Rare-earth metal methylidene complexes with Ln₃(μ₃-CH₂)(μ₃-Me)(μ₂-Me)₃ core structure†

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Tricentral rare-earth metal methylidene complexes with a Ln₃(μ₃-CH₂)(μ₃-Me)(μ₂-Me)₃ structural motif were synthesized by applying three protocols. Polymeric [LuMe₃]₌ (1-Lu) reacts with the sterically demanding amine H[N(SiMe₃)₂] (Ar = C₆H₄Py-2,6) in tetrahydrofuran via methane elimination to afford isolable monomeric [N(SiMe₃)₂][LuMe₄(thf)]₂ (4-Lu). The formation of tricentral rare-earth metal tetramethylidene complexes [N(SiMe₃)₂][Ln₃(μ₂-CH₂)(μ₂-Me)(μ₂-Me)₃(thf)]₉ (7-Ln; Ln = Y, Ho, Lu) via reaction of [LnMe₆]₄ (1-Ln; Ln = Y, Ho, Lu) with H[N(SiMe₃)₂] is proposed to occur via an “intermediate” species of the type [N(SiMe₃)₂][LnMe₄(thf)]₂ and subsequent C–H bond activation. Applying Lappert’s concept of Lewis base-induced methylaluminate cleavage, compounds [N(SiMe₃)₂][Ln(AlMe₄)₂] (5-Ln; Ln = Y, La, Nd, Ho) were converted into methylidene complexes 7-Ln (Ln = Y, Ho, Lu) in the presence of tetrahydrofuran. Similarly, tetramethylgallate complex [N(SiMe₃)₂][Y(GaMe₄)₂] (6-Y) could be employed as a synthesis precursor for 7-Y. The molecular composition of complexes 4-Ln, 5-Ln, 6-Y and 7-Ln was confirmed by elemental analyses, FTIR spectroscopy,¹¹ H and¹² C NMR spectroscopy (except for holmium derivatives) and single-crystal X-ray diffraction. The Tebbe-like reactivity of methylidene complex 7-Y with 9-fluorenone was assessed affording oxo complex [N(SiMe₃)₂][Nd₂(µ-O)(µ₂-Me)₄(thf)]₉ (8-Nd). The synthesis of 5-Ln yielded [N(SiMe₃)₂][Ln(AlMe₄)₂] (9-Ln; Ln = La, Nd) as minor side-products, which could be obtained in moderate yields when homoleptic Ln[AlMe₄]₂ were treated with two equivalents of K[N(SiMe₃)₂].

Introduction

Multiple metal–carbon bonds, predominantly alkylidyne units “M=CR₂”, continue to trigger immense research activities in organometallic synthesis and catalysis.¹–⁶ Schrock’s neopentylidene complex (tBuCH₂)₃Ta(=CH/BU)⁷,¹⁰ marked the first example of a stable transition metal alkylidyne complex, with the bulky tBu substituents at the α-carbon atom impeding intermolecular decomposition pathways. In contrast, methylidyne “CH₂” species are sterically less protected against bimolecular reactions, and hence present a particular challenge and are found to be kinetically labile. Although authenticated by single-crystal X-ray diffraction, the first transition metal methylidyne complex C₉H₆Ta(C₂H₄) (CH₃)₁¹,¹² decomposes bimolecularly forming ethylene complex C₂Ta(C₂H₄)₃(CH₃).¹¹ Current progress in the field of early transition metal terminal methylidyne complexes features Mindiola’s group 4 and group 5 derivatives (PNP)MM’(CH₂)(CH₃).¹³,¹⁴ Lewis-acid stabilized homometallic methylidyne complexes (CH₂),¹⁵–¹⁸ The most prominent example of a Lewis-acid stabilized heterobimetallic methylidyne complex is the Tebbe reagent Cp₂Ti[(μ₂-CH₂)(μ₂-Cl)AlMe₂]₅,¹⁹ whose structural elucidation proved to be delicate.²⁰ The Tebbe reagent also laid the ground work for a series of rare-earth metal variants, [LnIII]n[Ln(µ-CH₂)(µ-Me)(µ₂-Me)₃(thf)]₉ (1-Ln; Ln = Y, Ho, Lu; R = Me, ferrocenyl). Previous studies from our laboratory and others on rare-earth-metal(n) alkyl complexes [LnRR’] (L = C₆H₄Me₅(= Cp’), N(SiMe₃)₂[Ar], PhC(NC₆H₄Py-3,5)₂; Ln = Y, La, Ho, Lu; R, R’ = Me, AlMe₃, Cl) led to the isolation of “Lewis-acid-free” Ln₃” methylidyne complexes with a striking Ln₃(µ₃-CH₂) core structure (Scheme 1).¹⁰–¹²

