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Dialumenes – aryl vs. silyl stabilisation for small molecule activation and catalysis†

Catherine Weetman,  Amelie Porzelt, Prasenjit Bag, Franziska Hanusch and Shigeyoshi Inoue *

Main group multiple bonds have proven their ability to act as transition metal mimics in the last few decades. However, catalytic application of these species is still in its infancy. Herein we report the second neutral NHC-stabilised dialumene species by use of a supporting aryl ligand (**3**). Different to the *trans*-planar silyl-substituted dialumene (**3^{Si}**), compound **3** features a *trans*-bent and twisted geometry. The differences between the two dialumenes are explored computationally (using B3LYP-D3/6-311G(d)) as well as experimentally. A high influence of the ligand's steric demand on the structural motif is revealed, giving rise to enhanced reactivity of **3** enabled by a higher flexibility in addition to different polarisation of the aluminium centres. As such, facile activation of dihydrogen is now achievable. The influence of ligand choice is further implicated in two different catalytic reactions; not only is the aryl-stabilised dialumene more catalytically active but the resulting product distributions also differ, thus indicating the likelihood of alternate mechanisms simply through a change of supporting ligand.

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Introduction

The ability to isolate and stabilise complexes containing metal-metal bonds is of fundamental interest, providing both experimental and theoretical insights into the intrinsic nature of the metal centre.¹ Since the discovery that the so-called 'double bond rule' could be broken in the beginning of the last quarter of the 20th century,^{2–5} efforts within main group chemistry have strived towards isolating a plethora of both homo- and hetero-main group element multiply bonded compounds, which have been the subject of numerous reviews.^{6,7} Aside from curiosity, one of the driving forces behind this research area is the ability to use main group multiple bonds as transition metal mimics.^{8–10} This is possible due to similarly energetically accessible frontier molecular orbitals. Thus, reduction of small molecules, such as dihydrogen, under ambient conditions by sustainable main group metal centres is achievable.¹¹

Whilst the ability to mimic transition metals is now possible in regard to oxidative addition reactions, main group elements still fall short in terms of catalytic activity due to the resulting stability of the higher oxidation state complexes, *i.e.* the first step in a redox based catalytic cycle. In order to truly compete with transition metals that are currently employed in industry, the ability to influence the stability, and thus reactivity, of main

group metal centres is paramount. One method of influencing stability is through choice of stabilising ligand. If you consider disilenes, the choice of silyl, aryl and nitrogen-based ligands has been shown to influence the structural parameters around the double bond,^{12,13} with silyl groups tending towards *trans*-planar geometries¹³ and aryl groups promoting *trans*-bent character. It was not until the use of an N-heterocyclic imine (NHI) based ligand, which results in a highly *trans*-bent and twisted geometry, that dihydrogen activation was achieved.¹⁴

An electropositive silyl supporting ligand was used to stabilise the first neutral aluminium-aluminium double bond, namely dialumene.¹⁵ DFT calculations found the HOMO to consist of a π -bond formed from almost pure Al p-orbitals and as such a planar geometry was observed. As predicted, the dialumene behaved as a transition metal mimic towards a variety of small molecules, as well as enabling catalytic reduction of CO₂.¹⁶ Prior to the isolation of the first neutral dialumene, several compounds with Al–Al bond orders greater than 1 were isolated.¹⁷ These can be classed as radical mono-anionic species, one electron π -bonded compounds, a dianionic complex and masked dialumenes. The stick with latter, reported independently by Power¹⁸ and Tokitoh,¹⁹ proposed the intermediacy of aryl-stabilised dialumenes, with the masked species being a result of [2 + 4]-cycloaddition reaction due to the use of aromatic solvent. This was additionally accounted for through a series of [2 + 2]-cycloaddition reactions with internal alkynes. Tokitoh further showed that the benzene derived masked species was capable of activating dihydrogen;²⁰ however, upon switching to an anthracene derived masked species no reactivity towards dihydrogen was observed.

Department of Chemistry, Catalysis Research Center and Institute of Silicon Chemistry, Technische Universität München, Lichtenbergstra ße 4, 85748, Garching bei München, Germany. E-mail: s.inoue@tum.de

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On descending group 13, heavier digallenes and dithallenes have been isolated which show notable *trans*-bent character and have been known to dissociate to their corresponding monomers in hydrocarbon solutions.^{21–25} However, digallanes have been shown to react as the double bonded species, rather than the monomer with regards to cycloadditions of unsaturated C–C bonds and even dihydrogen activation.^{26–28}

Motivated by our group's previous efforts in dialumene chemistry, we targeted the isolation of a neutral aryl-stabilised dialumene to compare the intrinsic nature of the aluminium-aluminium double bond through the influence of ligand stabilisation. Whilst silyl and aryl groups have been routinely used in main group multiple bond chemistry, no direct comparisons of their influence on multiple bonds as reactive species have been drawn. As such, we proposed a systematic study of both dialumenes towards activation of a range of small molecules and their use in catalysis, with the aim of providing experimental and theoretical insight into the influence of these ligand classes on main group multiple bond reactivity.

Results and discussion

Synthesis of aryl-stabilised dialumene

Following on from the successful isolation of the first neutral dialumene, we focused our attention on expanding the scope of this class of compounds towards aryl stabilised systems. As such, we targeted the use of the Tipp ligand (Tipp = 2,4,6-tri-*iso*-propylphenyl) for the stabilisation of a new dialumene. In keeping with the previous dialumene, the choice of N-heterocyclic carbene (NHC) remained the same, $I^iPr_2Me_2$ ($I^iPr_2Me_2$ = 1,3-di-*iso*-propyl-4,5-dimethyl-imidazolin-2-ylidene). Direct reaction of $I^iPr_2Me_2AlH_3$ and LiTipp at $-78^\circ C$ resulted in formation of the monosubstituted aluminium dihydride complex $I^iPr_2Me_2Al(Tipp)H_2$ (**1**) (Scheme 1) in good yield (66%, ^{27}Al : δ 112.9 ppm).²⁹ The identity of compound **1** was confirmed upon inspection of the 1H NMR spectrum wherein three resonances for the *iso*-propyl groups were identified in a 2 : 2 : 1 ratio (NHC : *o*-Tipp : *p*-Tipp *iso*-propyl signals) as well

as a characteristic broad signal for the Al–H₂ protons (1H : δ 5.11 ppm). Additionally, a sharp IR stretching band at 1711 cm^{-1} (Al–H) was observed in the IR spectrum.

