# Neutral ligand induced methane elimination from rare-earth metal tetramethylaluminates up to the six-coordinate carbide state<sup>†</sup>

Ajay Venugopal,<sup>*a,b*</sup> Ina Kamps,<sup>*a*</sup> Daniel Bojer,<sup>*a*</sup> Raphael J. F. Berger,<sup>*a*</sup> Andreas Mix,<sup>*a*</sup> Alexander Willner,<sup>*a*</sup> Beate Neumann,<sup>*a*</sup> Hans-Georg Stammler<sup>*a*</sup> and Norbert W. Mitzel<sup>\**a,b*</sup>

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The reaction of 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC) with  $[La{Al(CH_3)_4}_3]$  resulted in C-H activation, leading to the formation of  $[(TMTAC)La{Al(CH_3)_4}{(\mu_3-CH_2)[Al(CH_3)_2(\mu_2-CH_3)]_2}]$ (1) containing a bis(aluminate) dianion and subsequent extrusion of methane. A similar reaction with  $[Y{Al(CH_3)_4}_3]$  led to the formation of CH<sub>4</sub>,  $[TMTAC{Al(CH_3)_3}_2]$  (2) and  $\{[(TMTAC)Y]|Y_2(\mu_2 - \mu_2 - \mu_3)|Y_2(\mu_2 - \mu_3)|Y_2(\mu_3 - \mu_3)|Y_2(\mu_3 - \mu_3)|Y_3(\mu_3 - \mu_3)|Y_3(\mu_3$ CH<sub>3</sub>)][{ $(\mu_6-C)$ [Al( $\mu_2$ -CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)]<sub>3</sub>}{ $(\mu_3-CH_2)(\mu_2-CH_3)$ Al(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (3), containing a six-coordinate carbide ion and two  $[CH_2Al(CH_3)_3]_2^-$  anions. Compound **3** is a product of multiple C-H activation. This reaction was monitored by in situ <sup>1</sup>H NMR spectroscopy. The analogous reaction with  $[Sm{Al(CH_3)_4}_3]$  led to the formation of 2, of  $[(TMTAC)Sm{(\mu_2-CH_3)(CH_3)_2Al}_2{(\mu_3-CH_3)(CH_3)_2Al}_2]$  $CH_{2}$  ( $CH_{3}$ )<sub>2</sub> (4), which contains a tris(aluminate) trianion, and [{(TMTAC)Sm}{Sm\_{2}(\mu\_{2}-1)}  $CH_{3}$  { $(\mu_{6}-C)$  [Al( $\mu_{2}-CH_{3}$ )<sub>2</sub>(CH<sub>3</sub>)]<sub>3</sub> { $(\mu_{3}-CH_{2})(\mu_{2}-CH_{3})$  Al(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (5), which is isostructural to 3. The products were characterised by elemental analyses (except 4, 5), 1 by multinuclear NMR spectroscopy and compounds 1, 2, 3, 4 and 5 by X-ray crystallography. Quantum chemical calculations were undertaken to support the crystallographic data analysis and confirm the structure of 3 and to compare it with an analogous compound where the central six-coordinate carbon has been replaced by oxygen. The investigations point to a mechanism of sterically induced condensation of  $[Al(CH_3)_4]$  groups in close proximity in the coordination spheres of the rare-earth metal atoms, which is dependent on the size of these metal atoms.

# Introduction

C-H bond activation in the coordination sphere of metals and alkane elimination reactions from metal bound alkyl substituents are key steps for the understanding of many important chemical processes. These include catalytic transformations, heterogenic as well as homogenous ones. Such reactions have been studied particularly in the context of olefin polymerisation.

On the one hand the examination of deactivation pathways of catalyst systems has produced a series of interesting results, for example the observation of multiple C–H activations and formation of so far unprecedented Ti/Al carbide clusters from titanium phosphinimides like Cp(R<sub>3</sub>PN)TiMe<sub>2</sub> with Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>.<sup>1</sup> Examples published by Stephan *et al.* are [CpTi( $\mu$ -SR)( $\mu$ -NP<sup>i</sup>Pr<sub>3</sub>)( $\mu$ <sub>4</sub>-C)( $\mu$ -SR)AlMe] (R = Ph, Bn),<sup>2</sup> [CpTi( $\mu$ -Me)( $\mu$ -NP<sup>i</sup>Pr<sub>3</sub>)( $\mu$ <sub>4</sub>-C)( $\mu$ -AlMe<sub>2</sub>)<sub>2</sub>(AlMe<sub>2</sub>)<sup>3</sup> and [CpTi( $\mu$ <sub>2</sub>-Me)( $\mu$ <sub>2</sub>-NPPh<sub>3</sub>)( $\mu$ <sub>5</sub>-C)(AlMe<sub>2</sub>)<sub>3</sub>( $\mu$ <sub>2</sub>-MeAlMe<sub>2</sub>)].<sup>4</sup>

Such C–H activation reactions also led to a number of highly coordinate methine species including the anion  $[(Me_2Al)_2(\mu$ 

CH)(AlCl\_2Me)\_2]^-  $^5$  as well as  $[(Cp*Zr)_4(\mu\text{-Cl})_5(Cl)(\mu\text{-CH})_2]$  and  $[(Cp*Zr)_5(\mu\text{-Cl})_6(\mu\text{-CH})_3],^6$  some carbaalanes^7 and also Zr–Al–C clusters.<sup>8</sup>

On the other hand attempts to understand the methane elimination from the reaction of  $Cp_2TiCl_2$  and  $Al_2(CH_3)_6^9$  in the context of studies on the titanocene and zirconocene Ziegler–Natta catalysts were undertaken. These led to the discovery of methylene bridged species, the most prominent being Tebbe's reagent,<sup>10</sup> which is nowadays used for the introduction of methylene units into carbonyl compounds in a Wittig-analogous reaction type.<sup>11</sup>

More recently, Anwander and co-workers contributed a series of examples, where C–H activation reactions take place in the coordination sphere of rare-earth elements. They found the formation of trinuclear ionic  $\mu_3$ -methylidene complexes by donor (THF) induced cleavage of tetraalkylaluminates of the rare-earth elements<sup>12</sup> and the formation of  $\mu_4$ -methine bridged yttrium aluminates of the formula [{(Cp\*Y)[ $\mu_2$ -HC(AlMe\_3)\_2](YCp\*)}\_2(\mu\_2-Me)\_2].

During recent studies to isolate trimethyllanthanum, it was found, that the action of PMe<sub>3</sub> onto  $[La{Al(CH_3)_4}_3]$  leads to multiple methyl group degradation, affording complex aggregates containing methylene, methine and carbide units, where the carbide is coordinated by five metal atoms.<sup>13</sup> It has been concluded, that the high charge densities of the hard carbon functionalities  $CH_2^{2-}$ ,  $CH^{3-}$  and  $C^{4-}$  drive the cluster formation with the relatively hard  $La^{3+}$  cations.

