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## Donor-free 9,10-dihydro-9,10-dialuminaanthracenes†

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Despite their promising potential, e.g., as ditopic, cooperatively binding Lewis acids, 9,10-dihydro-9,10-dialuminaanthracenes (DAA- $R_2$ ; R: terminal Al-bonded substituent) have remained unexplored for long due to the challenges in synthesizing the ligand-free species. We demonstrate that DAA- $Me_2$  is accessible via the reaction of 1,2-( $Me_3Sn$ ) $_2C_6H_4$  with  $AlMe_3$ , producing volatile  $SnMe_4$  as the sole byproduct. In non-coordinating solvents and in the solid state, DAA- $Me_2$  exists as a dimer (DAA- $Me_2$ ) $_2$ . Treatment of (DAA- $Me_2$ ) $_2$  with 4 equiv.  $AlBr_3$  cleaves the dimer, leads to quantitative Me/Br exchange, and forms the double  $AlBr_3$  adduct DAA- $Br_2 \cdot (AlBr_3)_2$ . Removal of  $AlBr_3$  with 2,2'-bipyridine gives free DAA- $Br_2$ , which also dimerizes in the absence of bases to form (DAA- $Br_2$ ) $_2$ . (DAA- $Me_2$ ) $_2$  and (DAA- $Br_2$ ) $_2$  readily react with mono- (e.g., pyridine) or ditopic Lewis bases (e.g., potassium pyrazolide) to afford *trans*-diadducts or triptycene-type frameworks. Upon addition of [ $nBu_4N$ ]Br, DAA- $Br_2 \cdot (AlBr_3)_2$  undergoes selective cleavage of Al-C bonds to produce the  $Br^-$  chelate complex of 1,2-( $Br_2Al$ ) $_2C_6H_4$ , a valuable synthon for 1,2-dideprotonated benzenes.

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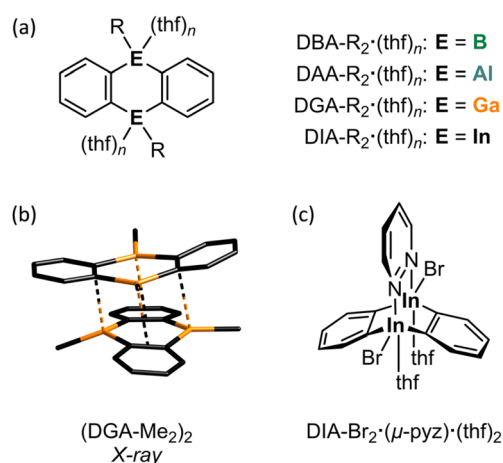
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## Introduction

The incorporation of p-block elements other than carbon into polycyclic aromatic hydrocarbons ('heteroatom doping') has emerged as a powerful tool for imparting new and valuable chemical and physical properties to these compounds.<sup>1</sup> Notable examples are 9,10-dihydro-9,10-diboraanthracenes (DBAs; Fig. 1a, E = B), which have found wide-ranging applications,<sup>2</sup> including their use as fluorophores<sup>3</sup> or homogeneous catalysts.<sup>4</sup> To further enhance the utility of DBAs, various substituted derivatives have been developed,<sup>5,6</sup> the B-doped acene scaffold has been expanded by benzannulation,<sup>7</sup> and additional heteroatoms (such as N, O, and S) have been introduced into the delocalized  $\pi$  system.<sup>8</sup>

Significantly less attention has been given to what is arguably the most impactful modification: the exchange of the B atoms for their higher homologues.<sup>9,10</sup> While a few anthracenes containing Al (DAAs),<sup>11,12</sup> Ga (DGAs),<sup>11,13</sup> or In (DIAs)<sup>11,14–18</sup> at the 9,10-positions are known, these compounds are typically isolated as their Lewis-base adducts, which inherently diminishes the desired reactivity. As an example, the synthesis of DAA- $Me_2 \cdot (thf)_n$  according to Bickelhaupt *et al.*<sup>11</sup> uses  $MeAlCl_2$

(ref. 19) and  $[Mg(thf)(o-C_6H_4)]_4$ , prepared from  $[Hg(o-C_6H_4)]_3$ ,<sup>20,21</sup> in THF;<sup>11,22</sup> DGA- $Me_2 \cdot (thf)_n$  and DIA- $Me_2 \cdot (thf)_n$  were synthesized in a similar manner (Fig. 1a, E = Al, Ga, or In;  $n \geq 2$ ).<sup>11</sup> The solubility requirements of the  $Mg^{2+}$  reagent necessitate the use of THF, which inevitably precludes the formation of ligand-free heteroanthracenes. Also in the synthesis of the octafluorinated congener of DAA- $Me_2 \cdot (thf)_n$ , where 1,2-( $Me_3Sn$ ) $_2C_6F_4$  and  $Me_2AlCl$  are employed as starting materials, the cyclocondensation of the initially formed intermediate into the target product must be



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Fig. 1 (a) General structures of thf adducts of heteroanthracenes (E = B, Al, Ga, or In). (b) Solid-state structure of (DGA- $Me_2$ ) $_2$  with all H atoms omitted for clarity. (c) Triptycene-type structure of DIA- $Br_2 \cdot (\mu-pyz) \cdot (thf)_2$ , where pyz = pyridazine.

initiated by adding THF.<sup>12</sup> Donor-free DGA-R<sub>2</sub> is accessible from 1,2-(ClHg)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and GaR<sub>3</sub> in *p*-xylene (R = Me, Et; 140 °C, 3 h).<sup>13</sup> This protocol, however, poses considerable risks due to the toxic or pyrophoric precursors and particularly the extremely harmful byproduct HgR<sub>2</sub>, which is released in 4 equivalents. DGA-R<sub>2</sub> dimerizes *via* Ga... $\pi$  interactions or Ga-C<sub>b</sub>-Ga two-electron three-center bonds (2e3c; C<sub>b</sub>: bridging C atom),<sup>23</sup> with (DGA-Me<sub>2</sub>)<sub>2</sub> (Fig. 1b) and (DGA-Et<sub>2</sub>)<sub>2</sub> having distinctly different molecular structures in the solid state (see below).