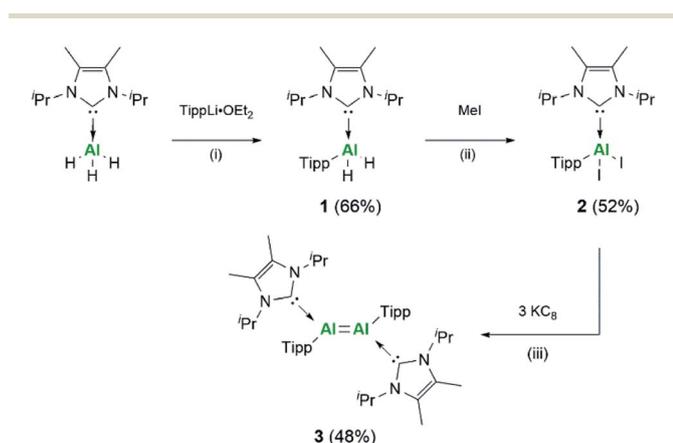
Conversion of **1** towards formation of $I^iPr_2Me_2Al(Tipp)I_2$ (**2**) could be achieved through reaction with $BI_3 \cdot dms$ (dms = dimethyl sulfide) or with a small excess of methyl iodide, with the latter resulting in higher and cleaner conversion; moreover, the concomitant formation of methane allows for facile reaction monitoring. Loss of signals relating to Al–H were observed in both the 1H NMR and IR spectra, and further characterisation by single crystal XRD confirmed the identity of **2** (Fig. S54[†]). Compound **2** is structurally analogous to the corresponding silyl supported complex (2^{Si}) with Al–C^{NHC} bond lengths essentially the same (**2**: 2.0645(18) Å; 2^{Si} : 2.0673(17) Å), indicating the dative nature of the NHC ligand. This is additionally confirmed on comparison with the Al–C^{Tipp} bond length (1.9887(19) Å), which is smaller than the sum of the covalent radii ($R_{Al-C} = 2.01$ Å).³⁰

Following the analogous synthetic protocol to the silyl dialumene, compound **2** was stirred vigorously with KC_8 at room temperature (Scheme 1). Through monitoring the reaction by 1H NMR, it was found that this reaction requires 72 hours rather than the 24 hours required for the previous case. Compound **3** was isolated as a black solid, and in contrast to the silyl stabilised dialumene (3^{Si}), **3** is highly soluble in a broad range of aromatic, alkyl and ethereal solvents. Both dialumenes are stable in the solid state in an inert atmosphere for prolonged periods; however, they decompose in solution after 24 hours. The 1H NMR spectrum of **3** shows a large broad signal at room temperature (~ 7.0 – 5.5 ppm) which resolves into distinct signals at 228 K for the *iso*-propyl groups, indicating a degree of rotational fluxionality in this system (Fig. S11[†]).

Single crystals were grown from a concentrated *n*-hexane solution at $5^\circ C$ and revealed a *trans*-bent and twisted geometry of the aryl stabilised dialumene (compound **3**, Fig. 1) ($\theta = 17.25^\circ$, 23.70° , $\tau = 12.06^\circ$), which contrasts with the *trans*-planar geometry observed previously. Furthermore, in 3^{Si} the NHC groups were found to be parallel to each other, whilst in **3** they are found to be almost perpendicular (85°). The change from a planar to a *trans*-bent and twisted geometry has also been observed in disilene chemistry on switching between aryl and silyl-based ligands.^{12,13} The Al–Al bond length is 2.4039(8) Å which is fractionally longer than that in the previous dialumene (3^{Si} : 2.3943(16) Å). Another notable difference between the two systems lies in the Al–C_{NHC} bond length (**3**: 2.0596(16), 2.0422(17); 3^{Si} : 2.073(3) Å). The shorter bond length in the case of aryl stabilisation likely indicates a decrease in dative character and thus an increase in the covalent nature of the Al–C_{NHC} bond (which is also supported by the calculated bond dissociation energy, see below).

Computational discussion of aryl-stabilised dialumene

To gain a deeper insight into the differences between these two classes of dialumenes, we performed density functional theory (DFT) calculations at the B3LYP-D3/6-311G(d) level of theory (for detailed information see the ESI[†]). The optimised



Scheme 1 Synthesis of aryl substituted Al compounds, Tipp = 2,4,6-tri-*iso*-propylphenyl. Reaction conditions: (i) TippLi·OEt₂, Et₂O $-78^\circ C$ to RT 48 h; (ii) MeI, toluene $0^\circ C$ to RT 24 h; (iii) 3 eq. of KC_8 , C₆H₆, RT 72 h.



