Introduction

Aluminium and its compounds are most commonly found in their zerovalent (metallic Al, Al⁰) and +3 oxidation states (trivalent Al, Al³⁺). Thus it is not surprising that compounds of aluminium in its +1 and +2 oxidation states – generally rare and unstable species – have a marked tendency to disproportionate into Al⁰ (metal) and Al³⁺ compounds. A number of Al¹ compounds ([:AlX], [AlH], [Al₂O]) have been realized by cryochemical methods. However, a major development in low-valent Al chemistry was the near-ambient temperature isolation of an Al⁰ compound, R₂Al-AlR₂ (R = CH(SiMe₃)₂), the first Al–Al bonded molecular species, by Uhl in 1988. Several dialanes have since been isolated using a similar strategy. A further breakthrough in low-valent Al chemistry was the generation of transient dialumenes R₉Al=AlR₉ (R = m-terphenyl, ary1, or silyl groups), featuring Al¹ atoms, which were trapped as cycloaddition products with aromatic species. Only recently, Inoue and coworkers reported a stable, neutral, doubly NHC-stabilised dialumene (I), which contains silyl substituents (Scheme 1a). Shortly, the same group presented a doubly NHC-stabilised diaryldialumene, II. These two compounds have shown exciting abilities in small-molecule activation and catalysis. In 2021, Krämer and Cowley reported the third stable dialumene (III), which bears amino substituents with chelating phosphine bases. Interestingly, this species was demonstrated to exhibit a reversible dissociation behavior.

Monovalent aluminium species (Al¹) have been known since 1991, with the isolation of the tetrameric Al¹ species Al₈Cp⁴⁺ (Cp* = pentamethylyclopentadienyl; IV, Scheme 1a), which was shown to dissociate into its monomer [AlCp⁺] upon heating. However, the isolation of a Al¹ compound with a β-diketiminato ligand by Roessky and coworkers (V, Scheme 1a) allowed access to a stable mono-Al¹ species. In 2018, our group reported the compound ([η⁵-Cp⁵]Al¹) (VI, Scheme 1a) (Cp* = 1,3,5-tri-tert-butylcyclopentadienyl), a monomeric species that showed several interesting reactivity patterns. We also reported a parent alumylene (i.e., Al¹H) species (VII, Scheme 1a) stabilised by two cyclic (alkyl)(amino)carbenes (CAACs) which showed 36% singlet diradical character (Al¹H). While these discoveries provided mono-Al¹ species for further reaction, they both bear further stabilising groups, meaning that neither is monocoordinate. A stunning recent discovery by Power et al. presented a first stable, monomeric, base-free, and mono-coordinate Al¹ species (VIII, Scheme 1a), bearing a sterically bulky terphenyl substituent. Shortly after this discovery, the groups of Liu and Hinz independently reported the synthesis of another base-free alumylene that carries a sterically hindered amino substituent (IX). We note that although various terminologies, including alanediy1,12 aluminylene,14 and aluminyl,
Compounds. Given that a base-free arylalumylene has been isolated,\(^{13}\) while attempts to isolate an NHC-bound analogue led only to isolation of a diaryl dialumene,\(^2\) we have been interested in developing a method to prepare an NHC-coordinated arylalumylene. We reasoned that the reduction of an NHC-stabilised dihaloalane bearing a superbulky aryl group (Ar*) i.e. \([\text{NHC} \text{AlI}_2\text{Ar}^*] \text{ (Ar}^* = \text{2,6-C}_6\text{H}_3\text{Mes}_2, \text{Mes} = \text{2,4,6-Me}_3\text{C}_6\text{H}_2, \text{NHC} = \text{NHCMe}_4, \text{X} = \text{I}) might lead to a stable, monomeric alumylene of the form \([\text{NHC} \text{Ar}^*\text{Al}]) – effectively an acyclic version of Roesky’s alumylene (V, Scheme 1a). This study has led instead to the discovery of highly unusual outcomes of reducing a dihaloalane: an intramolecular formal [2 + 2] cycloaddition product by deamortization of an outlying aryl group (Mes) by the generated dialumene of the form \(([[\text{NHC}\text{AlI}] = \text{AlAr}^*\text{(NHC)}]), and bicyclic bis(ala)ne products arising from the deconstruction of aromatic solvent molecules by the anticipated transient alumylene of the form \([\text{NHC}\text{Ar}^*\text{Al}]) (Scheme 1b). Insights gained through a combination of experiments and computations hint that from the reduction reaction, the initial species formed is a dialumene of the form \([\text{NHC}\text{Ar}^*\text{Al}])\, a species responsible for the intramolecular cycloaddition product. An additional hint gained was that the diaryldialumene can unravel into its monomeric alumylene \([\text{NHC}\text{Ar}^*\text{Al}]), which engages in deconstructing the less reactive arenes benzene and toluene.

