DOI: 10.1002/ejic.201100425

Subtle Size Effects in C–H Activation Reactions of Lanthanum and Praseodymium Tetramethylaluminates by Neutral Trinitrogen Bases

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Keywords: Triazacyclohexanes / C-H activation / Rare earths / Lanthanum / Praseodymium

The reaction of $Pr(AlMe_4)_3$ with 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC) leads to the formation of two isomeric products by C–H activation of the $AlMe_4^-$ ligands: $[(\eta^3\text{-TMTAC})Pr\{\eta^4\text{-}(Me_3AlCH_2AlMe_2CH_2AlMe_3)\}]$ (**1**), containing a linear tris(aluminate) trianion, and $[(\eta^3\text{-TMTAC})Pr(\eta^4\text{-}\{CH(AlMe_3)_3\})]$ (**2**), containing a branched tris(aluminate) trianion. The analogous reaction with the more bulkily substituted 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane (T*t*BuTAC) leads selectively to $[(\eta^3\text{-T}t\text{BuTAC})Pr\{\eta^4\text{-}(Me_3AlCH_2AlMe_2CH_2AlMe_3)\}]$ (**3**). The reaction of $La(AlMe_4)_3$ with T*t*BuTAC affords $[(\eta^3\text{-T}t\text{BuTAC})La\{\eta^4\text{-}(Me_3AlCH_2AlMe_2CH_2AlMe_3)\}]$ (**4**). All compounds were characterised by elemental analysis and crystal-structure determination. Isomers **1** and **2** could not be separated and form a cocrystalline product with a **1**/**2** ratio of 1:2 with two slightly different structures of **2** (**2a** and **2b**). In compounds **2**, **3** and **4** the tris(aluminate) ligand $[Me_3AlCH_2AlMe_2CH_2AlMe_3]^{3-}$ is bonded to the lanthanide ions in an η^4-mode through two CH_2 units and two terminal Me groups.

Introduction

A range of C–H bond activation reactions in the coordination sphere of metal atoms has been described in recent years. It is frequently observed that metal-bound alkyl groups can undergo deprotonation reactions, whereby other groups of the same type act as bases and are converted into alkanes. The deprotonated units can then be alkylidene, alkylidyne or even carbide units, which generally bridge some metal atoms. A textbook example, is the formation of Tebbe's reagent,[1] $Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_2$, by methane elimination in the reaction of Cp_2TiCl_2 and Al_2Me_6. Tebbe's reagent played an important role in the development of organometallic chemistry, e.g. in the development of olefin metathesis, and is still used as a methylene transfer agent in Wittig-type reactions with carbonyl compounds.[2]

Other examples studied in the context of deactivation pathways of olefin polymerization catalyst systems are Ti/Al carbide clusters formed from titanium phosphinimides such as $Cp(R_3PN)TiMe_2$ with Al_2Me_6,[3] which are the products of multiple C–H activation and were investigated by Stephan et al. The same authors described related reactions leading to $[CpTi(\mu\text{-}SR)(\mu\text{-}NPiPr_3)(\mu_4\text{-}C)(AlMe_2)_2(\mu\text{-}SR)AlMe]$ (R = Ph, Bn),[4] $[CpTi(\mu\text{-}Me)(\mu\text{-}NPiPr_3)(\mu_4\text{-}C)(\mu\text{-}AlMe_2)_2(AlMe_2)]$[5] and $[CpTi(\mu_2\text{-}Me)(\mu_2\text{-}NPPh_3)(\mu_5\text{-}C)(AlMe_2)_3(\mu_2\text{-}MeAlMe_2)]$.[6] Highly coordinate methylidyne species were also found in the anion $[(Me_2Al)_2(\mu\text{-}CH)(AlCl_2Me)_2]^{-}$[7] and in $[(Cp^*Zr)_4(\mu\text{-}Cl)_5(Cl)(\mu\text{-}CH)_2]$ and $[(Cp^*Zr)_5(\mu\text{-}Cl)_6(\mu\text{-}CH)_3]$,[8] as well as in some carbaalanes[9] and Zr–Al–C aggregates.[10]

