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## ARTICLE

## Dialumenes – Aryl vs. Silyl Stabilisation for Small Molecule Activation and Catalysis

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Main group multiple bonds have proven their ability to act as transition metal mimics in the last decades. However, catalytic application of those species is still in its infancy. Herein we report the second neutral NHC-stabilised dialumene species by usage of a supporting aryl ligand (**3**). Different to the *trans*-planar silyl-substituted dialumene (**3<sup>Si</sup>**), 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 onto the structural motif is disclosed, 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 differ. Thus, indicating the likelihood of alternate mechanisms simply through change of supporting ligand

## 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.<sup>1</sup> Since the discovery that the so called 'double bond rule' could be broken in the beginning of the last quarter of the 20th century,<sup>2-5</sup> 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.<sup>6-7</sup> Besides from curiosity, one of the driving forces behind this research area is the ability to use main group multiple bonds as transition metal mimics.<sup>8-10</sup> 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.<sup>11</sup>

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. 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 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,<sup>12-13</sup> with silyl groups tending towards *trans*-planar geometries<sup>13</sup> and aryl groups promoting *trans*-bent character. It was not until the use of a N-heterocyclic imine (NHI) based ligand, which results in a highly *trans*-bent and twisted geometry, that dihydrogen activation was achieved.<sup>14</sup>

An electropositive silyl supporting ligand was used to stabilise the first neutral aluminium–aluminium double bond, namely dialumene.<sup>15</sup> DFT calculations found the HOMO to consist of a  $\pi$  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 CO<sub>2</sub>.<sup>16</sup> Prior to the isolation of the first neutral dialumene, several compounds with Al–Al bond orders greater than 1 were isolated.<sup>17</sup> These can be classed as radical monoanionic species, one electron  $\pi$ -bonded compounds, a dianionic complex and masked dialumenes. The latter, reported independently by Power<sup>18</sup> and Tokitoh,<sup>19</sup> 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 the benzene derived masked species was capable of activating dihydrogen,<sup>20</sup> however upon switching to an anthracene derived masked species no reactivity towards dihydrogen was observed.

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.<sup>21-25</sup> 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.<sup>26-28</sup>

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Motivated by our groups 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 influence of ligand stabilisation. Whilst silyl and aryl groups have been routinely used in main group multiple bond chemistry, no direct comparisons upon their influence in 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 in main group multiple bond reactivity.

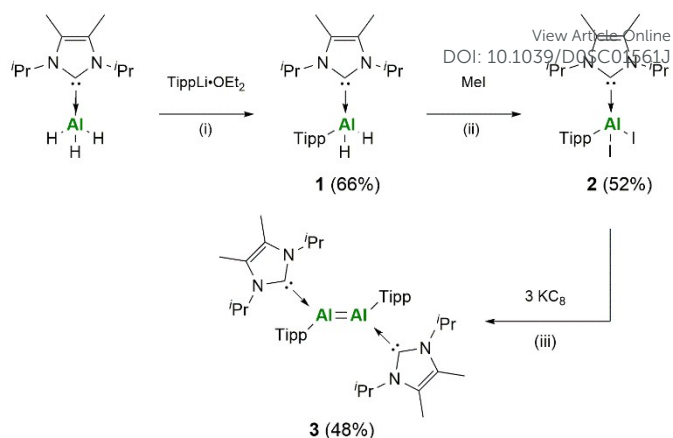
## Results and discussion

### 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 compound towards aryl stabilised systems. As such, we targeted the use of Tipp ligand (Tipp = 1,3,5-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,  $i^i\text{Pr}_2\text{Me}_2$  ( $i^i\text{Pr}_2\text{Me}_2$  = 1,3-di-*iso*-propyl-4,5-dimethyl-imidazolin-2-ylidene). Direct reaction of  $i^i\text{Pr}_2\text{Me}_2\text{AlH}_3$  and LiTipp at  $-78^\circ\text{C}$  resulted in formation of the monosubstituted aluminium dihydride complex,  $i^i\text{Pr}_2\text{Me}_2\text{Al}(\text{Tipp})\text{H}_2$  (**1**) (Scheme 1) in good yields (66 %,  $^{27}\text{Al}$ :  $\delta$  112.9 ppm).<sup>29</sup> The identity of compound **1** was confirmed upon inspection of the  $^1\text{H}$  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-H<sub>2</sub> protons ( $^1\text{H}$ :  $\delta$  5.11 ppm). Additionally, a sharp IR stretching band at  $1711\text{ cm}^{-1}$  (Al-H) was observed in the IR spectrum.

Conversion of **1** towards formation of  $i^i\text{Pr}_2\text{Me}_2\text{Al}(\text{Tipp})_2$  (**2**) could be achieved through reaction with  $\text{B}l_3\text{-dms}$  (dms = dimethyl sulfide) or with a small excess of methyl iodide. With the latter resulting in higher and cleaner conversions, moreover the concomitant formation of methane allows for facile reaction monitoring. Loss of signals relating to Al-H were observed in both the  $^1\text{H}$  NMR and IR spectra, and further characterisation by single crystal XRD confirmed the identity of **2** (Figure S54). Compound **2** is structurally analogous to the corresponding silyl supported complex (**2<sup>Si</sup>**) with Al-C<sup>NHC</sup> bond lengths essentially the same (**2**: 2.0645(18) Å; **2<sup>Si</sup>**: 2.0673(17) Å), indicating the dative nature of the NHC ligand. This is additionally confirmed on comparison with the Al-C<sup>Tipp</sup> bond length (1.9887(19) Å), which is smaller than the sum of the covalent radii ( $R_{\text{Al-C}} = 2.01\text{ \AA}$ ).<sup>30</sup>

Following the analogous synthetic protocol to the silyl dialumene, compound **2** was stirred vigorously with  $\text{KC}_8$  at room temperature (Scheme 1). Monitoring the reaction by  $^1\text{H}$  NMR found this reaction requires 72 hours rather than 24 hours required for the previous case. Compound **3** was isolated as a black solid, whereas in contrast to the silyl stabilised dialumene (**3<sup>Si</sup>**), **3** is highly soluble in a broad range of aromatic, alkyl and



**Scheme 1.** Synthesis of aryl substituted Al(III) compounds, Tipp = 1,3,5-tri-*iso*-propylphenyl. Reaction conditions (i) TippLi-OEt<sub>2</sub>, Et<sub>2</sub>O  $-78^\circ\text{C}$  to RT 48hrs; (ii) MeI, Toluene  $0^\circ\text{C}$  to RT 24hrs; (iii) 3 eq. of  $\text{KC}_8$ ,  $\text{C}_6\text{H}_6$ , RT 72hrs.