Results and discussion

We chose a bulky terphenyl moiety \((\text{2,6-C}_6\text{H}_3\text{Mes}_2, \text{Mes} = \text{2,4,6-Me}_3\text{C}_6\text{H}_2)) and a small N-heterocyclic carbene \((1,3,4,5\text{-}\text{tetramethylimidazol-2-ylidene, NHC Me}_4)) for our study. The bulky terphenyl-substituted, NHC-coordinated AlIII diiodide precursor 2 was synthesized by iodiumation of the corresponding hydride, 1, with an excess of methylidene in toluene at room temperature (Scheme 2).\(^{17a}\)

The NHCMe4-substituted terphenylalane 1 was prepared by reacting TerLi\(^{18}\) with the corresponding carbene-stabilised alane.\(^{17a}\) The synthetic routes to 1 and 2 are analogous to the procedures of Inoue.\(^{17}\) Formation of 1 and 2 were confirmed by \(^1\text{H}\) and \(^{27}\text{Al}[\text{\textit{H}}]\) NMR spectroscopy. The \(^1\text{H}\) NMR signal of the Al-bound hydrides of 1 appeared at high field 4.04 (br, s AlH2, FWHM: 257 Hz) ppm, while a \(^{27}\text{Al}[\text{\textit{H}}]\) NMR signal was found at low field 112.4 ppm compared to that of NHCMe4 AlH3 (\(^1\text{H}\): 4.45 (br, s AlH2, FWHM: 779 Hz) ppm; \(^{27}\text{Al}[\text{\textit{H}}]: 106.5\) ppm). These values match well with those of similar reported compounds.\(^{9}\) The identities of 1 and 2 as NHC-stabilised terphenylalanes were further confirmed by their solid-state structures (Fig. 1).

Reduction of 2 with four equivalents of KC8 at room temperature in benzene led to the compounds 3 and 4 (64% and 36% respectively, relative NMR conversion, Scheme 3). Separation of the compounds was achieved by taking advantage of their differing solubility. Repeated washing of the reaction mixture with hexanes allowed us to separate 4 (5% isolated yield, see ESI\(^{\dagger}\) for details). The remaining solid was dissolved in a minimum amount of benzene and allowed to evaporate slowly inside a glovebox to afford bright yellow crystals of 3 (20%, isolated yield). After extraction of 3 and 4, the remaining
Me3C6H2.

NMR spectroscopic signal of the vinylic carbon C5 was found at 5.14 ppm, while the signal for the vinylic proton of the activated mesityl group in 4 was poorly soluble while also being unstable in benzene, partly explaining its poor isolated yield. Partial decomposition of 4 was noted after ca. 4 h in the presence of benzene, as indicated by 1H NMR spectroscopy.

Despite the instability of the latter, X-ray quality single-crystals of 3 and 4 were obtained from saturated benzene solution contained a mixture of the two compounds, which we could not separate further. Both 3 and 4 were characterized by multinuclear solution NMR spectroscopy and solid-state molecular structure determination. The 1H NMR signal for the vinylic proton of the activated mesityl group in 3 (attached to C3, Scheme 3) appeared at 5.14 ppm, while the signal for the allylic proton (attached to C1) appeared much more upfield (0.7 ppm) than those of conventional allylic protons (ca. 1.8 ppm). This is likely due to aluminium attachment to the C1 center, making the proton attached to C1 more hydridic. The 13C{1H} NMR spectroscopic signal of the vinylic carbon C5 was found at 116 ppm (as confirmed by HSQC). The 1H NMR spectroscopic signal for the C1,4 vinylic protons of 4 was found at 5.01 ppm (d, 1J = 12 Hz), in the usual range for signals of vinylic protons but slightly upfield compared to that of 3. The signal for the C3,5 vinylic protons was found significantly further downfield (7.32 ppm), which is in line with the 1H resonances of analogous protons in a similar compound reported by Crimmin.19 Solid samples of 4 were poorly soluble while also being unstable in benzene, partly explaining its poor isolated yield. Partial decomposition of 4 was noted after ca. 4 h in the presence of benzene, as indicated by 1H NMR spectroscopy.

