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Donor-free 9-aluminafluorenes: molecular structures and reactivity†

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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 $AlMe_3$ in hexanes. The compound is a dimer, $(\mathbf{2})_2$, with *trans*-positioned Al*Me* substituents in the solid state. In solution, $(\mathbf{2})_2$ shows a dynamic *cis*/*trans*-interconversion rather than a monomer-dimer equilibrium (Tol-d_8, RT). Lewis bases L cleave $(\mathbf{2})_2$ into monomeric adducts **2**·L (L = OEt_2, thf, pyridine). Lewis acidic $AlBr_3$ transforms $(\mathbf{2})_2$ into a 2,2′-$(Br_2Al)_2$-1,1′-biphenyl (**3**), crystallographically characterized as dimeric $(\mathbf{3})_2$. $(\mathbf{3})_2$ is a synthetic equivalent for the elusive free Br-AlFlu: Treatment with donor molecules furnishes Br-AlFlu·L adducts (L = OEt_2, pyridine); the three-coordinate, monomeric aluminafluorene Mes*-AlFlu was prepared from $(\mathbf{3})_2$, Mes*Li, and a 2,2′-dilithio-1,1′-biphenyl in quantitative yield (Mes* = 2,4,6-$(t\mathrm{Bu})_3C_6H_2$).

Introduction

Doping organic π-electron systems with other p-block elements is an effective strategy to impart new chemical and physical properties to these species.[1] 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,[2,3] as a conjugation barrier (*i.e.*, the CH_2 fragment in the carbonaceous species) is removed and a vacant $B(p_z)$ orbital is introduced instead, which can now: (i) mediate electron delocalization and bring about novel optoelectronic properties,[4] (ii) facilitate reduction,[5,6] and (iii) act as a Lewis acid to promote bond-activation reactions[7] or the expansion of the five-membered central borole ring.[8]

Compared to the extensive research on BFlus, their heavier homologues, the 9-aluminafluorenes (AlFlus),[9,10] 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,[11] leading to a greater propensity to form structurally intriguing aggregates through Al⋯π(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_3 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*-biphenylyl(diphenyl)aluminum at 200 °C. Their claim was mainly based on the analysis of hydrolysis and iodinolysis products.[12,13] 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.[14,15] More recently, Braunschweig *et al.* disclosed the synthesis of various aluminafluorenes R-AlFlu [R = 1,2,4-$(t\mathrm{Bu})_3C_5H_2$ (92%; Fig. 1), $Ph_2(t\mathrm{Bu})Si$ (44%), 2-C_4H_3S (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 η^5-cyclopentadienide derivative, which is monomeric in the solid state, and the *t*Bu derivative, which crystallizes as a dimer.[16]

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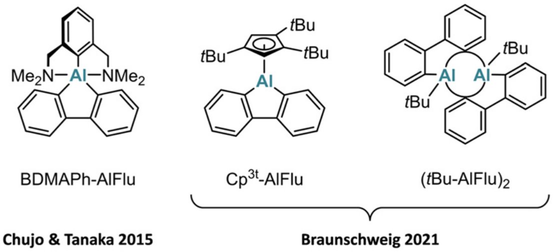
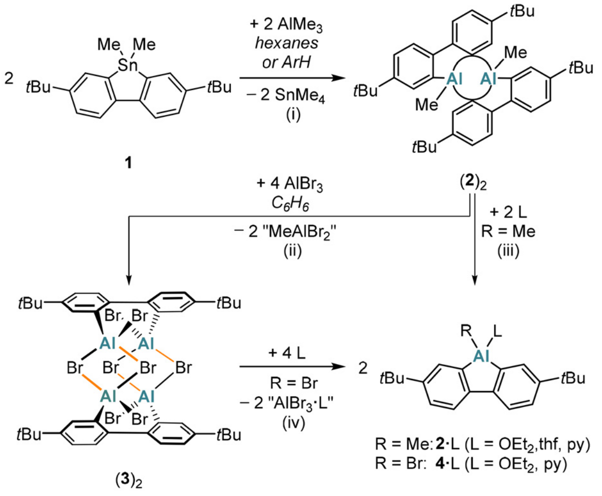


Fig. 1 Known mono- and dimeric 9-aluminafluorenes featuring 2,6-bis[(dimethylamino)methyl]phenyl (BDMAPh), 1,2,4-$(tBu)_3C_5H_2$ (Cp^{3t}), and *tert*-butyl (*t*Bu) substituents.