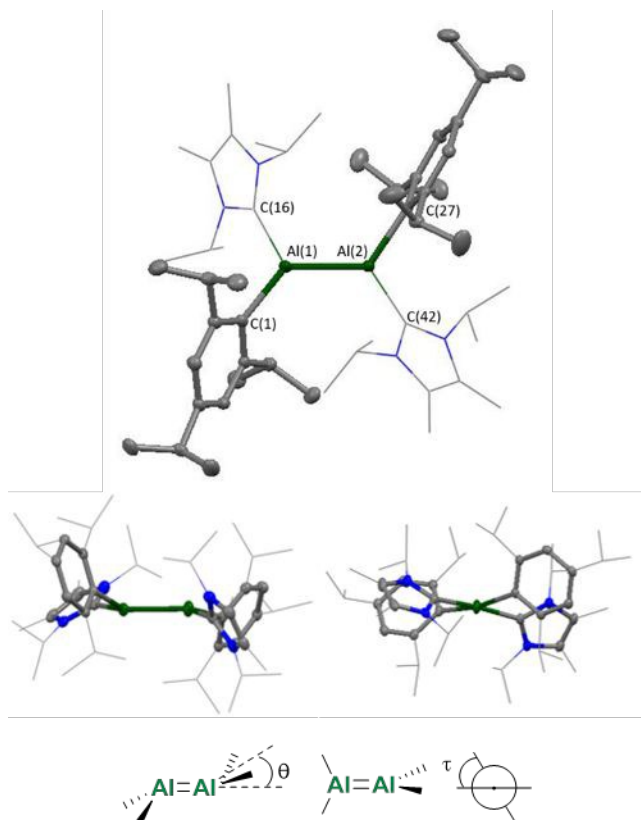
etheral solvents. Both dialumenes are stable in the solid state in an inert atmosphere for prolonged periods, however, decompose in solution after 24 hours. The  $^1\text{H}$  NMR spectrum of **3** shows a large broad signal at room temperature ( $\sim 7.0 - 5.5$  ppm) which resolves into distinct signals at 228 K for the *iso*-propyl groups indicating a degree of rotational fluxionality in this system (Figure S11).

Single crystals were grown from a concentrated *n*-hexane solution at  $5^\circ\text{C}$  and revealed a *trans*-bent and twisted geometry of the aryl stabilised dialumene (Compound **3**, Figure 1) ( $\theta = 17.25^\circ$ ,  $23.70^\circ$ ,  $\tau = 12.06^\circ$ ), which contrasts with the *trans*-planar geometry observed previously. Furthermore, in **3<sup>Si</sup>** the NHC groups were found to be parallel to each other, whilst in **3** they are found to be almost perpendicular ( $85^\circ$ ). The change from planar to *trans*-bent and twisted geometry has also been observed in disilene chemistry on switching between aryl and silyl-based ligands.<sup>12-13</sup> The Al-Al bond length is 2.4039(8) Å which is fractionally longer than the previous dialumene (**3<sup>Si</sup>**: 2.3943(16) Å). Another notable difference between the two systems lies within the Al-C<sup>NHC</sup> bond length (**3**: 2.0596(16), 2.0422(17); **3<sup>Si</sup>**: 2.073(3) Å). The shorter bond length in the case of aryl stabilisation likely indicates a decrease in dative character and thus increase in the covalent nature of the Al-C<sup>NHC</sup> bond (which is also supported by 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 Supporting Information). The optimised 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<sup>Si</sup>** including dispersion are given in the Supporting Information. Analysis of the frontier orbitals of **3** revealed similar features to **3<sup>Si</sup>**, in which the HOMO-1 and HOMO contain the Al-Al  $\sigma$  and  $\pi$  bonds, respectively, as well as the LUMO representing the Al-C<sup>NHC</sup>  $\pi$  bond (Figure 2). The main difference to **3<sup>Si</sup>** (see Figure S57 for the corresponding

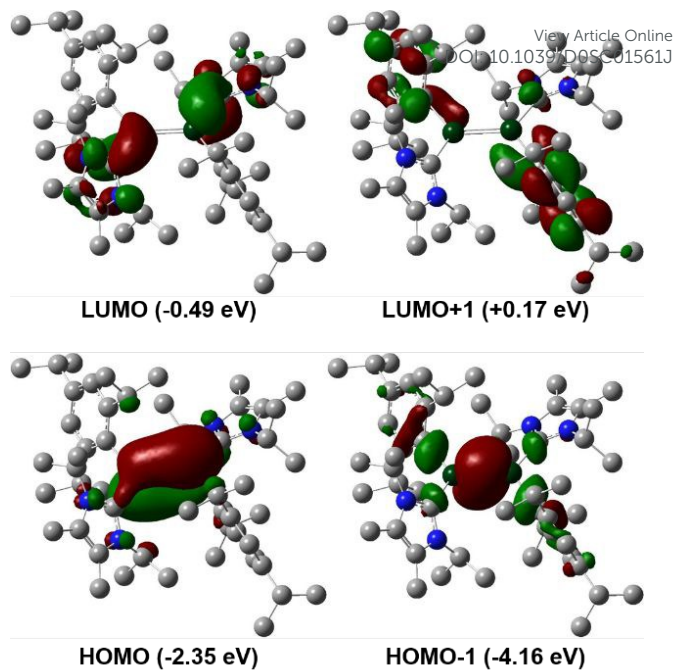




**Figure 1.** Molecular structure of compound **3** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and NHC ligands are depicted in wireframe for simplicity. Selected bond lengths (Å) and angles (°): Al(1)-Al(2) 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),  $\theta = 17.25, 23.70$ ,  $\tau = 12.06$ .

orbitals), is the loss of uniform arrangement of the HOMO on the two aluminium centres as well as additional  $\pi$  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<sup>NHC</sup> bonds in the SC-XRD structure and further evidenced by an increased Gibbs free energy of bond dissociation of 25.5 kcal/mol (cf. **3**<sup>Si</sup> = 16.9 kcal/mol). The conjugation towards the Al-C<sup>NHC</sup>  $\pi$  bond in **3** is also observed on inspection of the monomers (see SI for further details, Figure S62), which also gives rise to the decreased HOMO-LUMO gap in **3** compared to **3**<sup>Si</sup> (**3** = 1.86 eV, **3**<sup>Si</sup> = 2.24 eV) based on decreased overlap of the monomers being possible.

