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## COMMUNICATION

## Addition of *in-situ* reduced amidinato-methylaluminium chloride to acetylenes†‡

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**Two ethylene-bridged methylaluminium amidinates and one aluminium amidinate containing three terminal trimethylstannylethynyl groups interconnected by  $\pi$ -coordinated potassium ions were prepared *in-situ*. The re-oxidation of the ethylene-bridged compound by iodine followed by further reduction using the same activation procedure demonstrated versatility of the approach used. The reactivity of an ethylene-bridged methylaluminium amidinate towards hydrogen chloride in terms of building block concept was also studied. DFT calculations were carried out in order to get insight into the mechanism of the *in-situ* activation of diphenylacetylene.**

In the last few decades the seminal observations on activations of various small molecules and unsaturated systems by mainly low-valent main group metal complexes and their subsequent chemical transformations have attracted considerable attention.<sup>1</sup> The chemistry of low-valent aluminium<sup>2</sup> compounds such as Al<sup>I</sup> and/or Al<sup>II</sup> has been significantly developed when the first stable species with Al-Al arrangement - [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Al-Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> - were prepared and structurally characterized by Uhl<sup>3</sup> in 1988. However, the key milestone was Roesky's report in 2000 concerning the synthesis of stable monomeric aluminum(I) species (a stable aluminium analogue of carbene) decorated by a crowded bidentate diketiminato ligand.<sup>4</sup> Along with the synthetic routes yielding new low-valent aluminium complexes such as Al<sup>I</sup> species, dialumanes<sup>1i,2e,5</sup> and some metalloids/clusters<sup>2g,h,6</sup>, new reactivity patterns of the aforementioned compounds towards small/larger molecules<sup>7</sup> were disclosed.

An important part of the synthetic and structural studies is associated with the activation of the C-C multiple bond via either *in-situ* generated Al<sup>I</sup>/Al<sup>II</sup> species or via the stepwise

reaction with the isolable Al-Al/Al<sup>I</sup>/Al<sup>I</sup> intermediate. Both, the *in-situ* reduction of diiodoaluminium *N,N*-diketiminato in the presence of RC≡CR moiety (R = Ph or SiMe<sub>3</sub>)<sup>8</sup> and the stepwise activation of RC≡CR<sup>9</sup> (R = H, Ph, Me or SiMe<sub>3</sub>) by isolable LAI<sup>I</sup> intermediate afforded aluminacyclopropenes. However, dialuminacyclobutenes were obtained from the *in-situ* (reduction by KC<sub>8</sub>)<sup>10</sup> as well as the stepwise reaction (via Al-Al fragment)<sup>7b</sup> of Me<sub>3</sub>SiC≡CSiMe<sub>3</sub> with organoaluminium compounds containing sterically demanding ligands. To the best of our knowledge, only sole examples of dinuclear aluminium ethylene bridged<sup>5a</sup> or double bridged compounds prepared from bisamido-dialane and PhC≡CH<sup>5c</sup> followed by heating of the product in benzene (1,4-dialuminacyclohexadienes<sup>11</sup>) and PhC≡CPh, respectively, were described until now. The pioneering studies of the reactivity of trialkyl aluminium compounds with acetylenes activated by UV-light or sodium metal were also performed.<sup>5d,e</sup> Furthermore, the reaction of dichloroaluminium amide with an excess of acetylides of the alkali metals (Li<sup>12</sup>, Na and K<sup>12b</sup>) yielded ate-complexes consisting of ionic aluminium fragment carrying two/three terminal ethynyl groups involving alkali metal ions in bridging mode.

Herein, we report on the synthesis, structural properties and reactivity of products resulting from the *in-situ* reduction of chloromethylaluminium species supported by NCN chelating amidinato ligand with various acetylenes. The main idea of the studied approach stemmed from the previous work<sup>13</sup> in which the preparation of the starting LAIMECl (L = DippNC(Me)NDipp) and its reduction by a potassium mirror (yielding LAIME<sub>2</sub> and L<sub>2</sub>AlME) were investigated. The probable existence of the transient "LAIME" particle offered the possibility of its utilization in further studies as a trap for various unsaturated systems.