Experimental and theoretical studies on homometallic tricentral rare-earth metal methylidyne complexes L₃Ln₃(µ₃-CH₂) (µ₃-CH₂)(µ₃-CH₂)₃(thf)₉ (L = monoanionic ligand) revealed Tebbe-like reactivity in methylenation reactions (Scheme 1)
along with methylation of the carboxylic functionalities.\textsuperscript{31–33} In sharp contrast, treatment of \( \text{CP}'_3\text{TM}_3(\mu_2-\text{CH}_3)\) with a ketone would rather yield \( \text{CP}'_3\text{TM}_3(\mu_2-\text{CH}_3)(\text{OC}(\text{CH}_3)(\text{C}_6\text{H}_4))_3 \) as a result of methylidene transfer and simultaneous \textit{ortho}-metallation of benzophenone (not shown in Scheme 1).\textsuperscript{34} Moreover, Hou and coworkers accessed “Lewis-acid-free” cuboid clusters \( \text{[CP'}\text{Ln}(\mu_2-\text{CH}_3)]_n \) via prolonged thermal treatment of the respective trinuclear complexes \( \text{CP}'_3\text{TM}_3(\mu_3-\text{CH}_3)(\mu_2-\text{CH}_3)_{3n} \) or \( \text{CP}'_5\text{Lu}_3(\mu_2-\text{CH}_3)_6 \), respectively. While such Lewis-acid-free \( \text{Ln}(n)=\text{CH}_2 \) clusters revealed interesting reactivity toward (electronically uncharged) functional substrates (Scheme 1),\textsuperscript{15–37} seemingly less efforts were devoted to elucidate the formation of such rare-earth metal methylidene species. Herein, we present three synthesis approaches toward rare-earth metal tetramethylidene complexes capable of methylating ketones. The isolation of dimethyl complex \([\text{NSiMe}_3(\text{Ar})]\text{LuMe}_2(\text{thf})_2\) hints to a mechanism with one crucial C–H bond activation step. Part of the work on methylidene complexes \([\text{NSiMe}_3(\text{Ar})]\text{LnMe}_3(\mu_2-\text{CH}_3)(\mu_2-\text{CH}_3)_2(\text{thf})_3\) \((\text{7-Ln, Ln} = \text{Y, Ho, Lu})\) were recently communicated by our group.\textsuperscript{31}

Results and discussion

We have shown previously that treatment of \([\text{LnMe}_3]\) \((\text{1-Ln; Ln} = \text{Y, Ho, and Lu})\)\textsuperscript{31,38} suspended in \( \text{n}-\text{hexane} \) with one equivalent of \( \text{H}[\text{NSiMe}_3(\text{Ar})] \) subsequent addition of excess \text{thf} at ambient temperature, selectively yields the trinuclear rare-earth metal complexes \([\text{NSiMe}_3(\text{Ar})]\text{LnMe}_3(\mu_2-\text{CH}_3)(\mu_2-\text{CH}_3)_2(\text{thf})_3\) \((\text{7-Ln, Ln} = \text{Y, Ho, Lu; Scheme 2, route A})\).\textsuperscript{31} Due to the insolubility of \text{1-Ln} in aliphatic solvents, immediate reaction with \( \text{H}[\text{NSiMe}_3(\text{Ar})] \) in \( \text{n}-\text{hexane} \) to form putative \([\text{NSiMe}_3(\text{Ar})]\text{LnMe}_3 \) did not occur. It is anticipated that the donor solvent \( \text{thf} \) is necessary to break up the polymeric network of \text{1-Ln}, thus initiating the reaction. Re-investigation of the lutetium-reaction afforded single crystals of \([\text{NSiMe}_3(\text{Ar})]\text{LuMe}_2(\text{thf})_2\) \((\text{4-Lu, 33%})\), which could be isolated together with precipitated \([\text{NSiMe}_3(\text{Ar})]\text{Lu}(\mu_2-\text{CH}_3)(\mu_2-\text{Me})(\mu_2-\text{Me})_2(\text{thf})_3\) \((\text{7-Lu, 19%})\). The \(^1\text{H} \text{NMR} \) spectrum of \( \text{4-Lu} \) in \( \text{thf}-\text{d}_6 \) at ambient temperature features one set of signals for the amido ligand and the coordinated thf donor molecules. The Lu–CH\(_3\) moieties appeared as one narrow singlet at \(-1.06 \text{ ppm (6H)} \), indicating a highly fluxional nature of complex \( \text{4-Lu} \). Cooling a solution of \( \text{4-Lu} \) in \( \text{thf}-\text{d}_6 \) to \(-90 \text{ C} \) significantly shifted the resonances of the metal-bonded methyl groups, the silyl moeity and the methine groups (iPr) to lower field, while the signals for the aryl hydrogen atoms and the methyl groups appeared at higher fields (Fig. S9\textsuperscript{t}). The high thermal sensitivity of compound \( \text{4-Lu} \) allowed \(^1\text{C} \{^1\text{H}\} \) NMR spectroscopy only at low temperatures \((-35 \text{ C}) \) revealing the signal for the Lu–CH\(_3\) groups at 29.5 ppm.

Single-crystal X-ray diffraction of \( \text{4-Lu} \) revealed a geometry about the five-coordinate lutetium metal centre which can best be described as distorted trigonal bipyramidal with \( \text{C1, C2, and N1 occupying the positions in the equatorial plane and O1 and O2 in the apical positions (see Fig. 1). The Lu–CH\(_3\) bond lengths of 2.366(4) and 2.378(5) \text{ Å} \) of complex \( \text{4-Lu} \) are in the same range as in dimethyl complex \([\text{TPy}^{2\text{H,Me}}]\text{LuMe}_2 \) (avg. \( 2.370 \text{ Å} \))\textsuperscript{39} and ate complex \([\text{NSiMe}_3(\text{Ar})]\text{YbMe}(\mu-\text{Me})\text{Li}(\text{thf})_3\) \((\text{Ar} = \text{C}_6\text{H}_3^{2\text{,6}}; \text{Ln–C} 2.349(8) \text{ Å}; \text{Ln–N avg. 2.226} \text{ Å})\),\textsuperscript{40} but the \( \text{Ln–C} \text{ bond lengths of 2.376(2)} \text{ Å} \)\textsuperscript{41} of \( \text{4-coordinate [NSiMe}_3(\text{Ar})]\text{Lu(CH2SiMe3)2(thf)}_3 \) \((\text{Ar} = \text{C}_6\text{H}_3^{2\text{,6}}; \text{Ln–C} 2.382(7) \text{ Å}; \text{Ln–N avg. 2.226} \text{ Å})\),\textsuperscript{40} the Ln–N bond lengths of 1.06 ppm. The high thermal sensitivity of compound \( \text{4-Lu} \) allowed \(^1\text{C} \{^1\text{H}\} \) NMR spectroscopy only at low temperatures \((-35 \text{ C}) \) revealing the signal for the Lu–CH\(_3\) groups at 29.5 ppm.