Scheme 1 Synthesis of donor-free $(\mathbf{2})_2$ through Sn/Al exchange between the 9-stannafluorene **1** and $AlMe_3$ (ArH: C_6H_6/toluene). The addition of $AlBr_3$ to $(\mathbf{2})_2$ furnishes $(\mathbf{3})_2$. Lewis bases (L: Et_2O, THF, or pyridine), cleave $(\mathbf{2})_2$ or $(\mathbf{3})_2$ into the monomeric adducts **2**·L or **4**·L. (i) Hexanes, 140 °C, 3 d (74% yield) or C_6H_6/toluene, 120 °C, 3 d (91% yield); sealed glass ampoule. (ii) C_6H_6, room temperature, 1 d (95% yield). (iii) $\mathbf{2}\cdot OEt_2$: in Et_2O, room temperature; **2**·thf: C_6D_6, room temperature; **2**·py: C_6H_6, room temperature (quantitative conversions). (iv) $\mathbf{4}\cdot OEt_2$: C_6H_6, room temperature (quantitative conversion); **4**·py: C_6D_6, room temperature (not isolated). Note: in $(\mathbf{3})_2$, four bonds were arbitrarily chosen as formally intermolecular (highlighted in orange) to facilitate the distinction between the monomers M and M′.

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-$(tBu)_3C_6H_2$). All our AlFlus were equipped with *t*Bu groups in their 2,7-positions to enhance solubility in non-polar solvents and to facilitate NMR-spectroscopic analysis.

Results and discussion

Syntheses

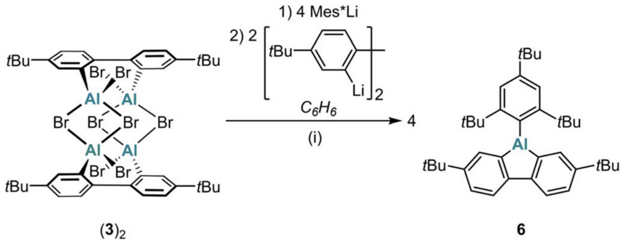
The base-free Me-AlFlu (**2**) was synthesized by heating the 9,9-dimethyl-9-stannafluorene **1** with 1 equiv. of $AlMe_3$ [17] in either hexanes or C_6H_6/toluene (Scheme 1). The only by-product formed is the volatile and relatively inert $SnMe_4$.[18,19] An advantage of using hexanes as the solvent is that the dimer $(\mathbf{2})_2$ precipitates in pure form already upon cooling the reaction mixture to room temperature (yield: 74%); when C_6H_6/toluene is employed, the yield of $(\mathbf{2})_2$ is higher (91%), but some further workup is required. In the presence of the donor molecules Et_2O, THF, or pyridine, $(\mathbf{2})_2$ is cleanly split into its constituting monomers to furnish the monoadducts $\mathbf{2}\cdot OEt_2$, **2**·thf, or **2**·py (Scheme 1).

Treatment of $(\mathbf{2})_2$ with 4 equiv. of $AlBr_3$ [17] in C_6H_6 results not only in quantitative AlMe/AlBr exchange but also in the incorporation of two $AlBr_3$ molecules to afford dimeric 2,2′-$(Br_2Al)_2$-1,1′-biphenyl [$(\mathbf{3})_2$, 95%; Scheme 1]. Upon addition of Et_2O to $(\mathbf{3})_2$ in C_6H_6, the donor adduct of Br-AlFlu, $\mathbf{4}\cdot OEt_2$, precipitates quantitatively as a colorless solid. In terms of yield, our overall synthesis cascade to $\mathbf{4}\cdot OEt_2$ improves upon the published protocol[16] by about 40 percentage points. Although pyridine can also reconstitute the AlFlu scaffold from $(\mathbf{3})_2$, it proved challenging to separate the target product **4**·py from by-products such as $[AlBr_2(py)_4][X]$ ([**5**][X]; X = Br^-, $AlBr_4^-$; Fig. S44 and S45†).

