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## Redox non-innocent bis-silylene aluminium complexes with a carborane backbone†

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The redox non-innocent bis-silylenyl *ortho*-carborane ligands [Si<sup>II</sup>(CC<sub>cage</sub>)Si<sup>II</sup>] (CC<sub>cage</sub> = *o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, Si<sup>II</sup> = ArC(N<sup>t</sup>Bu)<sub>2</sub>Si; Ar = C<sub>6</sub>H<sub>5</sub>, *p*-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>), with their particular chelating and electronic properties, have been employed for the synthesis of new donor-stabilized Si<sup>II</sup> → Al<sup>III</sup> complexes, potential precursors to low oxidation state aluminium complexes. Due to the redox non-innocence of the carborane backbone, [Al<sub>2</sub><sup>+</sup>] complexes with three ligand oxidation states were characterized: with neutral and radical anionic *closo*- as well as dianionic *nido*-C<sub>2</sub>B<sub>10</sub> cores. Reduction at the aluminium center could also be enacted with potassium/naphthalene leading to {K[Si<sup>II</sup>(CC<sub>cage</sub>)Si<sup>II</sup>]Al(C<sub>10</sub>H<sub>8</sub>)} derivatives from [1 + 4] cycloaddition reaction. The mechanism of this dearomatization reaction is proposed to occur *via* the formation of transient low oxidation state aluminium intermediates (radicals and/or aluminylenes) that are trapped by naphthalene.

## Introduction

Strong  $\sigma$ -donors are an important tool in the synthesis of zero-valent main group element complexes, which have garnered significant interest in the last decade.<sup>1–4</sup> Complexes of isolobal molecular ions supported by neutral ligands also rely on strong  $\sigma$ -donors for stabilization. Not only do such low valent compounds have interesting structures but they also possess unique potential applications. For example, they can act as ligands with unique bridging coordination modes, form otherwise difficult-to-realize molecules through oxidation, and have potential as novel single-source precursors for the synthesis of functional materials.<sup>5–9</sup> Among the group 13 elements, the first zero oxidation state B<sub>*n*</sub> (*n* = 1, 2, 4) compounds were isolated in recent years, mainly with carbene ligands.<sup>10–14</sup> Of these, the rather  $\pi$ -accepting cAACs have also been applied to the synthesis of donor-stabilized aluminium compounds, such as an extraordinary mononuclear Al<sup>I</sup> hydride reported by Braunschweig and coworkers, that also features significant diradical character at the carbene-C centers.<sup>15–19</sup> Whilst no zero oxidation state aluminium compounds have been proposed yet, the first Al<sup>I</sup> (aluminylene) cation **I** was synthesized in 2022 by Crossing and co-workers, with only

neutral AlCp\* substituents.<sup>20</sup> Related Ga<sup>I</sup> ion complexes with various donor ligands (*e.g.* PPh<sub>3</sub>, NHC) have been accessed from the useful salt complex [Ga(C<sub>6</sub>H<sub>5</sub>Me)<sub>2</sub>]<sup>+</sup>[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]<sup>−</sup> since 2010.<sup>21,22</sup> In 2017, the first B<sup>I</sup> (borylene) cation **II** (X = CO) was reported by Xie and Lin using a chelating bis-silylene ligand.<sup>23</sup> We have demonstrated that bis-silylenes can act as effective  $\sigma$ -donor ligands, enabling access to monoatomic zero oxidation state group 14 and 15 complexes.<sup>5,24–26</sup> Such compounds are capable of facile activation of small molecules such as H<sub>2</sub>, NH<sub>3</sub>, 9-BBN, CO and CO<sub>2</sub>.<sup>27–30</sup> Silylenes are defined as divalent silicon species, isoelectronic with singlet carbenes.<sup>31,32</sup> Amidinato-silylenes in particular can be fixed to many spacer molecules, establishing a family of highly adaptable  $\sigma$ -donating chelating ligands.<sup>33–36</sup>

The area of low oxidation state silicon–aluminium chemistry is still in its infancy with the first examples of such compounds published in 2022–2023.<sup>37–40</sup> Last year, we reported the transient pincer bis-silylene-supported aluminylene **III** (Ar = Ph), that dimerizes to give an Si<sub>2</sub>Al<sub>2</sub> heterocycle (Fig. 1).<sup>41</sup> Compound **III** could also be trapped as an iron(0) complex, from which we inferred its structure using density functional theory (DFT) calculations. Later, the isolable aluminylene **III** (Ar = Mes) was characterized by Mo and coworkers and agreed with our calculations.<sup>42</sup> We also investigated the neutral bis-silylene [Si<sup>II</sup>(Xant)Si<sup>II</sup>] (Xant = 9,9-dimethylxanthene) for the synthesis of aluminylene complexes, but found it unsuitable for the synthesis of aluminylene compounds except as an Fe<sup>0</sup> adduct **IV**.<sup>41,43</sup>

We turned our interest towards the bis-silylene [Si<sup>II</sup>(CC<sub>cage</sub>)Si<sup>II</sup>] **1a** based on an *ortho*-icosahedral carborane spacer [CC<sub>cage</sub> = *o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, Si<sup>II</sup> = LSi, L = PhC(N<sup>t</sup>Bu)<sub>2</sub>].<sup>44,45</sup> **1a** is a stronger  $\sigma$ -donor and  $\pi$ -acceptor ligand than [Si<sup>II</sup>(Xant)Si<sup>II</sup>], which has been demonstrated experimentally by their differing reactivity