Moving on to In offers novel perspectives for several reasons: (i) due to the 'inert-pair effect', In(i) halides are more stable and easier to handle than their Al(i) or Ga(i) counterparts. Consequently, [Hg(*o*-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]<sub>3</sub> in THF can conveniently be reacted with InBr in a combined transmetallation/redox reaction to furnish DIA-Br<sub>2</sub>·(thf)<sub>4</sub> and elemental Hg, which is a significantly less concerning byproduct compared to HgMe<sub>2</sub> mentioned earlier.<sup>14</sup> (ii) Due to its larger atomic radius, each In site in DIA-Br<sub>2</sub> can accommodate two Lewis bases within a trigonal-bipyramidal ligand sphere, instead of just one. Given the increasing significance of coordination networks and microporous solids,<sup>24,25</sup> it is noteworthy that DIA-Br<sub>2</sub>·(thf)<sub>4</sub>, when combined with rigid, ditopic Lewis bases such as 1,4-diazine, has been used to self-assemble molecular stairs and ladders.<sup>16</sup> When 1,2-diazine (pyridazine, pyz) is offered to DIA-Br<sub>2</sub>·(thf)<sub>4</sub> instead of 1,4-diazine, the system switches to a chelating mode, leading to the formation of a triptycene-type structure DIA-Br<sub>2</sub>·( $\mu$ -pyz)·(thf)<sub>2</sub> (Fig. 1c).<sup>17</sup> This outcome points to the potential application of DIA-Br<sub>2</sub>·(thf)<sub>4</sub> as a homogeneous Lewis acid catalyst with cooperating heteroatoms.<sup>18</sup>

Herein, we present efficient access routes to the first donor-free 9,10-dihydro-9,10-dialuminaanthracenes (DAA-Me<sub>2</sub>)<sub>2</sub>, (1)<sub>2</sub>, and (DAA-Br<sub>2</sub>)<sub>2</sub>, (2)<sub>2</sub>, which exist as dimers in non-coordinating solvents and in the solid state. We further describe selective reactions of (1)<sub>2</sub> and (2)<sub>2</sub> with (i) mono- and bidentate N- or O-Lewis bases and (ii) the Lewis acid AlBr<sub>3</sub>.<sup>19</sup> Beyond their intriguing electronic structures, these compounds hold promise as preorganized, ditopic Lewis acids<sup>26</sup> and rare *ortho*-dimetallated benzene building blocks for organic synthesis.

## Results and discussion

### Syntheses

A classical protocol for the synthesis of DBA-X<sub>2</sub> is based on reactions between 1,2-(Me<sub>3</sub>E)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and BX<sub>3</sub> in toluene, *n*-hexane, or under solvent-free conditions (E = Si, Sn; X = Cl, Br).<sup>3a,d,5</sup> To extend this approach to the synthesis of DAAs with the aim to avoid the use of [Hg(*o*-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]<sub>3</sub> and coordinating solvents, we explored whether 1,2-(Me<sub>3</sub>E)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> could also serve as a suitable *o*-phenylene source in the present case. Eisch *et al.* reported that the reaction of the corresponding stannane with AlCl<sub>3</sub> in toluene gives 1,2-(Cl<sub>2</sub>Al)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.<sup>27</sup> However, a serious drawback is that the Me<sub>3</sub>SnCl byproduct remains firmly complexed with the aryl alane, resulting in an inseparable polymeric ion pair. Although using AlMe<sub>2</sub>Cl somewhat mitigated this issue – yielding a weaker electron-pair acceptor in 1,2-(Me<sub>2</sub>Al)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> – the Me<sub>3</sub>SnCl could still not be completely removed.<sup>27</sup> Considering modified approaches, we noted that the tetrafluoro