Substitution of an  $[Al(CH_3)_4]^-$  anion in  $[Y{Al(CH_3)_4}_3]$ and  $[La{Al(CH_3)_4}_3]$  by a hydrotris(pyrazolyl)borate ligand (Trofimenko's scorpionate) was claimed to produce a unique

<sup>&</sup>lt;sup>a</sup>Universität Bielefeld, Fakultät für Chemie, Anorganische Chemie und Strukturchemie Universitätsstraße 25, 33615, Bielefeld, Germany. E-mail: mitzel@uni-bielefeld.de; Fax: +49 (0)521 106-6026; Tel: +49 (0) 521 106-6163

<sup>&</sup>lt;sup>b</sup>International Graduate School of Chemistry, Universität Münster, Corrensstraße 30, 48149, Münster, Germany

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ligand environment for the stabilisation of discrete rare-earth metal methyl-methylene species.<sup>14</sup>

In this contribution we demonstrate, that even neutral and comparatively less bulky substituents can initiate multiple C-H activation in rare-earth metal tris(tetramethylaluminates)  $[M{Al(CH_3)_4}_3]$  (M = La, Sm and Y).<sup>15</sup> We have now observed even the formation of hexa-coordinate carbon atoms of the carbide type in reactions of rare-earth metal tris(tetramethylaluminates) with TMTAC (1,3,5-trimethyl-1,3,5-triazacyclohexane). Our initial intention was to use the mixed metal precursors  $[M{Al(CH_3)_4}_3]$  to deprotonate TMTAC, leading to doubly amino-substituted carbanions, as recently described by us for a lithiated derivative [LiCH(NMeCH<sub>2</sub>)<sub>2</sub>NMe], which can serve as a nucleophilic acylation reagent analogous to the Corev-Seebach reagent.<sup>16</sup> We expected the reaction to proceed via liberation of highly reactive MMe<sub>3</sub> according to a route recently described to work upon addition of single-site Lewis bases to  $[M{Al(CH_3)_4}_3]^{17}$ and via the complex induced proximity effect (CIPE).<sup>18</sup>

#### **Results and discussion**

## Reaction of TMTAC with $[La{Al(CH_3)_4}_3]$

Upon addition of TMTAC to a solution of  $[La{Al(CH_3)_4}_3]$  in toluene at -30 °C we could detect no deprotonation of the TMTAC unit, but isolate complex 1, which precipitates in crystalline form after warming the reaction mixture to ambient temperature (Scheme 1). Complex 1 contains the neutral TMTAC ligand coordinated to the lanthanum atom, one  $[Al(CH_3)_4]^-$  unit and one  $[(CH_3)_3AlCH_2Al(CH_3)_3]^{2-}$  dianion. The latter is the product of a "condensation" of two  $[Al(CH_3)_4]^-$  units under extrusion of methane *via* C–H activation.



Scheme 1 Reaction of  $[La{Al(CH_3)_4}_3]$  with TMTAC.

In the <sup>1</sup>H NMR spectrum the metal bonded TMTAC ligand in 1 gives rise to two doublets for the geminal protons of its CH<sub>2</sub> units and a singlet for the methyl groups. Three signals at -1.22, -0.93 and -0.76 ppm correspond to the metal bound methyl and methylene units. The <sup>13</sup>C NMR shows the presence of the TMTAC ligand with resonances at 77.0 and 39.0 ppm and two broad resonances at -1.3 and -10.2 ppm and the presence of a very broad feature at -5.5 ppm assignable to the methylene unit. As the NMR spectra were obtained from D<sub>8</sub>-THF solutions, we cannot exclude the possibility, that THF adducts were under observation possibly also changing the binding characteristics of the ligands.

Nevertheless, the presence of two chemically distinct kinds of aluminate ions follows directly from the <sup>27</sup>Al NMR, showing a narrower signal at 153 ppm (which is in the region of the resonance of  $[La{Al(CH_3)_4}_3]$  at 162 ppm) and at 182 ppm, which is much broader reflecting the asymmetry of the Al site in the

 $[(CH_3)_3AlCH_2Al(CH_3)_3]^{2-}$  anion. The purity of the compound was also confirmed by elemental analysis.

# Structure of [(TMTAC)La{Al(CH<sub>3</sub>)<sub>4</sub>}{( $\mu_3$ -CH<sub>2</sub>)[Al(CH<sub>3</sub>)<sub>3</sub>- ( $\mu_2$ -CH<sub>3</sub>)]<sub>2</sub>]] (1)

The crystalline material of **1** allowed the determination of its molecular structure in the solid state by X-ray diffraction. The structure is depicted in Fig. 1. It shows the lanthanum atom bonded slightly asymmetric to the TMTAC ligand by two longer (2.830(2) and 2.826(2) Å) and one shorter (2.789(2) Å) La–N bonds. It is difficult to compare these values as the closest related compounds are TMTAC complexes of other rare-earth metal atoms, namely praseodymium and scandium ([Pr(TMTAC)<sub>2</sub>(OTf)<sub>3</sub>])<sup>9</sup> and [Sc(TMTAC)Cl<sub>3</sub>]);<sup>20</sup> these have coarsely similar metal-nitrogen distances.



Fig. 1 Molecular structure of  $[(TMTAC)La{Al(CH_3)_4}{(\mu_3-CH_2)-[Al(CH_3)_4(\mu_2-CH_3)]_2}]$  (1) in the crystalline state. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [°] are: La1–N1 2.789(2), La1–N2 2.830(2), La1–C13 2.860(2), La1–C7 2.748(3), La1–C10 2.549(2), La1–C13 2.763(2), La1–C14 2.754(3), La1–C17 2.773(3), Al1–C10 2.056(2), Al2–C10 2.054(2), Al1–C7 2.070(3), Al2–C13 2.082(3), Al3–C14 2.050(3), Al3–C17 2.044(3), La1–C7–Al1 83.8(1), La1–C13–Al2 83.0(1), La1–C10–Al1 89.3(1), La1–C10–Al2 89.2(1), Al1–C10–Al2 132.5(1), La1–C14–Al3 86.1(1), La1–C17–Al3 85.7(1).

The [Al(CH<sub>3</sub>)<sub>4</sub>]<sup>-</sup> ion binds in an  $\eta^2$ -fashion to the lanthanum atom. Three contacts between the lanthanum atom and the bis(aluminate) ion [(CH<sub>3</sub>)<sub>3</sub>AlCH<sub>2</sub>Al(CH<sub>3</sub>)<sub>3</sub>]<sup>2-</sup> can be described as binding: a shorter one to the central methylene unit (La1–C10 2.549(2) Å) and two longer ones to a methyl group of each Al(CH<sub>3</sub>)<sub>3</sub> unit (La1–C7 2.748(2) and La1–C13 2.763(2) Å). The shorter of these La–C bonds is close to that of the homoleptic three-coordinate [La{CH[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}<sub>3</sub>] at 2.515(9) Å.<sup>21</sup> It can also be compared to that in [Tp<sup>tBu,Me</sup>La{( $\mu_3$ -CH<sub>2</sub>)[Al(CH<sub>3</sub>)<sub>3</sub>( $\mu_3$ -CH<sub>3</sub>)]<sub>2</sub>}]<sup>22</sup> at 2.519(2) Å, and to those in cluster compounds like [La<sub>4</sub>Al<sub>8</sub>(CH)<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>20</sub>{P(CH<sub>3</sub>)<sub>3</sub>] (La–CH<sub>2</sub>: 2.588(4) and 2.629(4) Å), [La<sub>4</sub>Al<sub>8</sub>(C)(CH)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>22</sub>(toluene)] (2.549(7)– 2.889(7) Å)<sup>12</sup> and in [Cp\*<sub>3</sub>La<sub>3</sub>( $\mu$ -Cl)<sub>3</sub>( $\mu_3$ -Cl)( $\mu_3$ -CH<sub>2</sub>)(thf)<sub>3</sub>] (2.537(3)–2.635(3) Å).<sup>11</sup> The La–( $\mu$ -CH<sub>3</sub>) distances compare well with those in [Tp<sup>tBu,Me</sup>La{( $\mu_3$ -CH<sub>2</sub>)[Al(CH<sub>3</sub>)<sub>3</sub>( $\mu_2$ -CH<sub>3</sub>)]<sub>2</sub>}].<sup>22</sup>

The geometry within the  $[(CH_3)_3AlCH_2Al(CH_3)_3]^{2-}$  anion  $(Al-CH_2 2.055(av), Al-C-Al 132.5(1)^\circ)$  is not too far from other compounds with Al-CH<sub>2</sub>-Al linkages such as the neutral  $[CH_2{Al(CH(SiMe_3)_2)_2}]^{23}$  (Al-C 1.938(1) Å, Al-C-Al (Al-C-Al) (A

129.6(2)°) and lithium ate-complex Li<sub>2</sub>[CH<sub>2</sub>{Al(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>] (Al–C 2.060(5) Å, Al–C–Al 137.5(6)°),<sup>24</sup> both reported by Uhl and co-workers. This demonstrates that coordination of these anions does not lead to a fundamental rearrangement of their structure.

# Reaction of TMTAC with $[Y\{Al(CH_3)_4\}_3]$

Notwithstanding our expectation,  $[Y{Al(CH_3)_4}_3]$  reacts with TMTAC under liberation of methane to afford a mixture of complexes 2 and 3 (Scheme 2).