In a recent review on homoleptic rare earth metal complexes containing Ln–C σ-bonds,[11] Anwander et al. included the description of a series of methyl group degradation reactions, where C–H activation reactions are initiated in the coordination sphere of rare earth elements by the action of different bases in $Ln(AlMe_4)_3$ reagents.[12] Although single-site bases, such as diethyl ether, THF or PMe_3, lead to the formation of polymeric $LnMe_3$ in some cases, others have been observed in which complex mixtures of highly aggregated products including degraded methyl groups in the form of CH_2^{2-}, CH^{3-} and C^{4-} units have been detected.[13]

Better control of the products has been achieved in reactions of $Y(AlMe_4)_3$ with hydridotris(pyrazolyl)borates LH. In the case of $La(AlMe_4)_3$ this leads to $[LLa(Me_3AlCH_2AlMe_3)]$, which contains a CH_2^{2-} unit formally bound to one LLa^{2+} and two $AlMe_3$ units.[14]

In a series of contributions on the reactions of 1,3,5-trialkyl-1,3,5-triazacyclohexanes (T*R*TAC with *R* = alkyl) with $Ln(AlMe_4)_3$ reagents we have found a variety of reactivities.[15–18] These are unlike the reactions of T*R*TAC bases with butyllithium, where deprotonation reactions occur,[19] leading to unusual dinitrogen-substituted carbanions. The products of T*R*TAC/$Ln(AlMe_4)_3$ reactions depend on the size of the T*R*TAC ligands, the size of the rare earth metal (Ln) atoms involved, and the ability of these metal ions to undergo reduction reactions. The small ligand TMTAC (*R* = Me) reacts with $La(AlMe_4)_3$ to afford $[(TMTAC)La(AlMe_4)(\{\mu_3\text{-}CH_2\}\{AlMe_2(\mu_2\text{-}Me)\}_2)]$ containing a bis-

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(aluminate) dianion (one C–H activation step).[15] In contrast, the analogous reaction with $Sm(AlMe_4)_3$ leads to a two-step C–H activation and affords $[(TMTAC)Sm\{(\mu_2\text{-}Me)Me_2Al\}_2\{(\mu_3\text{-}CH_2)_2AlMe_2\}_2]$ containing a tris(aluminate) trianion, and the complex aggregate $[\{(TMTAC)Sm\}\text{-}\{Sm_2(\mu_2\text{-}Me)\}\{(\mu_6\text{-}C)\{Al(\mu_2\text{-}Me)_2Me\}_3\}\{(\mu_3\text{-}Me)(\mu_2\text{-}Me)\text{-}AlMe_2\}_2]$, which contains two CH_2^{2-} units and a previously unprecedented carbide unit C^{4-}, simultaneously bound to six strongly electropositive metal atoms. With $Y(AlMe_4)_3$, the latter reaction type with the formation of the analogous aggregate is observed exclusively.

C–H activation reactions are also observed to accompany base-induced reduction (BIR) reactions when combining $Sm(AlMe_4)_3$ and T*R*TAC with *R* groups larger than methyl.[16] With *R* = cyclohexyl (Cy), the methylidyne complex and C–H activation product $[(TCyTAC)Sm^{III}\text{-}(\mu_4\text{-}CH)\{AlMe_2(\mu_2\text{-}Me)\}_3]$ was found to be formed in addition to the reduction product $[(TCyTAC)(AlMe_4)Sm^{II}(\mu_2\text{-}AlMe_4)_2Sm^{II}(AlMe_4)(TCyTAC)]$. Closer investigation of this reaction with variation of *R* showed that the isomeric tris(aluminate) ion with two methylidene units had formed in C–H activation reactions besides BIR, namely $[(T\mathit{i}PrTAC)La(AlMe_4)(\{\mu_3\text{-}CH_2\}\{AlMe_2(\mu_2\text{-}Me)\}_2)]$ in the case of *R* = *i*Pr.[17]

A third type of reaction between $Ln(AlMe_4)_3$ and T*R*TAC ligands was observed for the combinations Ln = Y and *R* = Cy: in this case the formation of methyl cations of the formula $[(TCyTAC)_2YMe_2]^+$ with $AlMe_4^-$ counterions has been observed.[18] Such base-induced formation of methyllanthanide cations was also observed upon the action of crown ethers to $Ln(AlMe_4)_3$ reagents (Ln = Y, Pr).[20]