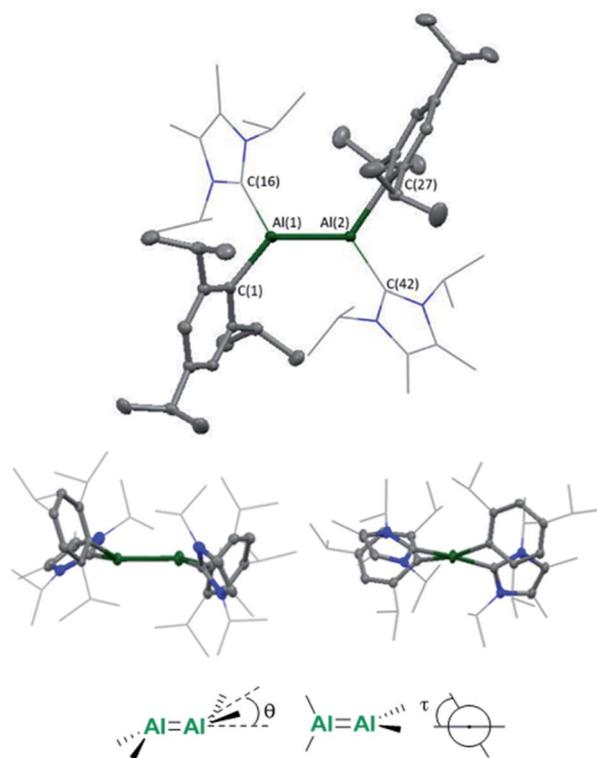


Fig. 1 Molecular structure of compound **3** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and NHC ligands are depicted in wireframe for simplicity. Selected bond lengths (Å) and angles (°): Al(1)–Al(2) 2.4039(8), Al(1)–C(16) 2.0596(16), Al(2)–C(42) 2.0422(17), Al(1)–C(1) 2.0292(16), Al(2)–C(27) 2.0180(16), C(16)–Al(1)–Al(2) 119.55(5), C(42)–Al(2)–Al(1) 114.13(5), C(1)–Al(1)–Al(2) 123.56(5), C(27)–Al(2)–Al(1) 129.55(5), C(1)–Al(1)–C(16) 110.28(6), C(27)–Al(2)–C(42) 112.84(7), $\theta = 17.25, 23.70$, $\tau = 12.06$.

geometry of **3** is in good agreement with experimental values, with the addition of the dispersion required to account for the *trans*-bent and twisted geometry. For comparison, all calculated values for **3^{Si}** including dispersion are given in the ESI.† Analysis of the frontier orbitals of **3** revealed similar features to **3^{Si}**, in which the HOMO–1 and HOMO contain the Al–Al σ - and π -bonds, respectively, as well as the LUMO representing the Al–C^{NHC} π bond (Fig. 2). The main difference to **3^{Si}** (see Fig. S57† for the corresponding orbitals) is the loss of uniform arrangement of the HOMO on the two aluminium centres as well as additional π -incorporation of the NHC present in **3**. We attribute this to the different orientation of the NHCs in **3**, enabling overlap with the p-orbital of the carbene carbon atom, which is experimentally observed as a shortened Al–C^{NHC} bond in the SC-XRD structure and further evidenced by an increased Gibbs free energy of bond dissociation of 26.0 kcal mol^{–1} (*cf.* **3^{Si}** = 16.9 kcal mol^{–1}). The conjugation towards the Al–C^{NHC} π -bond in **3** is also observed on inspection of the monomers (for further details see ESI Fig. S62†), which also gives rise to the decreased HOMO–LUMO gap in **3** compared to **3^{Si}** (**3** = 1.86 eV, **3^{Si}** = 2.24 eV) based on decreased overlap of the monomers being possible.

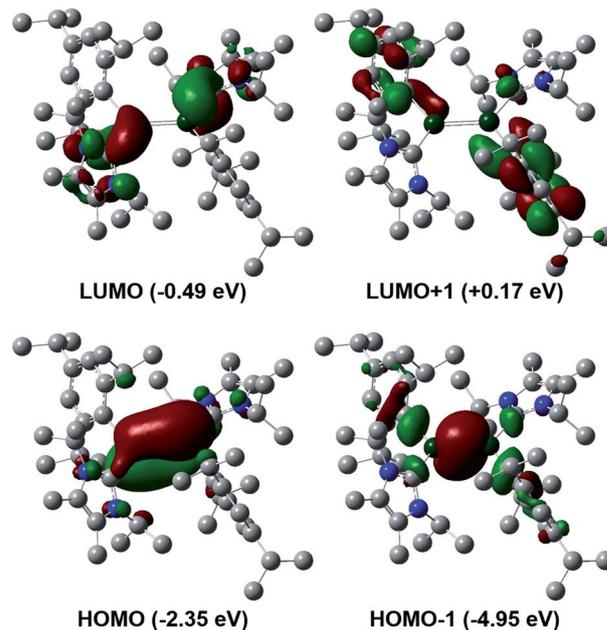


Fig. 2 Frontier orbitals of aryl substituted dialumene **3**.

TD-DFT calculations corroborated the experimental UV/vis spectrum of **3**. This showed an intense absorption band at 833 nm ($\epsilon = 6273$ L mol^{–1} cm^{–1}) (calc. value 794 nm), which can be assigned to the HOMO to LUMO transition and is responsible for the highly coloured compound.³¹ Natural bond orbital (NBO) analysis provided electronic insight into the nature of the Al–Al double bond. The Al–Al π -bond of **3** bears reduced *p*-character compared to **3^{Si}**. Moreover, this NBO orbital has a lower occupancy based on partial population of the π^* -orbitals of the C–N bonds of the NHC, rationalising the increased interaction of the NHC for **3**. This is based on its different orientation, which we mainly attribute to the reduced steric demand of the ligand. Furthermore, this is reflected in the decreased Wiberg bond index (WBI) of the Al–Al bond of 1.67 to 1.53 going from silyl to aryl (Fig. 3), yet still indicating a high degree of multiple bonding character in both systems.

Analysis of NPA charges clearly reflects the silyl effect (Fig. 3): the aluminium centres in **3^{Si}** bear a nearly neutral charge of +0.08, while in **3** they account for +0.48/+0.49. We attribute this to the silyl substituents, with their strong σ -donating properties, possessing a more effective orbital overlap with the aluminium centres in the σ (Al–Si) bonds. This also becomes evident upon examination of the results of NBO analysis for the

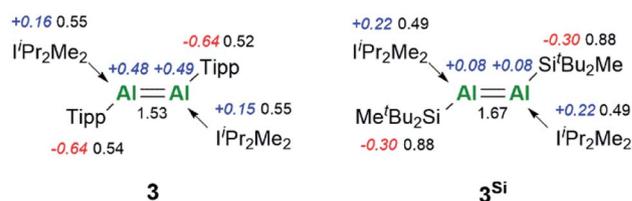


Fig. 3 Results of the NBO analysis of **3** and **3^{Si}**. NPA charges (blue and red) and WBIs (black).