Compound **3** has the composition  $[{(TMTAC)Y}{Y_2-(\mu_2-CH_3)}{(\mu_6-C)[Al(\mu_2-CH_3)_2(CH_3)]_3}{(\mu_3-CH_2)(\mu_2-CH_3)Al-(CH_3)_2}_2]$ . It contains a hexa-coordinate carbide ion surrounded by three aluminium atoms and three yttrium atoms, and two methylene units each linking one aluminium and two yttrium atoms. Compound **3** is a product of multiple C–H activation and its structure will be discussed in detail below.

The reaction proceeds slowly and takes three days to come to completion accompanied by methane evolution. During this time multiple C–H activations occur and numerous intermediates are formed and consumed again. We monitored this reaction by several independent investigations using a technique of *in situ* <sup>1</sup>H NMR spectroscopy, which allows starting the reaction at low temperature inside the NMR spectrometer.<sup>25</sup> Due to the extremely low solubility of product **3**, such an NMR monitoring can only show the initial steps. Fig. 2 shows a typical series of spectra obtained in the first 155 min of the reaction.

The spectra show, that the reactants are immediately converted into new products after mixing them at -75 °C. Obvious is the coordination of the TMTAC ligand, as its singlet of the methyl group disappears, while more signals in this region emerge. In the region of the metal bound methyl groups the single resonance is turned into two prominent signals and a few smaller peaks. Later (50 min) the mixture becomes more complicated, but the spectrum becomes simpler again upon warming and prolonged reaction. At this stage of the reaction an insoluble oil starts to separate from the solution and consequently a part of the mixture becomes no longer observable by NMR spectroscopy of the solution. Over the next three days solid products separate from this oily product, which have been identified as complexes **2** and **3**.

Performed on a preparative scale, the reaction proceeds in the same manner and the liberated methane can be collected and



Fig. 2  $^{-1}$ H NMR *in situ* monitoring of the initial steps of the reaction of  $[Y{Al(CH_3)_4}_3]$  with TMTAC for the first 155 min.

identified by means of <sup>1</sup>H NMR spectroscopy. While **2** is soluble in the supernatant solution reaction, product **3** is completely insoluble, not only in toluene but also in other inert hydrocarbon solvents. The compounds also immediately decompose upon attempts to dissolve them in diethyl ether or THF. Compound **3** is colourless and extremely sensitive to air and moisture. Its structure has been determined by X-ray diffraction and is described below together with an isostructural samarium complex.

The TMTAC adduct of  $Al(CH_3)_3$  [TMTAC{ $Al(CH_3)_3$ }\_2] (2) was identified by NMR spectroscopy (including comparison with data of a sample independently prepared from TMTAC and two equivalents of  $Al(CH_3)_3$ ) and by determination of its crystal structure (see below).

# Reaction of TMTAC with $[Sm{Al(CH_3)_4}_3]$

A reaction behaviour similar to that described before is observed when  $[Sm{Al(CH_3)_4}_3]$  is reacted with TMTAC in toluene (Scheme 3).

Again the liberation of methane is observed (identified by NMR spectroscopy). As above the intermediate formation of an oily substance is observed, too. From this well formed crystals precipitate during a period of three days at ambient temperature. The supernatant solution again contains the adduct [TMTAC{Al(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>] (2). Among the crystals we found two sorts with different shapes and colours, by which they can be distinguished and separately picked. In this way we obtained the compounds 4 (pale red) and 5 (yellow). They are both virtually insoluble in inert hydrocarbon solvents. In addition to the extremely low solubility, the paramagnetism of Sm(III) makes NMR investigations very difficult. These low solubilities seem unexpected due to the many alkyl groups in the periphery of these compounds, but can be rationalised by the extreme molecular



Scheme 3 Reaction of  $[Sm{Al(CH_3)_4}_3]$  with TMTAC.

dipole moments of the compounds, due to the stacked composition of neutral TMTAC, tricationic rare-earth metal ions, and organoaluminium anions (compound 5, for example, has a calculated dipole moment of 12.8 D at the RI-BP/SV(P)+COSMO level of theory, see below). This excludes hydrocarbons as solvents due to their insufficient polarities, while more polar solvents like ethers react with the compounds.

We performed a series of deuterolysis experiments of **5** (and also **3**) with D<sub>2</sub>O and CH<sub>3</sub>OD, which all led to vigorous methane evolution. Analysis of these gases by GC-MS (after drying over CaH<sub>2</sub>) showed unequivocally the presence of CH<sub>3</sub>D (m/z = 17), CH<sub>2</sub>D<sub>2</sub> (m/z = 18) and CD<sub>4</sub> (m/z = 20), but no signal at m/z = 19, reflecting the presence of formal CH<sub>3</sub><sup>-</sup>, CH<sub>2</sub><sup>2-</sup> and C<sup>4-</sup> units in these compounds but the absence of CH<sup>3-</sup> units. Finally, an unequivocal proof of identity of both compounds was obtained from repeated and independent crystal structure determinations.

Intriguingly and in contrast to the reaction of the yttrium compound [Y{Al(CH<sub>3</sub>)<sub>4</sub>}<sub>3</sub>], the reaction of [Sm{Al(CH<sub>3</sub>)<sub>4</sub>}<sub>3</sub>] with TM-TAC gives two different products (4 and 5) besides 2. Compound 4 can be described as [(TMTAC)Sm{( $\mu_2$ -CH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>Al}<sub>2</sub>{( $\mu_3$ -CH<sub>2</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]. The formation of its trianionic tris(aluminate) ligand can be described as a double condensation reaction with liberation of methane from the tris(tetramethyl)aluminate [Sm{Al(CH<sub>3</sub>)<sub>4</sub>}<sub>3</sub>]. This reaction can thus be viewed at as a continuation of the mono-condensation reaction observed for 1 (for a mechanistic discussion see below).

The formation of such a tris(aluminate) anion [{[( $\mu_2$ -CH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>Al( $\mu_3$ -CH<sub>2</sub>)]Al(CH<sub>3</sub>)<sub>2</sub>}]<sup>3-</sup> from similar precursors was only recently reported.<sup>22</sup> In this contribution [Y{Al(CH<sub>3</sub>)<sub>4</sub>}<sub>3</sub>] was shown to react with a protonated trispyrazolylborate, whereby a salt of the composition [H<sub>3</sub>CAl(Tp')]<sup>+</sup>[{(CH<sub>3</sub>)<sub>2</sub>Al( $\mu_2$ -CH<sub>3</sub>)<sub>2</sub>}Y{[( $\mu_2$ -CH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>Al( $\mu_3$ -CH<sub>2</sub>)]<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> was formed (Tp' = hydrotris(3-'butyl-5-methyl-pyrazolylborate).

The second product in the precipitate of the reaction described in Scheme 3, compound 5, has the composition  $\{[(TMTAC)Sm][Sm_2(\mu_2-CH_3)][\{(\mu_6-C)[Al(\mu_2-CH_3)_2(CH_3)]_3\}\{(\mu_3-CH_2)(\mu_2-CH_3)Al(CH_3)_2\}_2]$ . It is the samarium analogue to the yttrium compound 3. It is obviously the product of multiple C–H bond activation under methane elimination and later state of

degradation than **4**. The details of its structure will be discussed together with that of the isostructural yttrium compound **3** below.

# Structure of $[TMTAC{Al(CH_3)_3}_2]$ (2)

The molecular structure of  $[TMTAC{Al(CH_3)_3}_2]$  (2) in the solid state contains the N<sub>3</sub>C<sub>3</sub> ring in a chair conformation with one N–CH<sub>3</sub> group oriented equatorially and two axially. The latter two each bear an Al(CH<sub>3</sub>)<sub>3</sub> group in equatorial position relative to the ring. In the light of the Al–N bond length of the simple adduct Me<sub>3</sub>N·AlMe<sub>3</sub> at 2.099(10) Å,<sup>26</sup> the Al–N bond lengths in 2 of 2.098(2) (Al1–N1) and 2.089(2) Å (Al2–N2) are typical. The coordination geometry of the two aluminium atoms is distorted pyramidal, with the N–Al–C angles being less than the tetrahedral angle (101.3(1) to 105.3(1)°), while the C–Al–C angles are wider (114.0(1) to 115.4(1)°). More details on the structure can be extracted from the caption of Fig. 3.



