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Rare-Earth-Metal Alkyl Complexes

$LaAl_3Et_{12}$: A Homoleptic Ethyllanthanum Complex**

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In memory of Alfred G. Gahn

“By any criterion, simple transition metal alkyls are very unstable”.[1] This very general statement by Parshall and Mrowca in 1968 certainly does not differentiate between thermodynamic and kinetic factors, but it holds true nonetheless. Specifically referring to the simplest alkyl ligands methyl and ethyl, late-transition-metal complexes of the latter are considered exceedingly unstable owing to their propensity to decompose by β-H elimination.[2] In contrast, d^0 complexes seem to be kinetically stabilized with respect to β-H elimination, which is of major importance in early-transition-metal-based Ziegler–Natta polymerization catalysis.[3] In this regard, ethylaluminum reagents play a major role as cocatalysts by activating the transition-metal center by ethyl-group transfer.[4] Compared to their methyl congeners ethylaluminum reagents are considered beneficial 1) because of their relatively cost-effective synthesis, 2) because they imply higher solubility, and 3) therefore often enhance polymerization activity.[5] Unfortunately, ethyl complexes of the early transition metals, including the rare-earth metals, engage in further degradation reactions, as shown for α- and β-hydrogen abstraction as well as β-alkyl transfer, particularly in the absence of stabilizing ancillary ligands.[6] To date, only a small number of rare-earth homometallic ethyl complexes has been authenticated by X-ray structure analysis, while methyl derivatives clearly dominate the field of Ln–Al bimetallic Ziegler catalysis.[7] For scandium, N-donating ancillary ligands were shown to stabilize diethyl complexes such as $[\{ArNC(t\mathrm{Bu})CHC(t\mathrm{Bu})NAr\}ScEt_2]$ $(Ar = C_6H_3i\mathrm{Pr}_2\text{-}2,6)$[8] and $[\{N(SiMe_2CH_2Pi\mathrm{Pr}_2)_2\}ScEt_2]$,[9] while ethyl Grignard reagents were employed in salt metathesis protocols. The monoethyl complexes $[(dadmb)YEt(thf)_2]$ (dadmb = 2,2′-bis-[(*tert*-butyldimethylsilyl)amido]-6,6′-dimethylbiphenyl)[10] and $[Lu(\mu\text{-}Et)(\mu\text{-}H)\{\mu\text{-}Et_2Si(C_5H_4)(C_5Me_4)\}_2Lu]$[11] were obtained from the hydrido derivatives by ethylene insertion. Tetraethylaluminate $(AlEt_4)^-$ groups seem to be rather stable when bonded to divalent rare-earth-metal cations, as shown for the homoleptic complexes $[Ln(AlEt_4)_2]_n$ (Ln = Eu, Sm, Yb),[12] which readily form monomeric donor adducts, for example, $[Ln(AlEt_4)_2(thf)_2]$ (Ln = Yb, Sm).[13] Ln^{III} tetraethylaluminate complexes are scarce, probably because they display reactivity behavior reminiscent of $[LnEt(AlEt_3)]$ (“ethyl in disguise”), bearing close resemblance to the intrinsically unstable Group 4 congeners.[14] Only the heteroleptic metallocene complexes $[(C_5Me_5)_2Sm(AlEt_4)]$,[15] $[(C_5Me_5)_2Sm(AlEt_4)(thf)]$,[16] and *rac*-$[\{Me_2Si\text{-}(2\text{-}Me\text{-}C_9H_5)_2\}Y(AlEt_3Me)]$[17] and the lanthanum carboxylate $[(2,4,6\text{-}i\mathrm{Pr}C_6H_2CO_2AlEt_3)_2La(AlEt_4)]$[18] were analyzed by X-ray diffraction.