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solutions. The solid-state structure of 3 (Fig. 2) showed that one of the mesitylene rings loses its planarity (and thus also its aromaticity), forming an Al₃C₂ four-membered ring. The Al–Al distance in 3 is 2.6091(5) Å, significantly longer than those of the carbene-stabilised dialumene II [Al=Al: 2.4039(8) Å]¹⁹ and the 1,2-dialuminacyclobutene [R₂Al₂(CSiMe₃)₂] (R = 2,6-C₆H₃Dip₂, Dip = 2,6-C₆H₃[Ph₂]₂) Al–Al: 2.4946(9) Å,²⁰ slightly shorter than a carbene-stabilised dialuminacyclobutane, [(NHC)(iBu₂SiMe)AlCH₂CH₂Al[NHC][iBu₂SiMe]] (NHC = 1,3-diisopropyl-1,5-dimethylimidazol-2-ylidene) Al–Al 2.6503(10) Å (ref. 6a) but similar to a range of other Al–Al single-bond distances (2.5 to 2.95 Å). The four-membered Al₃C₂ ring deviates from planarity with an Al₁–Al₂–C₂–C₁ dihedral angle of 23.51(6)°, which matches well with previously reported Al₃C₂ rings.²⁰

The structure of 4 (Fig. 2) exhibits two fused five-membered rings resembling a dihydropentalene structure, connected in an endo fashion (torsion angle Al₁–C₃–C₆–Al₂: 118.36(7)°; C₂–C₃–C₆–C₅: 130.7(1)°). Each ring of the dihydropentalene structure contains one tetrahedral AlIII center, while the carbon backbone is clearly derived from the activation of the benzene solvent. A similar dearomatized product was observed in the reaction of biphenylene with Roesky’s AlI complex V, reported by Crimmin et al.,²⁵ however, this AlI complex does not undergo a similar activation of benzene or toluene.

The ring-opening of benzene derivatives is rare and is generally considered to be very difficult. An early work demonstrating the ring-opening of benzene by a main-group compound was reported by Meller in 1988 on the reduction of a dihaloaminoborane in a benzene/dimethoxyethane solvent mixture, which led to the formation of a diboron derivative of pentalene.²¹ In 2019, the groups of Goicoechea and Aldridge presented the reversible insertion of a reactive aluminium anion into benzene at 80 °C, the product of which was trapped using Me₂SnCl₂.²² In our case, to confirm that the solvent was the source of the backbone of the product 4, we repeated the reaction in toluene at room temperature. The ¹H NMR spectrum of the reaction mixture showed the formation of 3 (ca. 68%) along with two new peaks, a doublet of doublets and a singlet in the vinyl region, indicating the formation of 5 (ca. 28%, Scheme 4). Compound 5 is more soluble than 3, allowing its isolation by hexane washing and crystallization (3% isolated yield). The remaining yellow solid was dried, providing 3 in 40% isolated yield. Repeating the reaction with a short reaction time (ca. 10 h) and starting at −78 °C led to greater selectivity for 3, allowing its isolation in 70% yield. The ¹H NMR spectrum of 5 exhibited two characteristic signals for the proton attached to C₁ and C₄ at 5.01 ppm (dd, J = 2 Hz, J = 12 Hz) and 4.83 ppm (s), respectively. The signal for the proton attached to C₂ was found further downfield at 7.34 ppm as doublet-of-doublets (J = 3 Hz (coupling with bridging proton, confirmed by COSY), J = 12 Hz (coupling with vinylic proton, confirmed by COSY)). Like 4, 5 has a similar endo geometry but unlike 4 it has no center of inversion as observed from its solid-state structure (Fig. 2). The two localized C–C double bonds significantly differ in length: the length of C₂–C₁ (1.345(14) Å) is closer to that of the C₂–C₁ bond distance of 4, whereas the C₅–C₄ distance in 5 (1.45(2) Å) is longer than typical C–C double bonds. The structures of 4 and 5 indicate that they arise from the deconstruction of benzene and toluene, respectively, by a low-valent aluminium species. To further support this, and to provide 3 more selectively, we performed the reduction of 2 in hexane (Scheme 4). As expected, this reaction resulted in 3 almost exclusively according to ¹H NMR of the crude reaction mixture and afforded it in 90% isolated yield.