Fig. 3 Molecular structure of  $[TMTAC{Al(CH_3)_3}_2]$  (2) in the solid state. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Al1–C13 1.959(3), Al1–C12 1.962(3), Al1–C11 1.963(3), Al1–N1 2.098(2), Al2–N2 2.090(2), N1–C1 1.482(2), N1–C3 1.486(2), N1–C4 1.489(3), N2–C1 1.478(2), N2–C2 1.481(2), N2–C5 1.490(2), N3–C3 1.446(2), N3–C2 1.453(2); C13–Al1–C11 115.6(2), C12–Al1–C11 114.9(2), C13–Al1–N1 103.4(1), C12–Al1–N1 105.5(1), C11–Al1–N1 101.3(1), C1–N1–C3 108.4(1), C1–N1–C4 114.0(1), C3–N1–C4 110.4(1), N2–C1–N1 117.1(1).

# Structure of [(TMTAC)Sm{( $\mu_2$ -CH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>Al}<sub>2</sub>{( $\mu_3$ -CH<sub>2</sub>)<sub>2</sub>-Al(CH<sub>3</sub>)<sub>2</sub>}] (4)

Fig. 4 illustrates the structure of **4**. A neutral tridentate TMTAC ligand and the  $[(CH_3)_3Al-CH_2-Al(CH_3)_3]^{3-}$  trianion coordinate the Sm<sup>3+</sup> ion. The total coordination number at samarium is seven. As in **1**, the TMTAC ligand bonds almost symmetrically to the samarium atom, with the Sm–N bonds falling over a range of 2.626(5) and 2.640(5) Å. The  $[(CH_3)_3Al-CH_2Al(CH_3)_3]^{3-}$  trianion is bonded *via* two bridging terminal methyl groups with longer Sm–C distances of 2.663(7) and 2.706(7) Å and *via* the two methylene units with shorter Sm–C distances of 2.426(5) and 2.441(5) Å. This reflects the different charge on these carbyl units. The situation is thus similar to that in **1** and also to that in the anion  $[{Al(CH_3)_4}Y{[(CH_3)_3Al-CH_2]_2Al(CH_3)_2}]^-$  (Y–CH<sub>3</sub> 2.586(9), 2.589(8) and Y–CH<sub>2</sub> 2.344(8), 2.411(9) Å).<sup>22</sup> However, due to the different ligand symmetry (TMTAC in **4** *vs*. [Al(CH\_3)\_4]^- in the compound obtained by Anwander and



**Fig. 4** Molecular structure of **4** in the crystal. Only one of the two crystallographically independent molecules is shown. Also omitted are the toluene molecules in the crystal. Thermal ellipsoids are drawn at 50% probability level. The bonds within the TMTAC and the tris(aluminate) unit are drawn in filled mode for better visibility of the parts. Selected bond lengths [Å] and angles [°] of one molecule: Sm1–C7 2.663(7), Sm1–C10 2.426(5), Sm1–C13 2.441(5), Sm1–C16 2.706(7), Al1–C10 2.038(6), Al2–C10 2.080(5), Al2–C13 2.074(6), Al3–C13 2.061(6), Al1–C7 2.070(8), Al3–C16 2.067(8), Sm1–N1 2.636(5), Sm1–N2 2.640(5), Sm1–N3 2.626(5), C10–Sm1–C7 81.9(2), C10–Sm1–C13 85.3(3), C13–Sm1–C16 81.9(2), C10–Al1–C7 108.7(3), C13–Al2–C10 105.2(2), C13–Al3–C16 109.9(3).

co-workers) compound **4** shows a different conformation for the tris(aluminate) anion, being close to mirror symmetry.

The angles Al–C–Al are surprisingly similar to one another (Al1–C10–Al2 135.6(3)°, Al3–C13–Al2 136.2(3)°) and also reminiscent of the Al–C–Al angle in 1 as well as in Uhl's compounds  $[CH_2{Al(CH(SiMe_3)_2)}_2]^{23}$  and  $Li_2[CH_2{Al(CH_2SiMe_3)_3}_2]^{24}$  (see above). Also remarkably similar are the Sm–CH<sub>2</sub>–Al angles; they fall over a range between 84.6(2) and 88.0(2)° again nicely paralleling the situation in  $[{Al(CH_3)_4}Y{[(CH_3)_3AlCH_2]_2Al(CH_3)_2}]^-$  (values between 80.2(3) and 86.5(3)°).<sup>22</sup>

# Structure of the complexes {[(TMTAC)M][ $M_2(\mu_2$ -CH<sub>3</sub>)][{( $\mu_6$ -C)-[Al( $\mu_2$ -CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)]<sub>3</sub>}{( $\mu_3$ -CH<sub>2</sub>)( $\mu_2$ -CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>}] (M = Y (3), Sm (5))

The structures of both compounds (Fig. 5) were determined repeatedly from different crystals to ensure that the samples were of homogenous composition. The best structural data obtained for 5 allowed also the determination of all hydrogen atoms apart from those of a  $\mu_2$ -bridging methyl group between two samarium atoms (C40). For this purpose the structure of the isostructural species 3 was also calculated by first principle methods and confirmed the experimental results (see below). The calculations were carried out for 3 instead of 5, as 5 is paramagnetic and therefore might exhibit a complex electronic structure, which would impose a series of difficulties onto the calculations. These calculations predict the structure to deviate very slightly from  $C_s$  symmetry, and the variation is most pronounced for the orientation of the three hydrogen atoms at C40. As the crystal structures of 3 and 5 obey mirror symmetry, this deviation leads to a disorder of the three hydrogen atoms at C40, but even this minor detail in the structures of 3 and 5 could be resolved by the aid of the calculated data. Table 1



Fig. 5 Molecular structure of 5 in the crystal. The toluene molecule in the crystal is not shown. Compound 3 is isostructural. Thermal ellipsoids are drawn at 50% probability level. For better visibility, the bonds to the hexa-coordinate carbon atom are drawn as solid sticks, and carbon and hydrogen atoms are dawn as circles of arbitrary size. Structure parameters of 5 and 3 are listed in Table 1.

**Table 1** Selected bond lengths and angles in compounds **3** and **5** as determined by X-ray diffraction, and geometry results of calculations for the free molecules **3** and the  $O^{2-} vs$ .  $C^{4-}$  analogue (**6**) (see text) at the RI-DFT(BP86) level of theory augmented by calculations taking surrounding polarity effects into account (cosmo)