Herein we present the solid-state structure of homoleptic lanthanum(III) tetraethylaluminate **1** and elaborate on its thermal decomposition in solution by β-H transfer and ethane formation, as detected by NMR spectroscopy. A previous attempt to X-ray crystallographically analyze $[La(AlEt_4)_3]$ (**1**) produced only a connectivity structure[19] owing to the low quality of the crystals that resulted from an unoptimized reaction protocol and partial decomposition of **1**. We have now reinvestigated the synthesis of **1**, treating $[La(NMe_2)_3(LiCl)_3]$ instead of $[La\{N(SiHMe_2)_2\}_3(thf)_2]$ with excess $AlEt_3$, which enabled facile separation of byproduct $[(Et_2AlNMe_2)_2]$ thus allowing isolation of pure material in good yield. Highly twinned crystals of complex **1** with a featherlike morphology could be harvested from hexane at −40 °C. Under the same conditions, these crystals transformed into ordered clear blocks in the course of approximately one week.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. Experiments conducted at 203 and 103 K showed that the notorious disorder caused by rotating ethyl groups is eliminated at lower temperature (see Figure 1 and the Supporting Information).[20] The formally six-coordinate lanthanum center accommodates two differently arranged η^2-bonded $(AlEt_4)^-$ ligands, with the methyl groups of the terminally Al-bonded ethyl ligands being either both oriented toward the lanthanum center (Al1 and Al2: Al-C-C 117.24(13)–120.41(13)°) or one pointing away from it (Al3-C23-C24 113.17(17)°). In comparison, $[La(AlMe_4)_3]$ features three distinct tetramethylaluminate coordination modes: η^2, distorted-η^2, and η^3.[21] The exclusively η^2-coordinated ligands in **1** certainly reflect the enhanced steric bulk of the ethyl groups. On the other hand, the exchange of methyl for ethyl groups seems to have only a slight impact on the metal–carbon(η^2) bond lengths ($[La(AlMe_4)_3]$: La−C 2.696(3), 2.701(3), $Al{-}C_\mu$ 2.080(3), $Al{-}C_t$ 1.972(3), 1.965(4) Å). Generally, methylaluminate complexes including $[La(AlMe_4)_3]$ are thermally quite stable but can decompose in the presence of donor molecules to Tebbe-like

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Supporting information for this article, including additional analytical data for complexes **1** and **4** and details of NMR spectroscopy for **2** und **3**, is available on the WWW under http://dx.doi.org/10.1002/anie.201105251.

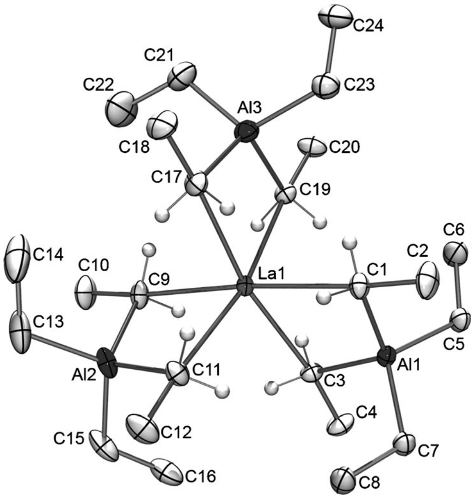
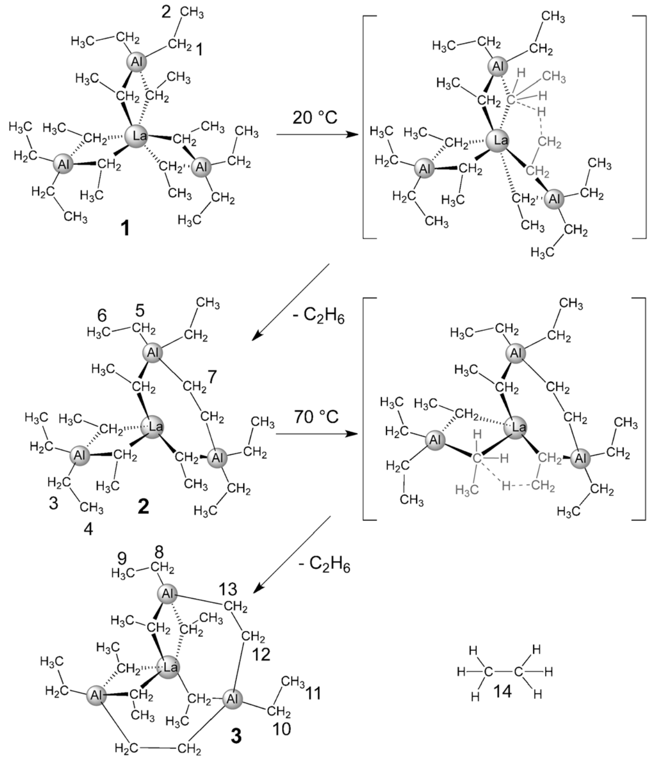