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† Electronic supplementary information (ESI) available. CCDC 2418300 (compound **2b**), 2418301 (compound **3**), 2418298 (compound **4a**), 2418297 (compound **4b**), 2418302 (compound **5b**). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5sc01104c>



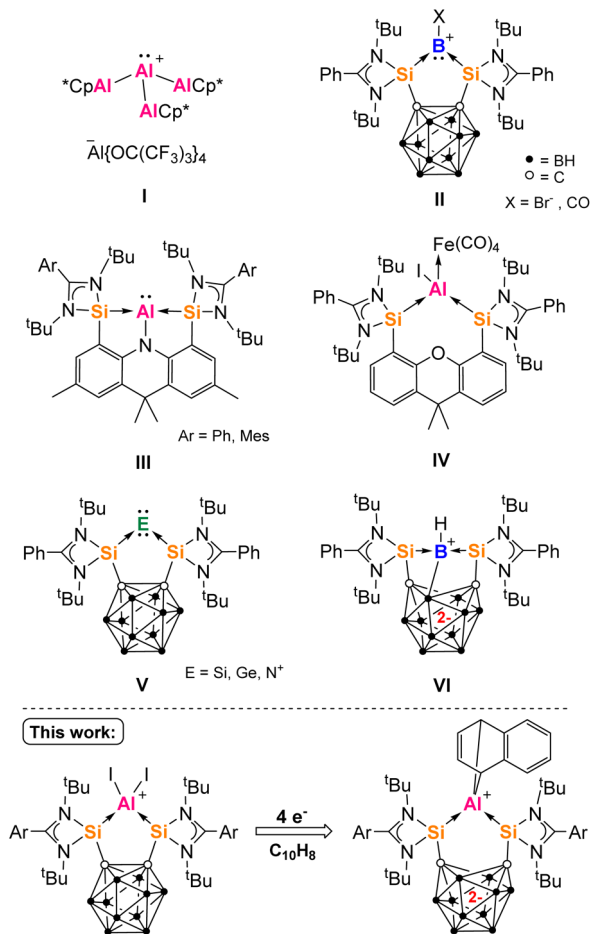


Fig. 1 An Al(I) complex supported only by neutral ligands (I), examples of group 13–15 bis-silylene complexes (II–VI) and the new bis-silylene aluminium complexes of this work.

towards CO and P<sub>4</sub>, and relates to the inductive withdrawing effect of carborane substituents.<sup>27,46–49</sup> **1a** is also highly rigid, has a fixed smaller bite angle and generates more stable five-membered rings on complexation to a single atom. Furthermore, (C<sub>2</sub>B<sub>10</sub>)-functionalized compounds are capable of reversibly accepting one or two electrons to give radical anion or dianion complexes respectively.<sup>50,51</sup> Accordingly, the two-electron reduction product  $\{(\text{K}^+(\text{THF})_4)_2[\text{Si}^{\text{II}}(\text{CC}_{\text{cage}})\text{Si}^{\text{II}}]^{2-}\}_n$  has been isolated.<sup>52</sup> We have used **1a** to furnish some exceptional redox non-innocent complexes of Si<sup>0</sup>, Ge<sup>0</sup> and N<sup>I</sup> **VII**, with other chelating carboranyl tetrylenes since being investigated.<sup>48,52–58</sup>

Complexes **II** and **V** (Fig. 1) are capable of redox-induced valence tautomerism or electron transfer (ET), rare for main group element complexes. This manifests as the unexpected flow of electrons in or out of the carborane cage away or towards the element center, often accompanied by E–E coupling.<sup>59,60</sup> For example, upon two-electron reduction, **II** (X = Br<sup>-</sup>) becomes **VI** (Fig. 1).<sup>61</sup> In this work, we investigated the suitability of **1** for the synthesis of primarily donor-stabilized aluminium compounds, that could potentially act as precursors to low oxidation state aluminium complexes. We were first able to isolate Al<sup>III</sup> complexes of **1** with three different ligand oxidation states.

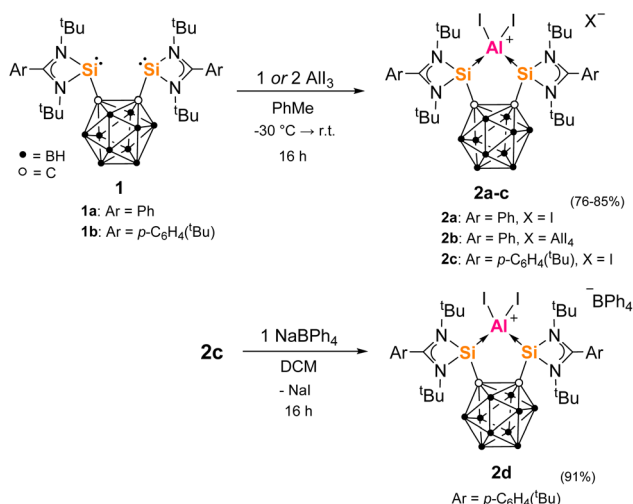
Further reduction with K(C<sub>10</sub>H<sub>8</sub>) leads to 1,4-naphthalene derivatives of Al<sup>III</sup>, which points to the existence of largely unknown low-valent aluminium intermediates.