Thus, the plausible reductive coupling (Scheme 1) of [DippNC(Me)NDipp]AlMECl with either PhCCPh or 4-Me<sub>3</sub>Si-C<sub>6</sub>H<sub>4</sub>CCPh and potassium at room or/and lower temperature yielded novel ethylene-bridged methylaluminium amidinates **1** (31 %) and **2** (27 %), respectively, along with aluminium amidinates LAIME<sub>2</sub> and L<sub>2</sub>AlME (L = DippNC(Me)NDipp) as side-products removable by crystallization (ESI†). In addition, the

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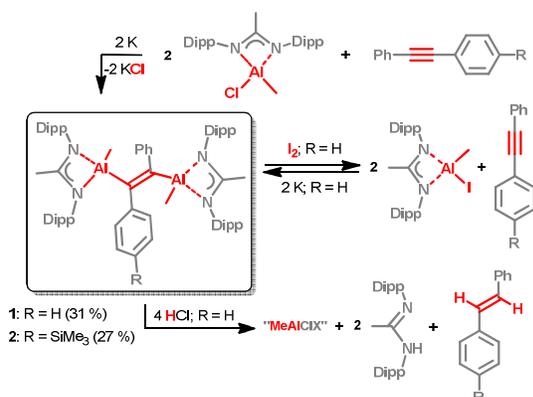
‡ Electronic Supplementary Information (ESI) available: Experimental details, spectroscopic characterization, computational details, and X-ray crystallographic data - CCDC 1406406 - 1406408 for **1** - **3** is available. See DOI: 10.1039/x0xx00000x.

† Dedicated to Dr. Bohumil Štíbr on the occasion of his 75<sup>th</sup> birthday in recognition of his outstanding contributions to the area of boron chemistry

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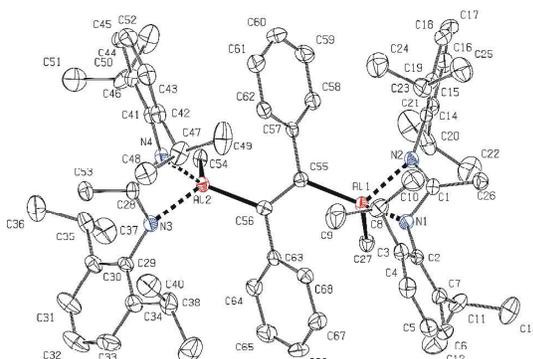
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blank test showed no reaction between both components without the presence of potassium. Notwithstanding that the activation of acetylenes within the three-component framework (*in-situ*) affording aluminacyclopropenes or dialuminacyclobutenes was already published by Roesky and others.<sup>8,10</sup>



**Scheme 1** Synthesis of dinuclear ethylene-bridged methylaluminum amidinates (**1** - **2**) within the three-component approach and the reactivity of **1** towards hydrogen chloride and iodine.

Both **1** and **2** were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in C<sub>6</sub>D<sub>6</sub>, elemental analyses as well as XRD techniques (**1** - Fig. 1 and S5 in ESI†; **2** - Fig. S6 and S7 in ESI†). Structures of both compounds **1** and **2** showing in both cases four-coordinated aluminium atoms with a distorted tetrahedral arrangement of the substituents. The most prominent feature of both dinuclear structures is the presence of a Al-C(Ph)=C(Ph)-Al chain fragment with twisted phenyl groups (torsion angles - 50.50 and 49.95°) in *trans* configuration. This structural arrangement may predetermine the nature of its further reactivity as well as the structural design of products. The diphenylethylene moiety (C=C found in **1** C55-C56 1.367(3) Å) serves as connecting agent (Al1-C55 1.985(2) and C56-Al2 1.987(3) Å in **1**) between two aluminium atoms decorated by a bidentately bonded amidinates.



**Fig. 1** The molecular structure of **1** (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1-C1 1.337(3); N2-C1 1.337(3); N4-C28 1.333(3); N3-C28 1.333(3); C1-Al1 2.386(2); C28-Al2 2.368(2); Al1-C27 1.971(2); Al2-C54 1.980(2); N1-Al1 1.937(2); N2-Al1 1.976(2); N3-Al2 1.960(2); N4-Al2 1.938(2); Al1-C55 1.985(2); C55-C56 1.367(3); C56-Al2 1.987(3); N1-

C1-N2 109.7(2); N3-C28-N4 110.4(2); C1-Al1-C55 129.10(9); C28-Al2-C56 132.30(9); Al1-C55-C56 120.06(18).