A particularly notable application of $(\mathbf{3})_2$ as a synthetic equivalent of donor-free Br-AlFlu is the preparation of Mes*-AlFlu (**6**): sequential addition of Mes*Li (4 equiv.) and 2,2′-dilithio-4,4′-di-*tert*-butyl-1,1′-biphenyl (2 equiv.) to $(\mathbf{3})_2$ in C_6H_6 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*-$(\mathbf{2})_2$; Fig. 2).[20] The individual monomers, M and M′, are linked by two Al⋯C interactions, resulting in two Al(1)⋯Al(1)′ bridging aryl rings (Ar_b) and two terminal rings (Ar_t), with bridging [C(11)] and terminal [C(21)] *ipso*-C atoms. The position of Ar_b 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 $(\mathbf{3})_2$ as a synthetic equivalent of the elusive Br-AlFlu. (i) C_6H_6, room temperature, 1 d (97% yield).

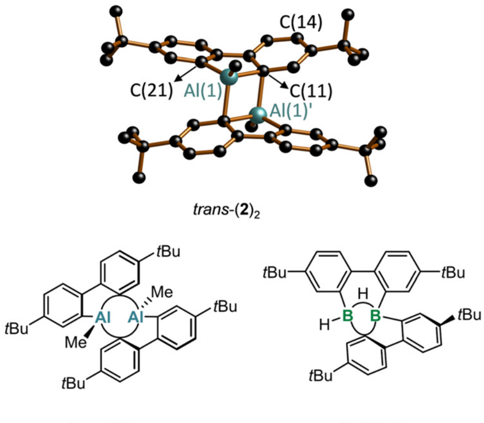


Fig. 2 Top: molecular structure of *trans*-(**2**)$_2$ in the solid state; H atoms omitted for clarity (C: black, Al: turquoise). Bottom: structural formulae of *trans*-(**2**)$_2$ and of the comparable 9-borafluorene dimer (H-BFlu)$_2$.

Al(1)′–C(11)–C(14) angle is significantly closer to 90° than the Al(1)–C(11)–C(14) angle can still be viewed as a remnant of the initial intermolecular Al⋯π(Ar) complex when the two heterofluorene 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$_b$ (1.382(5)–1.427(5) Å) is close to that in Ar$_t$ (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*-(**2**)$_2$ has very similar structural parameters to Braunschweig's (*t*Bu-AlFlu)$_2$,[16] while the comparable 9-borafluorene dimer (H-BFlu)$_2$ shows one B–(μ-H)–B two-electron–three-center bond and one B⋯B′-bridging aryl ring (the three other rings remain terminally bonded).[21]

X-ray crystallography reveals that the compound (**3**)$_2$ no longer contains the 9-aluminafluorene motif but instead forms a centrosymmetric 2,2′-(Br$_2$Al)$_2$-1,1′-biphenyl dimer (Fig. 3). The two Br$_2$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–(μ-Br)$_2$–Al(Br)R ring, is common not only for aluminum tribromide (R = Br) but also for numerous dibromo(organo)alanes.[22]

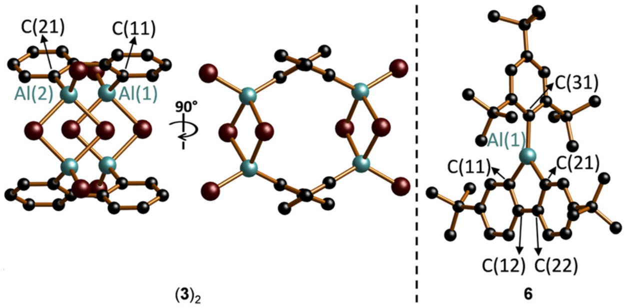


Fig. 3 Left: molecular structure of (**3**)$_2$ in the solid state, viewed from two different perspectives; *t*Bu-groups in the 2,7-positions of the biphenyl backbones and H atoms omitted for clarity. Right: molecular structure of **6** in the solid state; H atoms omitted for clarity (C: black, Al: turquoise,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