## Results and discussion

### Generation of bis-silylenyl carborane aluminium complexes

Many metallocarborane derivatives containing aluminium have been described since the 1970s.<sup>62–65</sup> Despite chelating ligands with carborane scaffolds being well known, only recently did a report of an aluminium complex bearing a carborane backbone appear, specifically a *nido*-C<sub>2</sub>B<sub>9</sub>-based salen [NOON] ligand.<sup>66,67</sup> We were able to prepare a series of *closo*-C<sub>2</sub>B<sub>10</sub>-based aluminium complexes straightforwardly using the bis-silylenes **1a** and **1b** (Scheme 1). Thus, adduct **2a** was produced as colorless precipitate in 79% yield from the reaction of one molar equiv of **1a** with one molar equiv AlI<sub>3</sub> in toluene at low temperature. **2a** exhibits very poor solubility in common aprotic solvents and decomposes instantly when dissolved in THF at room temperature. Its <sup>1</sup>H and <sup>1</sup>H/<sup>13</sup>C-coupled NMR spectra could therefore only be recorded in *o*-dichlorobenzene-D<sub>4</sub>. The marginally more soluble ion pair **2b** was prepared similarly in 85% yield using two molar equivs of AlI<sub>3</sub>. A few colorless crystals of **2b** were grown from Et<sub>2</sub>O solutions that were suitable for an scXRD analysis. Dissolution of **2b** in THF led to an orange solution and almost clean reformation of the free bis-silylene **1a** detected by <sup>1</sup>H NMR.

The cation of **2b** contains a symmetrical C<sub>2</sub>Si<sub>2</sub>Al five-membered ring with an Si–Al–Si angle of 89.07(8)°, as determined by the rigid geometry of **1a**, and with an average Si–Al bond length 2.493(3) Å (Fig. 2); the carborane C–C bond measures 1.729(8) Å. Compared to **2b**, the isostructural complex  $\{[\text{Si}^{\text{II}}(\text{Xant})\text{Si}^{\text{II}}]\text{AlI}_2\}^+\text{I}^-$  has a much larger Si–Al–Si bond angle of 123.01(5)° but a similar average Si–Al bond length of 2.463(13) Å.<sup>41</sup> Additionally, we later prepared the <sup>t</sup>Bu-functionalized analogue **1b**  $\{[\text{Si}^{\text{II}}(\text{CC}_{\text{cage}})\text{Si}^{\text{II}}]\}$  with Si<sup>II</sup> = L/Si, L' =



Scheme 1 Synthesis of complexes **2a–c** from bis-silylenes **1a–b** and AlI<sub>3</sub> and subsequent reaction of **2c** with NaBPh<sub>4</sub> to give **2d**.



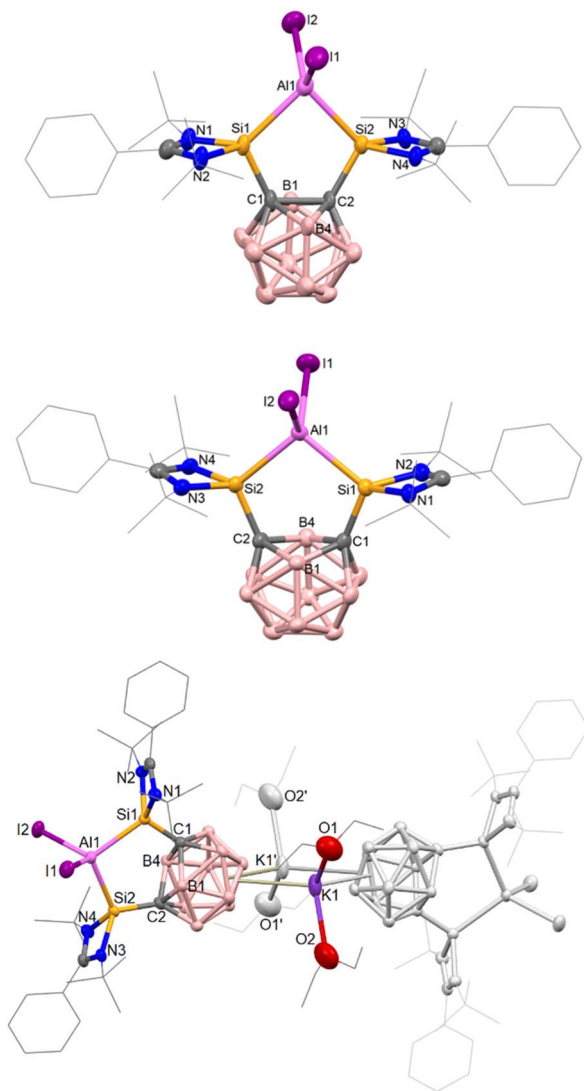
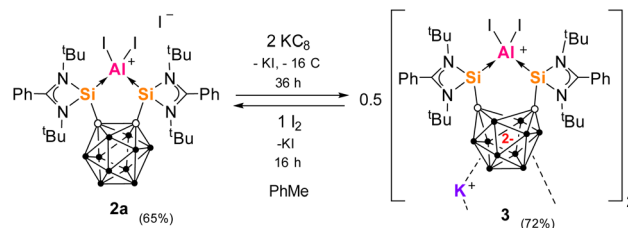


Fig. 2 Molecular structures of the  $\text{AlI}_2^+$ -containing complexes of **2b** (top,  $\text{All}_4^-$  counterion omitted), **4a** (middle) and  $[\mathbf{3}(\text{Et}_2\text{O})_4]$  (bottom) as determined by scXRD. Thermal ellipsoids have been set at 50% probability. Hydrogens and solvent molecules have been omitted and selected groups are shown in wireframe for clarity.