The isolation of dimethyl complex \([\text{NSiMe}_3(\text{Ar})]\text{LuMe}_2(\text{thf})_2\) \((\text{4-Lu}) \), as a plausible intermediate in the formation of the trinuclear complex \( \text{7-Lu} \) tempted us to speculate about a possible mechanism (see Scheme 3). The reaction proceeds presumably via a sequence of methane elimination \((\text{a}) \) or donor-induced tetramethylaluminate/gallate cleavage (vide infra) \((\text{b}) \) to yield dimethyl complexes \((\text{1} \text{ or } \text{4-Lu}) \), C–H bond activation following formation of \( \text{Ln}(n)=\text{CH}_2 \) \((\text{F}) \) and methane \((\text{c}) \) and subsequent agglomeration \((\text{d}) \) affording trinuclear compounds \( \text{7-Ln} \), which consist of a core with three rare-earth metal centres bridged by \( \mu_2-\text{Me}, \mu_2-\text{Me} \) and \( \mu_2-\text{CH}_3 \) moieties.

The formation of \( \text{7-Y} \) by donor-induced cleavage of bis(aluminate) complex \( \text{5-Y} \) (Scheme 2, route \textbf{B}; Scheme 3, \textbf{b-d}) was also previously communicated by us.\textsuperscript{31} We now found that route \textbf{B} can be adopted for the larger rare-earth metal centres, which is infeasible for route \textbf{A}. Reaction of homoleptic \( \text{Ln(AlMe}_4)_3 \) \((3-\text{Ln, Ln} = \text{Y, La, Nd, Ho})\)\textsuperscript{32,41} with one equivalent of potassium amide \([\text{KNSiMe}_3(\text{Ar})]_4\)\textsuperscript{42,45} in \( \text{n}-\text{hexane} \) at ambient temperature cleanly formed the respective rare-earth metal complexes.31
mono(amide) complexes \([\text{NSiMe}_3(\text{Ar})]\text{Ln(AlMe}_4\text{)}_2\) (5-Ln) in high yields (Scheme 2). The molecular composition of complexes 5-Ln was confirmed by elemental analyses, infrared spectroscopy, single-crystal X-ray diffraction and \(^1\text{H}/\text{\textsuperscript{13}C}\) NMR spectroscopy (except 5-Ho).

The \(^1\text{H}\) NMR spectra of the diamagnetic complexes 5-Ln (Ln = Y, La) showed the expected resonances for the NSiMe\(_3\)(Ar) ligand. The methyl groups of the Al(\(\mu\)-Me)\(_2\)Me\(_2\) moieties appeared as one narrow signal indicating a rapid exchange of bridging and terminal methyl groups (5-Y \(\delta = -0.24\) ppm, \(^2J_{\text{YH}} = 2.5\) Hz; 5-La \(\delta = -0.19\) ppm). Good quality \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra could also be obtained for the paramagnetic neodymium compound 5-Nd. However, due to significant paramagnetic shifts and broadening effects, assignment of the

Scheme 2 Syntheses of trinuclear rare-earth metal methylidene complexes 7-Ln supported by a bulky amido ligand.

Fig. 1 Molecular structure of 4-Lu (atomic displacement parameters are set at the 30% level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [:] Lu1–C1 2.366(4), Lu1–C2 2.378 (5), Lu1–O1 2.312(3), Lu1–O2 2.333(3), Lu1–N1 2.203(3), C6–N1–Lu1 112.8(2), O1–Lu1–O2 161.6(1), O1–Lu1–C1 88.1(1), O2–Lu1–C1 86.6(1), O1–Lu1–C2 83.1(1), O2–Lu1–C2 84.8(1), C1–Lu1–C2 122.3(2).

Scheme 3 Proposed reaction mechanism for the formation of multinuclear methylidene complexes 7-Ln.
signals – except for the AlMe₄ resonance at 11.27 ppm in the
¹H NMR spectrum – appeared to be difficult.

The X-ray crystallographic analyses of [NSiMe₃(Ar)]-Ln(AlMe₄)₂ (5-Ln) revealed structural motifs as found in the solid-state structures of half-sandwich bis(tetramethylaluminate) complexes Cp⁸Ln(AlMe₄)₂⁴⁶–⁴⁸ with one AlMe₄ ligand coordinating in the routinely observed planar η² fashion, and the second one showing a bent η¹ coordination (Fig. 2 and S1–S3). The geometry about the five-coordinate Ln(u) centre can best be described as distorted square pyramidal, with the four bridging methyl groups in the corner of the basal plane and the amido nitrogen atom in the apical position. As detected for Cp⁸Ln(AlMe₄)₂⁴⁶–⁴⁸ the Ln–C[µ-Me] bond lengths increase with increasing Ln(III) size, the bonds in the bent AlMe₄ ligand being significantly elongated compared to those in the planar tetramethylaluminate ligand, and C8 is tilted toward the rare-earth metal centre. The solid-state structures of 5-Ln feature additional short contacts between the metal centres and the ipso carbon atoms of the aryl rings. As a consequence, the aryl ring lies almost orthogonally to the Ln–N bond as evidenced by the acute C9–N1–Ln1 bond angles (Table 1). Interestingly, the feasibility of complexes 5-La and 5-Nd might provide access to methylidene complexes of type 7-Ln with large rare-earth metal centres.