Figure 1. Molecular structure of [La(AlEt$_4$)$_3$] (**1**) at 103 K, showing molecule 1 with atomic displacement parameters at the 50% level. Peripheral H atoms are omitted for clarity. Selected bond lengths [Å]: La1–C 2.6533(18)–2.7016(17), Al–C$_t$ 1.972(2)–2.002(2), Al–C$_\mu$ 2.0934(19)–2.1189(18), C$_\mu$-C 1.545(2)–1.548(3), C$_t$–C 1.520(3)–1.535(3).

alkylidene or alkylidyne complexes via α-CH abstraction.[22] In contrast, Group 4 and scandium alkyl complexes usually show weak interactions with alkyl aluminum reagents and only form stable M−AlR$_4$ coordination compounds in exceptional cases[23] or with groups R that increase the Lewis acidity of the Al center (e.g. (C$_6$F$_5$)$^-$).[24]

Solutions of complex **1** in aliphatic (*n*-hexane, cyclohexane) or aromatic (benzene, toluene) solvents are initially colorless, but turn brownish over time at ambient temperature, indicating decomposition. NMR spectroscopic investigations revealed similar spectral patterns with marginally shifted ethyl signals for the different solvents tested ([D$_6$]benzene, [D$_8$]toluene, [D$_{12}$]cyclohexane), making a reaction with the solvents unlikely and indicating intra- or intermolecular degradation of **1**. For the identification of the decomposition products, HMBC experiments proved diagnostic, showing a large range of couplings ($^1J\rightarrow{}^3J$), even over the Al nuclei. For the confirmation of the number of protons bound to carbon atoms, ^{1}H-coupled ^{13}C NMR spectra were recorded, which gave better and clearer results than DEPT spectra. The formation of ethane[25] was unequivocally confirmed, as was the presence of ethylene moieties of the type Al-CH$_2$-CH$_2$-Al, which showed chemical shifts comparable to the signals of the bridging ethyl groups observed in the low-temperature NMR spectrum of [(AlEt$_3$)$_2$] (see the Supporting Information). Over time and depending on the temperature, the generation of two different species **2** and **3** is proposed, the formation of which involves a La-promoted β-H transfer mechanism as the initial major decomposition pathway of **1** (Scheme 1, explanatory NMR spectra are shown in the Supporting Information).

Complex [(AlEt$_4$)La{(μ-Et)(AlEt$_2$)}$_2$(μ-CH$_2$CH$_2$)] (**2**) formed slowly as the major product at ambient temperature (20 °C; Figure 2, see also the Supporting Information). Only insignificant amounts of **3** were observed after long reaction times (two weeks). Unfortunately, owing to the slow reaction rate a complete conversion was not achieved in reasonable time periods, and all endeavors to separate **2** from remaining [La(AlEt$_4$)$_3$] (**1**) have failed to date, meaning that **1** could not be crystallized from mixtures with a high content of **2** and vice versa. The signals of the Al-CH$_2$-CH$_2$-Al group (7: ^{1}H NMR



Scheme 1. Decomposition of [La(AlEt$_4$)$_3$] by β-H abstraction yielding [(AlEt$_4$)La{(μ-Et)(AlEt$_2$)}$_2$(μ-CH$_2$CH$_2$)] (**2**) and [La{(Et$_3$Al)(μ-CH$_2$CH$_2$)(AlEt$_2$)(μ-CH$_2$CH$_2$)$_2$(AlEt$_3$)}] (**3**).

