

Ln₄(CH₂)₄ Cubane-Type Rare-Earth Methylidene Complexes Consisting of “(C₅Me₄SiMe₃)LnCH₂” Units (Ln = Tm, Lu)

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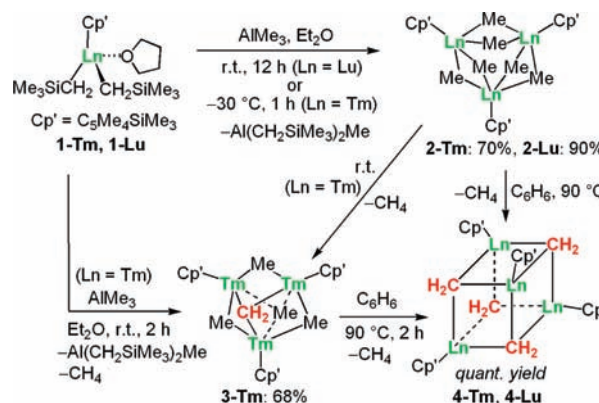
S Supporting Information

ABSTRACT: Tetranuclear cubane-type rare-earth methylidene complexes consisting of four “Cp’LnCH₂” units, [Cp’Ln(μ₃-CH₂)₄] (4-Ln; Ln = Tm, Lu; Cp’ = C₅Me₄SiMe₃), have been obtained for the first time through CH₄ elimination from the well-defined polymethyl complexes [Cp’Ln(μ₂-CH₃)₂]₃ (2-Ln) or mixed methyl/methylidene precursors such as [Cp’₃Ln₃(μ₂-Me)₃(μ₃-Me)(μ₃-CH₂)] (3-Ln). The reaction of the methylidene complex 4-Lu with benzophenone leads to C=O bond cleavage and C=C bond formation to give the cubane-type oxo complex [Cp’Lu(μ₃-O)]₄ and CH₂=CPh₂, while the methyl/methylidene complex 3-Tm undergoes sequential methylidene addition to the C=O group and ortho C–H activation of the two phenyl groups of benzophenone to afford the bis(benzo-1,2-diyl)ethoxy-chelated trinuclear complex [Cp’₃Tm₃(μ₂-Me)₃{(C₆H₄)₂C(O)Me}] (6-Tm).

Transition-metal carbene and alkylidene complexes have been extensively studied in the past four decades because of their importance in synthetic applications.¹ In contrast, studies on rare-earth-metal carbene and alkylidene complexes have been very limited, despite recent significant advances.^{2–9} This is mainly due to the extremely high reactivity (or instability) of the highly polar rare-earth–carbon double bonds, which renders them difficult to isolate and characterize. The formation of a rare-earth alkylidene species was first postulated in 1979,³ but the first structurally characterized “carbene”-type rare-earth complex bearing a pincerlike bis(imino-phosphorano)methylidene ligand was reported only recently in 2000.⁴ More recently, rare-earth methylidene complexes stabilized by chloride bridges⁶ or a Lewis acid such as AlMe₃^{7,8} as well as mixed methyl/methylidene complexes⁹ have been reported.

We report here a new class of rare-earth methylidene complexes, [Cp’Ln(μ₃-CH₂)₄] (4-Ln; Ln = Tm, Lu; Cp’ = C₅Me₄SiMe₃), which consist of only simple “Cp’LnCH₂” units and adopt a novel cubane-like Ln₄(CH₂)₄ core structure. The isolation and structure determination of the trinuclear polymethyl complexes [Cp’Ln(μ₂-CH₃)₂]₃ (2-Ln) and the mixed methyl/methylidene complex [Cp’₃Tm₃(μ₂-Me)₃(μ₃-Me)(μ₃-CH₂)] (3-Tm), which are precursors to the cubane-type methylidene complexes 4-Ln, has also been achieved. The reactions of the methylidene complexes with ketones were carried out to probe the competence of the complexes as methylidene transfer agents.