Further reactivity towards C–C multiple bonds was trialed with diphenylacetylene (PhCCPh). Addition of 1 eq. of PhCCPh to 3^{Si} failed to cause a reaction, and after prolonged heating only decomposition of 3^{Si} was observed. In contrast, PhCCPh was observed to react readily with **3**, notably through the instant colour change from the dark black solution of **3** to a yellow solution of compound **6**. This difference in reactivity was surprising, considering that both **3** and 3^{Si} reacted cleanly with both non-polar (ethylene to form **4** and 4^{Si}) and polar (phenylacetylene to form **5** and 5^{Si}) C–C multiple bonds. This difference in reactivity is thought to be a direct result of the choice of stabilising ligand. The flexibility of the Tipp ligand, due to the rotational *iso*-propyl groups, makes the central AlAl core more accessible for reactant molecules, thus enabling reactivity with more sterically demanding reagents. Moreover, the positive NPA charges of **3** make it more electrophilic in comparison to 3^{Si} , thus implying higher reactivity towards nucleophilic C–C multiple bonds.

Compounds **4** and **6** were crystallised from concentrated pentane solutions at $-30\text{ }^{\circ}\text{C}$. The XRD structures revealed addition of the C–C multiple bonds to the dialumene, resulting in the formation of 4-membered rings (Fig. 4). Loss of double bond character from the dialumene was confirmed due to elongation of the Al–Al bond (**4** 2.6035(13), **6** 2.5918(6) vs. **3**

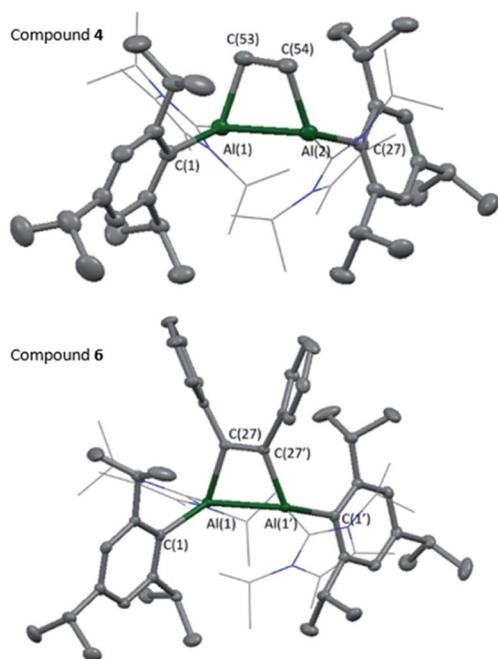


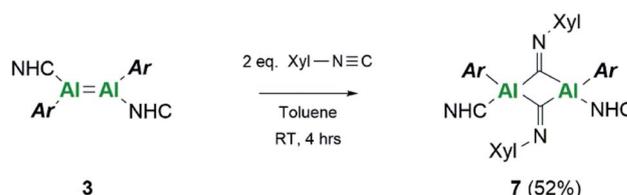
Fig. 4 Molecular structures of compounds **4** and **6** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and NHC ligands are depicted in wireframe for simplicity. Selected bond lengths (Å) and angles ($^{\circ}$): **4**: Al(1)–Al(2) 2.6035(13), Al(1)–C(1) 2.053(3), Al(1)–C(16) 2.079(3), Al(1)–C(53) 2.052(3), C(53)–C(54) 1.565(5), Al(2)–C(27) 2.048(3), Al(2)–C(42) 2.093(3), Al(2)–C(54) 2.040(3), Al(1)–Al(2)–C(54) 73.50(11), Al(2)–Al(1)–C(53) 72.94(11), C(54)–C(53)–Al(1) 101.33(19), C(53)–C(54)–Al(2) 101.23(19). **6**: Al(1)–Al(1') 2.5918(6), Al(1)–C(1) 2.0413(14), Al(1)–C(16) 2.1097(15), Al(1)–C(27) 2.0246(14), C(27)–C(27') 1.3701(19), Al(1')–Al(1)–C(27) 72.19(4), Al(1)–C(27)–C(27') 107.09(10).

2.4039(8) Å). Also noted to occur is the elongation of the Al–C^{NHC} bond lengths (**4** 2.079(3), 2.093(3), **6** 2.1097(15) vs. **3** 2.0596(16), 2.0422(17) Å). The 4-membered ring in **6** is almost planar (6.37° between Al–Al–C(27) planes), whilst **4** is puckered due to the presence of the sp^3 carbons.

Extension of this work towards C–N triple bonds focused on the use of 2,6-dimethylphenylisocyanide (XylNC). Previously, Tokitoh and co-workers had shown that reaction of their masked dialumene species resulted in homocoupling of isocyanides.³⁵ Reactions of varying equivalents of XylNC to 3^{Si} all resulted in an ill-defined mixture of species; unfortunately, attempts to separate species through fractional crystallisation failed. In contrast, reaction of 2 eq. of XylNC with **3** resulted in a clear colour change from black to red and produced a well-defined but complex ^1H NMR spectrum of compound **7** (Scheme 3). This complex contains bridging CNXyl units due to the observed downfield signal in the ^{13}C NMR spectrum at δ 303.4 ppm. This was similar to the previously observed bridging carbonyl fragment observed with 3^{Si} , in the rearrangement of CO_2 (δ 276.0 ppm)⁴⁶ and the bridging isocyanide intermediate reported by Tokitoh (δ 294.7 ppm).³⁵ Single crystals of **7** were grown from a 2 : 1 (toluene : hexane) mixture at $5\text{ }^{\circ}\text{C}$, revealing a butterfly configuration with two μ -CNXyl units (Fig. 5).