Compound 3 can be thought of as a pseudo-dialumene internally stabilised by [2 + 2] cycloaddition between an Al=Al bond and the π system of a peripheral mesitylene ring. Earlier studies by Power²⁶ and Tokitoh²⁷ independently disclosed the synthesis of bicyclic masked base-free dialumenes formed by [4 + 2] cycloaddition of toluene or benzene with the Al=Al bond of intermediate dialumenes. It is worth mentioning that while [2 + 2] cycloaddition is symmetry forbidden, it can occur with benzene or toluene, respectively, by a low-valent aluminium species. To further support this, and to provide 3 more selectively, we performed the reduction of 2 in hexane (Scheme 4). As expected, this reaction resulted in 3 almost exclusively according to ¹H NMR of the crude reaction mixture and afforded it in 90% isolated yield.

| Scheme 4 Reduction of 2 in toluene and hexanes to obtain 3 and 5. (Ter = 2.6-C₆H₃Mes₂, Mes = 2,4,6-Me₃C₆H₂) |
| --- |
| 2 |
| 3 (56%) |
| 3 (isolated) |
| 4 (28%) |
| 5 (isolated) |
room temperature. Calculations performed at the PBE1PBE-D3BJ/Def2TZVP/SMD(benzene)/PBE1PBE-D3BJ/Def2SVP level of theory on this reaction hinted that diiododialane formation from the homocoupling of the early NHC-stabilised iodo(aryl) aluminyl radical [(NHC)(I)Ar*Al] is highly likely, as the coupled species is markedly stable ($\Delta G = -25.2$ kcal mol$^{-1}$). Unfortunately, experiments invariably formed 3 and the starting material in a ratio ca. 2 : 3, contrasting the results of reducing a base-free diiododialane, wherein the diiododialane is the primary product. This may have resulted from reducing the in situ generated diiododialane to dialumene 6 more rapidly than the starting material 2.

Since compound 3 can be viewed as a masked dialumene, we anticipated that simple heating might allow the generation of a dialumene. However, no decomposition or changes were observed during a variable-temperature NMR experiment on a benzene solution of 3 from 25 °C up to 100 °C. Prolonged heating at 100 °C (24 h) led to the formation of 8, the product of a formal intermolecular C−H activation (Scheme 5), along with a small batch of crystals of 4. The reduction of 2 in benzene also provided a similar outcome, with 8 as the major product. The $^1$H NMR spectrum of 8 showed a distinctive, broad signal (FWHM = 129 Hz) at 4.41 ppm corresponding to the Al-bound hydride, which is somewhat downstream of that of aluminium hydride 1 but in the range of similar carbene-stabilised dialumene hydrides. A broad signal (FWHM = 75 Hz) at 1.68 ppm was also observed corresponding to the newly formed methylene group. Interestingly, in the solid-state structure of 8 (Fig. 3), the Al−Al bond (Al1−Al2 2.6228(5) Å) was found to be significantly longer than that of 3 (Al−Al: 2.6091(3) Å) (Fig. 3).

The outcome of this experiment suggests that upon heating, 3 first reverts to 6, which then transforms to 8 (Fig. 4). In other words, 3 is a kinetic product and 8 is a thermodynamic product from 6. The thermodynamics computed for 3, 6 and 8 are in line with our experimental observation that 3 is significantly more stable than 6 ($\Delta G = -13.0$ kcal mol$^{-1}$), while 8 is substantially more stable than 3 ($\Delta G = -24.4$ kcal mol$^{-1}$) and 6 ($\Delta G = -37.4$ kcal mol$^{-1}$). It can be assumed that 3 forms via an intramolecular [2 + 2] cycloaddition in 6. For 8, however, given that the added methylene and hydride functionalities in 8 are trans-oriented, a straightforward C−H activation across the Al=Al bond in 6 may not be viable as it can only lead to a cis-isomer of 8. Conversion of this cis-isomer to the obtained trans-isomer via rotation of the Al=Al single bond may not be feasible due to steric. Thus, we suggest 8 forms via an intramolecular C−H activation in alumiylene 7 that was generated from the

**Scheme 5** Thermolysis of 3 to form 8 and 4. Ter = 2,6-C₆H₃Mes₂, Mes = 2,4,6-Me₃C₆H₂.
dissociation of dialumene 6, leading to a hydridoalane intermediate (9), followed by a formal insertion of another 7 into the Al–H bond in 9 (Fig. 4). Only a minor amount of the pentalene product 4 obtained from the same thermal reaction signals that the dialumene 6 generated from the reduction reaction somehow reacts with benzene before self-stabilising to form 3. Even for this reaction, we propose the involvement of alumylene 7 via dissociation of 6 (Fig. 4).