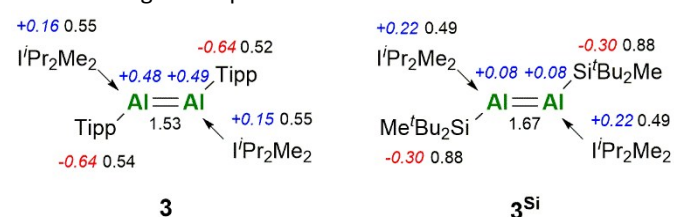
TD-DFT calculations corroborated the experimental UV/vis spectrum of **3**. This showed an intense absorption band at 833 nm ( $\epsilon = 6273 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) (calc. value 794 nm) which can be assigned as the HOMO to LUMO transition and is responsible for the highly coloured compound.<sup>31</sup> Natural bond orbital (NBO) analysis provided electronic insight to the nature of the Al-Al double bond. The Al-Al  $\pi$  bond of **3** bears reduced  $p$  character compared to **3**<sup>Si</sup>. Moreover, this NBO orbital has a lower occupancy based on partial population of the  $\pi^*$  of the C-N bonds of the NHC, rationalizing the increased interaction of the NHC for **3**. This is based on its different orientation, which we



**Figure 2.** Frontier Orbitals of aryl substituted dialumene **3**.

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 (Figure 3), yet still indicating a high degree of multiple bonding character in both systems.

Analysis of NPA charges clearly reflect the silyl effect (Figure 3): the aluminium centres in **3**<sup>Si</sup> bear a nearly neutral charge of +0.08 e, whereas in **3** they account to +0.48/+0.49. We attribute this to the silyl substituents, with their strong  $\sigma$  donating properties, possessing a more effective orbital overlap with the aluminium centres in the  $\sigma(\text{Al-Si})$  bonds. This also becomes evident upon examination of the results of NBO analysis for the Al-C<sup>Tipp</sup>/Al-Si bonds: the Al-C<sup>Tipp</sup> bonds are highly polarised (17% Al, 83% C<sup>Tipp</sup>) compared to Al-Si bonds in **3**<sup>Si</sup> (36% Al, 64% Si). This difference is also rationalised upon comparison of Al-C and Al-Si Pauling electronegativities ( $\Delta\chi$  Al-C 0.94;  $\Delta\chi$  Al-Si 0.29), thus resulting in less polarised Al-Si bonds.



**Figure 3.** Results of the NBO analysis of **3** and **3**<sup>Si</sup>. NPA charges (blue and red) and WBIs (black).

To elucidate the effect of sterics around the aluminium centre, we initially compared the steric demand of the Tipp and Si<sup>t</sup>Bu<sub>2</sub>Me ligands, these revealed similar percentage of buried volume values (%V<sub>bur</sub>) 29.9% (**3**) and 30.7% (**3**<sup>Si</sup>) (Figure S58, S59). However, the shape and thus distribution of kinetic stabilisation varies. Further calculation and comparison of



reduced model systems were performed with the  $I^iPr_2Me_2$  carbene replaced by  $IMe_4$  ( $IMe_4\mathbf{3}$  and  $IMe_4\mathbf{3}^{Si}$ , Figure S60).<sup>32</sup>

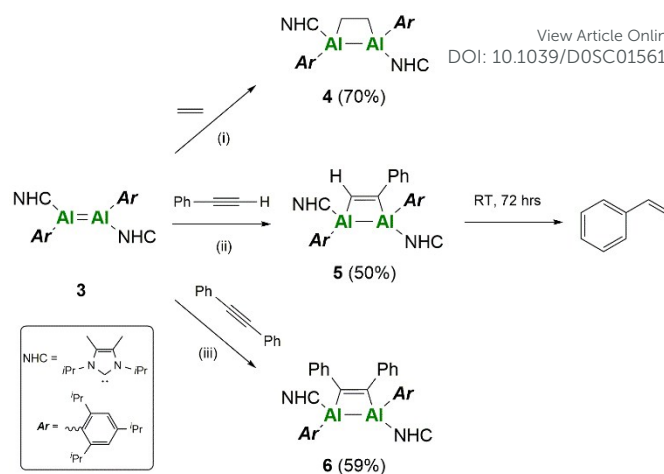
For  $IMe_4\mathbf{3}^{Si}$  the most stable isomer exhibits a strongly *trans*-bent and twisted geometry ( $\theta = 42.1^\circ$ ,  $30.4^\circ$ ,  $\tau = 11.7^\circ$ ) with the NHC planes orientated almost parallel and a substantially elongated Al-Al bond length of 2.43 Å. In the Tipp-substituted  $IMe_4\mathbf{3}$  the *trans*-bent character is decreased compared to  $\mathbf{3}$ , accompanied by a small increase of the Al-Al bond length due to further rotation of the NHC planes towards the Al-Al plane, enabling more effective  $\pi$ -interaction of NHC and the  $Al_2$  moiety. This also becomes more apparent upon examination of the corresponding frontier orbitals with  $IMe_4\mathbf{3}$ . This features enhanced delocalisation of the HOMO onto the NHC moiety, as a consequence of further rotation of the NHC planes towards the Al-Al bond (angle between NHC planes:  $49^\circ$ ). In contrast, the HOMO in  $IMe_4\mathbf{3}^{Si}$  exhibits contributions from the silyl groups, as conjugation towards the NHC  $\pi$ -system is not possible due to the different orientation. Moreover, the HOMO-LUMO gap decreases for aryl and increases for the silyl case, attributed to the decreased/increased *trans*-bent geometry.