species 1,2-(Me<sub>3</sub>Sn)<sub>2</sub>C<sub>6</sub>F<sub>4</sub> reacts with Me<sub>2</sub>AlCl to form dimeric [1,2-(Cl(Me)Al)<sub>2</sub>C<sub>6</sub>F<sub>4</sub>]<sub>2</sub> and SnMe<sub>4</sub> (rather than Me<sub>3</sub>SnCl).<sup>28</sup> This suggested that starting with AlMe<sub>3</sub> (ref. 19) could prevent the formation of difficult-to-remove chlorostannanes altogether. Indeed, when 1,2-(Me<sub>3</sub>Sn)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (ref. 29) is treated with an equimolar amount of AlMe<sub>3</sub> in hexanes at elevated temperatures (150 °C, 3 d, sealed glass ampoule), SnMe<sub>4</sub> is released and cyclocondensation to the heteroanthracene occurs (Scheme 1). The dimeric product (1)<sub>2</sub> precipitates in pure form from the reaction mixture upon cooling to room temperature (yield: 76%); (1)<sub>2</sub> is highly soluble in C<sub>6</sub>H<sub>6</sub>, toluene, CHCl<sub>3</sub>, or CH<sub>2</sub>Cl<sub>2</sub>. The volatile byproduct SnMe<sub>4</sub> can be easily removed and, in principle, subjected to a redistribution reaction with SnCl<sub>4</sub> to regenerate<sup>30</sup> the Me<sub>3</sub>SnCl required for the synthesis of the starting material 1,2-(Me<sub>3</sub>Sn)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. In the presence of Lewis-basic ligands such as tetrahydrofuran (THF) or pyridine (py), (1)<sub>2</sub> is cleaved into the monomers, which are obtained as the diadducts 1·(thf)<sub>2</sub> (ref. 11) and 1·(py)<sub>2</sub> (Scheme 1). Of particular interest is the coordination behavior of 1 toward bidentate ligands, as this reveals the potential of 1 as a preorganized, ditopic Lewis acid. Initial exploratory investigations with pyridazine (pyz) led to the following observations: (i) the room-temperature <sup>1</sup>H NMR spectrum of an equimolar mixture of (1)<sub>2</sub> and pyz in THF-*d*<sub>8</sub> showed only minor changes of  $\pm$  0.03 ppm compared to the chemical shift values of the signals of 1·(thf)<sub>2</sub> and free pyz. (ii) Upon gas-phase diffusion of *n*-hexane into such mixtures, however, the heteroadduct 1·(pyz)(thf) crystallized, which features a pyz ligand that coordinates to one Al site through one of its N atoms, while a thf ligand coordinates to the other Al site (Fig. S41†).<sup>16,31</sup> In contrast, the boron and indium congeners DBA-H<sub>2</sub> and DIA-Br<sub>2</sub> show triptycene-type structures with E-( $\mu$ -pyz\*)<sub>2</sub>-E' moieties

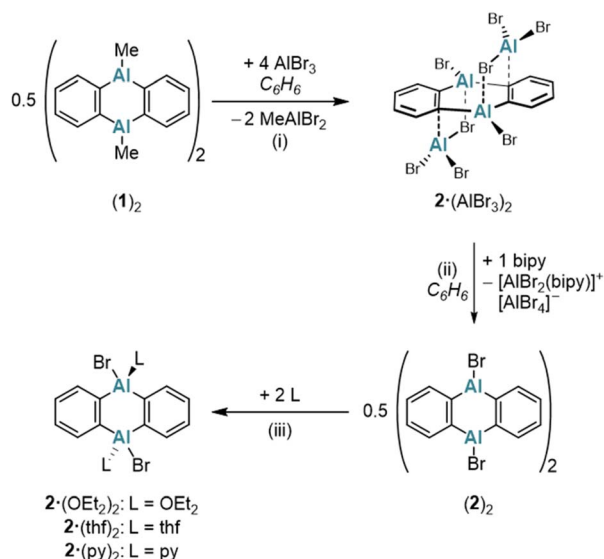


**Scheme 1** The Sn/Al exchange reaction of 1,2-(Me<sub>3</sub>Sn)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> with AlMe<sub>3</sub> leads to the formation of donor-free (1)<sub>2</sub>. In the presence of Lewis bases (THF or py), (1)<sub>2</sub> is cleaved into the monomeric diadducts 1·(thf)<sub>2</sub> or 1·(py)<sub>2</sub>. The heterotriptycene K[1·(μ-pz)] is synthesized by reacting (1)<sub>2</sub> with Kpz. (i) Hexanes, 150 °C, 3 d, sealed glass ampoule. (ii) 1·(thf)<sub>2</sub>: in THF, room temperature; 1·(py)<sub>2</sub>: 2.1 equiv. py, C<sub>6</sub>H<sub>6</sub>, room temperature. (iii) 1 equiv. Kpz, THF, room temperature.



under comparable conditions in the solid state ( $E = B, In$ ;  $pyz^* = \text{benzo}[d]\text{pyridazine}$ ).<sup>17,32</sup> A THF-stable heterotriptycene motif can also be imposed on **1** by using the negatively charged, five-membered pyrazolato ( $[pz]^-$ ) ligand instead of the neutral, six-membered  $pyz$  ligand (*cf.*  $K[1 \cdot (\mu\text{-}pz)]$ ; Scheme 1).

To expand the variety of donor-free DAAs, it would be desirable to obtain also an Al-halogenated derivative DAA- $X_2$ . One possibility is to start from  $(1)_2$  and to achieve the necessary Me/X exchange by the reaction with  $AlX_3$ .  $AlBr_3$  was selected for this purpose because, unlike  $AlCl_3$ , it is soluble in the non-coordinating solvent  $C_6H_6$ . Treatment of  $(1)_2$  in  $C_6H_6$  with 8 equiv.  $AlBr_3$  leads to the instantaneous precipitation of  $2 \cdot (AlBr_3)_2$ , which is generally poorly soluble in non-coordinating solvents (Scheme 2). If only 4 equiv.  $AlBr_3$  per  $(1)_2$  are used instead of 8 equiv., a structure similar to  $2 \cdot (AlBr_3)_2$  is obtained, but with the non-bridging Br positions partially occupied by Me groups [ $DAA-R_2 \cdot (AlBrR_2)_2$ ;  $R = \text{Me}$  or  $\text{Br}$ ; according to X-ray crystallography, Fig. S42†]. Having achieved the aimed-for Me/Br exchange on **1**, the next task is to remove the two coordinating  $AlBr_3$  molecules from  $2 \cdot (AlBr_3)_2$  to obtain the free heteroanthracene. The chelating ligand 2,2'-bipyridine (bipy) proved to be ideally suited for this purpose: In  $C_6H_6$ , the addition of 1 equiv. bipy to  $2 \cdot (AlBr_3)_2$  resulted in the formation of  $(2)_2$  after heating and sonication. NMR spectroscopy on the supernatant revealed exclusively signals of the free, dimeric  $(2)_2$ , with no detectable bipy resonances (Scheme 2). We assume that the solid consists of species such as  $[AlBr_2(\text{bipy})][AlBr_4]$ , which, due to their salt-like nature, quantitatively separate from the target product.<sup>33</sup> Similar to  $(1)_2$ ,  $(2)_2$  is converted to  $2 \cdot (OEt_2)_2$ ,