$p\text{-}^t\text{BuC}_6\text{H}_4\text{C}(\text{N}^t\text{Bu})_2$ .<sup>68</sup> The aluminium iodide adduct **2c** was prepared in the same way as **2a** and isolated as a pale-yellow precipitate in 76% yield (Scheme 1). **2c** was characterized by multinuclear NMR spectroscopy in dichloromethane (DCM) before slowly decomposing overnight. Akin to **2a**, **2c** is also unstable in THF and still poorly soluble in acetonitrile. Where anion exchange reaction of **2a** had failed using  $\text{NaBPh}_4$  and  $\text{AgOTf}$  when attempted in various solvents, we conveniently found that the iodide counterion of **2c** could be exchanged simply in DCM. The reaction of one molar equiv **2c** with one equiv  $\text{NaBPh}_4$  in DCM gives **2d** as a pale-yellow solid in 91% yield. **2d** is stable in DCM solution for weeks, whilst **2c** is not. This indicates that the iodide counterion is not purely a spectator ion and potentially aids the relatively slower



Scheme 2 Two-electron reduction of **2a** with  $\text{KC}_8$  to give dimer **3** and the reverse oxidation reaction with  $\text{I}_2$  to re-form **2a**.

decomposition process to give free bis-silylene (compared to **2a** in THF) which would go on to react with DCM (as known for silylenes).<sup>69</sup>

### Redox chemistry of the $o\text{-C}_2\text{B}_{10}$ -cage in bis-silylenyl carborane $\text{M}^{\text{III}}$ complexes ( $\text{M} = \text{Al}, \text{Ga}$ )

We first probed  $\text{KC}_8$  as a reducing agent, which has been successfully applied in the reduction steps to produce both **II** and **III** (Fig. 1). Reaction of one molar equiv **2a** with a large excess  $\text{KC}_8$  (5 equivs) in toluene for 36 h leads to a bright red solution (Scheme 2). Dark pink needle-shaped crystals grew from the filtrate and were revealed by scXRD to be the zwitterionic dipotassium salt  $[\mathbf{3}(\text{C}_6\text{H}_5\text{Me})_2]$ , isolated in 72% yield. **3** was characterized by multinuclear NMR spectroscopy in THF but decomposed significantly within 2 hours.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy confirmed a change of environment for the  $\text{B}_{10}$  cage atoms with four signals at  $\delta_{\text{B}} = -3.2, -7.2, -16.6$  and  $-32.6$  ppm [for **2c**  $\delta_{\text{B}} = 1.9, -3.5, -8.7$  and  $-13.2$  ppm ( $\text{CD}_2\text{Cl}_2$ )].

Crystals of  $[\mathbf{3}(\text{Et}_2\text{O})_4]$  suitable for scXRD analysis could be grown from  $\text{Et}_2\text{O}$  solutions at low temperature (Fig. 2). In the 'back-to-back' dimeric structure of **2**, the two  $\text{K}^+$  ions sit in-between the two carborane cages with the  $\text{AlI}_2^+$  moieties facing outward. The reduction of the  $o$ -carborane moiety is apparent from the increased  $\text{C}\cdots\text{C}$  distance. **3** features a  $nido\text{-C}_2\text{B}_{10}$  cluster core with a  $\text{C}\cdots\text{C}$  distance of 2.59 Å compared to 1.730(2) in **2b**. Accompanying this change, the  $\text{Si}\text{-Al}\text{-Si}$  angle increases slightly from 89.08(7) to 101.99(6)°. Other metal complexes of **1a**, such as the  $\text{Si}^{\text{I}}\text{-Si}^{\text{I}}$  and  $\text{Ge}^{\text{I}}\text{-Ge}^{\text{I}}$  dimers (derived from **V**, Fig. 1) or dipotassium compound, have one-dimensional chain structures with  $\text{K}^+$  ions also bridging the dianionic  $nido$ -carborane moieties.<sup>52,54</sup> The scXRD and  $^{11}\text{B}$  NMR data indicate that during reduction, two electrons are accepted by the  $\text{C}_2\text{B}_{10}$  cage whilst the oxidation state of aluminium is unchanged.

**3** can also be formed in an alternate synthesis, where **1a** is reduced first with two equivs  $\text{KC}_8$  in THF (to give the dipotassium salt complex *in situ*) then reacted with one molar equiv  $\text{AlI}_3$  at low temperature. We propose that in the reaction of **2a** with  $\text{KC}_8$ , reduction begins with one electron being accepted by the unsaturated amidinato ligand which then moves to the carborane backbone to give a carborane radical anion intermediate. A similar mechanism for reduction of ligand **1a** was demonstrated by DFT calculations investigating the reduction



of silylone **V**.<sup>52</sup> The initial formation of a transient aluminium radical intermediate is also possible. The formation of **3** contrasts with the formation of the related complexes of  $B^I$  **II** and  $Si^0$ ,  $Ge^0$  **V**, demonstrating how the *closo*- $C_2B_{10}$  cluster is reduced preferentially over  $Al^{III}$  but not over  $Si^{II}$ ,  $Ge^{II}$  or  $B^{III}$  under these reaction conditions.

