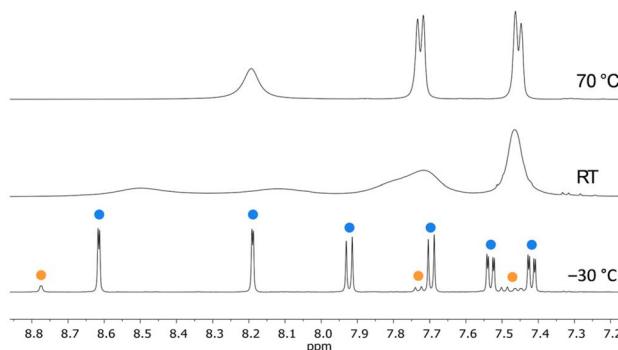


Fig. 4 Aromatic regions of  $^1\text{H}$  NMR spectra of  $(2)_2$  in  $\text{Tol-d}_8$  (500.2 MHz). Top: 70 °C. Middle: room temperature. Bottom: -30 °C. ●: *trans*-(2)<sub>2</sub>. ●: *cis*-(2)<sub>2</sub>.

1.28 ppm ( $2 \times 18\text{H}$ ), assignable to two equivalent  $\text{AlMe}$  substituents and two pairs of non-equivalent  $t\text{Bu}$  groups, respectively. In the aromatic region, four doublets ( $4 \times 2\text{H}$ ;  $2 \times ^3J_{\text{H,H}} = 8.2$  Hz,  $2 \times ^4J_{\text{H,H}} = 2.2$  Hz) and two doublets of doublets ( $2 \times 2\text{H}$ ) are observed, indicative of two pairs of non-equivalent  $\text{C}_6\text{H}_3$  fragments. In principle, these NMR features would align with both the molecular structure of the *cis*- and *trans*-(2)<sub>2</sub> dimer (as observed in the solid state). *Vice versa*, the minor signal set likely arises from *trans*- or *cis*-(2)<sub>2</sub>. At low temperatures, both isomers are present in an (essentially) static mixture, while some dynamic rearrangement equilibrium is established at higher temperatures. This preliminary conclusion raises two questions: (i) Does *cis*- or *trans*-(2)<sub>2</sub> dominate at low temperatures? (ii) Is the dynamic equilibrium at high temperatures due to monomer/dimer association/dissociation, or is it the result of a rapidly interconverting *cis*/*trans* dimeric form of (2)<sub>2</sub>?

To address question (i), quantum-chemical calculations predict that the crystallographically characterized *trans*-(2)<sub>2</sub> is 1.6 kcal mol<sup>-1</sup> more favorable in energy than *cis*-(2)<sub>2</sub> (Scheme S1†; experimental value, determined at -30 °C from the proton-integral values of the minor/major component:  $\Delta G^\circ = 0.7$  kcal mol<sup>-1</sup>). Furthermore, the relative proportion of the minor component increases with solvent polarity, consistent with the existing dipole moment of *cis*-(2)<sub>2</sub> ( $^1\text{H}$  NMR spectroscopic control; Table S1 and Fig. S1, S2†). Finally, the computed  $^{13}\text{C}$  chemical shift values for *cis*/*trans*-(2)<sub>2</sub> align more closely with the assumption that the major component is *trans*-(2)<sub>2</sub> rather than *vice versa* (Tables S9–S11†). It is therefore safe to assume that the major component in an equilibrating *cis*/*trans*-(2)<sub>2</sub> mixture is the *trans* isomer.

Regarding question (ii), we note that the computed energy required for cleaving *trans*-(2)<sub>2</sub> into its constituting monomers is 19.4 kcal mol<sup>-1</sup> (in  $\text{CH}_2\text{Cl}_2$ ). In contrast, the computed energy barrier of the *cis*/*trans* interconversion of (2)<sub>2</sub> is only  $\Delta G^\ddagger = 14.8$  kcal mol<sup>-1</sup>, which agrees well with the value of  $\approx 14.5$  kcal mol<sup>-1</sup> experimentally determined from the coalescence temperature ( $T_c$ ) in conjunction with the maximum peak separation ( $\Delta\nu$ ) in the slow-exchange limit ( $\text{CD}_2\text{Cl}_2$ ; see the

ESI† for full details). The observed NMR features are therefore more convincingly attributed to a dynamic *cis*/*trans* equilibrium rather than to a monomer/dimer association/dissociation equilibrium.

In the temperature range of -30 to 70 °C, (3)<sub>2</sub> exhibited only extremely broadened signals in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, providing no structural information.