The anticipated formation of a transient [NSiMe₃(Ar)]LnMe₂(thf) species is substantiated by synthesis approach B (Scheme 2), since addition of exess thf to n-hexane solutions of [NSiMe₃(Ar)]Ln(AlMe₄)₂ (5-Ln) afforded complexes 7-Ln in high yields. Single-crystal X-ray diffraction revealed the formation of trigonally rare-earth metal tetramethylmethylene complexes [NSiMe₃(Ar)]Ln₃[µ₃-CH₂][µ₃-Me][µ₂-Me]₃(thf)₃ (7-Ln, Ln = Y,³¹ Nd, Ho) as the product of sequential donor-induced cleavage of Ln[µ₂-Me]₂[AlMe₄] moieties.⁴⁹ C–H bond activation, and agglomeration (Schemes 2 and 3). Note that, treatment of 5-La with excess thf led to intractable, alkylated species.²⁴ Comparative studies on half-sandwich dialkyl complexes revealed that the capability of alkyl complexes to engage in C–H bond activation reactions strongly depends on the size of the rare-earth metal centre, the amount of Lewis base as well as the steric demand of the ancillary ligand. For example, Hou and coworkers showed that the reaction of Cp₃Ln(CH₅SiMe₃)₂(thf) [Cp = C₅Me₅SiMe₃] with AlMe₃ in diethyl ether at ambient temperature yielded [Cp₃LnMe₂]₂ for lutetium and Cp₃Ln[µ₂-CH₃][µ₂-Me]₂Me₃ for thulium.³⁴ We found that the donor-induced cleavage of Cp*Ln(AlMe₄)₂ (Ln = Y, Lu) with two equivalents of tetrahydrofuran led to trimeric [Cp*LnMe₄]₃, whereas the reaction with one equivalent thf produced methylidyne complex [Cp*₂Y₂(µ₂-CH₃)₂{(CH₃)Al(µ₂-CH₃)₂}₃(Cp*₂Y₂)₂].⁴⁷,⁵₀

Organoauminum moieties are well-known to promote C–H bond activation reactions at transition metals.¹⁹,⁵⁰–⁵² As such, we were interested to elucidate the influence of any co-ordinated alkylaluminate moieties on the formation of 7-Ln along pathway B. According to Pearson’s HSAB concept the methyl groups in GaMe₂ moieties should behave less basic than in AlMe₄. This is also in accord with the tendency of the tetramethylaluminate ligand to separate off GaMe₃. Hence we tackled the synthesis of [NSiMe₃(Ar)]Y(GaMe₄)₂ (6-Y) from homoleptic Y(GaMe₄)₃ (2-Y)⁵³,⁵⁴ which was obtained aluminium-free from [YNMe₃]₂[LiCl]₃ and GaMe₃. Reaction of 2-Y with one equivalent of potassium amide K[NSiMe₃(Ar)]⁴⁴,⁴⁵ in n-hexane at ambient temperature gave exclusively compound 6-Y in high yields (Scheme 2, route C). Comparable to aluminate complexes 5-Ln, 6-Y features a highly fluxional Ga[µ-Me]₂Me₂ coordination as evidenced by one narrow signal for the methyl groups at δ = 0.03 ppm. The ²⁹⁳Y NMR resonance of 6-Y (δ 477.2 ppm) is in the same range as for 7-Y (δ 498.0 ppm).³¹ The molecular structure of complex 6-Y is isomorphous to those of 5-Ln and similar to Cp⁺Y(GaMe₄)₂ (Cp* = C₅Me₅) regarding the coordination of the GaMe₃ ligands (Fig. 3).⁵⁵

The metal parameters of 6-Y are comparable to Cp⁺Y(GaMe₄)₂ with average Y–C[µ-CH₃] bond lengths of 2.616 Å and 2.520 Å for the bent and planar Ga[µ-Me]₂Me₂ moieties, respectively, being slightly shorter than in the respective half-

![Fig. 2](image-url) Molecular structure of [NSiMe₃(Ar)]Nd(AlMe₄)₂ (5-Nd), representative of the isostructural complexes 5-La, 5-Nd and 5-Ho. Atomic displacement parameters are set at the 30% level, hydrogen atoms have been omitted for clarity. The asymmetric unit contains two independent molecules with similar structural data.

| Table 1 | Selected structural parameters [Å, º] of complexes 5-La, 5-Nd, 5-Ho and 6-Ya |
|---------|-----------------|
| Ln-N1   | 2.295(4)        |
| Ln-C1   | 2.712(5)        |
| Ln-C2   | 2.716(5)        |
| Ln-C5   | 2.837(5)        |
| Ln-C6   | 2.717(5)        |
| Ln-M1   | 3.278(2)        |
| Ln-M2   | 3.013(1)        |
| Ln-C9   | 2.779(4)        |
| Ln-N1-C9| 93.8(2)         |
| Ln-C1-M1-C2| -0.4(2)     |
| Ln-C5-M2-C6| 45.2(5)     |

a Metric parameters of molecule 2 of 5-Nd and 5-Ho are listed in the ESL.
sandwich complex (average 2.679 and 2.555 Å). The Ln–C bond lengths of the related yttrium neosilyl complexes \([\text{NSiMe}_3(\text{Ar})\text{Y(Me}_2\text{SiMe}_3)_2\text{Li}(\text{thf})]\) (Ar = C\(_6\)H\(_5\)Pr\(_2\)-2,6; Y–C avg. 2.367 Å)\(^{31}\) and \([\text{NSiPr}_2(\text{Ar})\text{Y(TH}_2\text{SiMe}_3)_2\text{Li}(\text{thf})]\) (Ar = C\(_6\)H\(_5\)Pr\(_2\)-2,6; Y–C 2.373(3)–2.490(4) Å)\(^{36}\) are as expected shorter than in 6-Y, but the Ln–N(amido) bond lengths compare well (2.190(2) Å\(^{41}\), 2.259(3) Å\(^{56}\)) 6-Y, 2.172(4) Å.