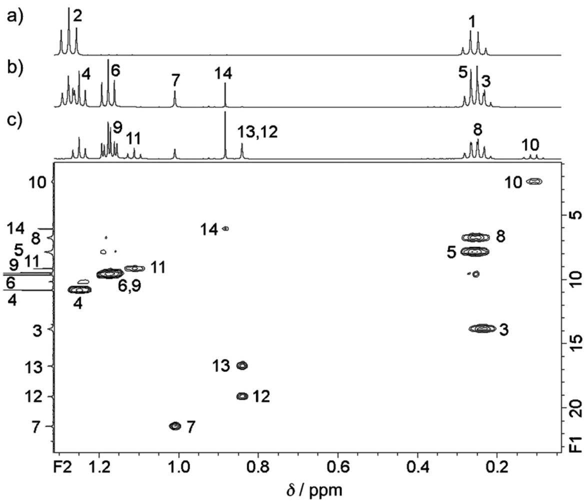


Figure 2. ^{1}H–^{13}C HSQC spectra in [D$_{12}$]cyclohexane of a mixture of complexes **2** and **3**, with peak assignment according to Scheme 1. The upper three ^{1}H NMR spectra show the formation of **2** and **3** from a) pure **1**, b) formation of **2** after ten days at 20 °C to give a mixture of **1** and **2**, and c) formation of **3** after additional heating to 70 °C for 12 h, to give a mixture of **2** and **3**.

(^{13}C NMR) at 20 °C: 0.81 (22.0) (in C_6D_6), 0.82 (21.7) (in C_7D_8), 1.01 ppm (21.4) (in C_6D_{12})), appear markedly shifted compared to the ethylene resonance found for scandium complex $[\{(C_5Me_4SiMe_2N\textit{t}Bu)Sc(PMe_3)\}_2(\mu\text{-}C_2H_2)]$ (^{1}H NMR: −0.17, ^{13}C NMR: 35.2 ppm in $[D_8]$toluene).[6]

The proton-coupled ^{13}C NMR spectrum of **2** exhibits a triplet with a considerably smaller coupling constant than the aforementioned scandium complex ($^1J_{CH} = 116$ vs. 142 Hz). The ethylene group gives one singlet signal in the ^{1}H and ^{13}C NMR spectra, in accordance with magnetic equivalency of the methylene groups, which implies high molecular symmetry and unhindered rotation of the ethylene ligand. This aspect would argue against a rigid coordination to the lanthanum center as discussed for the ethylene bonding in $[\{(C_5Me_4SiMe_2N\textit{t}Bu)Sc(PMe_3)\}_2(\mu\text{-}C_2H_2)]$.[6] The six ethyl groups of the $[Et_3Al\text{-}CH_2CH_2\text{-}AlEt_3]^{2-}$ moiety and the four of the $(AlEt_4)^-$ ligand give one signal set each, even at low temperatures, evidencing rapid exchange of bridging $La(\mu\text{-}CH_2CH_3)Al$ and end-on-coordinated $Al(CH_2CH_3)$ ethyl groups. Such high ethyl group mobility was also observed in a variable-temperature (VT) NMR spectroscopy experiment with **1**.