|              | Crystal structures <sup>a</sup> |                | Calculations   |         |
|--------------|---------------------------------|----------------|----------------|---------|
| Compd (M/X)  | <b>5</b> (Sm/C)                 | <b>3</b> (Y/C) | <b>3</b> (Y/C) | 6 (Y/O) |
| X33–M1       | 2.744(5)                        | 2.696(6)       | 2.694          | 3.504   |
| X33–M2       | 2.510(3)                        | 2.436(5)       | 2.442          | 2.617   |
| X33–A11      | 2.058(3)                        | 2.035(5)       | 2.064          | 1.967   |
| X33–A13      | 2.086(5)                        | 2.074(7)       | 2.109          | 1.993   |
| M1-C12       | 2.782(5)                        | 2.772(7)       | 2.838          | 3.308   |
| M1-C24       | 2.515(4)                        | 2.452(5)       | 2.480          | 2.434   |
| M1-N1        | 2.748(3)                        | 2.708(4)       | 2.844          | 2.615   |
| M1-N2        | 2.810(4)                        | 2.777(6)       | 2.878          | 2.579   |
| M2-C13       | 2.627(4)                        | 2.572(6)       | 2.623          | 2.538   |
| M2-C23       | 2.669(5)                        | 2.590(6)       | 2.651          | 2.452   |
| M2-C24       | 2.408(4)                        | 2.367(5)       | 2.404          | 2.392   |
| M2-C32       | 2.644(5)                        | 2.581(6)       | 2.623          | 2.570   |
| M2-C40       | 2.553(5)                        | 2.511(6)       | 2.555          | 2.503   |
| A12-C24      | 2.058(4)                        | 2.053(5)       | 2.102          | 2.149   |
| A11-X33-M1   | 84.8(2)                         | 85.4(2)        | 85.4           | 74.5    |
| A13-X33-M1   | 168.7(2)                        | 166.7(3)       | 167.7          | 155.5   |
| M2-X33-M1    | 87.7(1)                         | 86.7(2)        | 86.9           | 74.4    |
| M2-X33-A13   | 84.4(1)                         | 84.0(2)        | 83.9           | 83.6    |
| Al1-X33-Al3  | 102.5(2)                        | 103.1(2)       | 103.0          | 113.7   |
| All-X33-All' | 98.3(2)                         | 98.5(3)        | 98.9           | 100.7   |
| M1-C24-M2    | 95.4(1)                         | 94.0(2)        | 92.9           | 107.7   |
| M2-C24-Al2   | 88.5(1)                         | 87.3(2)        | 86.4           | 83.7    |
| M1-C24-Al2   | 175.6(2)                        | 178.7(3)       | 178.2          | 168.4   |
| M2-C40-M2'   | 89.9(2)                         | 87.2(2)        | 86.9           | 95.8    |
| A13-C32-M2   | 81.6(1)                         | 80.5(2)        | 79.9           | 89.4    |
| Al1-C12-M1   | 84.1(2)                         | 83.3(2)        | 82.8           | 98.9    |
| Al1-C13-M2   | 81.7(1)                         | 80.8(2)        | 79.8           | 88.4    |
| Al2-C23-M2   | 81.5(2)                         | 81.0(2)        | 79.9           | 82.3    |

<sup>*a*</sup> Symmetry transformation used to generate equivalent atoms:  $x, \frac{1}{2} - y, z$ .

contains some corresponding structural parameter values of **3** and **5** along with above mentioned calculated values.

The most striking feature in the structures of compounds **3** and **5** are the hexa-coordinate carbide units labeled C33. The distances between the hexa-coordinate carbon atom and the three aluminium atoms in **3** are 2.035(5) (C33–A11) and 2.074(7) Å (C33–A13) and in **5** are 2.058(3) (C33–A11) and 2.086(5) Å (C33–A13). Expectedly they are slightly longer than typical known Al–C bonds (*e.g.* 1.988(4)–2.014(4) Å in [Al{C(CH<sub>3</sub>)<sub>3</sub>}]).<sup>27</sup> Despite the high coordination number at C and due to the highly ionic contribution of the interaction of a carbide unit with the Al atoms, these distances are even shorter than the bridging Al–C bonds in Al<sub>2</sub>Me<sub>6</sub> at 2.125(2) Å, but longer than the terminal ones at 1.953(av).<sup>28</sup>

Compared to the Al–C distances, the three rare-earth metal atoms in both compounds have much more different distances from the hexa-coordinate carbon atom. The TMTAC bonded atoms Y1 (3) and Sm1 (5), which are coordinatively most saturated, have much longer distances of 2.696(6) (C33–Y1 for 3) and 2.744(5) Å (C33–Sm1 for 5), whereas the other two rare-earth atoms have shorter distances of 2.436(5) (C33–Y2 for 3) and 2.510(3) Å (C33–Sm2 for 5). In general these values are in the coarse range of literature established Sm–C distances (*e.g.* Sm( $\mu_2$ -Me<sub>2</sub>AlMe<sub>2</sub>)<sub>3</sub> 2.544(3)–2.568(3) Å).<sup>29</sup>

This bonding situation is unlike that in  $[La_4Al_8(C)(CH)_2(CH_3)_2(CH_3)_{22}(toluene)]$  recently reported by Anwander and coworkers.<sup>13</sup> This compound contains a five-coordinate carbide ion in a trigonal bipyramidal environment of three lanthanum atoms (equatorially) and two aluminium atoms (axially). The La–C distances in this compound are between 2.448(6) and 2.475(6) Å, which is surprising in the light that the lanthanum atom is bigger than the yttrium atom in **3** or the samarium atom in **5** (shorter Y–C and Sm–C bonds expected). However, as the carbide atoms in our **3** and **5** have higher coordination numbers an obverse effect can be expected leading to longer Y–C and Sm–C bonds. It is obviously the latter effect that dominates the situations in **3** and **5**.

A corresponding effect can be observed by comparison of the Al–C bond lengths in our **3** and **5** on one hand and  $[La_4Al_8(C)(CH)_2(CH_2)_2(CH_3)_{22}(toluene)]^{13}$  on the other. On average the Al–C distances in the latter are substantially shorter at 1.977 Å than in **3** at 2.064 and in **5** at 2.077 Å.

Expected for CAl<sub>3</sub>Y<sub>3</sub> and CAl<sub>3</sub>Sm<sub>3</sub> environments, respectively, the angles about the hexa-coordinate carbon atom deviate from an ideal octahedral environment; the angles involving rare-earth metal atoms are smaller than 90° (e.g. Sm2–C33–Al3 84.4(2)° in **5**), while that involving only aluminium atoms are larger (*e.g.* Al1–C33–Al3 102.5(2)° in **5**).

Two different types of coordination spheres are observed for the rare-earth metal atoms. The atoms Y1 and Sm1, respectively, are eight-coordinate. They are linked to the hexa-coordinate carbide ion, to two penta-coordinate methylene units, to two  $\mu_2$ -bridging methyl groups and to the three nitrogen atoms of the TMTAC ligand. The other two rare-earth metal atoms Y2 and Sm2, respectively, form links to the hexa-coordinate carbide ion, to one penta-coordinate methylene unit and to three  $\mu_2$ -bridging methyl groups. They are thus in a distorted octahedral coordination environment.

The methylene units (carbon atoms C24 and C24') have trigonal bipyramidal coordination environments, with the hydrogen atoms

and Y2/Sm2 lying in the equatorial plane and Al2 and Y1/Sm1 occupying the axial positions. The H<sub>2</sub>C–Al distances in **6** are 2.058(4) Å (and 2.053(5) for **3**) and are thus in the same range as the Al–CH<sub>2</sub> distances in **5** (2.038(6) to 2.080(5) Å). The distances of these methylene carbon atoms to Sm1 at 2.515(4) Å are longer than in **5** at 2.426(5) and 2.441(5) Å.

# $$\label{eq:constraint} \begin{split} &Quantum chemical calculations of 3 and its oxygen analogue \\ &of the complexes [{(TMTAC)Y}{Y_2(\mu_2-CH_3)}{(\mu_6-O)}]Al(\mu_2-CH_3)_2(CH_3)]_3}{(\mu_3-CH_2)(\mu_2-CH_3)Al(CH_3)_2}_2]^{2+} (6) \end{split}$$

In order to exclude any possibility of a misinterpretation of crystallographic plus elemental analysis results and to falsify the hypothesis that the central carbide atom could be in fact an oxygen atom, we have calculated the structure of **3** and that of a reference species **6**, [{(TMTAC)Y}{Y<sub>2</sub>(µ<sub>2</sub>-CH<sub>3</sub>)}{(µ<sub>6</sub>-O)[Al(µ<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)]<sub>3</sub>}{(µ<sub>3</sub>-CH<sub>2</sub>)(µ<sub>2</sub>-CH<sub>3</sub>)Al(CH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>. This is derived from **3** *via* isoelectronic substitution of the central carbide (C<sup>4-</sup>) by an oxide ion (O<sup>2-</sup>). The DFT calculations used the BP86 functional.<sup>30</sup> To account for crystal polarity effects on the structures, we also performed solvent modeling calculations using the COSMO routine for both structures.<sup>31</sup>

Comparison of the experimental data for 3 with that of the calculated shows an impressive agreement with the carbon centered structure 3, but not with the oxygen centered structure 6 (Table 1). This holds in particular true for the central structure element  $XY_3Al_3$  (X = C, O), where the carbon-metal distances are well reproduced, but there is a large deviation for X = O. The distance C33-Y1 for instance is calculated within the experimental standard deviation, but 0.9 Å larger for X = O. The other two Y–O distances are also far too long to represent a realistic alternative; the Al-O bonds on the other side are too short. A structure with central atom O would thus have a drastically different core structure, which is obviously due to the strong ionic contributions and the higher formal charge of C4- instead of O2-. The only larger deviations between experimental and calculated structure of 3 are the Y-N bond lengths, which however, are strongly affected by the inclusion of the effects of the polarity of the surrounding as seen by the serious improvement in the COSMO calculations. In essence the good agreement of experiment and calculations leave no doubt about the correct constitution of **3**.