If the organoaluminum moieties in \([\text{NSiMe}_3(\text{Ar})]\text{Ln(AlMe}_3)_2\) (5-Ln) would be crucial for the formation of methylidene species, the reaction of the respective methylgallate \([\text{NSiMe}_3(\text{Ar})\text{Y(GaMe}_4)_2\) with a Lewis base might yield a species like \([\text{NSiMe}_3(\text{Ar})\text{YMe}_2\) with \(\text{CH}_2\text{SiMe}_3\) Li(\text{thf})]. However, upon treatment of 6-Y with thf we could isolate \([\text{NSiMe}_3(\text{Ar})\text{Y}(\text{CH}_2\text{SiMe}_3)_2\text{Li}(\text{thf})]\) (7-Y) in almost quantitative yield.

The rare-earth metal tetramethyl methylidene complexes 7-Ln are sparingly soluble in \(n\)-hexane, but readily dissolve in aromatic solvents and thf, which allowed for elaborate NMR spectroscopic investigations of the diamagnetic representatives 7-Y and 7-Lu.\(^{31}\) The interpretation of the \(^1\)H NMR spectra of compounds 7-Ln (Ln = Nd, Ho) is affected by paramagnetic shifts and line broadening.

Representatively for the isostructural complexes 7-Ln, Fig. 4 and 5 illustrate the molecular and core structure of the neodymium derivative 7-Nd (7-Ho: Fig. S5†). Complexes 7-Nd and 7-Ho are isomorphous to the previously reported 7-Y and 7-Lu,\(^{31}\) crystallizing in the monoclinic space group \(P2_1/n\). In the solid state, each Ln is six-coordinate by one amido ligand, one thf, three bridging methyl groups, and one \(µ_2\)-bridging methyldiene group. The core atoms of the complex (Fig. 5, left) adopt a distorted hexagonal bipyramid with alternating Ln and \(µ_2\)-bridging methyl groups in the equatorial, and the \(µ_1\)-methyl and the methyldiene groups in the apical positions. Together with the methyldiene group all three amido ligands are residing on one side of the plane spanned by the Ln metal centres. It seems that the amido substituents provide a protective enclosure for the methyldiene moiety reminiscent of a picket fence, thus impeding intermolecular deactivation.\(^{57}\) The Ln\(_3\)(µ\(_3\)-CH\(_2\)) unit in 7-Ln resembles those previously found in complexes L\(_2\)Ln\(_3\)(µ\(_3\)-CH\(_2\))\(_2\)(µ\(_3\)-Me)\(_2\)(µ\(_2\)-Me)\(_2\)(thf)\(_x\)

\(\text{Ln = Sc, Y, Ho, Tm, Lu; } x = 0, 1\).\(^{31,32,34}\) The Ln–C(CH\(_2\)) bond lengths of 2.356(10)–2.428(10) Å in 7-Ho (7-Nd: 2.425(7)–2.505(8) Å) are in accord with the distances reported for 7-Y (2.345(5)–2.424(4) Å),\(^{31}\) but are significantly shorter than the values for \(\text{Cp}^*_\text{Ln}^3(µ_2\text{C}_2)(µ_2\text{Cl})(µ_2\text{Cl})_3\) (Y: 2.424(2)–2.450(2) Å, La: 2.537(3)–2.635(3) Å)\(^{10}\) considering the differences of the ionic radii. As expected, the Ln–C bond lengths of the \(µ_3\)-CH\(_2\) moieties are between the values for \(\text{Ln}^3(µ_2\text{C}_2)(µ_2\text{Cl})_2\) and \(\text{Ln}^3(µ_3\text{C}_2\text{H}_4)\) (Table 2).

**Reaction of 7-Ln with ketones**

In the presence of carbonylic substrates, methylidene complexes 7-Ln act as Schrock-type nucleophilic carbenes. Moni-

**Table 2.** Selected average bond lengths (Å) and angles (°) for 7-Nd, 7-Ho and 8-Nd

|          | 7-Nd | 7-Ho | 8-Nd |
|----------|------|------|------|
| Ln–C(µ\(_2\)C\(_2\)) | 2.475 | 2.391 |
| Ln–C(µ\(_2\)C\(_2\)) | 2.817 | 2.737 |
| Ln–C(µ\(_2\)C\(_2\)) | 2.635 | 2.547 | 2.676 |
| Ln–O(xox) | 2.239 |
| Ln–N | 2.369 |
| Ln–O(thf) | 2.568 | 2.466 | 2.543 |
| Ln–C\(_{ipso}(\text{Ar})\) | 3.021 | 3.086 | 3.076 |
torating the reactions of 7-Ln with 1 equivalent of 9-fluorenone, benzophenone, and cyclohexanone, respectively, by $^1$H NMR spectroscopy, clearly revealed the formation of the expected methylenated products (see Scheme 4) and concomitantly led to methylation products.\(^{31}\) If compared to the original Tebbe reagent, which allows a variety of functional substrates (esters, lactones) suppressing the formation of undesired side-products,\(^{30}\) complexes of type 7-Ln are certainly less efficient and selective.\(^{30}\) Theoretical studies on [PhC(NC\(_6\)H\(_3\)idene-fluorene and [NSiMe\(_3\)(Ar)]\(_3\)Nd\(_3\)(µ\(_3\)-O)(µ\(_2\)-Me)\(_4\)(thf)\(_3\) (1 : 1 ratio) in