It is well established that ethyl ligands bound to d^0 metal centers readily engage in σ-bond metathesis,[3b,26,27] leading to C−H bond activation of neighboring alkyl ligands, with β-hydride elimination and β-hydride transfer as the two common reaction pathways.[8] Particularly, two adjacent ethyl groups are prone to react with each other through β-hydrogen abstraction, affording a $C_2H_4^{2-}$ ligand and release of ethane.[28] This mechanism was recently confirmed for the formation of $[Li(tmed)]_2[Et_4Hf(C_2H_4)]$ (tmed = tetramethylethylenediamine) by use of the partly deuterated ligand $(CH_2CD_3)^-$, which gave CH_2DCD_3 as a degradation product.[28c] Previously, ethylene ligands were also accessed by addition of ethylene to low-valent Group 4 complexes,[29] ligand exchange,[30] or fragmentation of titanacyclopentadiene.[31] To our knowledge, complex $[\{(C_5Me_4SiMe_2N\textit{t}Bu)Sc(PMe_3)\}_2(\mu\text{-}C_2H_4)]$ is the only reported rare-earth-metal complex featuring a $[C_2H_4]^{2-}$ ligand, formed from $[(C_5Me_4SiMe_2N\textit{t}Bu)Sc(PMe_3)Et]$ generated in situ.[6] $[\{ArNC(\textit{t}Bu)CHC(\textit{t}Bu)NAr\}NScEt_2]$ was reported to decompose by C−H activation of phenyl-bonded isopropyl groups and ethane formation.[8] Binuclear complexes bearing ethylene ligands are scarce, although the first examples date back to 1974, when Kaminsky et al. succeeded in identifying $Zr\text{-}CH_2CH_2\text{-}Zr$ and $Zr\text{-}CH_2CH_2\text{-}Al$ moieties as well as ethane as products of the decomposition reaction of $[(C_5H_5)_2ZrCl_2]$ and $AlEt_3$.[32] Moreover, ate complexes $[Li(tmed)]_2[Et_4Hf(C_2H_4)]$[28c] and $[\{[Me_2Si(C_5Me_4)_2]Zr(\eta^2\text{-}C_2H_4)H\}_2Mg]$[33] as well as the Group 5 metal complex $[(C_5Me_5)_2Ta(H)(C_2H_4{\cdot}AlEt_3)]$[34] nicely demonstrate the coordination possibilities of this ligand.

Heating of the reaction mixture from ambient temperature (Figure 2b) to 70 °C led to total consumption of the initial precursor $[La(AlEt_4)_3]$ (**1**) and formation of a second ethane elimination product, $[La\{(Et_3Al)(\mu\text{-}CH_2CH_2)(AlEt_2)(\mu\text{-}CH_2CH_2)_2(AlEt_3)\}]$ (**3**) within 2 h. The assumed strong binding of the originally formed $[Et_3Al\text{-}CH_2\text{-}CH_2\text{-}AlEt_3]^{2-}$ in **2** suggests that this sequential ethane elimination leading to **3** proceeds intramolecularly. Alternatively, an intermolecular elimination reaction involving organoaluminum bridged lanthanum centers, as found in the solid-state structure of **4** (see below), and consecutive ligand redistribution might occur. In complex **3**, the $[Et_3Al\text{-}CH_2CH_2\text{-}AlEt_2\text{-}CH_2CH_2\text{-}AlEt_3]^{3-}$ backbone exhibits two chemically inequivalent CH_2 groups. Assuming an AA′BB′ spin system of higher order, in aliphatic $[D_{12}]$cyclohexane only one pseudo singlet was visible for both CH_2 groups, while a superimposed multiplet pattern with very small coupling constants could be observed in aromatic solvents. The ^{13}C signals for the two CH_2 groups appear clearly separated, which facilitated separation of the ^{1}H peaks using 2D spectroscopy. The ethyl groups of the $AlEt_3$ and the $AlEt_2$ fragments show only one signal set each, as a result of a likewise high mobility already observed for complexes **1** and **2**. It should be mentioned that $^3J(^1H,^{13}C)$ couplings over Al were observed in the HMBC spectra for $(CH_3\mathit{CH_2})_3Al\text{-}\mathit{CH_2}CH_2\text{-}Al(CH_2CH_3)_2\text{-}CH_2\mathit{CH_2}\text{-}Al(\mathit{CH_2}CH_3)_3$ and $(CH_3CH_2)_3Al\text{-}CH_2\mathit{CH_2}\text{-}Al(\mathit{CH_2}CH_3)_2\text{-}CH_2CH_2\text{-}Al(CH_2CH_3)_3$ but not for $(CH_3CH_2)_3Al\text{-}CH_2\mathit{CH_2}\text{-}Al(CH_2CH_3)_2\text{-}\mathit{CH_2}CH_2\text{-}Al(CH_2CH_3)_3$. Nevertheless, we propose a molecular composition of **3** as shown in Scheme 1, for symmetry reasons and based on the integrals found after semiempirical deconvolution of the ^{1}H NMR spectra. The high solubility of **3** and remaining **2** impeded their separation by fractionating crystallization. Prolonged heating (two weeks at 70 °C) generated additional ethane and new products. Although the interpretation of the resulting NMR spectra was not conclusive, 2D spectroscopy hints at several proton signals assignable to new $M\text{-}CH_2CH_2\text{-}M$ (M = Al, La) moieties. This result suggests consecutive decomposition involving additional C−H bond activation reactions similar to those proposed for the formation of complexes **2** and **3**. The splitting of the new signals is in accordance with a more rigid behavior of these groups than observed in **2** and **3**.[36]