The central hexacoordinate carbon atom C33 in **3** is linked to three aluminium and three samarium atoms. The distance to the atom Sm1 is longer (2.744(5) Å) than to the two symmetry equivalent atoms Sm2 and Sm3 (2.510(3) Å).

Internal comparison is possible with the other Sm–C distances within the molecule: there is a shorter Sm2–C24 bond at 2.408(4) Å to a CH<sub>2</sub> unit, a similar Sm2–C40 bond at 2.553(5) Å of two Sm atoms to a bridging CH<sub>3</sub> group of medium length and the two longer bonds Sm2–C23 (2.669(5) Å) and Sm2–C32 (2.644(5) Å) to the CH<sub>3</sub> groups of tetra-coordinate C–Al(CH<sub>3</sub>)<sub>3</sub> units.

#### A proposed mechanism of methyl group degradation

The donor induced cleavage of tetramethylaluminates has been demonstrated a working principle in many cases.<sup>22,32</sup> Anwander *et al.* have discussed a mechanism for the hydrogen abstraction in the tris(tetramethyl)aluminates, which involves in a first step the loss of one equivalent of  $Al(CH_3)_3$  as a donor adduct upon

addition of this donor.<sup>13</sup> This mechanism assumes the primary interaction to be between the donor and an aluminium atom. It was quoted as pathway for the ether induced formation of rare-earth metal trimethyl compounds from  $[M{Al(CH_3)_4}] (M = Y, Lu)$ ,<sup>33</sup> but was also used to explain the extensive methyl group degradation in  $[La{Al(CH_3)_4}]$  upon addition of P(CH<sub>3</sub>)<sub>3</sub>.<sup>13</sup> The resulting methyl group bound to the rare-earth metal atom is then able to abstract a hydrogen atom from an  $[Al(CH_3)_4]^-$  unit leading to methane and a trimethylaluminium complexed methylene dianion unit  $[CH_2Al(CH_3)_3]^{2-}$ .

Although this mechanism is plausible for those reactions, where the donor is not found as a ligand bonded to the rare-earth metal in the final product, we were not able to explain the formation of our products containing the TMTAC ligand, which seems to be bonded to the rare-earth metal atom first. A good model for the description of C–H activation chemistry is the complex-induced proximity effect (CIPE),<sup>18</sup> used extensively and most successfully in organic carbanion chemistry. In the following paragraphs we want to apply this model to present an alternative possible pathway of methyl group degradation.

Scheme 4 shows a mechanism, which explains the formation of compounds 1 and 4 and the follow-up mechanisms for rationalisation of the formation of 3 and 5 are shown in Schemes 5 and 6 (the compounds in boxes are isolated compounds, the others postulated intermediates; note also that "arrows" do



Scheme 4 Proposed mechanism of the steric activation of steps of stepwise methyl group condensation in the reaction of  $[Al(CH_3)_4]$  ligands in  $[M{Al(CH_3)_4}_3]$  induced by successive coordination of TMTAC.



**Scheme 5** Proposed alternative mechanism of activation of a methylene C–H function of a bis(aluminate) anion  $[(CH_3)_3AlCH_2Al(CH_3)_3]^2$  explaining the formation of **2** during the increase of the nuclearity in M.

not correspond to transfer of full electron pairs due to morecenter bonding). Due to electron density accumulation at the N atom (Lewis base) and depletion at the rare-earth metal atom (Lewis acid), a TMTAC ligand is attracted to the central metal atom of an  $[M{Al(CH_3)_4}_3]$  molecule. This induces steric congestion among the tetramethylaluminate ligands and brings the carbanionic methyl groups in close proximity. A methyl anion can thus abstract a proton from a neighbour  $[Al(CH_3)_4]^-$  ligand, leading to CH<sub>4</sub>, a  $[H_2CAl(CH_3)_3]^2$ - dianion and a methyl-bridged  $[Al(CH_3)_3]$  unit (Scheme 4, step **b**). The latter two units combine to give a bis(aluminate) anion  $[(CH_3)_3AlCH_2Al(CH_3)_3]^2$ - leaving one mono-aluminate  $[Al(CH_3)_4]^-$  unit at the metal atom M unchanged (Scheme 4, step **c**).

If M is big enough, as is the case for  $M = La^{34}$  the steric stress on the aluminate ligands is already released by this methane elimination, as is shown to be the case for product 1 (Scheme 4, intermediate **D**).

If M is smaller, as is the case for M = Sm, the situation about the metal atom is more crowded and a further condensation step may occur (Scheme 4, step **d** intermediate



Scheme 6 Proposed mechanism of formation of the carbide  $C^{+}$  and introduction of a third nucleus M into the aggregates.

E). Intramolecular aggregation of E gives the tris(aluminate) trianion  $[(CH_3)_3AlCH_2Al(CH_3)_2CH_2Al(CH_3)_3]^{3-}$  as is observed experimentally in the product **4** (Scheme 4, step **e** intermediate **F**).

An alternative degradation pathway of intermediate **D** is depicted in Scheme 5. Here intermediate D is postulated not to react at its peripheral C-H function of a methyl group of the bis(aluminate) ligand, but at the central methylene unit. The result is an intermediate H, which contains a tris(aluminate) trianion of the composition  $[HC{Al(CH_3)_3}_3]^3$ , which is a protonated variety of the  $[C{Al(CH_3)_3}_3]^4$  units found in 3 and 5. If this H reacts with intermediate C (or also the equivalent D with a CH<sub>2</sub>-Al(CH<sub>3</sub>)<sub>3</sub> bond) via its hard anionic formal  $CH_2^{2-}$  unit in a way, that this CH22- acts as a nucleophile towards the metal atom M of intermediate H, the TMTAC ligand in C can shift with two (or all donor sites) away from metal atom M of intermediate C towards the aluminium atoms of  $[Al(CH_3)_3]$  or  $[Al(CH_3)_4]^-$  units, in the latter case inducing a cleavage reaction as proposed in Anwander's mechanism leading to an M-CH<sub>3</sub> unit. After readjusting donor and acceptor sites in intermediate I, the resulting double Al(CH<sub>3</sub>)<sub>3</sub> adduct of TMTAC, can be cleaved off as a stable leaving unit. It is this product 2 we observed in both reactions of TMTAC with  $[Y{Al(CH_3)_4}_3]$  and with  $[Sm{Al(CH_3)_3}_4]$ .

Scheme 6 describes the final proposed steps on the way to the carbide cluster compounds **3** and **5**. The M–CH<sub>3</sub> function and the C–H unit of the  $[HC{Al(CH_3)_3}_3]^3$  ligand in intermediate **J** come into close proximity with methane elimination being the result. This leads to the formation of a carbide species **K** which can accept another unit **C** under loss of another equivalent of **2**.

In absence of an abstractable proton as in intermediate L the  $M-CH_3$  function shares its methyl group with the other undercoordinate atom M finally leading to the product M, which was isolated in the products 3 (M = Y) and 5 (M = Sm).