We then investigated oxidation reactions of **3** that would release the two electrons from the *nido*-carborane cage. Test reactions with one or two equivs of  $AgOTf$  or  $FcPF_6$  ( $Fc$  = ferrocenium) in THF led to complex NMR spectra of unknown decomposition products. This can at least be in part explained by the instability of **2** in THF. **3** also decomposed in *o*-difluorobenzene (*o*-DFB), exhibited by a color change to dark brown (due to the formation of dark green precipitate). With polar solvents unsuitable, we used elemental iodine as an oxidizing agent. Thus, 0.5 molar equivs of dimer **3** were allowed to react with one molar equiv  $I_2$  in toluene, re-forming **2a** in 65% isolated yield (Scheme 2). Attempts to determine the redox potentials of **2c** in DCM by cyclic voltametric measurement were unsuccessful. Additionally, no  $K^+$  sequestration of **3** could be achieved with 18-crown-6 (18-c-6) or [2.2.2]-cryptand in THF. **3** also showed no reactivity towards  $NaBPh_4$  or  $CsBPh_4$ . This lack of reactivity for **3** demonstrates that the  $K^+$  and  $I^-$  ions are strongly bound within the complex, to the carborane dianions and cationic aluminium centers respectively. In contrast, the structurally related  $N^I$  cation complex  $\{K[Si^{III}(CC_{cage})Si^{III}]N\}$  can form an ion-separated pair with 18-c-6 which is stable and undergoes one- and two-electron oxidation of the carborane cage with  $AgOTf$ .<sup>53</sup>

From the reaction of one molar equiv of **2a** with a smaller excess of  $KC_8$  (2.5 equivs), the radical anion **4a**, proposed as an intermediate in the formation of **3**, was isolated in 24% yield (Scheme 3). The dark red crystals of **4a** were suitable for scXRD analysis. The paramagnetic nature of **4a** was evident from its NMR silence. EPR measurements at room temperature and below identified a strong isotropic radical signal at  $g = 2.007$  and line width of 23.4 G, which suggests a delocalized carborane-based radical; no hyperfine coupling could be resolved (Fig. 3). In the solid-state structure of **4a**, the  $C \cdots C$  carborane distance is increased similarly to **3**, at 2.43 Å (Fig. 2). The smaller carborane core opening agrees with the acceptance of one electron by the cluster to give a carboranyl radical anion. The geometry and bond distances around the Al center in **4a** are generally similar to those in **3**. Reduction of **4a** with excess of

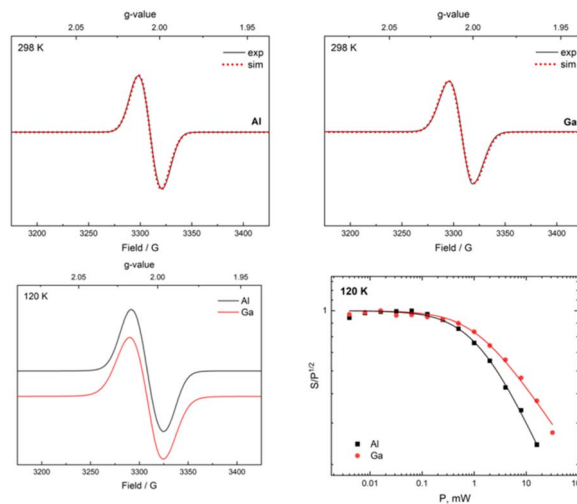


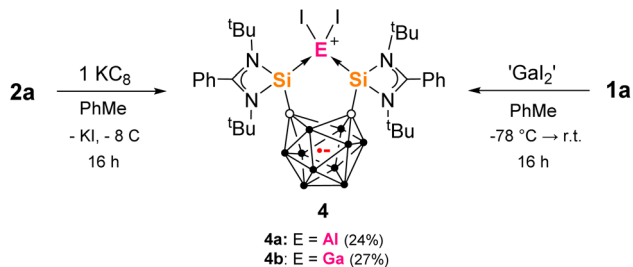
Fig. 3 EPR data of the radical complexes **4a** (top, left) and **4b** (top, right) at room temperature. Cryogenic EPR spectra at 120 K (bottom, left) and the corresponding power saturation of **4a** and **4b** (bottom, right).

$KC_8$  (2.4 molar equivs) in  $Et_2O$  also produces **3**, additionally confirming **4a** as a likely intermediate in the formation of **3** from **2a**.

We were also able to isolate the gallium analogue **4b** from the reaction of **1a** with 1.4 molar equivs of ' $GaI_2$ ' in toluene at low temperature (Scheme 3). ' $GaI_2$ ' is a solid prepared from the reaction of elemental gallium and iodine in a 1 : 2 ratio.<sup>70,71</sup> **4b** could be isolated as a mixture of dark red and yellow crystals from red-orange toluene solutions in 27% yield. Radical **4b** has an almost identical EPR signature to **4a** with a strong isotropic radical signal at  $g = 2.008$  and line width of 23.1 G, with no hyperfine coupling (Fig. 3). **4b** and its water adduct [**4b** +  $(H_2O)_5$ ] were additionally detected as molecular ions in mass spectrometry.