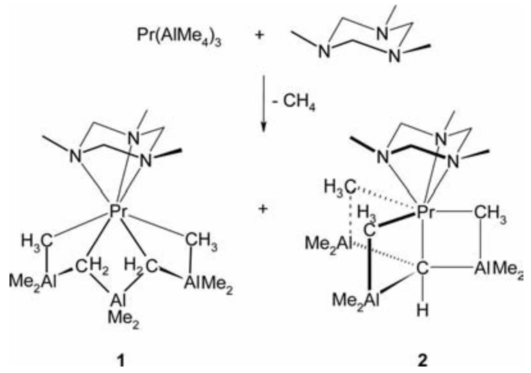
The many reaction types and the formation of mixtures make it desirable to understand the factors for selectivity and to find conditions under which certain species can be prepared exclusively and in high yield. In this contribution we show that selectivity for the formation of the aluminate dianions $[Me_3AlCH_2AlMe_2CH_2AlMe_3]^{3-}$ and its isomer $[CH(AlMe_3)_3]^{3-}$ can be steered by the correct choice of ligand size (*R*) and the appropriate metal ion (Ln).

Results and Discussion

Reaction of $Pr(AlMe_4)_3$ with TMTAC

Unlike the reaction of $La(AlMe_4)_3$ with TMTAC, which led to a single-step C–H activation (described above), that of $Pr(AlMe_4)_3$ with the same trinitrogen base leads to two products, **1** and **2** (Scheme 1), which both are the result of a two-step C–H activation. They are isomeric and contain the anions $[Me_3AlCH_2AlMe_2CH_2AlMe_3]^{2-}$ (in **1**) and $[CH(AlMe_3)_3]^{2-}$ (in **2**).

Surprisingly, examination of the crystalline product by X-ray diffraction showed the presence of both isomers, **1** and **2**, in the same crystals in a ratio of 1:2. Consequently, elemental analysis data do not allow us to distinguish between **1** and **2**, but represent the composition of the cocrystalline material.



Scheme 1. Reaction of $Pr(AlMe_4)_3$ with TMTAC.

Figure 1 shows the structure of **1**. Accounting for the larger ionic radius of Pr (0.03 Å),[21] the bond lengths to the Pr atom in **1** are similar to those in the analogous Sm compound described earlier.[15] The two Pr–C bonds to the methylidene units are 2.456(6) and 2.489(5) Å and are longer than the corresponding Sm–C bonds of the Sm analogue [2.442(6) and 2.441(5) Å]. The same is observed for the Pr–C bonds, compared to the Sm–C bonds, to the bridging methyl groups [C(39) and C(46)], which are 2.687(6) and 2.763(7) Å in the Pr compound, and shorter for the Sm compound [2.663(7) and 2.706(7) Å]. The trend for longer bonds in the Pr compound is also observed for the Pr–N distances, which fall into a range between 2.638(4) and 2.733(4) Å, whereas the corresponding Sm–N bonds are between 2.626(5) and 2.640(5) Å.

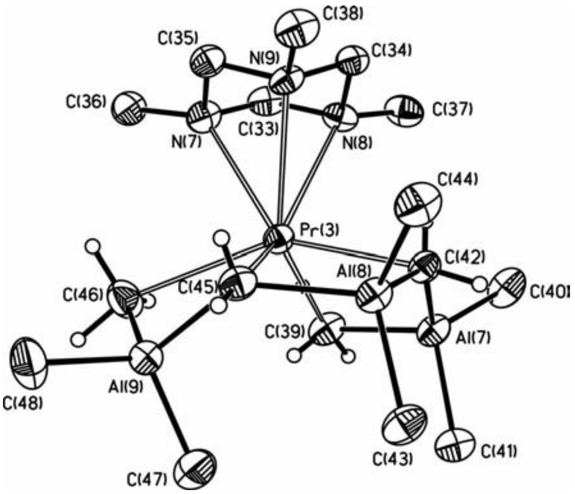


Figure 1. Molecular structure of **1**. Hydrogen atoms except at C(45), C(46), C(42) and C(39) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pr(3)–N(7) 2.690(4), Pr(3)–N(8) 2.733(4), Pr(3)–N(9) 2.638(4), Pr(3)–C(42) 2.489(5), Pr(3)–C(45) 2.456(6), Pr(3)–C(39) 2.687(6), Pr(3)–C(46) 2.763(7); C(39)–Pr(3)–C(42) 80.8(3), C(45)–Pr(3)–C(46) 78.6(2), C(39)–Al(7)–C(42) 108.5(2), C(42)–Al(8)–C(45) 105.7(2), C(45)–Al(9)–C(46) 107.3(3).