In essence five products 1 to 5 identified in this contribution fit in the proposed mechanism to explain the multiple C–H degradation from the tris(tetramethylaluminates)  $[M{Al(CH_3)_4}_3]$ to the carbide/methylene clusters 3 and 5. In addition we have evidence from experiments with other tripodal N-ligands containing bulkier substituents at N for the existence of a trisaluminate  $HC[Al(CH_3)_3]_3^{3-}$  unit.<sup>35</sup>

## Conclusions

We have established a reactivity of the tris(tetramethylaluminato) rare-earth metal complexes  $[M{Al(CH_3)_4}_3]$  induced by a neutral tripodal amine ligand (TMTAC), which leads to multiple C-H abstraction reactions. The degree of methyl group degradation is dependent on the size of the rare-earth metal atom involved. With the largest atom M = La, only one step of condensation of two [Al(CH<sub>3</sub>)<sub>4</sub>] ligands into a bis(aluminate) [(H<sub>3</sub>C)<sub>3</sub>Al-CH<sub>2</sub>- $Al(CH_3)_3$ <sup>2-</sup> occurs, while at the smaller samarium a double methane extrusion occurs, leading to the tris(aluminate) ion  $[(H_3C)_3Al-CH_2-Al(CH_3)_2-CH_2-Al(CH_3)_3]^{3-}$ . In this reaction also an aggregate of higher nuclearity concerning M is formed, pointing to the presence of alternative mechanisms. This contains besides other units a carbide ion C<sup>4-</sup> bound to three trimethylaluminium units to form a  $[C{Al(CH_3)_3}_3]^4$  further bonded to three metal atoms M. This type of reactivity is exclusively observed for the smallest M under investigation, M = Y.

In contrast to other mechanisms discussed in the literature our findings indicate that the donor ligand binds first to the rare-earth metal atom M. This leads to a steric congestion of the other ligands in the coordination sphere of M and leads to condensation reactions under extrusion of methane. The mechanism we proposed for this reactivity is based on the complexinduced proximity effect (CIPE),<sup>18</sup> a concept which proved to be very successful in typical carbanion chemistry.

Both, **3** and **5** are the first isolable examples of molecular species containing hexa-coordinate carbon atoms surrounded solely by very electropositive metal atoms. These examples thus complement the transition metal clusters with interstitial carbon atoms and are closer related to the so far elusive  $CLi_{6}$ .<sup>36</sup> This species has only been generated in the gas phase, but is so far not accessible as isolated compound. Due to the importance for our understanding of hypervalent compounds,  $CLi_{6}$  has of course attracted considerable theoretical interest.<sup>37</sup> Hexa-coordinate carbon atoms have so far been only described as interstitial carbon atoms in clusters of late transition elements. Examples include clusters of gold(I) atoms arranged about a central carbon centre,  $[C(AuPPh_3)_6]^{2+38}$  and  $[C(AuPPh_3)_5]^{+,39}$  but also in  $[Fe_6(\mu_6-C)(CO)_{16}]^{2-}$ ,  $[Rh_6(\mu_6-C)(CO)_{15}]^{2-}$  and  $[Re_7(\mu_6-C)(CO)_{21}]^{3-,40}$ 

Future work in our group is directed to establish the reactivity of other polydentate neutral bases to metal tetramethylaluminates in order to prove the concept of applicability of the CIPE mechanism in the chemistry of rare-earth elements and other heavier main group elements. Quantumchemical investigations will also be undertaken to shed more light onto the mechanistic details outlined in this contribution. It would have interesting consequences if one could predict the grade of such alkyl group degradation reactions on the basis of space requirement parameters governed by the size of the central metal atom and the space requirement of the reaction inducing ligand. Such work also requires the generation of more soluble compounds by changing substituents of the multi-donor ligands. It can be expected that C–H activation can then also be reached with such neutral donor molecules, opening up an area of new heterobimetallic reagents with mixed metal synergy.

# Experimental

All manipulations were performed under a rigorously dry and oxygen-free inert atmosphere of argon using standard Schlenk or glove box techniques. THF, toluene and pentane were dried with Na/benzophenone. They were freshly condensed from LiAlH<sub>4</sub> before being employed in reactions. THF-d<sub>8</sub> and toluene-d<sub>8</sub> were dried over Na/K alloy. NMR spectra were recorded using a Bruker Avance 400 and Bruker DRX 500 spectrometers, the *in situ* <sup>1</sup>H NMR measurements using a Bruker Avance 600 spectrometer according to a literature-described procedure.<sup>25</sup> Elemental analyses were carried out on Vario E1 III CHNS and LECO CHNS 932 instruments. [M{Al(CH<sub>3</sub>)<sub>4</sub>}] (M = La, Sm, Y) were synthesised according to the literature.<sup>29</sup> 1,3,5-Trimethyl-1,3,5-triazacyclohexane was dried over molecular sieves (3 Å) and freshly distilled before being employed in the reactions. IR spectra

## $[La{Al(CH_3)_4}{(CH_3)_3AlCH_2Al(CH_3)_3}(TMTAC)] (1)$

In a glove box a solution of TMTAC (64 mg, 0.50 mmol) in toluene (5 mL) was added dropwise to a toluene solution of  $[La{Al(CH_3)_4}]$  (200 mg, 0.50 mmol in 10 mL) with vigorous stirring at -30 °C. The mixture was stirred allowed to reach ambient temperature and stirred for further 20 h. Upon standing for 15 min, well formed crystals of 1 precipitated from the clear solution (which were suitable for crystal structure determination). Another crop of microcrystalline product was obtained by concentration of the solution in vacuum. Total yield 169 mg (66%). <sup>1</sup>H NMR (500 MHz, 20 °C, THF-d<sub>8</sub>)  $\delta = -1.22$  (s, broad, Al(CH<sub>3</sub>)<sub>4</sub>), -0.93 (s, broad, Al(CH<sub>3</sub>)<sub>3</sub>), -0.76 (s, broad, Al<sub>2</sub>CH<sub>2</sub>), 2.42 (s, NCH<sub>3</sub>), 3.03 (d,  ${}^{2}J_{\text{HH}} = 8.9$  Hz, N<sub>2</sub>CH<sub>2</sub>), 4.10 (d,  ${}^{2}J_{\text{HH}} = 8.9$  Hz, N<sub>2</sub>CH<sub>2</sub>);  $^{13}C{^{1}H} NMR (125 MHz, -10.2 (s, broad, Al(CH_3)_4), -5.5 (s, very)$ broad, Al<sub>2</sub>CH<sub>2</sub>), -1.3 (s, broad, Al(CH<sub>3</sub>)<sub>3</sub>), 39.0 (s, NCH<sub>3</sub>), 77.0 (s, N<sub>2</sub>CH<sub>2</sub>); <sup>27</sup>Al NMR (130 MHz, 20 °C, THF-d<sub>8</sub>)  $\delta$  = 153 (s,  $v_{\frac{1}{2}} = 180$  Hz,  $Al(CH_3)_3$ ), 183 (s,  $v_{\frac{1}{2}} = 1700$  Hz,  $Al(CH_3)_4$ ); CHN analysis, calcd: C 39.77, H 9.23, N 8.18, found C 39.42, H 9.17, N 8.19.

## Reaction of [Y{Al(CH<sub>3</sub>)<sub>4</sub>}<sub>3</sub>] with TMTAC

 $[Y{Al(CH_3)_4}_3]$  (0.525 g, 1.50 mmol) was dissolved in toluene (10 mL) and cooled to -35 °C. 1,3,5-Trimethyl-1,3,5-triazacyclohexane (TMTAC) (0.193 g, 1.50 mmol) was added to