Smallest possible model systems, by reducing  $I^iPr_2Me_2$  to  $I^iH_4$  as well as Tipp/ $Si^iBu_2Me$  to phenyl/TMS, were calculated and yield comparable results:  $\mathbf{5}\mathbf{3}$  and  $\mathbf{5}\mathbf{3}^{Si}$  both possess *trans*-bent but no twisted configuration. In  $\mathbf{5}\mathbf{3}^{Si}$  a slightly shorter Al-Al bond length and a decreased *trans*-bent angle ( $21.2^\circ$  vs.  $31.8^\circ$  for  $\mathbf{5}\mathbf{3}$ ) are observed however, in each case the NHC planes are rotated towards the Al=Al bond (see Figure S61). Hence, *trans*-bent structures are obtained for the aryl and the silyl substituted dialumenes bearing minimal steric effects. Thus, it is clearly demonstrated that the steric effects of both NHC and the ligands govern the binding motif of dialumenes. The shape of the ligand influences the interaction with the NHC: either only a weak and purely  $\sigma$ -donating type of interaction, as observed in planar  $\mathbf{3}^{Si}$ , or more flexible coordination of the NHC, with the  $p$ -orbital of the  $C^{Carbene}$  able to form a slipped  $\pi$  bond with the AlAl core as obtained for  $\mathbf{3}$ . The *trans*-bent and twisted structure obtained for  $\mathbf{3}$  is therefore a result of the difference in steric demand of the Tipp ligand compared to  $Si^iBu_2Me$ .

From the different aspects, sterically as well as electronically, discussed above we thus conclude: the structural difference between  $\mathbf{3}$  and  $\mathbf{3}^{Si}$  is caused by the different steric demand of the ligands. From the electronic side of view the change of silyl to Tipp ligand in the dialumene changes the orbital situation at the central AlAl core, which is accompanied by a reduced HOMO-LUMO gap. Moreover, the polarisation of the aluminium centres are diverging, based on differences in electronegativity between C and Si. We thus anticipate differences in reactivity in respect to activation of strong bonds, such as those in small molecules, as well as an increased accessibility towards bigger range of reagents molecules of  $\mathbf{3}$ , based on the increased flexibility of this system.

### Reactivity of Dialumenes

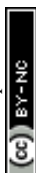
Further differences between these two systems were sought experimentally. Firstly, reactivity towards a series of C-C multiple bonds were examined (Scheme 2). In the case of

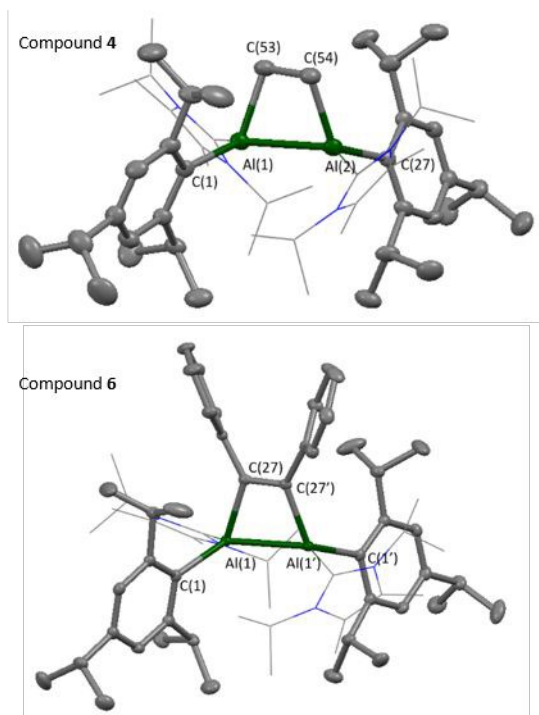


**Scheme 2.** Reactivity of dialumene ( $\mathbf{3}$ ) towards C-C multiple bonds. (i-iii) Toluene, RT, 4 hrs

ethylene, compound  $\mathbf{3}$  underwent formal [2+2]-cycloaddition to yield the dialuminacyclobutane compound  $\mathbf{4}$ , akin to the reactivity observed with  $\mathbf{3}^{Si}$ .<sup>15</sup> Upon reaction with 1 equivalent of phenylacetylene clean formation of a single species by NMR spectroscopy was noted to occur to form compound  $\mathbf{5}$ . This is in contrast to reactivity of  $\mathbf{3}^{Si}$  where both [2+2]-cycloaddition ( $\mathbf{5}^{Si}$ ) and C-H activation were observed. Varying the number of equivalents of phenyl acetylene (2:1 and 3:1 with respect to  $\mathbf{3}$ ) did not result in further incorporation of phenyl acetylene into the complex even at elevated temperatures. However, compound  $\mathbf{5}$  was found to decompose in solution to yield styrene (see Supporting Information Figure S37, 38). Monitoring a  $C_6D_6$  solution of  $\mathbf{5}$  showed this occurs intramolecularly, with the additional protons required to make styrene likely the result of C-H activation. In further support of an intramolecular C-H activation, addition of a hydrogen source e.g. dihydrogen, phenyl silane, pinacol borane or amine borane, failed to provide any notable increase in the rate of styrene formation. Unfortunately, attempts to identify the fate of resulting aluminium containing species were unsuccessful. It is proposed that initial [2+2]-cycloaddition occurs to form compound  $\mathbf{5}$ , followed by C-H activation of the *iso*-propyl groups of the Tipp ligand, as this was not observed with the analogous silyl complex. Intramolecular C-H activation of  $Mes^*$  ligand ( $Mes^* = 1,3,5$ -tri-*tert*-butylphenyl) has been previously observed by thermolysis of  $(Mes^*)_2AlH$ ,<sup>33</sup> whilst 1-germapropadiene which contains a  $Ge=C$  double bond supported by Tipp ligands, also undergoes C-H activation of the Tipp ligand.<sup>34</sup>