The Al–C bonds from the central aluminium atom Al(8) to the two methylidene units [C(42) and C(45)] are 2.063(4) and 2.073(6) Å and thus longer than those to the terminal methyl groups [C(43), C(44)], which are 1.986(5) and

1.989(5) Å; a similar pattern is observed for the bonds involving the terminal Al atoms Al(7) and Al(9).

The second product contained in these crystals, **2**, is present with two molecules in the cocrystals (**2a** and **2b**). The structure of **2a** is displayed in Figure 2. In both structures all $AlMe_3$ units are bonded to the methylidyne carbon atom through their aluminium atoms. They have further bonds between their methyl groups and the Pr atom. In two of each, one carbon atom per $AlMe_3$ unit binds to Pr, and two methyl groups are clearly terminal. The third $AlMe_3$ unit is oriented differently in a way that only one Me group is terminal and pointing away from the Pr atom, and two are closer to the Pr atom. These $AlMe_3$ groups show a different binding in the structures of **2a** and **2b**. The structure shown in Figure 2 is more asymmetrically bound in this respect, with one of the Pr–C contacts, Pr(1)–C(11), being shorter at 2.738(6) Å, whereas the other, Pr(1)–C(13), is longer at 3.169(7) Å. In contrast, the structure of **2b** contains two similar Pr–C bonds, Pr(2)–C(27) and Pr(2)–C(29), which are 2.870(8) and 2.814(7) Å, respectively. This demonstrates that Pr prefers to adopt a coordination number of eight in these arrangements, whereas the smaller Sm atom in [(TCyTAC)Sm{CH($AlMe_3$)$_3$}][16] adopts a coordination number of seven, with three almost identically bound $AlMe_3$ groups. The hapticity isomerism of the $AlMe_3$ units is capable of accounting for the demand for coordinative saturation of the different metal ions.

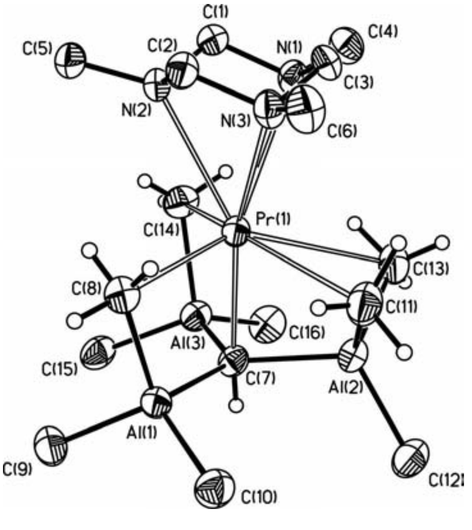


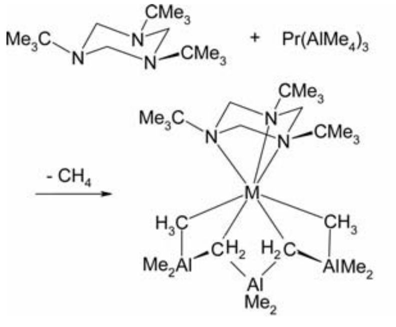
Figure 2. Molecular structure of **2a** (**2b** is similar but not the same). Hydrogen atoms except at C(11), C(13) and C(8) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pr(1)–N(1) 2.737(4), Pr(1)–N(2) 2.744(4), Pr(1)–N(3) 2.788(4), Pr(1)–C(7) 2.357(5), Pr(1)–C(8) 2.633(6), Pr(1)–C(11) 2.738(6), Pr(1)–C(14) 2.692(7); Al(1)–C(7)–Al(2) 116.7(3), Al(2)–C(7)–Al(3) 119.1(3), Al(1)–C(7)–Al(3) 123.6(3), Al(1)–C(7)–Pr(1) 90.0(2), Al(2)–C(7)–Pr(1) 81.3(2), Al(1)–C(7)–Pr(1) 90.6(2).