The scXRD analyses confirmed that both crystal types of **4b** contain the same molecular structure. The yellow-colored crystals of **4b** gave better metric data and the experimental bond lengths and angles were found to be almost identical to those of **4a** (Fig. S36†). The different colored crystals of **4b** result from different crystal packing and systems [yellow – orthorhombic, red – monoclinic]. The darker-colored crystals form predominantly from more concentrated solutions. In this two-fold reaction, the bis-silylenyl *o*-carborane accepts one electron and becomes bound to a  $GaI_2^+$  fragment in the final product. The exact mechanism of how this might happen is unclear but overall, the ' $GaI_2$ ' acts as a source of the  $GaI_2^+$  radical.

The EPR spectra of **4a** and **4b** recorded at 120 K verified that their isotropic radical signals are conserved at 120 K, exhibiting a small but significant difference in power saturation. The line shape, power and temperature dependency of **4a** and **4b** determined by EPR strongly suggest that the spin is delocalized in the  $C_2B_{10}$  core. Whilst the spin of other paramagnetic aluminium complexes is typically ligand-based, such compounds tend to exhibit hyperfine coupling.<sup>16,72–75</sup>



Scheme 3 Formation of the bis-silylenyl-carborane radical complexes **4a** and **4b** from **2a** and  $KC_8$  or **1a** and ' $GaI_2$ ' respectively.



With **2a**, **3** and **4a** in hand, we have established an interconvertible redox series of carborane-derived aluminium complexes, with three oxidation states characterized. This series based on **2a** is unique for featuring an inorganic (carborane) electron storage unit (rather than aromatic/organic) that is not directly coupled or bonded to the Al center. The aluminum cation center is additionally only attached to the compound through donor bonds. There is a growing body of aluminium complexes with non-innocent ligands that can access several ligand oxidation states, all with charged N- or O-ligands, many of which are catalytically active.<sup>76–79</sup> These complexes typically affect proton-coupled (PC)-ET or proton transfer (PT) reactions rather than ‘pure’ ET reactions, of which the few examples are rather diverse.<sup>77,80–82</sup> We have demonstrated that carboranyl aluminium derivatives can act as reversible electron acceptors and that with further study have potential in catalytic ET reactions.

### Trapping of low valent aluminium with $K(C_{10}H_8)$ **3**

Thereafter, we wondered if further reduction of **3** would lead to a reduced aluminium center. With **3** in hand, we probed its reduction with excess  $KC_8$ , also in the presence of 1,3-dienes,  $PCy_3$  or  $AlCl_3$ . This only gave complicated mixtures resulting from significant decomposition. Therefore, we tested the reaction of 0.5 equivs of dimer **3** with two molar equivs  $K(C_{10}H_8)$  in THF in an NMR tube. The reagents reacted instantaneously on solvation forming a dark red solution and colourless precipitate. The  $^1H$  NMR spectrum showed the formation of one equiv of free  $C_{10}H_8$  and one major species **5a** (Scheme 4), with no decomposition observed after 3 weeks. In the scaled-up reaction, **5a** was isolated as orange crystals from toluene in 22% yield. The  $^1H$  NMR spectrum of **5a** strongly suggested that it was a 1,4-naphthalene derivative, with a characteristic set of multiplets (dd) at  $\delta_H = 3.05, 6.38, 6.80$  and  $6.93$  ppm. We attributed the low isolated yield of **5a** to its very poor solubility in inert solvents (except THF). Therefore, we undertook a one-pot reaction with the potentially more soluble analogue **2c**. One equiv of **2c** was reacted with four molar equivs of  $K(C_{10}H_8)$  in THF at low temperature (Scheme 4). This furnished the expected product **5b**, which was isolated as orange crystals from

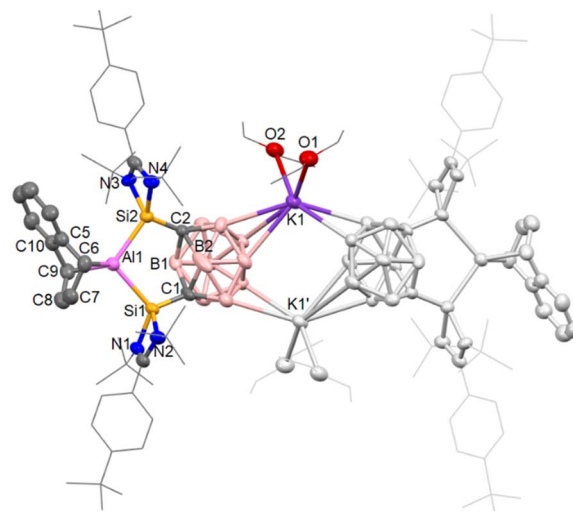
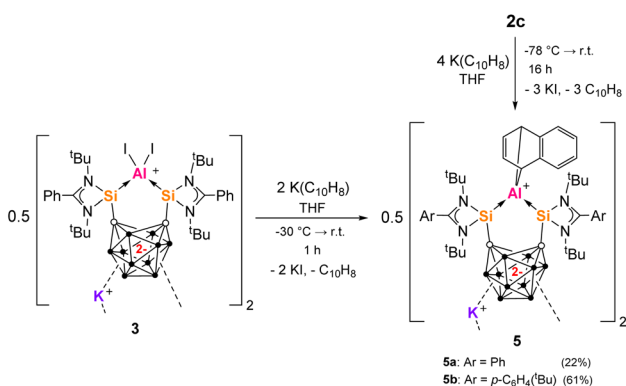


Fig. 4 Molecular structure of  $[5b(Et_2O)_4]$ . Thermal ellipsoids have been set at 50% probability. Hydrogens and solvent molecules have been omitted and selected groups are shown in wireframe for clarity.