Further reactivity towards C-C multiple bonds was trialed with diphenylacetylene ( $PhCCPh$ ). Addition of 1 eq. of  $PhCCPh$  to  $\mathbf{3}^{Si}$  failed to react, after prolonged heating only decomposition of  $\mathbf{3}^{Si}$  was observed. In contrast,  $PhCCPh$  reacts readily with  $\mathbf{3}$  notably through the instant colour change from the dark black solution of  $\mathbf{3}$  to a yellow solution of compound  $\mathbf{6}$ . This difference in reactivity was surprising, considering both  $\mathbf{3}$  and  $\mathbf{3}^{Si}$  reacted cleanly with both non-polar (ethylene to form  $\mathbf{4}$  and  $\mathbf{4}^{Si}$ ) and polar (phenylacetylene to form  $\mathbf{5}$  and  $\mathbf{5}^{Si}$ ) C-C multiple bonds. This difference in reactivity is thought to be a direct result of the choice of stabilizing ligand. The flexibility of





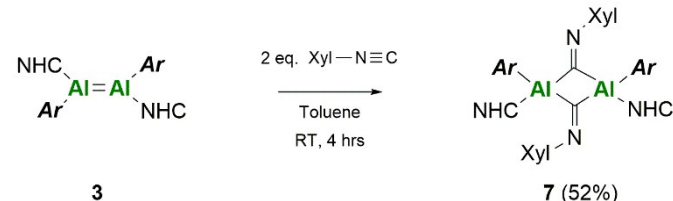
**Figure 4.** Molecular structures of compounds **4** and **6** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and NHC ligands are depicted in wireframe for simplicity. Selected bond lengths (Å) and angles (°): **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).

the Tipp ligand, due to the rotational *iso*-propyl groups, makes the central Al=Al core more accessible for reactant molecules. Thus, enabling reactivity with more sterically demanding reagents. Moreover, the positive NPA charges of **3** makes it more electrophilic in comparison to **3<sup>Si</sup>**, thus implying higher reactivity towards nucleophilic C-C multiple bonds.

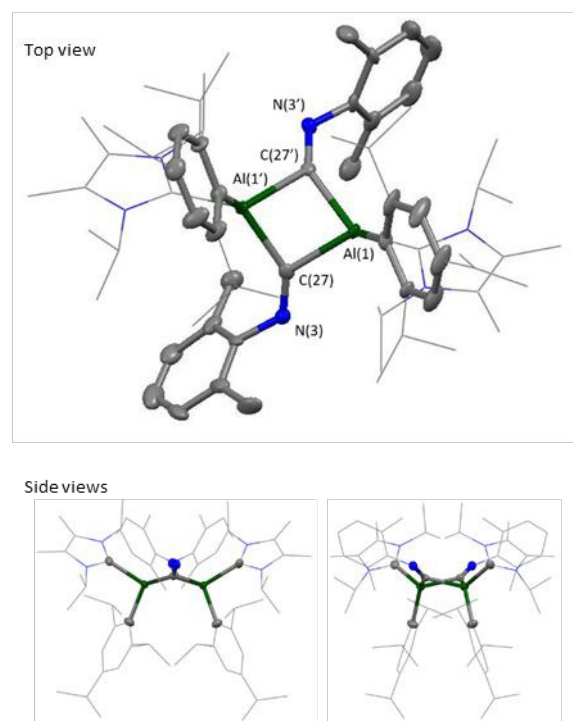
Compounds **4** and **6** were crystallised from concentrated pentane solutions at -30 °C. The XRD structures revealed addition of the C-C multiple bonds to the dialumene, resulting in the formation of 4-membered rings (Figure 4). Loss of double bond character from the dialumene was confirmed due to elongation of the Al-Al bond (**4** 2.6035(13), **6** 2.5918(6) vs **3** 2.4039(8) Å). Also noted to occur is the elongation of the Al-C<sup>NHC</sup> 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 planes), whilst **4** is puckered due to the presence of the *sp*<sup>3</sup> carbons.

Extension of this work towards C-N triple bonds focused on the use of 2,6-dimethylphenylisocyanide (XylINC). Previously Tokitoh and co-workers had shown that reaction of their masked dialumene species resulted in homocoupling of isocyanides.<sup>35</sup> Reactions of varying equivalents of XylINC to **3<sup>Si</sup>**, all resulted in an ill-defined mixture of species, unfortunately attempts to separate species through fractional crystallisation failed. In contrast reaction of 2 eq. with **3** resulted in a clear

colour change from black to red and produced a well defined but complex <sup>1</sup>H NMR spectrum of compound **7** (Scheme 3). This complex contains bridging CNXyl units due to the observed downfield signal in the <sup>13</sup>C NMR spectrum at δ 303.4 ppm. This was similar to the previously observed bridging carbonyl fragment observed with **3<sup>Si</sup>**, in the rearrangement of CO<sub>2</sub> (δ 276.0 ppm)<sup>16</sup> and the bridging isocyanide intermediate reported by Tokitoh (δ 294.7 ppm).<sup>35</sup> Single crystals of **7** were grown from a 2:1 (Toluene: Hexane) mixture at 5 °C, revealing a butterfly configuration with two  $\mu$ -CNXyl units (Figure 5).



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



**Figure 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) 2.053(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(1)-C(28) 126.3(2).

The central Al-C-Al-C core in compound **7** is puckered (34.3° between the two C-Al-C 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<sup>Si</sup>**. However, the reasons for such change in conformation were unclear. Again, elongation of the Al-C<sup>NHC</sup> bond lengths is observed (Al-C<sup>NHC</sup> 2.109(3) Å), with the change in Al-C<sup>Tipp</sup> negligible (**7** 2.042(7) vs **3** (2.0292(16) Å). Reduction of the C-N



triple to 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.<sup>36-39</sup> Additionally, the change in angle around the nitrogen in XylNC from linear to bent (126.3 (2) °) confirms reduction of C-N triple bond. This butterfly configuration has been previously observed with transition metal complexes,<sup>40-47</sup> however, these all contain a M-M bond, those without M-M bonds contain a planar central ring.<sup>48-52</sup>

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: 1544 cm<sup>-1</sup> vs. calculated: 1568 cm<sup>-1</sup>). Orbital analysis (Figure 6) revealed the HOMO as orbital overlap of aluminium and π\*(C=N). The LUMO represents the combination perpendicular to the HOMO, including conjugation across the central ring. NBO calculations confirmed no C-C or Al-Al bond is present in **7** (WBI (C<sup>27</sup>C<sup>27</sup>):0.06; WBI (Al<sup>1</sup>Al<sup>1</sup>): 0.04).