**Scheme 2** The addition of  $AlBr_3$  to  $(1)_2$  results in the immediate precipitation of  $2 \cdot (AlBr_3)_2$ . Donor-free  $(2)_2$  is formed by the reaction of  $2 \cdot (AlBr_3)_2$  with bipy. In the presence of Lewis-bases ( $Et_2O$ , THF, or py),  $(2)_2$  is cleaved into the monomeric diadducts  $2 \cdot (OEt_2)_2$ ,  $2 \cdot (\text{thf})_2$ , or  $2 \cdot (\text{py})_2$ . (i) 4 equiv.  $AlBr_3$  per monomeric unit **1**,  $C_6H_6$ , room temperature, 1 d. (ii) 1 equiv. bipy,  $C_6H_6$ , 70 °C, 2 h, sonication. (iii)  $2 \cdot (OEt_2)_2$ : exc.  $Et_2O$ ,  $C_6H_6$ , room temperature;  $2 \cdot (\text{thf})_2$ : 2.1 equiv. THF,  $C_6H_6$ , room temperature;  $2 \cdot (\text{py})_2$ : 2.1 equiv. py,  $C_6H_6$ , room temperature.



**Scheme 3** The reaction of  $2 \cdot (AlBr_3)_2$  with  $[nBu_4N]Br$  yields the 1,2-dialumino-substituted benzene derivative  $[nBu_4N][3]$ . (i) 2 equiv.  $[nBu_4N]Br$ ,  $C_6H_6$ , 70 °C, 1.5 h, sonication.

$2 \cdot (\text{thf})_2$ , or  $2 \cdot (\text{py})_2$  upon addition of  $Et_2O$ , THF, or py, respectively (Scheme 2).

In another attempt to generate the  $AlBr_3$ -free  $(2)_2$ ,  $Br^-$  ions were used as alternative ligands instead of bipy. However, the reaction between  $[nBu_4N]Br$  (2 equiv.) and  $2 \cdot (AlBr_3)_2$  in  $C_6H_6$  furnished the 1,2-dialumino-substituted benzene derivative  $[nBu_4N][3]$ , rather than the initially expected products  $(2)_2$  and  $[nBu_4N][AlBr_4]$  (Scheme 3). Formally,  $2 \cdot (AlBr_3)_2$  is a dimer of 1,2- $(Br_2Al)_2C_6H_4$ , and  $[3]^-$  is the  $Br^-$  adduct of this ditopic, chelating Lewis acid (a comparable  $F^-$  adduct of the boron-based ditopic Lewis acid 1,2- $[(C_6F_5)_2B]_2C_6F_4$  has been characterized by NMR spectroscopy).<sup>34</sup>

### Solid-state structures

**Note:** Whenever we want to indicate individual DAA units in a molecular structure, we will hereafter use dashed lines for any interactions between a respective unit and the rest of the molecule. This is not intended to imply any judgements about the nature or strength of the interaction.

The crystal of  $(2)_2$  is a true racemate of discrete chiral  $C_2$ -symmetric units, best described as dimers of DAA- $Br_2$  molecules (Fig. 2a; note that the corresponding B-doped DBA- $Br_2$  is monomeric in the solid state<sup>3a</sup>).<sup>35</sup> The  $Al_2C_4$  cores of the individual monomers adopt distorted, shallow boat conformations [dihedral angles  $Al(1)C(1)C(7)/C(1)C(2)C(7)C(8) = 35.3(2)^\circ$ ,  $Al(2)C(2)C(8)/C(1)C(2)C(7)C(8) = 6.0(2)^\circ$ ]. The Al atoms of monomer M (or M') interact with two C(*ipso*) atoms, both bonded to the same Al atom of monomer M' (or M), as schematically depicted in Fig. 3a. The corresponding bond lengths  $Al(1')-C(2)$  and  $Al(2')-C(8)$  measure 2.261(3) and 2.191(3) Å, respectively; the angles including these Al-C bonds and the  $C(2) \cdots C(5)$  or  $C(8) \cdots C(11)$  vectors across the corresponding phenylene rings are  $Al(1')-C(2) \cdots C(5) = 101.9(1)$  and  $Al(2')-C(8) \cdots C(11) = 111.6(2)^\circ$ . In summary,  $(2)_2$  forms a cage structure with six-membered rings serving as the base and top, and one four-membered, two five-membered, and one six-membered ring(s) constituting the belt (Fig. S44 and S45†). To facilitate the analysis of  $M \cdots M'$  interactions in  $(2)_2$ , we assume that each bridging  $C_b$  is  $sp^2$ -hybridized, neglecting contributions from Wheland-type<sup>36</sup> electronic structures with  $sp^3$ -hybridized  $C_b$  atoms. Within this model, an Al' atom from monomer M' can engage with monomer M either through the unhybridized  $p_z$  orbital of  $C_b$  ( $Al \cdots \pi(\text{Ar})$  interaction) or *via* the  $Al-C_b$   $\sigma$  bond (to generate a  $2e3c$  bond). Of the four  $M \cdots M'$  interactions present



Fig. 2 Molecular structures in the solid state: (a)  $(2)_2$ ; (b)  $(1)_2^A$  viewed as a dimer of DAA monomers M, M' (left) and as a tetramer of equivalent  $C_6H_4-Al(Me)$  fragments (right); (c)  $2 \cdot (AlBr_3)_2$  shown as a  $AlBr_3$  diadduct of  $DAA-Br_2$  (left) and viewed from the side (right). H atoms omitted for clarity. C: black, Br: brown, Al: turquoise.