The central Al–C^{Xyl}–Al–C^{Xyl} core in compound **7** is puckered (34.3° between the two C^{Xyl}–Al–C^{Xyl} planes), with the supporting NHC and Tipp ligands now *cis* to the ring. This change from *trans* to *cis*-conformation has been observed previously for the C–H activated phenylacetylene product on reaction with 3^{Si} . However, the reasons for such a change in conformation are unclear. Again, elongation of the Al–C^{NHC} bond lengths are observed (Al–C^{NHC} 2.109(3) Å), with the change in Al–C^{Tipp} negligible (**7** 2.042(7) vs. **3** (2.0292(16) Å). Reduction of the C–N triple bond to a double bond is confirmed on inspection of the bond length (C(27)–N(3) 1.292(4) Å), which is in line with average C=N bond lengths.^{36–39} Additionally, the change in angle around the nitrogen in XylNC from linear to bent ($126.3(2)^{\circ}$) confirms reduction of the C–N triple bond. This butterfly configuration has been previously observed with transition metal complexes;^{40–47} however, they all contain a M–M bond, and those without M–M bonds contain a planar central ring.^{48–52}

To confirm the nature of the bonding within compound **7** DFT studies were performed again, at the B3LYP-D3/6-311G(d) level of theory. The optimised structure is in good agreement with the one obtained experimentally by SC-XRD, including the calculated C=N IR stretching frequencies (experimental: 1545 cm^{-1} vs. calculated: 1568 cm^{-1}). Orbital analysis (Fig. 6)



Scheme 3 Reactivity of dialumene (**3**) towards isocyanide.



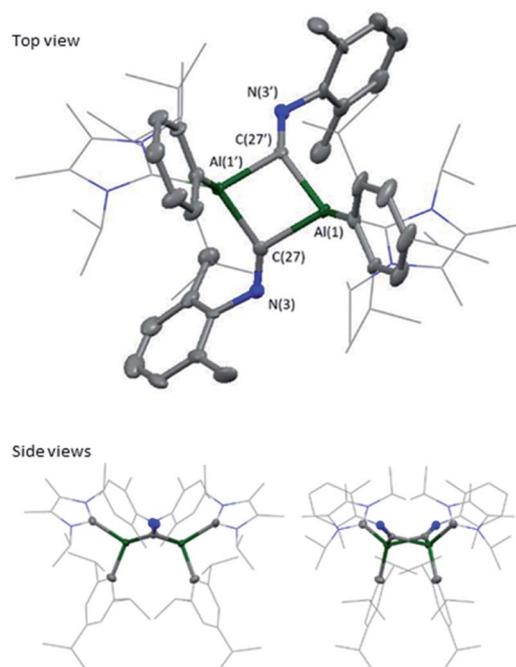
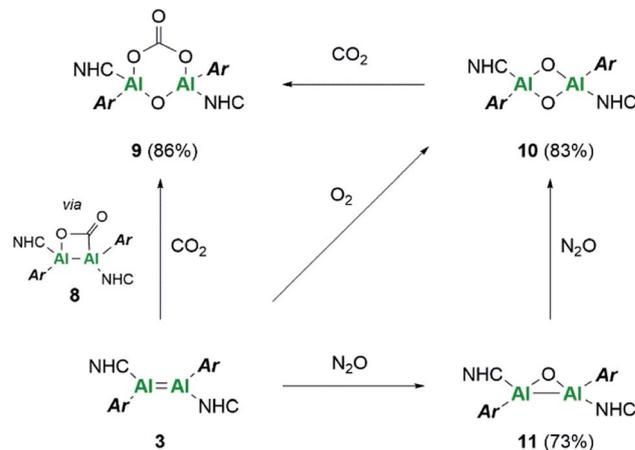


Fig. 5 Molecular structure of compound 7 in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and NHC ligands and iso-propyl groups are depicted in wireframe for simplicity. Selected bond lengths (Å) and angles (°): Al(1)–C(1) 2.042(7), Al(1)–C(16) 2.109(3), Al(1)–C(27) 2.059(3), C(27)–N(3) 1.292(4), Al(1)–C(27)–Al(1') 91.59(11), C(27)–Al(1)–C(27') 82.74(11), C(27)–N(3)–C(28) 126.3(2).

revealed the HOMO as an orbital overlap of aluminium and $\pi^*(\text{C}=\text{N})$. The LUMO represents the combination perpendicular to the HOMO, including conjugation across the central ring. NBO calculations confirmed that no C–C or Al–Al bond is present in 7 (WBI (C²⁷C^{27'}):0.06; WBI (Al¹Al^{1'}): 0.04).

Small molecule activation

Further reactivity differences were sought through investigation towards small molecules (Scheme 4). Previously, reaction of 3^{Si} towards carbon dioxide (CO₂) resulted in an initial CO₂ fixation complex.¹⁶ This subsequently underwent C–O cleavage reaction, in the absence of additional CO₂ through rearrangement to a bridging carbonyl complex, whilst in the presence of CO₂, formation of a carbonate species with elimination of CO was observed. On reaction of 3 with CO₂ immediate loss of the black



Scheme 4 Reactivity of dialumene (3) towards small molecules, CO₂, O₂ and N₂O.

colour and formation of a colourless solution was observed. On inspection of the ¹³C NMR spectrum, the presence of CO (δ 184.4 ppm) and CO₃ (δ 159.12 ppm) was observed, indicating the formation of the carbonate complex compound 9. In contrast to 3^{Si}, attempts to isolate the CO₂ fixation product were unsuccessful as it rapidly converted to compound 9. Use of the labile I^tPr₂Me₂–CO₂ species allowed for the formal [2 + 2]-cycloaddition product (compound 8) to be observed due to its characteristic ¹³C resonance at δ 207.7 ppm (8^{Si} δ 209.9 ppm). However, this reaction resulted in multiple species as well as compound 9, owing to the higher reactivity of the Tipp dialumene (compound 3), thus indicating that formation of 9 proceeds through the CO₂ fixation species in a similar manner to 3^{Si}.