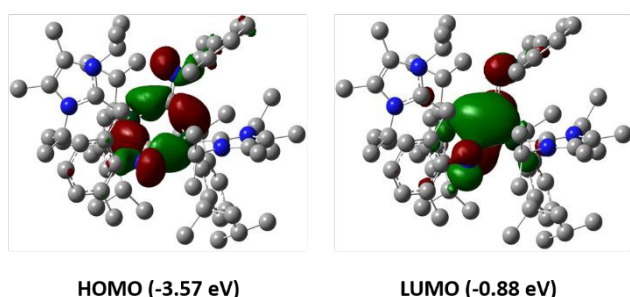
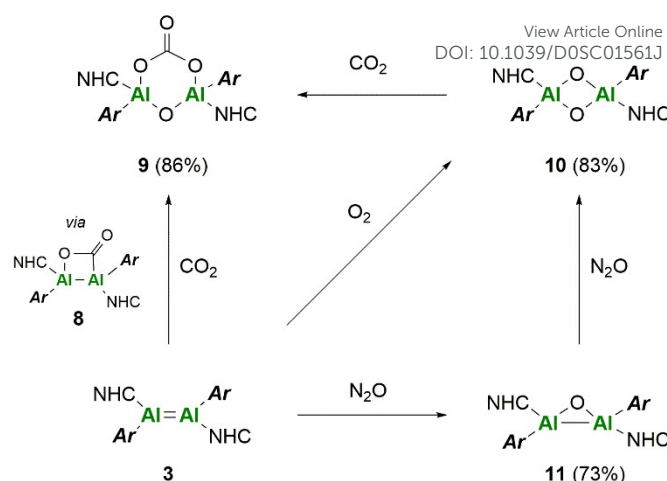


Figure 6. Frontier orbitals of compound **7**.

### Small Molecule Activation

Further reactivity differences were sought through investigation towards small molecules (Scheme 4). Previously reaction of **3**<sup>Si</sup> towards carbon dioxide (CO<sub>2</sub>) resulted in an initial CO<sub>2</sub> fixation complex.<sup>16</sup> This subsequently underwent C-O cleavage reactivity, in the absence of additional CO<sub>2</sub> through rearrangement to a bridging carbonyl complex. Whilst in the presence of CO<sub>2</sub> formation of a carbonate species with elimination of CO was observed. On reaction of **3** with CO<sub>2</sub> immediate loss of the black colour and formation of a colourless solution was observed. On inspection of the <sup>13</sup>C NMR spectrum, CO formation (δ 184.4 ppm) and CO<sub>3</sub> (δ 159.12 ppm) was observed indicating the formation of the carbonate complex compound **9**. In contrast to **3**<sup>Si</sup>, attempts to isolate the CO<sub>2</sub> fixation product were unsuccessful as it rapidly converted to compound **9**. Use of the labile <sup>i</sup>Pr<sub>2</sub>Me<sub>2</sub>-CO<sub>2</sub> species allowed for the formal [2+2]-cycloaddition product (Compound **8**) to be observed due to its characteristic <sup>13</sup>C resonance at δ 207.7 ppm (**8**<sup>Si</sup> 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 formation of **9** proceeds through the CO<sub>2</sub> fixation species in a similar manner to **3**<sup>Si</sup>.

Reaction of **3** with O<sub>2</sub> resulted in the expected dioxo product, compound **10**, same as the previously reported



Scheme 4. Reactivity of dialumene (**3**) towards small molecules, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>O.

reactivity of **3**<sup>Si</sup>. In a similar manner to **10**<sup>Si</sup>, compound **10** can also be reacted with CO<sub>2</sub> resulting in carbonate complex **9**. In a notable difference to the silyl supported reactivity, addition of N<sub>2</sub>O to compound **3** resulted in a dark red solution at room temperature (**3**<sup>Si</sup> yielded colourless compound **10**<sup>Si</sup>). This red solution was observed to slowly fade to colourless over a few hours and the formation of compound **10** was confirmed by <sup>1</sup>H 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 the glovebox freezer however at room temperature and in solution further oxidation to compound **10** occurs. Whilst <sup>1</sup>H NMR showed similar environments for both **10** and **11** (Figure S39), compound **11** is intensely coloured (UV/vis = 512 nm, ε = 1155 L mol<sup>-1</sup> cm<sup>-1</sup>) 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** (Figure S55). To provide further insight, calculations were also performed on compounds **10** and **11**. The optimised structure of **10** is symmetric relating to the Al-O bonds, as previously observed for the analogous silyl compound (**10**<sup>Si</sup>).<sup>16</sup> 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 Figure 7, reminiscent of the disilaoxirane reported by our group.<sup>53</sup> The LUMO represents the non-filled π(Al-C<sup>NHC</sup>) bond. TD-DFT calculations verified the experimentally observed red colour (UV-vis 512 nm) with a good accordance (calc. 519 nm) and are 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**<sup>Si</sup> was freeze-pump-thawed degassed then backfilled with approximately 1 atm of H<sub>2</sub>. After 24 hours at room temperature no reaction was noted to have