this solution under vigorous stirring. A gas evolution was observed (identified as CH<sub>4</sub> by condensing it in a trap and dissolving it in D<sub>8</sub>-toluene: <sup>1</sup>H NMR:  $\delta = 0.18$  (s)). An oily substance separated from this solution and assembled at the bottom of the Schlenk tube. The mixture was stirred for 1 day. A colourless precipitate separated from the oil during the next 2 d, while the oily phase disappeared. The mixture was filtered, the filtrate concentrated to 1 mL and kept for crystallisation at room temperature. Well formed colourless crystals precipitated from the oily phase upon standing for 2 d, identified as  $\{[(TMTAC)Y][Y_2(\mu_2-CH_3)]]\{(\mu_6-C)[Al(\mu_2-CH_3)]]\}$  $CH_{3}_{2}(CH_{3})_{3} \{ (\mu_{3}-CH_{2})(\mu_{2}-CH_{3})Al(CH_{3})_{2} \}_{2} \}$  (3). The remaining solution was cooled to -20 °C, which led to the precipitation of crystals of [TMTAC(AlMe<sub>3</sub>)<sub>2</sub>] (2), confirmed by <sup>1</sup>H NMR  $(\delta = (-0.6 \text{ (s, 18H, Al}(CH_3)_3), 2.12 \text{ (s, 9H, NCH_3)}, 3.15 \text{ (br, 6H, }))$  $NCH_2$ ) and X-ray diffraction. The colourless precipitate formed in the reaction mixture was also found to be 3, confirmed by IR spectroscopy and elemental analysis. Yield: 0.345 g (85%). IR (CsI, nujol) : v (cm<sup>-1</sup>) = 1263 (s), 1210 (s), 1167 (w), 1099 (w), 1012 (s), 941 (s), 719 (w), 681 (w). Elemental analysis (%) calculated for C<sub>25</sub>H<sub>67</sub>N<sub>3</sub>Al<sub>5</sub>Y<sub>3</sub>(C<sub>7</sub>H<sub>8</sub>)<sub>1/6</sub> C 38.01 H 8.33 N 5.08; found C 38.05, H 8.04, N 5.00 (two equivalents of toluene are contained in the crystal structure, but loss of toluene is observed upon drying in vacuum).

## Reaction of [Sm{Al(CH<sub>3</sub>)<sub>4</sub>}<sub>3</sub>] with TMTAC

 $[Sm{Al(CH_3)_4}_3]$  (0.411 g, 1.00 mmol) was dissolved in toluene (10 mL) and cooled to -35 °C. TMTAC (0.129 g, 1.00 mmol) was added to this solution under vigorous stirring. Gas evolution was observed (identified as CH<sub>4</sub> by <sup>1</sup>H NMR). A brown oily substance separated from the reaction mixture. The mixture was stirred for 3 days during which a microcrystalline precipitate separated, while the oily phase was consumed. The resulting mixture was filtered, the filtrate concentrated to 1 mL and kept for crystallisation at room temperature; crystals of 4 (pale yellow) and 5 (red) were obtained and identified by several independent single crystal X-ray diffraction experiments. The remaining solution was cooled to -20 °C to get crystals of [TMTAC(AlMe<sub>3</sub>)<sub>2</sub>] (2), confirmed by <sup>1</sup>H NMR and XRD.

## Crystal structure determinations

Crystals were mounted under inert perfluoropolyether at the tips of glass fibers mounted on the goniometer head. Details of the X-ray diffraction experiments are listed in Table 2. The structures were solved by direct method and refined by full-matrix least squares procedure against  $F^{2,41}$  In the structures of  $3 \cdot C_7 H_8$  and  $5 \cdot C_7 H_8$ , the hydrogen atoms at C40 were restrained to have equal distances, modeling a disorder described in the text and indicated by the ab initio calculations of 3. 3 and 5 also contain a toluene molecule disordered over a special position. The other hydrogen atoms of 3 and 5 were freely refined.

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| Compound   | 1   | $2 \cdot C_7 H_8$              | $3 \cdot C_7 H_8$              | $4 \cdot C_7 H_8$              | $5 \cdot \mathbf{C}_7 \mathbf{H}_8$ |
|--|---|--------------------------------|--------------------------------|--------------------------------|-------------------------------------|
| formula  | C <sub>17</sub> H <sub>47</sub> N <sub>3</sub> Al <sub>3</sub> La | $C_{19}H_{41}N_3Al_2$          | $C_{32}H_{75}N_{3}Al_{5}Y_{3}$ | $C_{23}H_{51}N_3Al_3Sm$        | $C_{32}H_{75}N_{3}Al_{5}Sm_{3}$     |
| fw [g/mol]   | 513.43  | 365.51                         | 903.58                         | 600.96                         | 1087.9                              |
| cryst syst   | orthorhombic  | monoclinic                     | monoclinic                     | orthorhombic                   | monoclinic                          |
| space group  | $P2_{1}2_{1}2_{1}$  | $P2_{1}/c$                     | $P2_1/m$                       | $Pna2_1$                       | $P2_1/m$                            |
| diffractometer   | Nonius Kappa CCD  | STOE IPDS-I                    | STOE IPDS-I                    | Bruker APEX                    | Bruker APEX                         |
| a [Å]  | 10.8824(6)  | 10.683(2)                      | 9.540(2)                       | 35.417(4)                      | 9.560(3)                            |
| <i>b</i> [Å]   | 14.4357(14)   | 29.104(4)                      | 17.210(2)                      | 17.334(5)                      | 17.289(2)                           |
| c [Å]  | 16.9846(9)  | 7.840(2)                       | 14.068(2)                      | 10.101(3)                      | 14.173(4)                           |
| $\beta$ [deg]  | 90  | 96.98(2)                       | 97.87(2)                       | 90                             | 97.61(2)                            |
| V [Å <sup>3</sup> ]  | 2668.2(3)   | 2419.5(6)                      | 2288.1(6)                      | 6201.7(12)                     | 2322.0(5)                           |
| Z  | 4   | 4                              | 2                              | 8                              | 2                                   |
| $D_{\text{calcd}}$ [Mg m <sup>-3</sup> ]                         | 1.278   | 1.003                          | 1.312                          | 1.287                          | 1.556                               |
| $\mu [\text{mm}^{-1}]$   | 1.705   | 0.126                          | 3.891                          | 1.992                          | 3.860                               |
| F(000)   | 1064  | 808                            | 940                            | 2488                           | 1078                                |
| temperature [K]  | 150(2)  | 163(2)                         | 153(2)                         | 153(2)                         | 153(2)                              |
| crystal size [mm]  | $0.17 \times 0.12 \times 0.06$                                    | $0.60 \times 0.40 \times 0.30$ | $0.60 \times 0.50 \times 0.10$ | $0.23 \times 0.16 \times 0.05$ | $0.30 \times 0.20 \times 0.20$      |
| θmax [deg]   | 27.50   | 26.93                          | 26.98                          | 30.04                          | 30.03                               |
| reflns collected   | 26594   | 32699                          | 35996                          | 70204                          | 26856                               |
| reflns unique  | 6091  | 4985                           | 5097                           | 18019                          | 6979                                |
| R(int)   | 0.0292  | 0.1258                         | 0.1648                         | 0.0544                         | 0.0308                              |
| completeness [%]   | 99.6  | 95.4                           | 99.0                           | 99.8                           | 99.6                                |
| refins with $I > 2\sigma(I)$                                     | 5386  | 4985                           | 5097                           | 16348                          | 6979                                |
| refined parameters   | 394   | 297                            | 365                            | 481                            | 331                                 |
| $R_1[I > 2\sigma(I)]$  | 0.0197  | 0.0492                         | 0.0555                         | 0.0535                         | 0.0378                              |
| $wR_2 [I > 2\sigma(I)]$  | 0.0332  | 0.0997                         | 0.1244                         | 0.1156                         | 0.0778                              |
| $R_1$ [all data]   | 0.0283  | 0.0906                         | 0.0860                         | 0.0612                         | 0.0424                              |
| $wR_2$ [all data]  | 0.0352  | 0.1104                         | 0.1398                         | 0.1187                         | 0.0793                              |
| $\rho_{\rm fin}  {\rm max}/{\rm min}  [{\rm e}  {\rm \AA}^{-3}]$ | 0.282/-0.361  | 0.289/-0.172                   | 0.915/-1.505                   | 2.537/-1.451                   | 1.536/-1.093                        |
| absolute struct param  | 0.001(8)  |                                |                                | 0.020(11)                      | _                                   |
| CCDC No.   | 711481  | 679432                         | 679431                         | 679434                         | 679433                              |

 $\textbf{Table 2} \quad Crystal \ data \ of \ compounds \ \textbf{1}, \ \textbf{2} \cdot C_7 H_8, \ \textbf{3} \cdot C_7 H_8, \ \textbf{4} \cdot C_7 H_8 \ and \ \textbf{5} \cdot C_7 H_8$ 

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