$^2$La–Ln, however, indicated that methylenide transfer rather than methyl transfer occurs.\(^{33}\)

Upscaling of the reaction between 7-Nd and 9-fluorenone (1 : 1 ratio) in \(n\)-hexane/thf led to the formation of 9-methylidene-fluorene and [NSiMe\(_3\)(Ar)]\(_2\)Nd\(_3\)(µ\(_3\)-O)(µ\(_2\)-Me)\(_4\)(thf)\(_3\) (8-Nd) as indicated by an immediate colour change from blue to green (Fig. S21). NMR-scale reactions using 1–5 equivalents of the carbonylic reagent in benzene-$d_6$ revealed that after addition of the third equivalent of substrate the mixture kept a brown colour. Additional signals assignable to a paramagnetically shifted 9-methyl-9-H-fluoren-9-yl oxy moiety were observed as well, however, due to the existing paramagnetism, a quantification of methylation versus methylation was infeasible. Single-crystal X-ray diffraction of complex 8-Nd revealed that the core structure of 7-Nd (Fig. 5, left) was replaced by Nd\(_3\)(µ\(_3\)-O)(µ\(_2\)-Me)\(_4\) with the Nd\(^{III}\) metal centres being bridged by one \(\mu_3\)-oxo moiety and four \(\mu_2\)-Me groups (Fig. 5, right). In contrast to 7-Nd, two of the amido ligands and the oxo are now located on the same side of the plane spanned by the Ln\(_3\) metal centres. The coordination of the thf donor molecules is opposite to the amido ligands (Fig. 6). The Nd–O bond lengths (avg. 2.239 Å) are slightly longer than in [Cp*Nd(NC\(_3\)H\(_4\)NC\(_3\)H\(_3\)])\(_2\)(µ-O) (2.157(2) Å).\(^{39}\) Similarly, the benzamidinato-supported complexes [PhC(NC\(_6\)H\(_3\)idene-fluorene and [NSiMe\(_3\)(Ar)]\(_3\)Nd\(_3\)(µ\(_3\)-O)(µ\(_2\)-Me)\(_4\)(thf)\(_3\) (8-Nd) could be obtained in moderate yields via salt metathesis of Ln(AlMe\(_4\))\(_3\) (2-Ln) with two equivalents of K[NSiMe\(_3\)(Ar)] in \(n\)-hexane at ambient temperature (Scheme 5).

The $^1$H and $^{13}$C($^1$H) NMR spectra of complex 9-La revealed one set of signals for the amidog ligands and the AlMe\(_4\) moiety, except for the diastereotopic aryl isopropyl groups. While the $^1$H NMR resonances for the NSiMe\(_3\)(Ar) ligand are shifted to lower fields compared to 5-La, a high-field shift was observed for the signal of the AlMe\(_4\) ligand (δ = 0.47 ppm, 12H; 5-La: δ = 0.19 ppm). The resonance of the AlMe\(_4\) ligand in paramagnetic 9-Nd appeared at 10.73 ppm. Blue (9-Nd) and colourless (9-La) single crystals were obtained from saturated \(n\)-hexane solutions. Previously reported Nd[NSiMe\(_3\)(Ar)]\(_2\)Cl(thf)\(_6\) is somewhat comparable to isomorphous 9-La featuring also a four-coordinate Ln metal centre (Fig. 7). Such simple complexes (NRR')\(_2\)Ln(alkyl) and (NRR')\(_2\)Ln(alkyl)\(_2\) coordinated by non-chelating alkyl and amido ligands, however, seem to be rather scarce.\(^{40,41,56}\) Complexes 9-Ln display distorted tetrahedral coordination geometries as evidenced by large N1–Ln–C(µ\(_2\)-CH\(_3\)) angles e.g., 9-La, 122.5(2)°; 9-Nd, 123.33(3)° (Table 3). Pronounced interactions of the Ln\(^{III}\) metal centre with the amido ligand is also evidenced by close contacts to

**Scheme 4** Synthesis of [NSiMe\(_3\)(Ar)]\(_3\)Nd\(_3\)(µ\(_3\)-O)(µ\(_2\)-Me)\(_4\)(thf)\(_3\) (8-Nd).

**Scheme 5** Synthesis of [NSiMe\(_3\)(Ar)]\(_2\)Ln(AlMe\(_4\))\(_3\) (9-Ln, Ln = La, Nd).

**Fig. 6** Molecular structure of 8-Nd (atomic displacement parameters are set at the 30% level). Isopropyl groups and hydrogen atoms, except for Nd–CH\(_3\) moieties, have been omitted for clarity.
Fig. 7 Molecular structure of [NSiMe3(Ar)]2Nd(AlMe4) (9-Nd), representative of the isomorphous complexes 9-La and 9-Nd. Atomic displacement parameters are set at the 30% level, hydrogen atoms have been omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for 9-La and 9-Nd

|                | 9-La              | 9-Nd              |
|----------------|-------------------|-------------------|
| Ln1–N1         | 2.356(3)          | 2.2968(8)         |
| Ln1–C16        | 2.719(4)          | 2.650(1)          |
| Al1–C16        | 2.072(4)          | 2.073(1)          |
| Al1–C17        | 1.979(4)          | 1.980(1)          |
| Ln1···Al1      | 3.296(2)          | 3.2302(4)         |
| Ln1···C1       | 2.791(3)          | 2.7502(9)         |
| N1–Ln1–C16     | 103.73(11)        | 103.10(3)         |
| N1–Ln1–C1      | 91.95(18)         | 92.29(5)          |