Complex **1** reacts by protonolysis with HC_5Me_5 in a similar way to its methyl congeners,[35,36] but the resulting metallocene **4** is already formed at ambient temperature. It crystallizes at −40 °C as the dimer $[\{(C_5Me_5)_2La(AlEt_4)\}_2]$ with $\mu\text{-}\eta^1{:}\eta^1$ bridging ethylaluminate ligands (Figure 3). For comparison, the corresponding samarium complex $[(C_5Me_5)_2Sm(AlEt_4)]$, crystallized at −20 °C from hexane, shows a monomeric solid-state structure.[15] The bond lengths and angles in **4** match those found in $[\{(C_5Me_5)_2La(AlMe_4)\}_2]$[37] ($La\text{−}C_\mu$ 2.848(2)–2.849(2), $Al\text{−}C_\mu$ 2.042(2)–2.043(2) Å, $C_\mu\text{-}La\text{-}C_\mu$: 87.36°; $La\text{-}C_\mu\text{-}Al$: 175.05(7)–175.74(8)°), except for a considerably wider $C_\mu\text{-}Al\text{-}C_\mu$ angle (100.76(7) vs. 112.3(2)°). VT-NMR spectroscopy revealed a monomer–dimer equilibrium of **4**, a well-known behavior of such complexes (see the Supporting Information).[38]

In conclusion, high-purity $[La(AlEt_4)_3]$ can be produced in good yields and shows similar reaction patterns to its methyl congener $[La(AlMe_4)_3]$, for example, in the protonolytic formation of $[(C_5Me_5)_2La(AlEt_4)]$. In contrast to the thermally stable $[La(AlMe_4)_3]$, decomposition takes place quickly in solution. The observed release of ethane originates from a β-H abstraction involving the attack of a highly basic ethyl ligand at a neighboring ethyl moiety. This decomposition pathway has precedence in Group 4 chemistry in particular,