The methylidyne unit has a pentacoordinate carbon atom in **2a** and **2b**. The Pr–C distances are 2.357(5) and 2.382(5) Å, respectively, which are longer than in [(TCyTAC)Sm{CH($AlMe_3$)$_3$}],[16] where the corresponding Sm–C distance is 2.340(2) Å. In both structures there are two Pr–C–Al angles close to 90°, which are those to the $AlMe_3$ units with two terminal Me groups. The remaining Pr–C–Al angle involving the methylidyne carbon atom is close to 80° in both structures and involves the $AlMe_3$ group bonded to the Pr atom by two methyl bridges.

The Pr–N bonds in both structures of **2** (2.757 Å on average) are slightly longer than those in **1** (2.687 Å on average), which is explained by the smaller coordination number of **1**.

Reactions of $Pr(AlMe_4)_3$ and $La(AlMe_4)_3$ with T*t*BuTAC

In contrast to above reaction, that of $Pr(AlMe_4)_3$ with T*t*BuTAC (*R* = *t*Bu) results in the formation of a sole product, the double methylidene complex **3** (Scheme 2). This product was characterised by elemental analysis and crystal structure determination. NMR investigations were complicated due to the limited solubility of **3** in inert solvents and the paramagnetic nature of Pr^{3+}.



3 (M = Pr)
4 (M = La)

Scheme 2. Reactions of $Pr(AlMe_4)_3$ and $La(AlMe_4)_3$ with T*t*BuTAC.

The analogous reaction with $La(AlMe_4)_3$ results in the lanthanum compound **4**. This was also identified by elemental analysis and crystal structure determination. Despite the fact that La^{3+} is diamagnetic, NMR spectroscopy was still difficult due to the limited solubility of **4** in most inert solvents. Hydrocarbons do not dissolve suitable amounts and ethers are cleaved. We found bromobenzene to dissolve a small amount of the sample and could perform a ^1H NMR experiment in bromopentadeuteriobenzene. The spectrum shows two doublets for the N_2CH_2 groups with the typical geminal coupling (9.1 Hz) at δ = 3.91 and 2.60 ppm and the a signal for the *tert*-butyl protons at δ = 0.69 ppm. The methylidenene protons of the $LaAl_2CH_2$ units also give two doublets, one at δ = 1.81 ppm and one at δ = –1.01 ppm, linked by a cross peak in the HH-COSY spectrum. The remaining signals of the metal-bound methyl groups cannot be assigned with certainty. As often observed in such compounds, exchange on the NMR time scale is similar, but poor solubility prohibits more detailed studies at low temperature.

The molecular structures of **3** and **4** (Figure 3, only that of **3** is shown) are similar to one another and to that of **1**. In these compounds the tris(aluminate) trianions $[Me_3AlCH_2AlMe_2CH_2AlMe_3]^{3-}$ are η^4-bound to the lanthanide ion through their two methylidene units and two terminal methyl groups. These methylidene and methyl carbon atoms are each five-coordinate.