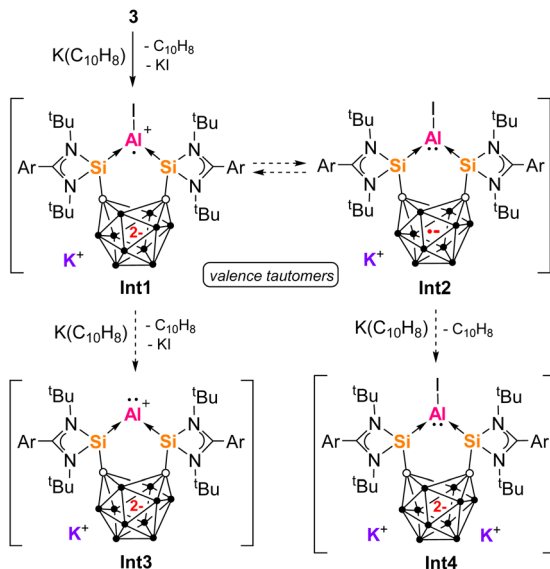
$Et_2O$  in 61% yield. **5a** and **5b** were characterized by multinuclear NMR spectroscopy in THF and benzene, respectively.

Akin to **3**, **5a** did not react with [2.2.2]-crypt, which might have aided the crystallization of single crystals of **5a**. Eventually, after many crystallization attempts, suitable crystals of **5b** from  $Et_2O$  solution were obtained and measured by scXRD analysis (Fig. 4). The angles and distances measured for **5b** are consistent with **3**. The carborane C...C distance is maintained at approximately 2.60 Å as well as the Si–Al–Si bite angle at  $100.95(5)^\circ$ . The  $Al(C_{10}H_8)$  unit manifests as two Al–C bonds of lengths of 2.056(4) and 2.066(4) Å, with a C–Al–C angle of  $77.49(17)^\circ$ . The  $^{29}Si$  NMR spectrum of **5b** revealed two resonances at  $\delta_{Si} = 29.5$  and 39.1 ppm. The non-equivalence of the  $^{29}Si$  nuclei can be explained by the orientation of the naphthalene group. **5a** and **5b** show consistent NMR and structural data with other  $Al(C_{10}H_8)$ -complexes resulting from  $Al^I$  activation of aromatics.<sup>83–86</sup> This contrasts with the cooperative silylene-aluminylene reactivity of the pincer aluminylene **III**, which activates aromatic 2-methylquinoline through a 1,4-addition across the Al–Si bond instead.<sup>42</sup>

The naphthalene-derived products **5a** and **5b** indicate a [1 + 4] cycloaddition reaction involving low oxidation state Al intermediates. Multiple reaction pathways are possible. Since **2c** and **3** both generate the same product **5**, we propose that **3** is also an intermediate in the reaction of **2c** (Scheme 4). One-electron reduction of **3** with  $K(C_{10}H_8)$  would generate **Int1** with an aluminium radical cation center first (Scheme 5). Due to presence of two electrons in the carborane backbone, one electron could be transferred to the Al center to give iodoaluminylene **Int2** with an Al-based electron pair. **Int1** and **Int2** are valence tautomers or electromers. **Int1** and **Int2** would react with a second equivalent of  $K(C_{10}H_8)$  to generate aluminylene species **Int3** and **Int4** respectively. It is additionally possible than **Int1** undergoes a radical cycloaddition with  $[C_{10}H_8]^{1-}$  directly, while aluminylene species **Int2–Int4** would undergo [1 + 4] cycloaddition with  $C_{10}H_8$  generated in the reaction (as



Scheme 4 Formation of 1,4-naphthalene derivatives **5a** and **5b** from **3** or **2c** and  $K(C_{10}H_8)$  respectively.



Scheme 5 The structures of the fleeting aluminium intermediates **Int1**–**Int4** proposed to form from one- or two-electron reduction.

previously demonstrated by other aluminylene species).<sup>84–86</sup> Such transient species as **Int1**–**Int4** are unprecedented for aluminium, but have been proposed as boron intermediates *vide infra*. In a similar manner, transient boron(i) hydrides have also been captured as [1 + 2] cycloaddition products of naphthalene from reaction with Na(C<sub>10</sub>H<sub>8</sub>).<sup>87,88</sup> Contrastingly, we did not observe C<sub>10</sub>H<sub>8</sub> incorporation in our previous work with aluminium halide complexes of bidentate donor ligands [Si<sup>II</sup>(Xant)Si<sup>II</sup>] or a bis(NHC)-ligand (bis(*N*-dipp-imidazole-2-ylidene)methylene).<sup>41,89</sup> Therefore this cycloaddition reactivity is unique to the Al complexes derived from ligand **1**. We expect this difference is related to the stabilizing effects of the dianionic carborane backbone on the low-valent Al center, through countering the positive charge at Al or possibly even reducing the Al center through valence tautomerism.