The 2,4,6-(*t*Bu)$_3$C$_6$H$_2$-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°, 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$_z$) orbital is positioned parallel or orthogonal to the vacant Al(p$_z$) orbital [Al(1)–C(11)/C(21)/C(31) = 1.9611(14)/1.9516(14)/1.9606(13) Å]. Within the five-membered AlC$_4$ 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),[23] 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$_6$H$_6$ (1.39 Å).[24] Taken together, this analysis of bond lengths suggests that the AlFlu moiety of **6** preserves two largely unperturbed Clar sextets within its two C$_6$H$_3$ fragments, with no indication of a delocalized (antiaromatic) π-system, nor any significant Al(1)═C(11)/C(21) double-bond character in the AlC$_4$ heterocycle.

The donor adducts **2**·OEt$_2$, **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$_6$H$_3$–C$_6$H$_3$ units of **2**·py and **4**·py were found to differ by no more than 3σ (and much less for most bonds).[25] This observation again suggests that the vacant Al(p$_z$) orbital exerts no significant electron-withdrawing mesomeric effect on the π-electron system.

NMR analysis

At room temperature, **2** gives severely broadened ^{1}H NMR signals, providing limited diagnostic value (Tol-d_8; 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 ^{1}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 ^{13}C{^{1}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 ^{1}H NMR spectrum reveals one singlet at −0.67 ppm (6H), and two additional singlets at 1.47 and

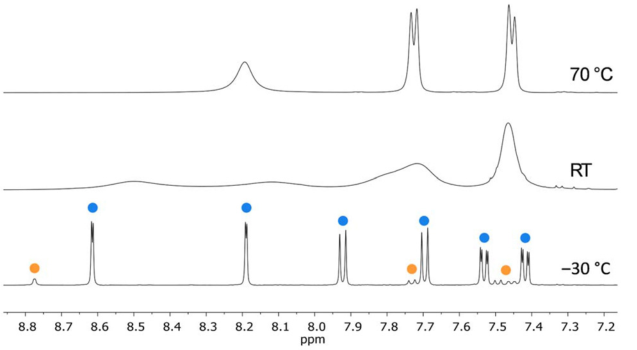


Fig. 4 Aromatic regions of ^1H NMR spectra of $(\mathbf{2})_2$ in Tol-d_8 (500.2 MHz). Top: 70 °C. Middle: room temperature. Bottom: −30 °C. 🔵: *trans*-$(\mathbf{2})_2$. 🟠: *cis*-$(\mathbf{2})_2$.

1.28 ppm (2 × 18H), assignable to two equivalent Al*Me* substituents and two pairs of non-equivalent *t*Bu groups, respectively. In the aromatic region, four doublets (4 × 2H; 2 × $^3J_{H,H}$ = 8.2 Hz, 2 × $^4J_{H,H}$ = 2.2 Hz) and two doublets of doublets (2 × 2H) are observed, indicative of two pairs of non-equivalent C_6H_3 fragments. In principle, these NMR features would align with both the molecular structure of the *cis*- and *trans*-$(\mathbf{2})_2$ dimer (as observed in the solid state). *Vice versa*, the minor signal set likely arises from *trans*- or *cis*-$(\mathbf{2})_2$. 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*-$(\mathbf{2})_2$ 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 $(\mathbf{2})_2$?