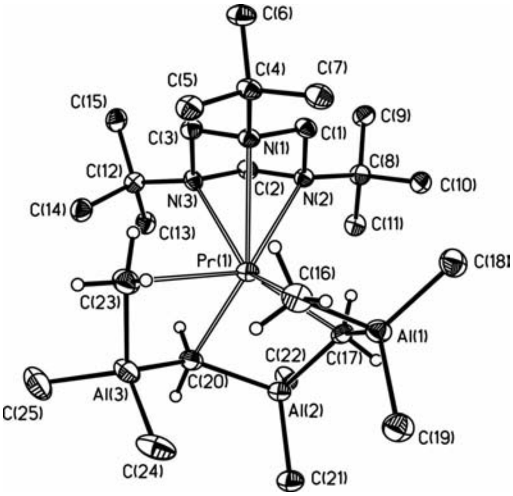


Figure 3. Molecular structure of **3** (**4** is isomorphous). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms except at C(17), C(20), C(16) and C(23) are omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: Pr(1)–N(1) 2.752(2), Pr(1)–N(2) 2.831(2), Pr(1)–N(3) 2.743(3), Pr(1)–C(16) 2.702(4), Pr(1)–C(23) 2.854(4), Pr(1)–C(17) 2.436(3), Pr(1)–C(20) 2.459(3), Al(1)–C(17) 2.060(3), Al(2)–C(17) 2.072(3), Al(2)–C(20) 2.066(3), Al(3)–C(20) 2.043(3), Al(1)–C(16) 2.072(4), Al(3)–C(23) 2.077(4); C(16)–Pr(1)–C(17) 80.4(2), C(20)–Pr(1)–C(23) 77.3(2), C(17)–Al(1)–C(16) 106.9(2), C(17)–Al(2)–C(20) 103.8(2), C(20)–Al(3)–C(23) 108.0(2). Selected bond lengths [Å] and angles [°] for **4**: La(1)–N(1) 2.890(2), La(1)–N(2) 2.801(2), La(1)–N(3) 2.788(2), La(1)–C(16) 2.759(3), La(1)–C(23) 2.871(3), La(1)–C(17) 2.491(3), La(1)–C(20) 2.502(3), Al(1)–C(17) 2.059(3), Al(2)–C(17) 2.089(3), Al(2)–C(20) 2.059(3), Al(3)–C(20) 2.045(3), Al(1)–C(16) 2.077(4), Al(3)–C(23) 2.069(3); C(16)–La(1)–C(17) 79.1(1), C(20)–La(1)–C(23) 76.7(1), C(17)–Al(1)–C(16) 108.1(2), C(17)–Al(2)–C(20) 105.1(2), C(20)–Al(3)–C(23) 108.8(2).

The two Pr–C bonds to the methylidene units in **3** are 2.436(3) Å to C(17) and 2.459(3) Å to C(20) and thus in the same range as those in **1**. Due to the larger ionic radius of La^{3+} (La 1.21 Å, Pr 1.16 Å) the corresponding bonds in **4** are expected to be about 0.05 Å longer, which is the case: 2.491(3) Å to C(17) and 2.502(3) Å to C(20). The La–C bonds in **4** are also shorter than the La–$CH_2(Al)_2$ bond in [(TMTAC)(η^2-$AlMe_4$)La($Me_3AlCH_2AlMe_3$)] at 2.549(2) Å, which is explained by the higher coordination number of eight in the latter (seven in **4**).

A similar trend is found by comparing the *M*–C bonds to the bridging methyl groups [*M* = Pr (**1**, **3**), La (**4**)]; they are again about 0.05 Å shorter for **1** [*M* = Pr, 2.702(4) Å to C(16), 2.854(4) Å to C(23)] than in **4** [2.759(3) Å to C(16), 2.871(3) Å to C(23)]. Not surprisingly, the *M*–N bond lengths follow the same pattern and show the same slightly unsymmetrical binding mode of the T*t*BuTAC ligands.

Reaction of La($AlMe_4$)$_3$ with T*i*PrTAC

We employed a triaminal ligand with a steric bulk of nitrogen substituents between that of TMTAC and T*t*BuTAC. The reaction of La($AlMe_4$)$_3$ with T*i*PrTAC (*R* = *i*Pr) yielded **5**, which is analogous to **4**. Within a large amount of solid precipitate only few crystals could be isolated, therefore, we can only report the crystal structure of this compound (Figure 4) and no further characterisation. There are some differences between the geometries of **5** and **4** due to the different steric requirements of the nitrogen substituents. Expectedly, the La–N bonds in **5** (2.762 Å on average) are shorter than those in the bulkier **4** (average 2.826 Å). The same applies to the La–C bonds to the outer methyl groups of the $Me_3AlCH_2AlMe_2CH_2AlMe_3$ ligand; average values are 2.752 Å for **5** and 2.788 Å for **4**. Surprisingly, the situation is reversed for the La–C bonds to the CH_2^{2-} units of the $Me_3AlCH_2AlMe_2CH_2AlMe_3$ ligand; they are longer for **5** (average 2.532 Å) and shorter for **4** (average 2.497 Å).