Fig. 3 Schematic representations to illustrate the intermonomer contacts in (a)  $(2)_2$ , (b)  $(DACHd)_2$ , and (c)  $(1)_2$ .

in  $(2)_2$ , two are pairwise identical. Intrinsic bond orbitals (IBOs) of the remaining two distinct interaction types are illustrated in Fig. S52.† Both types have contributions from  $Al \cdots \pi(Ar)$  and  $2e3c$  interactions, but to varying degrees: Based on the interpretation of IBOs, Wiberg bond indices (WBIs), and Mayer bond orders (MBOs), the two  $M \cdots M'$  interactions within the four-membered ring of the belt appear to be dominated by  $2e3c$  bonding, whereas the other two intermonomer bonds are predominantly of the  $Al \cdots \pi(Ar)$  type (Fig. S52 and S53†).  $(2)_2$  can be compared with the dimeric 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene  $[(DACHd)_2]$ , where the two non-planar monomers are rotated by  $90^\circ$  relative to each other and are linked *via* four  $Al \cdots \pi(olefin)$  bonds (Fig. 3b). The distance between two Al atoms of different monomers within the same dimer is about  $3.00 \text{ \AA}$ , which was regarded as 'relatively short'; according to *ab initio* calculations,  $Al \cdots Al'$  interactions contribute to the stability of the system.<sup>37</sup> Indeed, the dimers remained intact under mass spectrometry conditions up to temperatures of  $140^\circ \text{C}$ .<sup>38</sup> In  $(2)_2$ , the  $Al \cdots Al'$  distances range from  $2.717(2) \text{ \AA}$  (across the four-membered ring) to  $3.635(2) \text{ \AA}$  (across the six-membered ring). A third dimeric structural motif comparable to  $(2)_2$  and  $(DACHd)_2$  is observed in  $(DGA-Me_2)_2$  (Fig. 1b): the primary distinction among these three cases lies in the degree of rotation of the monomer units relative to each other.<sup>13</sup>

$(1)_2$  crystallizes with three crystallographically independent molecules in the unit cell, each displaying approximate  $D_{2d}$  symmetry  $[(1)_2^A - (1)_2^C]$ .<sup>39</sup> Since their key structural parameters

are very similar (Fig. S35†), only  $(1)_2^A$  will be discussed in detail. Although its molecular formula corresponds to a dimer of  $DAA-Me_2$ , the assignment of two distinct DAA units within the total ensemble is less unambiguous than in the case of  $(2)_2$ , owing to the higher symmetry of  $(1)_2^A$ . For the purposes of the discussion to follow, the six-membered rings containing  $Al(1)/Al(4)$  and  $Al(2)/Al(3)$  are defined as belonging to monomers M and M' (Fig. 2b, left; an alternative definition is possible but leads to the same conclusions). Both monomeric units exhibit twist-boat conformations. Unlike  $(2)_2$ , the Al atoms of monomer M (or M') in  $(1)_2^A$  interact with two diagonally opposite C(*ipso*) atoms attached to different Al atoms of monomer M' (or M) (cf. Fig. 3c). The respective 'intermonomeric' Al-C bond lengths range from  $2.100(2)$  to  $2.132(2) \text{ \AA}$ , which are shorter than those of  $(2)_2$ . While these findings are informative for the comparison of the solid-state structures of  $(1)_2$  and  $(2)_2$ , an alternative analysis of the  $(1)_2$  scaffold is more appropriate to account for its high symmetry: the cluster comprises four equivalent  $C_6H_4-Al(Me)$  fragments, each featuring a  $C(Ar)-Al$   $\sigma$  bond; the second deprotonated *o*-phenylene C atom bridges two additional Al atoms, forming an  $Al'-C_b-Al''$   $2e3c$  bond (Fig. 2b, right). Consequently, each Al vertex is tetracoordinated by C atoms. The  $Al_4$  core of  $(1)_2$  adopts a strongly distorted tetrahedral geometry with  $Al \cdots Al$  distances of av.  $2.666$  and av.  $3.611 \text{ \AA}$ . Overall, the framework of  $(1)_2$  resembles that of  $(DGA-Et_2)_2$  (ref. 13) and of the *o*-phenylene magnesium tetramer  $[Mg(thf)(o-C_6H_4)]_4$ , with the Al atoms replaced by Mg atoms and the Me substituents by thf ligands (Fig. S36 and S37†).<sup>21</sup> To conclude the discussion of structures  $(1)_2$  and  $(2)_2$ , we find it remarkable that both species prefer to form discrete dimers in a cluster-like arrangement rather than coordination polymers with  $Al-(\mu-Me/Br)_2-Al'$  bridges, as seen in  $Al_2Me_6$  (ref. 40) and  $Al_2Br_6$ ;<sup>41</sup> the diboraanthracene  $(DBA-H_2)_\infty$  is indeed polymeric *via*  $B-(\mu-H)_2-B'$  linkages in the solid state.<sup>42</sup> Furthermore, it is worth noting the following result from quantum chemical calculations (SMD( $C_6H_6$ )/ $\omega$ B97XD/def2-TZVPP//SMD( $C_6H_6$ )/ $\omega$ B97XD/def2-TZVPP): after Me/Br or Br/Me exchange, the resulting  $(1^{Br})_2$  or  $(2^{Me})_2$  remain minima on the potential-energy surface. For  $R = Me$ , the crystallographically observed structure  $(1)_2$  is more stable than  $(2^{Me})_2$  by  $4.9 \text{ kcal mol}^{-1}$ . Yet, for  $R = Br$ , structure  $(2)_2$  is less stable than  $(1^{Br})_2$  by  $3.5 \text{ kcal mol}^{-1}$ , in the absence of crystal-packing effects.<sup>43</sup>