Two plausible mechanisms were previously proposed by Roesky<sup>8</sup> for the reduction of the similar aluminium complex LAlI<sub>2</sub> in the presence of alkynes, suggesting either the formation of the aluminium centred radical LAlI<sup>•</sup>, which couples with alkynes or the electron-transfer from K to alkyne and the formation of the radical anion K<sup>+</sup>(RCCR)<sup>•-</sup>, which substitutes the iodide in the LAlI<sub>2</sub>. In both pathways, the same intermediate LAlI(RCCR)<sup>•</sup> is formed, yielding the desired product via a further electron-transfer reaction. For our system, the latter pathway could be ruled out because only one electron-transfer reaction can take place and therefore the alkyne coupling would be observed instead of the formation of **1**.

Based on these facts, DFT computations were carried out to elucidate the plausible reaction mechanism, suggesting one of the aforementioned pathways along with another possible pathway containing experimentally postulated dialumane intermediate<sup>5a</sup> (Fig. 2 and S16 in ESI†, Table S2 in ESI†). Both start with the reduction of the chloromethylaluminum complex **R** yielding radical **INT-1**. The first pathway comprises the formation of the dialumane intermediate in either *anti* (**INT-2A**) or *syn* conformation (**INT-2A'**), which subsequently reacts with the diphenylacetylene to form the corresponding final product with the *trans* (**P**) or *cis* (**P'**) type of structural arrangement, respectively. The *trans* and *anti* isomers are 7.1 and 6.9 kcal.mol<sup>-1</sup> lower in energy than the respective *cis* and *syn* isomers, which is in good agreement with the experimental results. Moreover, the prolonged reaction time and lower yields correlate well with the slightly positive ΔG of the second step of the reaction sequence. The second pathway is similar to the mechanism proposed by Roesky,<sup>8</sup> suggesting the reaction of the methylaluminum radical **INT-1** with the diphenylacetylene, which generates the intermediate **INT-2B**. The coupling of the aluminium-diphenylethylene radical **INT-2B** with the methylaluminum radical **INT-1** leads to the formation of the expected product **P** (**P'**). Similarly as in the first pathway, the rate-determining step of the reaction mechanism is the activation of a C≡C triple bond, which has in this case a slightly negative ΔG. Therefore, the second pathway seems to be thermodynamically more favoured, however the negligible differences in ΔG (-0.9 kcal.mol<sup>-1</sup> vs. 2.4 kcal.mol<sup>-1</sup>) do not allow for the definite exclusion of the first one.

Finally, the two radicals occurring in the proposed reaction pathways were investigated, revealing that **INT-1** is an aluminum-centered radical (Mulliken spin density at Al 82%) while in the case of **INT-2B** the spin density is more delocalized (Mulliken spin density at C<sub>ethylene</sub> 58%) into the π-system of the phenyl ring (Fig. S15 in ESI†).