Reaction of 3 with O₂ resulted in the expected dioxo product, compound 10, same as the previously reported reaction of 3^{Si}. In a similar manner to 10^{Si}, compound 10 can also be reacted with CO₂ resulting in carbonate complex 9. In a notable difference to the silyl supported reactivity, addition of N₂O to compound 3 resulted in a dark red solution at room temperature (3^{Si} yielded colourless compound 10^{Si}). This red solution was observed to slowly fade to colourless over a few hours and the formation of compound 10 was confirmed by ¹H NMR spectroscopy. Use of 1 eq. of an oxygen donor reagent, namely *N*-methylmorpholine-*N*-oxide, with 3 allowed for clean isolation of the red species, compound 11. Compound 11 is stable in the solid state for up to two months in a glovebox freezer; however, at room temperature and in solution, further oxidation to compound 10 occurs. Whilst ¹H NMR showed similar environments for both 10 and 11 (Fig. S39[†]), compound 11 is intensely coloured (UV/vis = 512 nm, ϵ = 1155 L mol⁻¹ cm⁻¹) whilst 10 is colourless. As such compound 11 was tentatively assigned as a bridging aluminium(II) mono-oxide species, rather than a terminal aluminium(III) mono-oxide complex. Unfortunately, SC-XRD analysis did not provide clear structural parameters for the mono-oxide species due to superposition with compound 10 (Fig. S55[†]). To provide further insight, calculations were also performed on compounds 10 and 11. The optimised structure

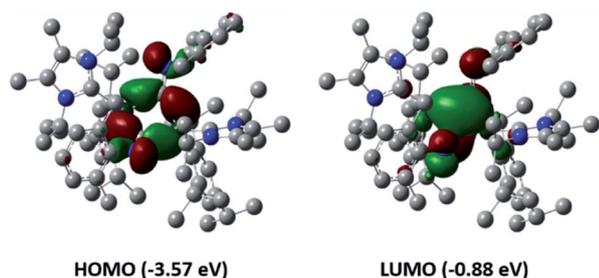


Fig. 6 Frontier orbitals of compound 7.

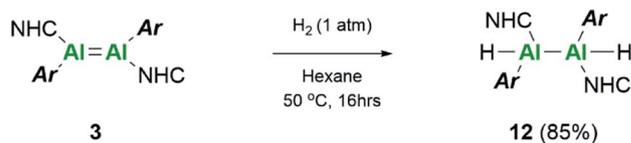


of **10** is symmetric relating to the Al–O bonds, as previously observed for the analogous silyl compound (**10^{Si}**).¹⁶ TD-DFT calculations revealed the highest transition at 259 nm, in line with the experimental colourless appearance. In contrast, compound **11** bears substantial π -electron density between the two aluminium centres in the HOMO as depicted in Fig. 7, reminiscent of the disilaoxirane reported by our group.⁵³ The LUMO represents the unoccupied π (Al–C^{NHC}) bond. TD-DFT calculations verified the experimentally observed red colour (UV-vis 512 nm) with good accordance (calc. 519 nm), assigned to the HOMO to LUMO transitions of **11**.

Extension of this small molecule reactivity towards dihydrogen was investigated. Firstly, a J-Young NMR tube containing a purple solution of **3^{Si}** was freeze–pump–thaw degassed and then backfilled with approximately 1 atm of H₂. After 24 hours at room temperature no reaction was noted to have occurred; increasing the temperature to 60 °C and regular monitoring only resulted in the observed decomposition of **3^{Si}**.

Repetition of this reaction with the aryl stabilised dialumene, compound **3**, also resulted in no reaction at room temperature. After 16 h at 50 °C, however, the black colour of **3** had faded to a dark brown/yellow solution (Scheme 5). On inspection of the ¹H NMR spectrum, no Al–H signals could be observed owing to the quadrupolar nature of the Al centre. Additionally, three distinct *iso*-propyl signals similar to that observed for compound **1** were identified. These, however, were not identical and therefore complete hydrogenation and cleavage of the Al–Al bond can be ruled out. Thus, it is likely that compound **12** consists of either terminal or bridging hydrides.

IR spectroscopy was utilised to differentiate between the two likely structures; two broad but distinct peaks at 1593 and



Scheme 5 Reactivity of dialumene (**3**) towards dihydrogen.

1634 cm⁻¹ were observed. Compounds containing no Al–Al bond but both terminal and bridging hydrides are found at approximately 1880 cm⁻¹ and 1350 cm⁻¹, respectively,^{20,54} whilst terminal hydrides within complexes containing Al–Al bonds are found within 1680–1835 cm⁻¹,⁵⁵ thus pointing more in the direction of a terminal hydride with Al–Al bonds. Additionally, for the previous terminal hydride in the related silyl system, from C–H activation of phenyl acetylene, this Al–H was found at 1666 cm⁻¹.¹⁵ Unfortunately, attempts to grow crystals suitable for SC-XRD were unsuccessful. Therefore, additional insight for this structure was sought computationally. Different possible isomers of product **12** were calculated, including bridging, terminal, and combinations of both as well as different rotational isomers (H: *cis* or *trans*; NHC and Tipp ligands: *cis* or *trans*).

The two lowest lying isomers were found to possess terminal hydrides in the *cis* and *trans* configurations (Fig. 8). The Al–H stretching frequencies were calculated to be 1634 and 1676 cm⁻¹, respectively, which is in good agreement with the experimentally obtained values (for detailed information see the ESI†). It is, therefore, suggested that the activation of hydrogen by **3** results in both the *cis* and *trans* isomers of compound **12**.

Catalysis

Further comparisons between the two dialumenes examined their use in catalytic applications. Two archetypal catalytic reactions (hydroboration and dehydrocoupling) were studied due to their prevalence in main group catalysis, as well as the implication of metal-hydrides in facilitating turnover.^{56,57} With the ability to form dialuminium-hydrides in the case of **3** and not for **3^{Si}**, differences in activity and mechanistic pathways are anticipated.