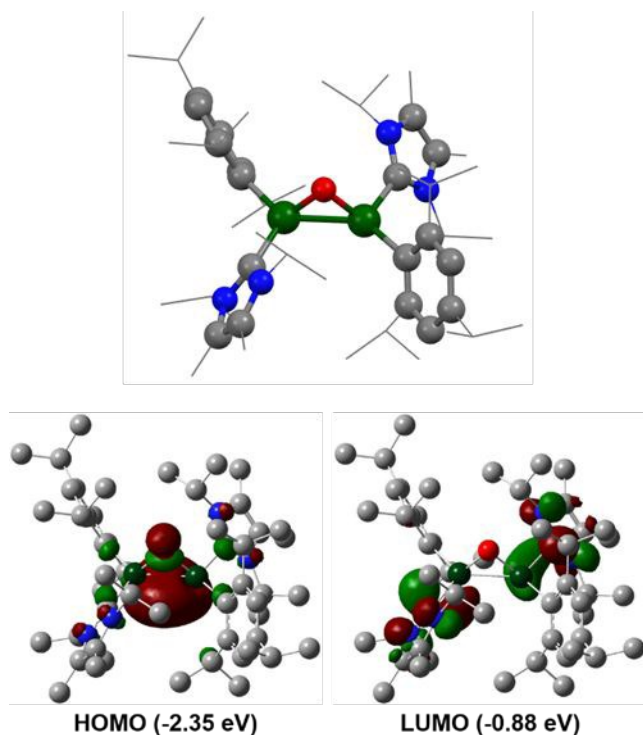
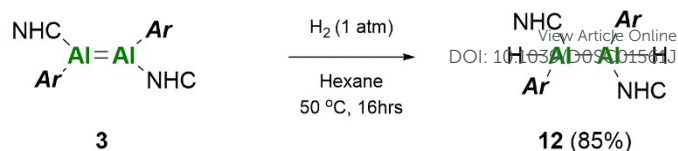


Figure 7. Calculated molecular structure of compound **11** and its frontier orbitals.

occurred, increasing the temperature to 60 °C and regular monitoring, only resulted in the observed decomposition of **3<sup>Si</sup>**. Repetition of this reaction with aryl stabilised dialumene, compound **3**, also resulted in no reaction at room temperature. After 16 hrs at 50 °C, however, the black colour of **3** had faded to a dark brown/yellow solution (Scheme 5). On inspection of the <sup>1</sup>H 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 1634 cm<sup>-1</sup> were observed. Compounds containing no Al-Al bond but both terminal and bridging hydrides are found at approximately 1880 cm<sup>-1</sup> and 1350 cm<sup>-1</sup>, respectively.<sup>20, 54</sup> Whilst terminal hydrides within complexes containing Al-Al bonds are found within 1680-1835 cm<sup>-1</sup>.<sup>55</sup> Thus, pointing more in the direction of a terminal hydride with Al-Al bonds. Additionally, the previous terminal hydride in the related silyl system, from C-H activation of phenyl acetylene, this Al-H was found at 1666 cm<sup>-1</sup>.<sup>15</sup> 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, combinations of both as well as different rotational isomers (H: *cis* or *trans*; NHC and Tipp ligands *cis* or *trans*).



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

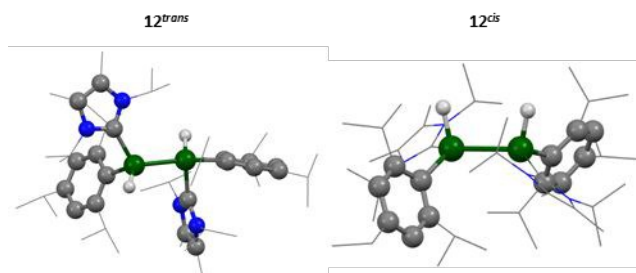


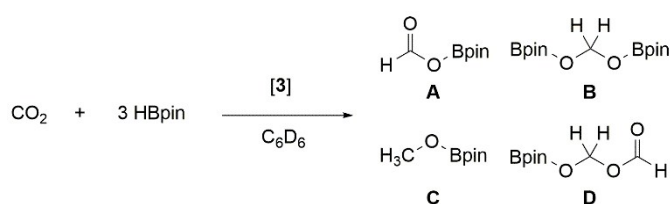
Figure 8. Calculated molecular structure of **12<sup>trans</sup>**/**12<sup>cis</sup>**.

The two lowest lying isomers were found to possess terminal hydrides in the *cis* and *trans* configurations (Figure 8). The Al-H stretching frequencies were calculated at 1634 and 1676 cm<sup>-1</sup>, respectively, which is in good agreement with the experimentally obtained values (for detailed information see the Supporting Information). 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.<sup>56,57</sup> With the ability to form dialuminium-hydrides in the case of **3** and not for **3<sup>Si</sup>**, differences in activity and mechanistic pathways are anticipated.

**CO<sub>2</sub> Hydroboration** Previously, **3<sup>Si</sup>** was found to selectively catalyse the reduction of CO<sub>2</sub> to a formic acid equivalent (Product A, Scheme 6) with pinacol borane (HBpin).<sup>16</sup> Whilst this reaction does proceed at room temperature this required up to 1 week and 10 mol% of **3<sup>Si</sup>** (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 CO<sub>2</sub> at room temperature was carried out (Table 1, entry 3). On regular monitoring through <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy the consumption of HBpin was noted to occur along with the formation of new B-O containing species. The corresponding <sup>1</sup>H 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**.





**Scheme 6.** Catalytic hydroboration of CO<sub>2</sub> mediated by dialumene (**3**).

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 hrs (at RT) as with 5 mol% (Table 1, entry 4), however resulting product distribution differs. With higher temperatures favoring the formation of the triply-reduced methanol equivalent (product **C**, Scheme 6).

The formation of higher reduced species indicates a likely change in the mechanism. Previously, **3**<sup>Si</sup> showed no reactivity towards HBpin and as such a non-hydridic mechanism based on the initial formation of **9**<sup>Si</sup> was proposed. Computational analysis found that coordination of HBpin and subsequent reduction of the exocyclic carbonyl of **9**<sup>Si</sup> was found to be rate determining. Turnover was achieved through coordination /insertion of an additional CO<sub>2</sub> on the opposite side of the Al---Al plane resulting in formation of an 8-membered ring which collapses to reform **9**<sup>Si</sup> with release of the formic acid equivalent. This mechanism also further supports the observed selectivity towards product **A**.<sup>16</sup>

**Table 1.** Catalytic hydroboration of CO<sub>2</sub> by dialumenes (**3** and **3**<sup>Si</sup>).

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

<sup>a</sup> Conversion of HBpin based on <sup>11</sup>B NMR integrals; <sup>b</sup> Ratio of products based on <sup>1</sup>H NMR integrals.