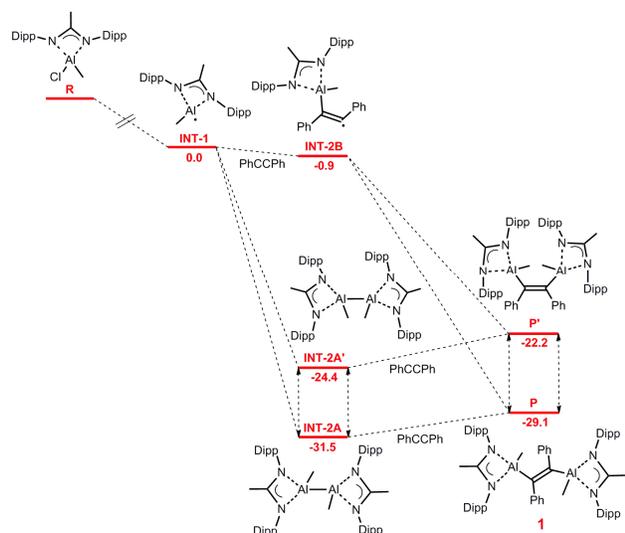


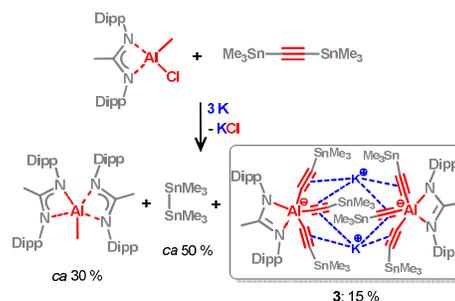
Fig. 2 Energetic profiles (Gibbs free energies in kcal mol<sup>-1</sup>) for the *in-situ* interaction of [DippNC(Me)NDipp]AlMeCl (**R**) with potassium and diphenylacetylene.

The oxidation of **1** by molecular iodine led to a clear mixture (<sup>1</sup>H and <sup>13</sup>C NMR - Fig. S9 - S10 in ESI†) of diphenylacetylene and [DippNC(Me)NDipp]AlMeI (Fig. S1 - S2 in ESI†). The reaction mixture was used without further workup for a re-reduction using the same approach. The reaction proceeded to the same product **1** in 34% yields. In addition, the attempt to oxidize **1** by the oxygen gas afforded a complex mixture of products with a major proportion of benzil and DippNC(Me)NHDipp, along with a small amount of diphenylacetylene and other by-products.

The importance of the structural arrangement of diphenylethylene moiety is demonstrated on reactivity of complex **1** towards small molecules (Scheme 1). A quantitative chemical transformation (based on <sup>1</sup>H - Fig. S11, <sup>13</sup>C NMR spectra- Fig. S12 and EI-MS - Fig. S14 in ESI†) of the diphenylethylene fragment after the reaction with two equivalents of hydrogen chloride to *trans*-stilbene was observed. This "hydrogen substitution" process was completed by the formation of amidine DippNC(Me)NHDipp (<sup>1</sup>H, <sup>13</sup>C NMR and EI-MS) and unidentified "methylaluminium chloride-containing" species (Fig. S13 in ESI†) as by-products formed due to the decomposition of the initially formed [DippNC(Me)NDipp]AlMeCl.

The analogous *in-situ* reduction of suitable [DippNC(Me)NDipp]AlMeCl in the presence of bis(trimethylstannyl)acetylene (Scheme 2) resulted in the formation of ca. 15% of the ate-complex **3** identified by NMR and XRD techniques. In the reaction mixture the aluminium-amidinate **3** was accompanied by Me<sub>3</sub>SnSnMe<sub>3</sub> (-109 ppm in the <sup>119</sup>Sn NMR spectrum)<sup>14</sup> and L<sub>2</sub>AlMe (L = DippNC(Me)NDipp)<sup>13</sup> as major by-products. This structural arrangement on the aluminium atom, however, is not entirely surprising. A couple of examples of these rare types of aluminium ate-complexes are known from the reaction of amido-aluminium dichloride with a large excess of alkali metal acetylide.<sup>12</sup> Most probably the potassium atom attacks the Sn-

C bond in the first step to form KCCSnMe<sub>3</sub><sup>15</sup> which further reacts with the MeAlCl fragment of the starting component.



Scheme 2 Reduction of [DippNC(Me)NDipp]AlMeCl in the presence of bis(trimethylstannyl)acetylene.

The signals corresponding to terminally bonded trimethylstannyl-ethynyl groups in **3** were found at 110.1 ppm (broad signal for C-Al) and 97.2 ppm (for C-Sn) in the <sup>13</sup>C NMR spectrum and at -88 ppm in the <sup>119</sup>Sn NMR spectrum (116.2 ppm and -81 ppm, respectively, for Me<sub>3</sub>SnCCSnMe<sub>3</sub>). This correlates well with the data found for the previously described ate-complexes [LAl(C≡C-Ph)<sub>3</sub>]M (M = Li, Na or K; broad signal at ~110 ppm)<sup>12b</sup> and [LAl(C≡C-SiMe<sub>3</sub>)<sub>3</sub>]Li (95.3 ppm for C-Si)<sup>12a</sup>. The value of the chemical shift of the central carbon atom of NCN moiety (165.9 ppm) in the <sup>13</sup>C NMR spectrum indicates the presence of a anisobidentately bonded ligand, which was also supported by the XRD analyses of **3** (N1-Al1 1.881(4); N2-Al1 2.413(4)). The structure of the centrosymmetric dimer **3** (Figs 3 and S8) displays distorted trigonal bipyramidal geometry (C-Al-C angles 100.46°, 100.65° and 116.04°) around both five-coordinated aluminium atoms with the Al-C distances 1.970(3), 1.974(3) and 2.041(4) Å. The [(DippNC(Me)NDipp)Al(C≡C-SnMe<sub>3</sub>)<sub>3</sub>] cores are stabilized by π-coordination (2.986 - 3.223 Å, comparable with [(LAl(C≡C-Ph)<sub>3</sub>]M)<sub>2</sub> (M = Na or K)<sup>12b</sup>) with two potassium atoms, each atom being connected to four ethynyl groups.