Conclusions

The unique [Ln3(µ2-CH3)(µ2-CH3)(µ2-CH3)]3 core structure has been achieved via three synthesis pathways. Such rare-earth metal methylidene complexes do form in the absence of any organoaluminium components as proven by applying alkylaluminium-free synthesis protocols. The generation of [NSiMe3(Ar)]nLn3(µ2-CH3)(µ2-CH3)(µ2-CH3)(thf)3 seems to be rather driven by steric constraints. A possible mechanism involves the formation of intermediate [NSiMe3(Ar)]LnMe2(thf)2 species, which upon C–H bond activation agglomerate to the target compound. The dianionic CH22− moiety seems to be preferentially stabilized by Ln3 “cluster-like” entities being protected from intermolecular deactivation by a picket-fence arrangement of the amido ligands. Nevertheless the methylidene ligand retains its nucleophilic character as revealed by Tebbe-like methylenation reactions with carboxylic substrates, which concomitantly form isolable rare-earth metal oxo clusters.

Experimental section

General procedures

All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun MBLab; <1 ppm O2, <1 ppm H2O). Toluene, n-hexane, and tetrahydrofuran were purified by using Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. Benzenes-d6 and toluene-d8 were obtained from Aldrich, degassed, dried over Na for 24 h, and filtered. Tetrahydrofuran-d8 was obtained from Aldrich, degassed, dried over CaH2 for four days and vacuum transferred. 9-Fluorenone was obtained from Fluka and sublimed prior to use. [LuMe3]n (1-Lu),18 homoleptic Ln(AlMe4)2 (2-Ln) (Ln = Y, Nd, Ho, Lu)42,43 and Y(GaMe4)353 were prepared according to literature methods. H[NSiMe3(Ar)] and K[NSiMe3(Ar)] were synthesized by a modification of the published procedure.44,45 The NMR spectra of air and moisture sensitive compounds were recorded by using J. Young valve NMR tubes at 26 °C on a Bruker-Avance II 400 (1H: 400.13 MHz, 13C: 100.61 MHz) and a Bruker-Avance II 500 (1H: 500.13 MHz; 13C: 125.76 MHz). 1H and 13C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. Coupling constants are given in Hertz. IR and DRIFT spectra were recorded on a NICOLET 6700 FTIR spectrometer using dried KBr and KBr windows or as Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an Elementar Vario EL III and an Elementar Vario Micro Cube.

General procedure for the synthesis of [NSiMe3(Ar)]-Ln(AlMe4)2 (5-Ln).

In a glovebox, a solution of Ln(AlMe4)Cl2 (2-Ln) in n-hexane (3 ml) was added to a vigorously stirred
suspension of $\text{K}_2\text{[NSiMe}_3\text{(Ar)}\text{]}$ in $n$-hexane (2 ml) at ambient temperature. The reaction mixture was stirred for 2 h and the $n$-hexane solution then separated by centrifugation, decantation, and filtration. Compounds 6–Ln were obtained by crystallization from a saturated $n$-hexane solution at $-35^\circ\text{C}$.

**[NSiMe₃(Ar)]₂La(AlMe₄)₂ (5-La).** Following the procedure described above, La(AlMe₄)₃ (160 mg, 0.40 mmol) and K[NSiMe₃(Ar)] (115 mg, 0.40 mmol) yielded 5-La as colourless crystals. Compound 5-La was purified and separated from co-product [NSiMe₃(Ar)]₃La(AlMe₄) (9-La) by fractional crystallization (136 mg, 0.24 mmol, 60%).

1H NMR (400 MHz, C₆D₆, 26 °C): $\delta = 7.09-6.98$ (m, 3H, $H_{meta}$, $H_{para}$ Ar), 3.12 (sept, 2H, $J_{HH} = 6.7$ Hz, $CH(CH_3)_2$), 1.15 (d, 6H, $J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 0.96 (d, 6H, $J_{HH} = 6.6$ Hz, $CH(CH_3)_2$), 0.24 (s, 9H, Si(CH₃)₃), $\sim$0.19 (s, 24H, Al–CH₃) ppm. 13C{¹H} NMR (101 MHz, C₆D₆, 26 °C): $\delta = 149.2$ (C$_{gas}$, Ar), 139.0 (C$_{orth}$ Ar), 127.6 (C$_{meta}$ Ar), 127.1 (C$_{para}$ Ar), 28.8 (CH(CH₃)₂), 26.7 (CH₃), 23.9 (CH₃), 4.6 (Al–CH₃), 4.1 (Si–CH₃) ppm. IR (nujol) (ν(nujol)) = 1362, 1286, 1192, 1109, 1024, 960, 833, 775, 580 cm⁻¹. Anal. Calcd (%) for C$_{23}$H$_{50}$Al$_2$LaNSi: C 49.19, H 8.97, N 2.47. Found: C, 50.71; H, 7.96; N, 2.86. IR (KBr): 3041s, 2957s, 2868m, 1583w, 1459m, 1418s, 1379w, 1313m, 1240s, 1193m, 1193s, 1142s, 1019s, 1022s, 915s, 877m, 835s, 774s, 743s, 658s, 588s, 487m, 434m cm⁻¹. 1H NMR (400 MHz, C₆D₆, 26 °C): $\delta = 13.05, 12.35, 7.98, 6.28, 3.19, 2.34, 2.10, 1.23, 0.88, -1.25$ ppm. Anal. Calcd (%) for C$_{23}$H$_{50}$Al$_2$LaNSi: C, 50.71; H, 7.96; N, 2.86. Found: C, 51.28; H, 8.29; N, 2.73.