To address question (i), quantum-chemical calculations predict that the crystallographically characterized *trans*-$(\mathbf{2})_2$ is 1.6 kcal mol^{-1} more favorable in energy than *cis*-$(\mathbf{2})_2$ (Scheme S1†; experimental value, determined at −30 °C from the proton-integral values of the minor/major component: $\Delta G°$ = 0.7 kcal mol^{-1}). Furthermore, the relative proportion of the minor component increases with solvent polarity, consistent with the existing dipole moment of *cis*-$(\mathbf{2})_2$ (^1H NMR spectroscopic control; Table S1 and Fig. S1, S2†). Finally, the computed ^{13}C chemical shift values for *cis*/*trans*-$(\mathbf{2})_2$ align more closely with the assumption that the major component is *trans*-$(\mathbf{2})_2$ rather than *vice versa* (Tables S9–S11†). It is therefore safe to assume that the major component in an equilibrating *cis*/*trans*-$(\mathbf{2})_2$ mixture is the *trans* isomer.

Regarding question (ii), we note that the computed energy required for cleaving *trans*-$(\mathbf{2})_2$ into its constituting monomers is 19.4 kcal mol^{-1} (in CH_2Cl_2). In contrast, the computed energy barrier of the *cis*/*trans* interconversion of $(\mathbf{2})_2$ is only $\Delta G^‡$ = 14.8 kcal mol^{-1}, which agrees well with the value of ≈14.5 kcal mol^{-1} experimentally determined from the coalescence temperature (T_c) in conjunction with the maximum peak separation ($\Delta\nu$) in the slow-exchange limit (CD_2Cl_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, $(\mathbf{3})_2$ exhibited only extremely broadened signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra, providing no structural information.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of all adducts formed between our R-AlFlus 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, $^{13}C\{^1H\}$ NMR spectroscopy is also a valuable tool for mapping the π-charge density distribution in conjugated systems, as the shielding of a specific C(sp^2) atom depends linearly on the corresponding π-electron density at that position.[26] Given this background, we compared the ^{13}C chemical shift values of the C atoms constituting the C_6H_3–C_6H_3 fragment of **6** with those of the equivalent atoms in the corresponding fragments of the adducts **2**·OEt$_2$, **2**·thf, **2**·py, **4**·OEt$_2$, and **4**·py. Except for the Al-bonded *ipso*-C atoms, whose shift differences varied from δ(**6**)–δ(adduct) = 3.3 to −4.7 ppm without a systematic trend, the Δδ(^{13}C) values for all other structurally analogous C atoms were less than ±1.8 ppm. In other words, we found no evidence of an overall ^{13}C-deshielding effect or π-electron depletion in **6** that could be attributed to a mesomerically electron-withdrawing Al(sp^2) center.

$^{13}C\{^1H\}$ 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.[27] For **2**·py/**4**·py, our observations consistently indicate that Me-AlFlu is the stronger acid, comparable in this respect to BPh$_3$.[28] 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.[28] 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 $(\mathbf{2})_2$ through X-ray crystallography and VT NMR spectroscopy (Tol-d_8). The key to this success was the highly selective reaction between the 9,9-dimethyl-9-stannafluorene **1** and AlMe$_3$,[17,18] which proceeds in non-donor solvents and releases volatile SnMe$_4$ as the sole by-product. Unlike the bulky *tert*-butyl group in *t*Bu-AlFlu,[16] 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_2, thf, py). In terms of an umpolung 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).[10] The resulting product, $[\mathbf{2}]^{2-}$, could potentially serve as an Al-centered nucleophile – analogous to the $[\text{H-BFlu}]^{2-}$ dianion, which is a valuable B-centered nucleophile.[3,6,29]

Treatment of $(\mathbf{2})_2$ with $AlBr_3$ furnishes the 2,2′-$(Br_2Al)_2$-1,1′-biphenyl $(\mathbf{3})_2$. 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_2, py), in the presence of Lewis bases. The use of Mes*Li, which provides the extremely bulky, negatively charged Lewis base $[\text{Mes*}]^-$, grants unprecedented access to three-coordinate, monomeric aluminafluorenes, specifically Mes*-AlFlu (**6**), *via* LiBr elimination. This reaction proves the utility of $(\mathbf{3})_2$ 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 π-electron withdrawing effect and does not mediate significant π-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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