Compelling evidence for the dissociation of compounds with heavier main group multiple bonds under mild conditions has been known for nearly five decades. However, only very recently, a report by Krämer and Cowley demonstrated the reversible dissociation of a doubly base-stabilised dialumene, III, for which the dissociation energy (ΔG_diss) was calculated to be small (7.1 kcal mol\(^{-1}\)) (vide supra) with benzene before self-stabilising to form 3. Even for this reaction, we propose the involvement of alumylene 7 via dissociation of 6 (Fig. 4).

Intriguingly, this intermediate presents similar kinetics and that they may both be (almost equally) competing to form the pentalene product 4. The computed pathways show that the initial process involved in the reaction of alumylene 7' with benzene is a [1 + 2] cycloaddition, leading to the aluminare intermediate 13'. Intriguingly, this intermediate presents similar kinetics and thermodynamics in the next stage to form the bicyclic intermediate 10' and the insertion intermediate 14'. This paves the way for divergent pathways for the arene deconstruction reaction. Forming 10' from 7' and benzene directly via the [1 + 4] cycloaddition transition state TS(7'-10'), as proposed by Crimmin for the biphenylene deconstruction, can be less regarded, as this route holds a relatively large activation barrier. As intermediates 10' and 14' lie only slightly uphill from their starting materials, 7' and benzene, and hold easily attainable, reversible activation barriers, we propose they form reversibly from their starting materials. In contrast, the C–H activation intermediate 9' (red profile), which we presumed to form at high temperatures from 7' and to be responsible for the formation of 8', while having a larger barrier than predicted for forming 10' and 14', lies significantly lower in energy from its starting material 7'; thus, the reversibility of this step is less likely. These disparities explain why 8 was the major product when the

![Fig. 5](image_url) Computed structure (a) and frontier orbitals (±0.05 isovalue) (b) of alumylene 7. HLG: HOMO–LUMO gap. Hydrogens are omitted for clarity. Mesityl groups of the terphenyl substituent and the methyl groups of the NHC are depicted in wireframe style for simplicity. Selected bond lengths [Å] and bond angles [°]: Al1–C1 2.072, Al1–C3 2.128, C1–Al1–C3 96.4, C2–C1–Al1–C3 69.2, N1–C3–Al1–C1 61.6.
reduction was carried out at high temperatures and when the benzene solution of 3 was heated.

**Conclusions**

We report that reducing an NHC-stabilised diiodoalane bearing a sterically encumbered aryl substituent, 2,6-dimesitylphenyl, in different hydrocarbon solvents leads to different outcomes. In hexanes, a highly unusual self-stabilised dialumene species was the product, instead of the anticipated acyclic, dicoordinate alumylene (AlI). In benzene or toluene, the primary product was a dialuminadihydrotentalene arising from C–C bond activation and deconstruction of the respective arene solvent. Subsequent probing through experiments and DFT calculations showed that the self-stabilised dialumene and its dialumene precursor dissociate to form the initially-sought alumylene before reacting with benzene and toluene. This reactivity of the transient alumylene suggests that it is more reactive than the previously reported di- and monocoordinate AlI species of Roesky and Power, respectively. We envisage that careful tuning of the aryl and base groups could enable isolation of a similar base-stabilised alumylene and allow the full exploitation of the fascinating reactivity of this family of compounds.

**Data availability**

Full experimental and computational details are provided as part of the ESI.†

**Author contributions**

H. B. supervised the project. D. D. carried out the synthetic work. D. D. and M. H. carried out the X-ray crystallographic analyses. A. J. carried out the computational studies. D. D., R. D. D. and A. J. prepared the manuscript. D. D. and A. J. prepared the ESI. All authors discussed the results and commented on the manuscript.

**Conflicts of interest**

There are no conflicts to declare.
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Notes and references

§ The ground state for alunylene is singlet ($\Delta G_{\text{singlet-triplet}} = 17.0$ kcal mol $^{-1}$).

¶ Note that the proportion mentioned is only a relative ratio as per $^1$H NMR spectroscopic data, and it is not scaled against any external standard.

† A few mechanistic steps computed on both pathways using the full experimental system displayed similar energetics to the truncated model, suggesting that the model used can reliably represent the pathways followed by the experimental system.

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