In the  $C_i$ -symmetric compound  $2 \cdot (\text{AlBr}_3)_2$ , two  $\text{AlBr}_3$  moieties coordinate to opposite sides of the  $\text{DAA-Br}_2$  core, which consequently adopts a chair conformation (Fig. 2c).<sup>44</sup> Similar to  $(1)_2$ , the binding sites are two diagonally opposite *C(ipso)* atoms (*cf.* Fig. 3c). The respective bonds are relatively short ( $\text{Al}(2)-\text{C}(1) = 2.032(4) \text{ \AA}$ ), and the  $\text{C}(1)$  atoms are strongly pyramidalized ( $\text{Al}(2)-\text{C}(1) \cdots \text{C}(4) = 134.0(2)^\circ$ ,  $\text{Al}(1)-\text{C}(1') \cdots \text{C}(4') = 124.0(2)^\circ$ ). Each  $\text{Al}(2)-\text{C}(1)$  bond is reinforced by a Br atom that bridges the Al atoms of  $\text{DAA-Br}_2$  and  $\text{AlBr}_3$  ( $\text{Al}(1)-\text{Br}(2) = 2.449(1) \text{ \AA}$ ,  $\text{Al}(2)-\text{Br}(2) = 2.411(1) \text{ \AA}$ ). In summary, the largely symmetric  $\text{Al}(1) \cdots \text{Al}(1')$ -bridging mode of the phenylene ring in  $2 \cdot (\text{AlBr}_3)_2$  more closely resembles the situation in  $(1)_2^A$  than in  $(2)_2$ . Compound  $2 \cdot (\text{AlBr}_3)_2$  is formally the dimer of  $1,2-(\text{Br}_2\text{Al})_2\text{C}_6\text{H}_4$ . The related  $[1,2-(\text{Cl}(\text{Me})\text{Al})_2\text{C}_6\text{F}_4]_2$ , which was characterized by Gabbai *et al.* with X-ray diffraction, has a markedly different molecular structure: It features two stacked 1,2-phenylene rings, two distinct types of  $\text{Al} \cdots \text{Al}'$ -bridging  $\text{Cl}^-$  ions, and lacks any  $\text{Al}-\text{C}_b-\text{Al}$  2e3c bonds.<sup>28</sup>

The compound  $[n\text{Bu}_4\text{N}][3]$  is asymmetric in the solid state, although the anionic component approximates the  $C_{2v}$  point group (Fig. 4a).  $[3]^-$  can be described as a ditopic Lewis acid (*i.e.*,  $1,2-(\text{Br}_2\text{Al})_2\text{C}_6\text{H}_4$ ), where the two vicinally positioned Al sites cooperate in bonding to the same  $\text{Br}^-$  anion, with an average bond length of  $\text{Al}-(\mu\text{-Br}) = 2.443 \text{ \AA}$ . As expected, these bonds are longer than the Al-Br bonds to the terminal Br atoms, which range from  $2.282(2)$  to  $2.294(2) \text{ \AA}$ . When the bridging  $\text{Br}^-$  ion is excluded from consideration, the sum of angles within the remaining  $\text{AlBr}_2$  fragments averages  $343.7^\circ$ , which lies between the typical values of a planar ( $360^\circ$ ) and a tetrahedral geometry ( $328.5^\circ$ ). The endocyclic angles  $(\mu\text{-Br})-\text{Al}-\text{C}$  and  $\text{Al}-(\mu\text{-Br})-\text{Al}$  are *av.*  $101.8^\circ$  and  $90.7(1)^\circ$ , respectively.

In the crystal lattice,  $[\text{K}(\text{thf})_{1.5}][1 \cdot (\mu\text{-pz})]$  forms a one-dimensional coordination polymer, with  $[\text{K}(\text{thf})_2]^+$  and  $[\text{K}(\text{thf})_2]^+$  cations bonding simultaneously to phenylene rings of two different anions (Fig. S40†). The anion  $[1 \cdot (\mu\text{-pz})]^-$  represents a rare heterotriptycene with Al atoms at the bridgehead positions (Fig. 4b).<sup>45–47</sup> The Al-N bonds to the bridging pyrazolato ( $[\text{pz}]^-$ ) ring (*av.*  $1.973 \text{ \AA}$ ) are longer than the Al-N(pz) bonds in  $[\text{R}_2\text{Al}-(\mu\text{-pz})_2-\text{AlR}_2]$  ( $\text{R} = \text{Me}$ : *av.*  $1.921 \text{ \AA}$ , *t*Bu: *av.*  $1.929 \text{ \AA}$ )<sup>48</sup> or in bicyclic  $[\text{HAL}(\mu\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-CH}_2\text{N}t\text{Bu})\text{AlH}]$  (*av.*  $1.914 \text{ \AA}$ ).<sup>45</sup>

The monomeric complexes  $1 \cdot (\text{py})_2 \times \text{C}_6\text{H}_6$  and  $2 \cdot (\text{py})_2 \times \text{C}_6\text{H}_6$  are isostructural in the crystalline state and show planar,  $C_i$ -symmetric  $\text{DAA-R}_2$  units coordinated by two py ligands from

opposite sides (*trans* configuration;  $\text{R} = \text{Br}, \text{Me}$ ). Also, the thf diadducts  $1 \cdot (\text{thf})_2$  and  $2 \cdot (\text{thf})_2$  adopt *trans* configurations. Remarkably, the  $\text{OEt}_2$  ligands in the corresponding diadduct  $2 \cdot (\text{OEt}_2)_2$  are positioned in a *cis* arrangement in the solid state (full details are given in the ESI†).