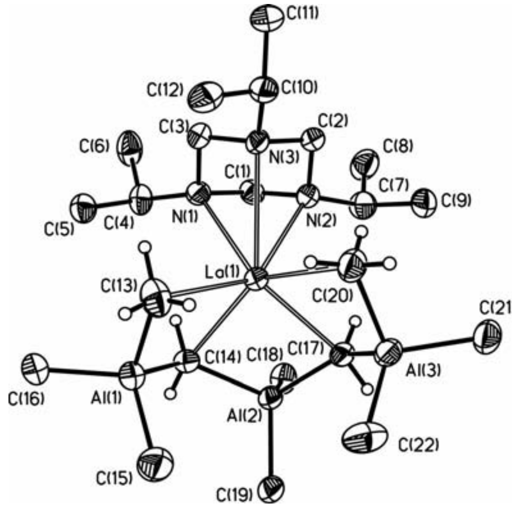


Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms except at C(16), C(17), C(20) and C(23) are omitted for clarity. Selected bond lengths [Å] and angles [°]: La(1)–N(1) 2.749(3), La(1)–N(2) 2.725(3), La(1)–N(3) 2.813(3), La(1)–C(14) 2.542(4), La(1)–C(17) 2.521(4), La(1)–C(13) 2.754(5), La(1)–C(20) 2.749(5), Al(1)–C(13) 2.084(5), Al(1)–C(14) 2.067(4), Al(2)–C(14) 2.077(4), Al(2)–C(17) 2.067(4), Al(3)–C(17) 2.049(4), Al(3)–C(20) 2.084(5); C(14)–La(1)–C(17) 81.5(1), C(13)–La(1)–C(14) 78.5(1), C(17)–La(1)–C(20) 78.2(2), C(14)–Al(2)–C(17) 105.7(2), Al(1)–C(14)–Al(2) 132.0(2), Al(2)–C(17)–Al(3) 140.7(2).

Conclusions

This work demonstrates the dependence of the products of reactions between rare earth tetramethylaluminates and polybases, such as triazacyclohexanes, on the steric requirements of both, the size of the substituents at the trinitrogen rings and the size of the metal ions. It is possible to find certain combinations that allow the isolation of uniform products in good yield, which contain only one species of C–H activation product. Initial reactivity tests demonstrate the transferability of the methylidene units. This and transfer reactions to other metal systems are presently under investigation.

Table 1. Crystallographic data for **1**–**5**.

	1/2a/2b	**3**	**4**	**5**
Empirical formula	$C_{16}H_{43}Al_3N_3Pr$	$C_{25}H_{61}Al_3N_3Pr$, C_7H_8	$C_{25}H_{61}Al_3N_3La$, C_7H_8	$C_{22}H_{55}Al_3LaN_3$
M_r	499.38	717.75	715.75	581.54
T [K]	100(2)	100(2)	200(2)	100(2)
Crystal size [mm]	0.30 × 0.05 × 0.03	0.18 × 0.09 × 0.06	0.16 × 0.14 × 0.14	0.15 × 0.14 × 0.09
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	9.9719(3)	11.0863(5)	11.2003(2)	18.1276(8)
b [Å]	16.7780(6)	12.4325(9)	12.5227(4)	11.0260(4)
c [Å]	24.1684(8)	15.3298(10)	15.4531(3)	17.6901(9)
α [°]	102.5540(15)	81.912(3)	81.7322(10)	90
β [°]	96.467(2)	86.584(4)	86.9471(9)	119.067(2)
γ [°]	105.7278(17)	66.310(3)	66.7038(9)	90
V [Å^3]	3735.3(2)	1915.6 (2)	1970.01(6)	3090.5(2)
Z	6	2	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.332	1.244	1.207	1.250
μ [mm^{-1}]	2.07	1.36	1.17	1.48
$F(000)$	1548	760	756	1216
Θ range [°]	2.9–27.5	3.0–25.0	3.0–27.5	3.0–27.5
Index range	$-12 \le h \le 12$	$0 \le h \le 12$	$-14 \le h \le 14$	$-23 \le h \le 23$
	$-21 \le k \le 21$	$-13 \le k \le 14$	$-16 \le k \le 16$	$-14 \le k \le 14$
	$-29 \le l \le 31$	$-18 \le l \le 18$	$-20 \le l \le 20$	$-22 \le l \le 22$
Reflections collected	62324	12545	62990	38913
Unique reflections	16827	6322	9011	7040
Observed reflections (2σ)	11709	5498	8170	5281
R_{int}	0.098	0.037	0.037	0.095
Data/restraints/parameters	16827/0/780	6322/0/408	9011/0/408	7040/0/314
GoF (F^2)	0.976	1.039	1.042	1.032
R_1, wR_2 [$I > 2\sigma(I)$]	0.0488, 0.1023	0.0311, 0.0611	0.0295, 0.0728	0.0430, 0.0994
R_1, wR_2 (all data)	0.0856, 0.1178	0.0410, 0.0645	0.0343, 0.0750	0.0660, 0.1085
$\Delta_{max/min}$ [e Å^{-3}]	1.62/–1.27	0.63/–0.73	1.51/–0.78	1.19/–0.82
CCDC-	-812632	-812633	-812634	-821938