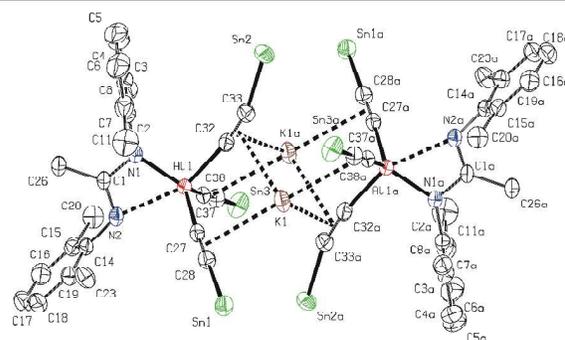


Fig. 3 The molecular structure of **3** (ORTEP view, 50% probability level). Hydrogen atoms and methyl groups from trimethylstannyl and 2,6-diisopropylphenyl moiety are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1-C1 1.350(5); N2-C1 1.293(4); N1-Al1 1.881(4); N2-Al1 2.413(4); Al1-C37 1.974(3); Al1-C27 1.970(3); Al1-C32 2.041(4); C37-C38 1.214(4); K1-C27 3.014(4); K1-C28 3.030(4); K1-C32 2.986(3); K1-C32a 2.989(3); K1-C33 3.233(4); K1-C33a 3.220(4); K1-C37a 3.036(3); K1-C38a 3.050(4); N1-C1-N2 113.3(4); C1-Al1-C27 106.42(15); C27-Al1-C32 100.46(15).

The internal ethynyl groups, which are bridged by two potassium atoms, reveal significant difference in K-C distances (K1-C32a vs. K1-C33a - see Caption of Fig. 3) of 0.23 Å while other K-C distances were found to be close to K1-C32a. The deviation from linearity among the Al-C≡C fragment (angles from 170.53° to 176.15°) in **3** was also found in structures of  $\{[LA(C\equiv C-Ph)_3]M\}_2$  (M = Li, Na or K)<sup>12b</sup> and could be explained as small energy differences in a linear and a non-linear Al-C≡C arrangement.

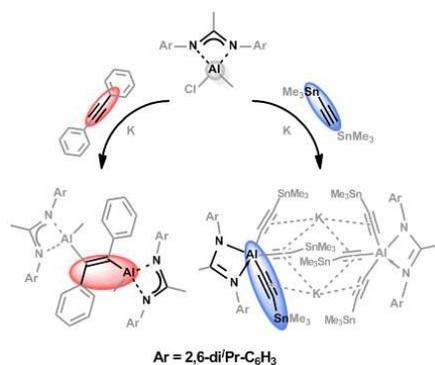
In conclusion, we described *in-situ* activation of the unsaturated CC multiple bond via reduction of the amidinato-methylaluminium chloride in the presence of various acetylenes (partially reversible by the oxidation of iodine with re-reduction). The structure of the products is strongly affected by the nature of the substituents of C≡C group (C-substituent vs. Sn-substituent). Moreover, we have postulated two potential reaction mechanisms on the model compound **1** using DFT calculations. In addition, the use of the building block concept was briefly demonstrated by the reactivity of **1** towards the hydrogen chloride resulting in the formation of *trans*-stilbene.

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## TOC



Addition of *in-situ* reduced amidinato-methylaluminium chloride to acetylenes was observed. The structure of products - ethylene-bridged motive vs. terminally bonded ethynyl groups - as well as their further reactivity is closely related to the nature of substituents anchored on the C≡C group.