CO₂ hydroboration

Previously, **3^{Si}** was found to selectively catalyse the reduction of CO₂ to a formic acid equivalent (product **A**, Scheme 6) with

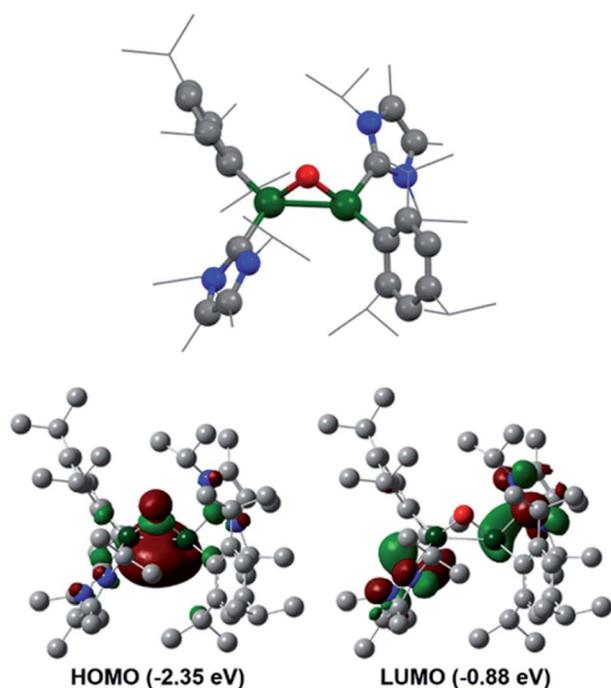


Fig. 7 Calculated molecular structure of compound **11** and its frontier orbitals.

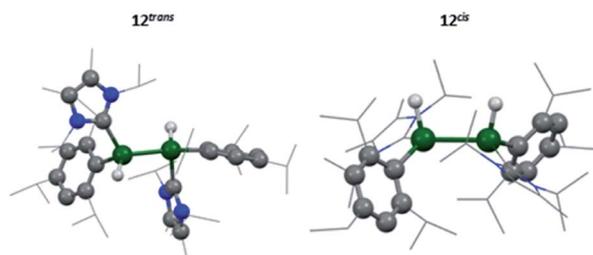
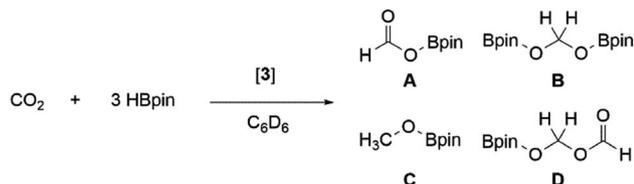


Fig. 8 Calculated molecular structure of **12^{trans}**/**12^{cis}**.



Scheme 6 Catalytic hydroboration of CO₂ mediated by dialumene (3).

pinacol borane (HBpin).¹⁶ Whilst this reaction does proceed at room temperature, it required up to 1 week and 10 mol% of **3**^{Si} (Table 1, entry 1); use of higher temperatures allowed for reduced catalyst loadings and decreased reaction times (Table 1, entry 2). As **3** has so far shown increased reactivity, a trial reaction with 5 mol% of **3** towards hydroboration of CO₂ at room temperature was carried out (Table 1, entry 3). On regular monitoring through ¹H and ¹¹B NMR spectroscopy the consumption of HBpin was noted to occur along with the formation of new B–O containing species. The corresponding ¹H NMR spectrum showed the presence of further reduced species (A–D, Scheme 6), indicating that **3** is not only more catalytically active, but also proceeds through an alternate mechanism due to the presence of B–C.

Again, through use of a higher temperature (60 °C), the catalyst loading could be decreased down to 1 mol% (Table 1, entry 5). This resulted in the same consumption of HBpin after 24 h (at RT) as with 5 mol% (Table 1, entry 4); however, the resulting product distribution differs, with higher temperatures favouring the formation of the triply reduced methanol equivalent (product C, Scheme 6).

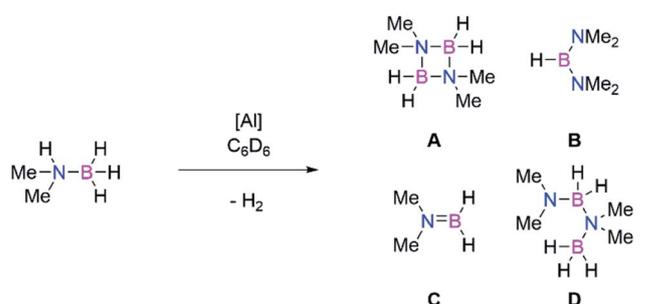
The formation of more highly reduced species indicates a likely change in the mechanism. Previously, **3**^{Si} showed no reactivity towards HBpin and as such a non-hydridic mechanism based on the initial formation of **9**^{Si} was proposed. From computational analysis, coordination of HBpin and subsequent reduction of the exocyclic carbonyl of **9**^{Si} was found to be rate determining. Turnover was achieved through coordination/insertion of an additional CO₂ on the opposite side of the Al···Al plane resulting in formation of an 8-membered ring which collapses to reform **9**^{Si} with release of the formic acid equivalent. This mechanism also further supports the observed selectivity towards product A.¹⁶

In this instance, use of **3** results in the formation of products B–D in notable amounts; therefore, an alternative mechanism for the hydroboration of CO₂ is highly likely. As such, **3** was reacted with 1 eq. of HBpin; the ¹¹B NMR spectrum showed complete consumption of HBpin and formation of a new upfield doublet at δ 2.57 ppm (*J*_{HB} = 112.18 Hz). The same signal and coupling were observed from the reaction of HBpin and I^tPr₂Me₂; therefore it is proposed that the stoichiometric reaction of **3** and HBpin results in NHC abstraction. Notably, this does not result in H–B bond cleavage and formation of an Al(H)–Al(Bpin) type species, which was observed with diborene⁵⁸ and disilyne⁵⁹ chemistry. Addition of CO₂ to this I^tPr₂Me₂–HBpin adduct did not result in formation of any reduced CO₂ species, or any reaction after 24 h at room temperature; therefore it is unlikely that this is the catalytically active species. It is of note that NHCs have been shown to catalyse hydroboration (with HBpin) of carbonyl compounds, in acetonitrile.⁶⁰