### NMR analysis

For all molecules presented in this work, the  $^{27}\text{Al}$  NMR resonances were broadened beyond detection. NMR spectroscopic analysis was not possible for  $2 \cdot (\text{AlBr}_3)_2$  and  $[n\text{Bu}_4\text{N}][3]$ , due to their low solubility in all suitable solvents. In the cases of the  $\text{Et}_2\text{O}/\text{thf}/\text{py}$  diadducts of **1** and **2** as well as  $[\text{K}[1 \cdot (\mu\text{-pz})]]$  and  $(1)_2$ , the number of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals, their chemical shift values, and the integral ratios of the proton resonances were consistent with the (symmetry-averaged) molecular structures determined by X-ray analysis (full details are given in the ESI†).  $(2)_2$  is the only example that requires a more thorough consideration: Its solid-state structure has insufficient symmetry to align with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra obtained in solution ( $\text{C}_6\text{D}_6$ ), which show only two and three signals, respectively. There are two possible explanations for the observed NMR features: (i)  $(2)_2$  may dissociate in solution into the monomeric units **2**. (ii) The dimeric structure may persist but experience significant fluctuations due to librational motion of the monomers relative to each other, resulting in an average  $D_{2d}$  symmetry. A quantum-chemical analysis renders the conversion of  $(2)_2 \rightarrow 2 \times 2$  unlikely, as it would be endergonic with  $\Delta G = 28.0 \text{ kcal mol}^{-1}$  (which is in line with the shortened  $\text{Al} \cdots \text{Al}'$  distances discussed in the crystallographic section). In contrast, any activation barrier to be overcome during the librational motion does not exceed  $\Delta G^\ddagger = 3.0 \text{ kcal mol}^{-1}$  (Scheme S1†), which makes option (ii) more probable.

### Potential of $[n\text{Bu}_4\text{N}][3]$ as synthesis equivalent of the 1,2-dideprotonated benzene nucleophile

The arylaluminum species described here, while interesting in their own right, also hold potential as *ortho*-dimetallated starting materials for organic synthesis. Such nucleophilic building blocks, which complement their ubiquitous, polarity inverted *o*-dihalogenated analogues, are just as valuable as they are difficult to access.<sup>49</sup> A major challenge is to avoid the unwanted formation of benzyne on the way to  $1,2\text{-M}_2\text{C}_6\text{H}_4$  ( $\text{M} = \text{Li}, \text{MgBr}$ ). The key starting material for most *o*-dimetallated benzenes therefore still remains *o*-phenylene mercury,  $[\text{Hg}(\text{o-C}_6\text{H}_4)]_3$ , which is obtained from  $1,2\text{-Br}_2\text{C}_6\text{H}_4$  and sodium amalgam in a process that takes several days.<sup>50,51</sup>  $[\text{Hg}(\text{o-C}_6\text{H}_4)]_3$  can subsequently be converted into the organolithium, -magnesium, or -zinc species  $1,2\text{-Li}_2\text{C}_6\text{H}_4$ ,  $[\text{Mg}(\text{thf})(\text{o-C}_6\text{H}_4)]_4$ , or  $[\text{Zn}(\text{thf})_2(\text{o-C}_6\text{H}_4)]_n$  [ $n = 2$  (crystalline state) or 3 (solution)] by reaction with metallic Li,<sup>50,52</sup> Mg,<sup>21</sup> or Zn,<sup>53</sup> respectively; the required reaction times range from half a day to weeks. Taken together, the widespread use of *o*-dimetallated benzenes is hindered not only by the well-recognized environmental and health concerns associated with organomercury compounds but also by the apparently poor reproducibility in the synthesis of  $[\text{Hg}(\text{o-C}_6\text{H}_4)]_3$ : while Wittig claimed to have obtained yields of 50%,

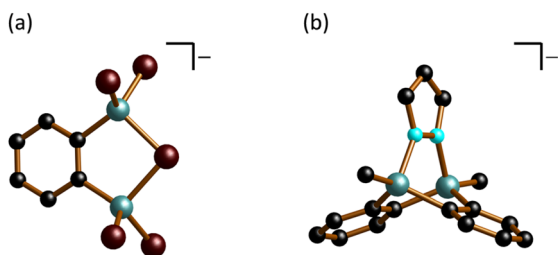


Fig. 4 Molecular structures in the solid state: (a)  $[n\text{Bu}_4\text{N}][3]$ ; (b)  $[\text{K}(\text{thf})_{1.5}][1 \cdot (\mu\text{-pz})]$ . Counter cations and H atoms omitted for clarity. C: black, Br: brown, Al: turquoise, N: cyan.