**[NSiMe₃(Ar)]₃Ln₃(µ₃-CH₂)(µ₂-Me)(µ₃-Me)(thf)₃ (7-Ln).** To a solution of [NSiMe₃(Ar)]₃Ln(AlMe₄)₂ (5-Ln) (60.7 mg, 0.1 mmol) in $n$-hexane (2 ml) ten drops of thf were added. The reaction mixture was shaken and left standing for 10 min at ambient temperature. The product could be crystallized from a thf/$n$-hexane mixture at $-35^\circ\text{C}$ to yield blue crystals (45.5 mg, 0.03 mmol, 90% cryst. yield). IR (KBr): 3041s, 2957s, 2868m, 1583s, 1458m, 1416s, 1380s, 1359s, 1313m, 1293s, 1193m, 1193s, 1142s, 1017s, 1041s, 1022s, 915s, 877m, 835s, 774s, 743s, 658s, 588s, 487m, 434m cm⁻¹. 1H NMR (400 MHz, C₆D₆, 26 °C): $\delta = 13.05, 12.35, 7.98, 6.28, 3.19, 2.34, 2.10, 1.23, 0.88, -1.25$ ppm. Anal. Calcd (%) for C$_{23}$H$_{50}$Al$_2$LaNSi: C, 50.71; H, 7.96; N, 2.86. Found: C, 51.28; H, 8.29; N, 2.73.
(400 MHz, C₆D₆): δ = 12.17, 10.28, 8.66, 8.57, 0.50, 0.27, 0.14, −0.19, −0.41, −0.54, −3.76, −4.26 ppm. IR (KBr): 2957s, 2868m, 1457s, 1374s, 1359w, 1311m, 1251m, 1237vs, 1192m, 1107w, 1025w, 921s, 913m, 871s, 853vs, 774m, 746w, 660w cm⁻¹. Anal. Calcd (%) for C₃₄H₆₄AlN₂LaSi₂: C 56.35, H 9.94, N 3.88.

[NiSe₂[(Ar),₂La(AlMe₄)] (9-La). Following the procedure described for 5-ln, La(AlMe₄)₃ (80 mg, 0.20 mmol) and K[NiSe₂(aryl)] (115 mg, 0.40 mmol) yielded 9-La as colourless crystals (64 mg, 0.09 mmol, 44%). ¹H NMR (400 MHz, C₆D₆, 26 °C): δ = 7.12 (d, J̈HH = 7.7 Hz, 4H, H-meta, Ar), 7.02 (t, J̈HH = 7.9 Hz, 2H, H-para, Ar), 3.35 (sept, 4H, J₃H = 6.8 Hz, CH(CH₃)₂), 1.31 (d, 12H, J̈HH = 6.5 Hz, CH(CH₃)₂), 0.24 (s, 18H, Si(CH₃)₃), −0.47 (s, 12H, Al-CH₃) ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆, 26 °C): δ = 146.4 (Cipso, Ar), 143.3 (C-ortho, Ar), 127.7 (C-metax, Ar), 125.8 (Cpara Ar), 28.5 (CH(CH₃)₂), 26.8 (CH₃), 24.8 (CH₃), 4.6 (Si(CH₃)₃), 4.2 (Al-CH₃), 1.09 (d, 12H, J̈HH = 6.5 Hz, CH(CH₃)₂), 7.9 Hz, 2H, H-para, Ar), 6.43, 6.26, 6.10, 5.79 (s, 2H, CH₂), 4.86, 3.72, 0.12, −0.56, −2.46, −3.99 ppm.

X-ray crystallography and crystal structure determination of 4-Lu, 5-Ln, 6-Y, 7-Ln, 8-Nd, and 9-Ln

Crystals of 5-Ln, 6-Y and 9-Ln were grown by standard techniques from saturated solutions using n-hexane or n-hexane/thf (4-Lu, 7-Ln and 8-Nd) at −40 °C. Suitable single crystals for X-ray structure analyses were selected in a glovebox and coated with Parabar 10312 and fixed on a nylon loop/glass fiber. Data for 4-Lu, 5-Ln, 7-Ln, 7-Ho, 7-Nd, 7-Ho and 8-Nd were collected on a Stoe IPDS 2T instrument equipped with a fine focus sealed tube and graphite monochromator using MoKα radiation (λ = 0.71073 Å) performing ω scans. Raw data were collected and integrated using Stoe’s X-Area software package. A numerical absorption correction based on crystal shape optimization was applied using Stoe’s X-Red and X-Shape. X-ray data for 9-Ln were collected on a Bruker AXS, TXS rotating anode instrument using a Pt CCD detector, and graphite monochromator using MoKα radiation (λ = 0.71073 Å). The Data collection strategy was determined using COSMO employing ω- and φ scans. Raw data were processed using APEX and SAINT, corrections for absorption effects were applied using SADABS. The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F² using SHELXTL and ShelXle. All Graphics were produced employing ORTEP-3 and POVRay. Further details of the refinement and crystallographic data are listed in Table S1 and in the CIF files. CCDCs 1410385–1410394 data contain all the supplementary crystallographic data for this paper.

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