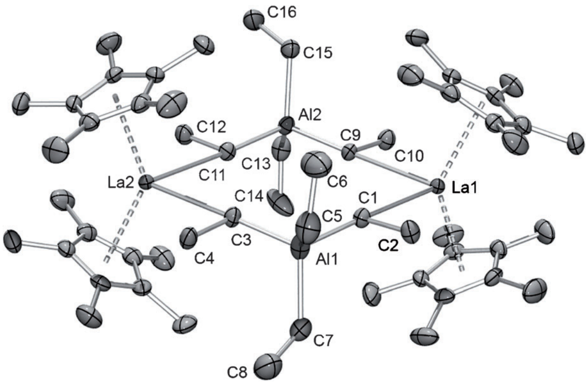


Figure 3. Molecular structure of $[\{(C_5Me_5)_2La(AlEt_4)\}_2]$ (**4**), shown with atomic displacement parameters at the 50% level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: La–Ctr 2.547–2.561, La1–C_μ 2.896(4)–2.929(4), Al–C_t 1.974(5)–1.990(5), Al–C_μ 2.012(4)–2.058(4), C_μ–C 1.539(5)–1.542(5), C_μ–C 1.477(7)–1.541(7); Ctr1-La1-Ctr2 135.54, Ctr1-La1-C1 109.67, La1-C1-C2 80.7(2), La1-C1-Al1 170.48(19), C1-La1-C9 79.13(11), C3-La2-C11 79.05(11). Ctr1, Ctr2 = ring centroids.

with fundamental implications for multinary Ziegler catalysts with ethylaluminum components. The temperatures applied in commercial polymerization reactions make such C–H activations very likely. The proposed decomposition products $[(AlEt_4)La\{(\mu\text{-}Et)(AlEt_2)\}_2(\mu\text{-}CH_2CH_2)]$ and $[La\{(Et_3Al)(\mu\text{-}CH_2CH_2)(AlEt_2)(\mu\text{-}CH_2CH_2)_2(AlEt_3)\}]$ are very rare examples of ethylene-bridged organometallic aluminum complexes. This very decomposition of $[La(AlEt_4)_3]$ and the to date elusive homoleptic derivatives of the smaller rare-earth metals emphasize the high importance of these findings for commercial neodymium-based Ziegler polymerization catalysis, where ethylaluminum reagents are routinely employed as alkylating reagents.

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Keywords: aluminates · C–H activation · ethyl · ethylene · lanthanoids

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[20] Compound **1** ($C_{24}H_6Al_3La$, $M_r = 568.57$) crystallizes from hexane in the triclinic space group $P\bar{1}$ with $a = 11.2418(9)$, $b = 14.2020(11)$, $c = 21.6548(17)$ Å, $\alpha = 71.3800(10)$, $\beta = 74.2460(10)$, $\gamma = 89.8990(10)°$, $V = 3139.6(4)$ Å^3, and $d_{calcd} = 1.203\ g\,cm^{-3}$ for $Z = 4$. Data were collected at 103 K on a BRUKER APEX II CCD system. The structure was solved by direct methods, and least-square refinement of the model based on 19192 (all data) and 18168 reflections ($I > 2.0\sigma(I)$) converged to a final $wR2 = 0.0689$ and $R1 = 0.0285$, respectively. An additional data set for **1** was taken at 203 K (see the Supporting Information). Compound **4** ($C_{56}H_{100}Al_2La_2$, $M_r = 1105.14$) crystallizes from a hexane/toluene mixture in the monoclinic space group $P2_1/c$ with $a = 18.1011(7)$, $b = 17.9190(7)$, $c = 19.3919(7)$ Å, $\beta = 116.0060(10)°$, $V = 5653.0(4)$ Å^3, and $d_{calcd} = 1.299\ g\,cm^{-3}$ for $Z = 4$. Data were collected at 123 K on a BRUKER-AXS 2K CCD system. The structure was solved by direct methods, and least-square refinement of the model based on 16618 (all data) and 10770 reflections ($I > 2.0\sigma(I)$) converged to a final $wR2 = 0.1182$ and $R1 = 0.0432$, respectively. CCDC 835110 (**1**, 103 K), 835111 (**1**, 203 K), 835112 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[36] We also kept an eye on any potential formation of ethylene or insertion products thereof, such as alkyls resulting from an "Aufbau" reaction, as an indicator for β-H elimination reactions. Although we did not observe any signals in the NMR spectrum assignable to ethylene gas, two sets of symmetric low-intensity signals were found to develop in the low-field region after two weeks at 70°C in all solvents, indicative of the formation of small amounts of olefinic products. Careful hydrolysis of thermally pretreated **1** with D_2O clearly points to the formation of DH_2CCH_3 and DH_2CCH_2D (see the Supporting Information); this finding is supportive of the scenario shown in Scheme 1.

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