Experimental Section

General Methods: All manipulations were performed under rigorously dry argon by using advanced Schlenk and glove-box techniques and freshly dried solvents. Toluene was dried with potassium, degassed and condensed from $LiAlH_4$ before use. The triazacyclohexane derivatives were prepared according to our earlier reports.[15–18] [La(AlMe$_4$)$_3$] and [Pr(AlMe$_4$)$_3$] were synthesised by a literature method.[12] NMR measurements were recorded with Bruker DRX 500 and Avance 600 spectrometers. Elemental analyses were performed with a LECO CHNS 932.

General Procedure for the Syntheses of 1, 2 and 3: In a glove box, a solution of the triazacyclohexane (0.5 mmol) in toluene was slowly added dropwise to a toluene solution of [Ln(AlMe$_4$)$_3$] (0.5 mmol) at room temperature. An instant precipitation of a greenish (Ln = Pr) or colourless (Ln = La) solid was observed accompanied by gas evolution. After stirring for 18 h, the reaction mixture was filtered, and the clear solution concentrated to 3 mL. Well-formed crystals (suitable for X-ray structure determination) were obtained after 3–7 d.

[(TMTAC)Pr{(μ-CH$_3$)Al(CH$_3$)$_2$}$_2${(μ$_3$-CH$_2$)$_2$Al(CH$_3$)$_2$}][(TMTAC) Pr{CH(AlMe$_3$)$_3$}]$_2$ (1 and 2): Yield: 168 mg (67 %). $C_{16}H_{43}Al_3N_3Pr$ (401.6): calcd. C 38.48 H 8.68 N 8.41; found C 38.52 H 8.76 N 8.12.

[(T*t*BuTAC)Pr{(μ-CH$_3$)Al(CH$_3$)$_2$}$_2${(μ$_3$-CH$_2$)$_2$Al(CH$_3$)$_2$}] (3): Yield: 224 mg (72 %). $C_{32}H_{69}Al_3N_3Pr$ (620.0): calcd. C 48.15 H 9.86 N 6.74; found C 48.25 H 9.91 N 6.32.

[(T*t*BuTAC)La{(μ-CH$_3$)Al(CH$_3$)$_2$}$_2${(μ$_3$-CH$_2$)$_2$Al(CH$_3$)$_2$}] (4): Yield: 247 mg (79 %). ^{1}H NMR (500 MHz, 20 °C, C_6D_5Br): δ = 3.91 (d, J = 9.1 Hz, 1 H), 2.60 (d, J = 9.2 Hz, 1 H), 1.81 (d, J = 12.4 Hz, 1 H), 0.77 (s, 1 H), 0.69 (s 9 H), –0.12 (s, 1 H), –0.60 (s, 3 H), –0.62 to –0.76 (m), –0.64 (m, 1 H), –0.89 (s, 1 H), –1.01 (d, J = 12.4 Hz, 1 H) ppm. $C_{25}H_{61}Al_3N_3La$ (623.6): calcd. C 48.15 H 9.86 N 6.74; found C 48.33 H 10.15 N 6.45.

Crystallographic Structure Determinations: Single crystals suitable for X-ray diffraction measurement were chosen inside the glovebox, suspended in a Paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer. The crystal data for **1/2a/2b**, **3**, **4** and **5** were collected with a Bruker Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined by full-matrix least-square cycles (programs SHELXS-97 and SHELXL-97).[22] Figures were prepared by using ORTEP.[23] More details on the crystallographic measurements can be found in Table 1. The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC deposition numbers are listed in Table 1.

Acknowledgments

We thank Klaus-Peter Mester for recording the NMR spectra and Brigitte Michel for performing the elemental analyses.

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Received: April 19, 2011