**Scheme 4** Synthesis of 1,2-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> or DBA-Br<sub>2</sub> by the reaction of [nBu<sub>4</sub>N][3] and Me<sub>3</sub>SiCl or BBr<sub>3</sub>, respectively. (i) 2 equiv. Me<sub>3</sub>SiCl, C<sub>6</sub>D<sub>6</sub>, room temperature, 1 d. (ii) Excess BBr<sub>3</sub>, room temperature.

Massey explicitly stated that, despite ‘10 years of experience in the field’, they consistently observed yields as low as 1–2%.<sup>50,51</sup> Even though, in favorable cases, the *in situ* generation of nucleophilic intermediates from 1,2-Br<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and Mg can be achieved in the presence of the electrophile, resulting in satisfactory yields (as demonstrated in the synthesis of 1,2-(Me<sub>3</sub>Sn)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>),<sup>29</sup> there is a persistent demand for efficient access to additional *o*-dimetallated benzenes.

Recognizing the potential of our aryl aluminium compound [nBu<sub>4</sub>N][3] as an ideal candidate to address this need, we conducted several proof-of-concept experiments. For this purpose, we selected target compounds with published synthesis protocols that require prolonged reaction times and/or high temperatures (Scheme 4). This allows us to identify potential advantages of our new starting material through direct comparison: For instance, the reaction between [nBu<sub>4</sub>N][3] and 2 equiv. Me<sub>3</sub>SiCl in C<sub>6</sub>D<sub>6</sub> furnished the disubstituted benzene 1,2-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> at room temperature after 1 d (quantitative conversion according to NMR spectroscopy; Fig. S25†). In contrast, the established synthesis of the same product from 1,2-Br<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, Mg, and Me<sub>3</sub>SiCl *via* a Grignard-type reaction in THF requires stirring for 2 d, with the temperature gradually increasing from 0 °C to room temperature.<sup>54</sup> Particularly noteworthy is the conversion of [nBu<sub>4</sub>N][3] with neat BBr<sub>3</sub>, which instantaneously affords the corresponding 9,10-dihydro-9,10-diboraanthracene already at room temperature (Scheme 4). The traditional route to DBA-Br<sub>2</sub> *via* 1,2-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and BBr<sub>3</sub> requires heating to 120 °C for 6 d.<sup>34,55</sup>

Already this selection of straightforward conversions highlights the potential of [3]<sup>−</sup> as a synthetic equivalent of 1,2-dideprotonated benzene. Despite its poor solubility in non-polar solvents like C<sub>6</sub>H<sub>6</sub>, it still undergoes smooth heterogeneous reactions. The products, however, are nicely soluble in C<sub>6</sub>H<sub>6</sub>, allowing for easy separation from any unreacted starting material and Al-containing byproduct salts, which greatly simplifies the purification process.

## Conclusions

Anthracenes incorporating Group 13 elements at the 9,10-positions have significant potential as redox-active systems and versatile ditopic Lewis acids, offering a broad range of applications. Their planar structures expose the reactive heteroelement sites, while the rigid 1,2-phenylene bridges bring these sites into close proximity, promoting acid–base binding cooperativity. Additionally, the delocalized  $\pi$  systems enable

electronic communication between the dopant atoms. While 9,10-dihydro-9,10-diboraanthracenes have been extensively studied and higher homologues have received some attention, 9,10-dihydro-9,10-dialuminaanthracenes (DAA-R<sub>2</sub>; R: terminal Al-bonded substituent) have remained almost entirely unexplored, despite Al being by far the most earth-abundant Group 13 element.

In this work, we synthesized DAA-Me<sub>2</sub> (1) in the absence of stabilizing ligands, resulting in its dimerization through Al $\cdots\pi$ (Ar) interactions to form (1)<sub>2</sub>. Despite dimerization, (1)<sub>2</sub> serves as an effective synthesis equivalent for ‘free’ DAA-Me<sub>2</sub>, as it readily reacts with mono- or bidentate Lewis bases to afford *trans*-diadducts such as 1·(py)<sub>2</sub>, or triptycene-type structures like K[1·(μ-pz)] (py: pyridine; Hpz: pyrazole). Notably, (1)<sub>2</sub> can be cleaved into its monomers not only by Lewis bases but also by the strong Lewis acid AlBr<sub>3</sub>, which displaces the original DAA-Me<sub>2</sub> partner by establishing new Br<sub>3</sub>Al $\cdots\pi$ (Ar) bonds and Al–Br–Al’ bridges in its place. This reaction also exchanges all Al-bonded Me substituents of DAA-Me<sub>2</sub> for Br atoms, leading to 2·(AlBr<sub>3</sub>)<sub>2</sub>, the double AlBr<sub>3</sub> adduct of DAA-Br<sub>2</sub> (2), which can also be viewed as a dimer of 1,2-(Br<sub>2</sub>Al)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. The donor-free (2)<sub>2</sub> can be liberated from 2·(AlBr<sub>3</sub>)<sub>2</sub> using 2,2’-bipyridine. In contrast, treatment of 2·(AlBr<sub>3</sub>)<sub>2</sub> with Br<sup>−</sup> ions splits two Al–C bonds to give the adduct [nBu<sub>4</sub>N][3], in which one molecule of 1,2-(Br<sub>2</sub>Al)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> chelates one Br<sup>−</sup> ion. The anion [3]<sup>−</sup> has proven to be an excellent synthon for a 1,2-dideprotonated benzene. Such compounds are rare but of exceptional synthetic value; the broader utility of [3]<sup>−</sup> in this regard is currently under investigation in our laboratories.

## Data availability

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

## 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.

## Conflicts of interest

There are no conflicts to declare.

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