The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of all adducts formed between our R-AlPlus and Lewis bases are in accord with the proposed molecular structures, as is the case for ligand-free **6** (see the ESI† for the fully assigned spectra). In addition to aiding in structure elucidation,  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy is also a valuable tool for mapping the  $\pi$ -charge density distribution in conjugated systems, as the shielding of a specific  $\text{C}(\text{sp}^2)$  atom depends linearly on the corresponding  $\pi$ -electron density at that position.<sup>26</sup> Given this background, we compared the  $^{13}\text{C}$  chemical shift values of the C atoms constituting the  $\text{C}_6\text{H}_3\text{—C}_6\text{H}_3$  fragment of **6** with those of the equivalent atoms in the corresponding fragments of the adducts 2-OEt<sub>2</sub>, 2-thf, 2-py, 4-OEt<sub>2</sub>, and 4-py. Except for the Al-bonded *ipso*-C atoms, whose shift differences varied from  $\delta(\mathbf{6}) - \delta(\text{adduct}) = 3.3$  to -4.7 ppm without a systematic trend, the  $\Delta\delta(^{13}\text{C})$  values for all other structurally analogous C atoms were less than  $\pm 1.8$  ppm. In other words, we found no evidence of an overall  $^{13}\text{C}$ -deshielding effect or  $\pi$ -electron depletion in **6** that could be attributed to a mesomerically electron-withdrawing Al(sp<sup>2</sup>) center.

$^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy on 2-py and 4-py provides a method to evaluate the relative Lewis acidities of free, monomeric Me-AlFlu and Br-AlFlu: in pyridine complexes of main-group elements, stronger acids induce increased shielding of the C-2,6 and deshielding of the C-3,4,5 nuclei of the ligand.<sup>27</sup> For 2-py/4-py, our observations consistently indicate that Me-AlFlu is the stronger acid, comparable in this respect to BPh<sub>3</sub>.<sup>28</sup> X-ray crystallography, however, offers a contrasting view: 4-py exhibits a shorter Al-N bond and a more pyramidalized Al center, implying higher Lewis acidity for Br-AlFlu.<sup>28</sup> Given the small differences in the key NMR and structural parameters between 2-py and 4-py, these conflicting observations highlight the limitation of relying on a single method to determine Lewis acidity, emphasizing the need for complementary approaches.

## Conclusions

We synthesized the donor-free 9-aluminafluorene Me-AlFlu (**2**), which was characterized as its dimer (**2**)<sub>2</sub> through X-ray crystallography and VT NMR spectroscopy (Tol-d<sub>8</sub>). The key to this success was the highly selective reaction between the 9,9-dimethyl-9-stannafluorene **1** and AlMe<sub>3</sub>,<sup>17,18</sup> which proceeds in non-donor solvents and releases volatile SnMe<sub>4</sub> as the sole byproduct. Unlike the bulky *tert*-butyl group in *tBu*-AlFlu,<sup>16</sup> the sterically less demanding methyl substituent in Me-AlFlu allows relatively unhindered access to the electrophilic Al center, as demonstrated by the straightforward formation of

various base adducts **2**·L (L = OEt<sub>2</sub>, thf, py). In terms of an uppolung of the Al center, exploring the reduction of **2** on a preparative scale could be promising (a non-benzannulated alumole has previously been reduced to its corresponding dianion).<sup>10</sup> The resulting product, [2]<sup>2-</sup>, could potentially serve as an Al-centered nucleophile – analogous to the [H-BFlu]<sup>2-</sup> dianion, which is a valuable B-centered nucleophile.<sup>3,6,29</sup>

Treatment of (2)<sub>2</sub> with AlBr<sub>3</sub> furnishes the 2,2'-(Br<sub>2</sub>Al)<sub>2</sub>·1,1'-biphenyl (3)<sub>2</sub>. Although this ring-opened product no longer retains the AlFlu motif, it rearranges back to afford Br-AlFlu adducts, such as **4**·L (L = OEt<sub>2</sub>, py), in the presence of Lewis bases. The use of Mes\*Li, which provides the extremely bulky, negatively charged Lewis base [Mes\*]<sup>-</sup>, grants unprecedented access to three-coordinate, monomeric aluminafluorenes, specifically Mes\*·AlFlu (**6**), *via* LiBr elimination. This reaction proves the utility of (3)<sub>2</sub> as a synthetic equivalent for the still-elusive free Br-AlFlu. A comparison of characteristic structural and NMR features of **6** with those of 2·L/4·L reveals that the three-coordinate Al center exerts only a negligible  $\pi$ -electron withdrawing effect and does not mediate significant  $\pi$ -electron delocalization.

## Author contributions

P. L. L. performed the experimental studies and characterized all new compounds. P. L. L. and J. G. performed the quantum-chemical calculations. A. V. performed the X-ray crystal structure analyses of all compounds. H.-W. L. and M. W. supervised the project. The manuscript was written by P. L. L. and M. W. and edited by all co-authors.

## Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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