Whilst these experimental observations preclude definitive mechanistic analysis, it is proposed that the aryl stabilised dialumene (**3**) acts as a pre-catalyst, with CO₂ hydroboration occurring through an initial hydroalumination of CO₂ and subsequent Al–O/B–H σ-bond metathesis, in line with other previously reported main group hydroelementation of CO₂ mechanisms.^{61–70}

Amine borane dehydrogenation

Main group catalysts (largely group 1, 2, and 13) have also been shown to be viable dehydrocoupling catalysts.^{56,57,71,72} These reactions largely proceed through formation of M–H and M–E

Scheme 7 Catalytic dehydrocoupling of Me₂NHBH₃ mediated by aluminium catalysts.Table 1 Catalytic hydroboration of CO₂ by dialumenes (**3** and **3**^{Si})

Entry	Catalyst	Loading/mol%	Time/h	Temp/°C	Conversion ^a /%	Product distribution ^b /%			
						A	B	C	D
1	3 ^{Si}	10	110	20	86	86	7	7	0
2	3 ^{Si}	5	4	60	68	94	2	4	0
3	3	5	58	20	81	39	27	34	0
4	3	5	24	20	66	65	15	17	3
5	3	1	24	60	62	49	7	41	3

^a Conversion of HBpin based on ¹¹B NMR integrals. ^b Ratio of products based on ¹H NMR integrals.



Table 2 Catalytic dehydrocoupling of Me₂NHBH₃ by aluminium catalysts

Entry	Catalyst	Loading/mol%	Time/hr	Temp/°C	Conversion ^a /%	Product distribution ^b /%			
						A	B	C	D
1	3	5	5	20	72	25	5	—	27
2	3	5	44	20	78	35	5	—	23
3	3^{Si}	5	16.5	20	17	5	1	—	11
4	3	1	2	20	28	8	1	<1	13
5	3	1	16.5	20	60	45	1	<1	14
6	1	5	24	20	0	0	0	0	0
7	1	5	24	60	31	11	—	—	15

^a Conversion of Me₂NHBH₃ based on ¹¹B NMR integrals. ^b Ratio of products based on ¹¹B NMR integrals.

bonds, *via* σ -bond metathesis reactions due to the differing protic and hydridic substrates. Therefore, to probe the intermediacy of aluminium hydrides we examined the use of both dialumenes in amine-borane dehydrocoupling catalysis. Use of 5 mol% of **3** and **3^{Si}** with Me₂NHBH₃ in C₆D₆ showed rapid evolution of gas at room temperature in the case of the aryl substituted dialumene (**3**). Regular monitoring of both reaction mixtures at room temperature by ¹H and ¹¹B NMR spectroscopy confirmed the formation of H₂ and showed several boron containing species by ¹¹B NMR (Scheme 7, products **A–D**). After 5 h approximately 70% of the Me₂NHBH₃ had been consumed in the case of **3** (Table 2, entry 1); in contrast, the silyl dialumene **3^{Si}** after three times as long resulted in 17% consumption of Me₂NHBH₃ (Table 2, entry 3). Notably, prolonged reaction times in the case of the **3** did not lead to significant or complete consumption of Me₂NHBH₃ (Table 2, entry 2), and only a small change in the product distribution was observed with increased reaction times.

It was also possible to use 1 mol% of **3**; again, fast consumption of Me₂NHBH₃ was observed within the first few hours (Table 2, entry 4) with the reaction rate slowing with increased Me₂NHBH₃ consumption (Table 2, entry 5). As aluminium-hydrides have been used in amine borane catalysis previously,⁷³ and to rule out complete hydrogenation and Al–Al bond cleavage during the reaction, compound **1** was tested for dehydrocoupling activity. After 24 h at room temperature (Table 2, entry 6) no conversion of Me₂NHBH₃ was observed; on increasing the temperature to 60 °C (Table 2, entry 7), some formation of H₂ and products **A–D** was observed. Due to the increased temperature and prolonged reaction times required for compound **1**, it is proposed that the retention of an Al–Al bond accounts for the increased catalytic activity.

Comparable to hydroboration reactions, the aryl stabilised dialumene (**3**) was found to be more catalytically active than the silyl-stabilised counterpart (**3^{Si}**). Mechanistically speaking, amine-borane dehydrocoupling reactions generally occur through formation of M–H and M–E bonds.⁵⁷ As such, it has been shown that formation of Al–H bonds is more accessible from **3** compared to **3^{Si}**, therefore accounting for the difference in catalytic activity. Both reactions show initial formation of a catalytic equivalent of HB(NMe₂)₂ (product **B**, Scheme 7) which then remains constant throughout the catalysis. It has

previously been shown by Wright and co-workers that formation of **B** is the result of the formation of the catalytically active Al–H containing species from Al(NR₃)₃ (R = Me, iPr).⁷⁴ Furthermore, Braunschweig and co-workers recently showed that Me₂NHBH₃ can be used to isolate hydrogenated diborenes; thus, analogous reactivity is anticipated.⁷⁵ However, in our hands, stoichiometric reactions of **3** and Me₂NHBH₃ resulted in a mixture of species, whilst reaction with a higher number of equivalents of Me₂NHBH₃ resulted in the dehydrocoupling products. We therefore conclude that the dialumene acts as a pre-catalyst in this reaction and the active catalyst is generated *in situ*.

Conclusions

In conclusion, we have shown the fundamental differences between aryl and silyl supporting ligands for the stabilisation of dialumenes and their subsequent influence on reactivity. The increased flexibility of the *trans*-bent and twisted structure for the aryl dialumene (**3**) enables reactivity with more sterically demanding substrates, and in addition is now able to activate dihydrogen. Further differences are observed in the catalytic ability of the two dialumenes, with the latter exhibiting higher activity. This is likely due to different mechanisms in the catalytic cycle and the ability of the aryl dialumene to stabilise a metal-hydride intermediate in contrast to the silyl ligand.

Conflicts of interest

There are no conflicts to declare.

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