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 CO<sub>2</sub> is highly likely. As such, **3** was reacted with 1 eq. of HBpin, the <sup>11</sup>B NMR spectrum showed complete consumption of HBpin and formation of a new upfield doublet at δ 2.57 ppm (*J*<sub>HB</sub> = 112.18 Hz). The same signal and coupling was observed from reaction of HBpin and *i*-Pr<sub>2</sub>Me<sub>2</sub>, 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 a Al(H)-Al(Bpin) type species, which was observed with diborene<sup>57</sup> and disilyne<sup>59</sup> chemistry. Addition of CO<sub>2</sub> to this *i*-Pr<sub>2</sub>Me<sub>2</sub>-HBpin adduct did not result in formation of any reduced CO<sub>2</sub> species, or any reaction after 24hrs 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.<sup>60</sup>

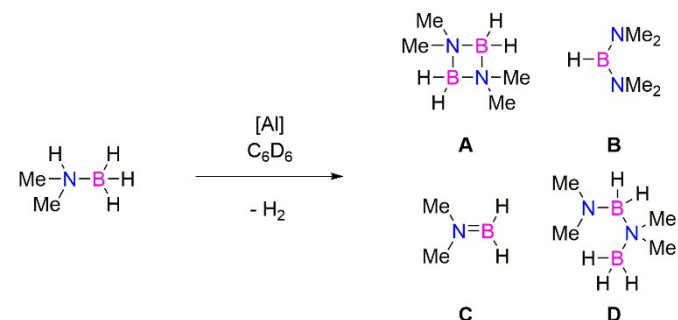
Whilst these experimental observations preclude definitive mechanistic analysis, it is proposed that the aryl stabilised dialumene (**3**) acts as a pre-catalyst. With CO<sub>2</sub> hydroboration occurring through an initial hydroalumination of CO<sub>2</sub> then subsequent Al-O/B-H σ-bond metathesis, in line with other previously reported main group hydroelementation of CO<sub>2</sub> mechanisms.<sup>61-70</sup>

**Amine Borane Dehydrogenation** Main group catalysts (largely group 1, 2, and 13) have also shown to be viable as dehydrocoupling catalysts.<sup>56-57,71,72</sup> These reactions largely

proceed through formation of M-H and M-E 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**<sup>Si</sup> with Me<sub>2</sub>NHBH<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> 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 <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy confirmed the formation of H<sub>2</sub> and showed several boron containing species by <sup>11</sup>B NMR (Scheme 7, products **A-D**). After 5 hrs approximately 70% of the Me<sub>2</sub>NHBH<sub>3</sub> had been consumed in the case of **3** (Table 2, entry 1), in contrast the silyl dialumene **3**<sup>Si</sup> after three times as long resulted in 17% consumption of Me<sub>2</sub>NHBH<sub>3</sub> (Table 2, entry 3). Notably, prolonged reaction times in the case of the **3** did not lead to significant or complete consumption of Me<sub>2</sub>NHBH<sub>3</sub> (Table 2, entry 2), only a small change in the product distribution was observed through increased reaction times.

**Scheme 7.** Catalytic dehydrocoupling of Me<sub>2</sub>NHBH<sub>3</sub> mediated by aluminium catalysts.

It was also possible to use 1 mol% of **3**, again fast consumption of Me<sub>2</sub>NHBH<sub>3</sub> was observed within the first few



hours (Table 2, entry 4) with the reaction rate slowing with increased Me<sub>2</sub>NHBH<sub>3</sub> consumption (Table 2, entry 5). As aluminium-hydrides have been used in amine borane catalysis previously,<sup>73</sup> and to rule out complete hydrogenation and Al-Al bond cleavage during the reaction, compound **1** was tested for dehydrocoupling activity. After 24hrs at room temperature (Table 2, entry 6) no conversion Me<sub>2</sub>NHBH<sub>3</sub> was observed, on increasing the temperature to 60 °C (Table 2, entry 7) some formation of H<sub>2</sub> 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.

**Table 2.** Catalytic dehydrocoupling of Me<sub>2</sub>NHBH<sub>3</sub> by aluminium catalysts

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



7	1	5	24	60	31	11	-	-	15
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<sup>a</sup> Conversion of Me<sub>2</sub>NHBH<sub>3</sub> based on <sup>11</sup>B NMR integrals; <sup>b</sup> Ratio of products based on <sup>11</sup>B NMR integrals.

Comparable to hydroboration reactions, the aryl stabilised dialumene (**3**) was found to be more catalytically active than the silyl-stabilised counterpart (**3**<sup>Si</sup>). Mechanistically speaking, amine-borane dehydrocoupling reactions generally occur through formation of M-H and M-E bonds.<sup>57</sup> As such, it has been shown that formation of Al-H bonds is more accessible from **3** compared to **3**<sup>Si</sup> therefore accounting for the difference in catalytic activity. Both reactions show initial formation of a catalytic equivalent of HB(NMe<sub>2</sub>)<sub>2</sub> (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(NR<sub>3</sub>)<sub>3</sub> (R = Me, iPr).<sup>74</sup> Furthermore, Braunschweig and co-workers recently showed that Me<sub>2</sub>NHBH<sub>3</sub> can be used to isolate hydrogenated diborenes thus analogous reactivity is anticipated.<sup>75</sup> However, in our hands stoichiometric reactions of **3** and Me<sub>2</sub>NHBH<sub>3</sub> resulted in a mixture of species, whilst reaction with a higher number of equivalents of Me<sub>2</sub>NHBH<sub>3</sub> 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.

## Acknowledgements

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## Notes and references

Crystallographic data for **2** (CCDC 1989167), **3** (CCDC 1989168), **4** (CCDC 1989169), **6** (CCDC 1989170), **7** (CCDC 1989171) and **11** (CCDC 1989172) have been uploaded to the Cambridge Crystallographic Database. Further spectroscopic, crystallographic, and computational data are included in the Supporting Information.

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