Donor-stabilized haloaluminylens have only been isolated as metal carbonyl complexes (*e.g.* **IV**, Fig. 1), while no donor-stabilized low valent aluminium cations have been reported.<sup>41,89–92</sup> It is noted that a Al<sup>I</sup> hydride [(cAAC)<sub>2</sub>AlH], Al<sup>I</sup> cation [Al(AlCp\*)<sub>3</sub>]<sup>+</sup> (**I**, Fig. 1) and a silyl-substituted Al<sup>III</sup> cation [R<sub>3</sub>Si-Al-SiR<sub>3</sub>]<sup>+</sup> have been isolated and characterized.<sup>15,20,93</sup> Radical cations, *e.g.* [AlH]<sup>•+</sup> and [AlF]<sup>•+</sup>, have only been synthesized in matrix conditions.<sup>94,95</sup> However, a neutral Al<sup>III</sup> radical [(R<sub>3</sub>Si)<sub>3</sub>Al]<sup>•</sup> has been synthesized and mononuclear Al<sup>II</sup> radicals [R<sub>2</sub>Al]<sup>•</sup> have also been recently detected *in situ* with EPR.<sup>75,96</sup> Al<sup>II</sup> radicals have also been proposed as intermediates in aluminium-directed reduction of H<sub>2</sub>, aromatics or alkynes.<sup>83,97–99</sup> To our knowledge, electromerism (or valence tautomerism) resulting in the formation of an Al<sup>I</sup> centre has not been reported.<sup>59</sup> For the related boron complexes of ligand **1**, species related to **Int1**–**Int3** have been proposed as intermediates or isolated.<sup>23</sup> One-electron reduction of bromoborylene **II** (Fig. 1) with Na(C<sub>10</sub>H<sub>8</sub>) gives an isolable B<sup>II</sup> radical complex of ligand **1a** (analogous to **Int1**), *via* the initial formation of its

valence tautomer (analogous to **Int2**).<sup>61</sup> Two-electron reduction of **II** yields **VI** (Fig. 1), with DFT calculations supporting the formation of a transient borylene cation (like **Int3**) that then reacts with a nearby cage B–H bond. Such a borylene or aluminylene cation like **Int3** would be isolobal with the isolable zero-valent beryllium compound [(cAAC)<sub>2</sub>Be].<sup>100</sup>

Carbenes, specifically cAACs, have been used to tame or trap aluminium radical complexes *in situ*, where TEMPO is unsuitable.<sup>16,19,75</sup> To find out more about the low-valent intermediates that form in the reaction to give **5a** and **5b**, we attempted reductions of **2c** and **3** in the presence of <sup>Me</sup>cAAC-5 with dropwise addition of THF solutions of crystalline [K(THF)(C<sub>10</sub>H<sub>8</sub>)] (of varying equivalents) at –78 °C (see ESI†).<sup>17,101</sup> Formation of **5** was prevented but no cAAC-containing products were identified. To remove the option of C<sub>10</sub>H<sub>8</sub> addition entirely, we carried out reduction reactions of **2** and **3** with K/KI (5% w/w) powder. Most promising was the reduction of the BPh<sub>4</sub> salt **2d** with one equiv <sup>Me</sup>cAAC-5 and five equivs K/KI powder in Et<sub>2</sub>O (see ESI†).<sup>102</sup> We observed color changes from colorless, *via* red, to dark blue within a few hours (Fig. S1 and S2†). <sup>1</sup>H NMR aliquots of the reaction mixture in benzene showed no notable products, despite the maintaining the intense color for at least 2 weeks, and unfortunately, no viable single crystals for scXRD were isolated. Despite these experimental challenges, there is still more to uncover about the nature of such low valent Al species supported by **1**. Further theoretical study could shine light on this and support the development of new ligand systems.

## Conclusions

Building on our previous work to access low oxidation state aluminium–silicon compounds, we employed the bis-silylenyl *o*-carborane ligands **1a** and **1b** to synthesize the respective bis-silylene Al<sup>III</sup> complexes **2a**–**2d**. Using KC<sub>8</sub>, the two-electron reduction of **2a** could be achieved leading to the bis-silylenyl Al<sup>III</sup> *nido*-C<sub>2</sub>B<sub>10</sub> dianion complex **3**, whilst one-electron reduction affords the corresponding Al<sup>III</sup> carborane radical anion complex **4a**. Thus, we establish a redox series of aluminium complexes with three interconvertible oxidation states characterized. The analogous gallium radical complex **4b** was also isolated from the reaction of **1a** with ‘GaI<sub>2</sub>’. Using K(C<sub>10</sub>H<sub>8</sub>), the AlI<sub>2</sub><sup>+</sup> center of **3** or **2c** was reduced furnishing the 1,4-naphthalene complexes **5a** and **5b**, respectively. Such products indicate the formation of transient donor-stabilized low-valent aluminium intermediates. These include the aluminium radical cation **Int1** which could react further to form iodo- or cationic aluminylene intermediates **Int2**–**Int4**. Overall, it is evident that tunable chelating silylene ligands and redox non-innocent ligands have important roles to play in the continued development of donor-stabilized low oxidation state aluminium complexes towards zero valent aluminium.

## Data availability

All experimental data associated with this work are available in the ESI.†



## Author contributions

A. S. carried out the synthetic experiments, analyzed the experimental data and wrote the original manuscript. S. Y. carried out the scXRD refinement of the compounds and edited the manuscript. C. L. collected and analyzed the EPR data. M. D. supervised the work and edited the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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