Scheme 1. Synthesis of Polymethyl and Methylidene Complexes



The reaction of [Cp’Lu(CH₂SiMe₃)₂(THF)] (1-Lu)¹⁰ with 1 equiv of AlMe₃ in ether at room temperature for 12 h gave the corresponding trinuclear hexamethyl complex [Cp’Lu(μ₂-CH₃)₂]₃ (2-Lu) in 90% isolated yield through the CH₂SiMe₃/Me exchange reaction between the “Lu(CH₂SiMe₃)₂” unit in 1-Lu and the “AlMe₃” part in AlMe₃ followed by trimerization (intermolecular Lu–Me interactions) of the resulting “Cp’LuMe₂” species (Scheme 1). In contrast, the similar reaction of [Cp’Tm(CH₂-SiMe₃)₂(THF)] (1-Tm)^{10b} with AlMe₃ at room temperature gave the tetramethyl/methylidene complex [Cp’₃Tm₃(μ₂-Me)₃(μ₃-Me)(μ₃-CH₂)] (3-Tm) in 68% isolated yield, while a hexamethyl complex analogous to 2-Lu was not observed. However, when the reaction of 1-Tm with 1 equiv of AlMe₃ was carried out at –30 °C, the analogous hexamethyl complex 2-Tm was obtained selectively. When it was warmed to room temperature, 2-Tm rapidly transformed into the tetramethyl/methylidene complex 3-Tm with release of CH₄ (Scheme 1).

Unlike 2-Tm, the Lu hexamethyl analogue 2-Lu is stable at room temperature. To see whether a mixed methyl/methylidene Lu complex analogous to 3-Tm could be formed at higher temperatures, 2-Lu was heated in C₆D₆ in a sealed NMR tube. Surprisingly to us, when 2-Lu was heated at 90 °C for 2 h, the tetranuclear tetramethylidene complex [Cp’Lu(μ₃-CH₂)₄] (4-Lu) was obtained quantitatively with release of CH₄ (Scheme 1). Similarly, heating the

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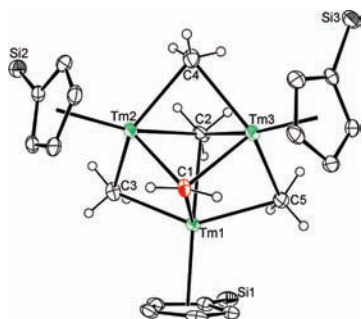


Figure 1. ORTEP drawing of **3-Tm** with 30% thermal ellipsoids. H atoms (except for those on Tm–CH₂ and Tm–Me units) and Me groups on Cp' rings and Si atoms have been omitted for clarity. Selected bond lengths (Å): Tm(1)–C(1), 2.364(5); Tm(2)–C(1), 2.330(5); Tm(3)–C(1), 2.365(5); Tm(1)–C(2), 2.636(5); Tm(2)–C(2), 2.682(5); Tm(3)–C(2), 2.652(6); Tm(1)–C(3), 2.492(6); Tm(2)–C(3), 2.493(5); Tm(2)–C(4), 2.504(6); Tm(3)–C(4), 2.524(5); Tm(1)–C(5), 2.495(6); Tm(3)–C(5), 2.467(5); Tm(1)–Cp(av), 2.63(2); Tm(2)–Cp(av), 2.63(2); Tm(3)–Cp(av), 2.64(1).

hexamethyl complex **2-Tm** or the methyl/methylidene complex **3-Tm** at 90 °C afforded the analogous methylidene complex [Cp'Tm(μ₃-CH₂)₄] (**4-Tm**) in quantitative yield.

Complexes **2-Lu** and **2-Tm** possess similar trinuclear structures, as shown by X-ray diffraction analyses (see the Supporting Information). The six CH₃ groups in each complex adopt a μ₂-bonding fashion, and each edge of the triangular metal framework is equally bridged by two CH₃ groups. The average bond lengths of the Ln–(μ₂-CH₃) bonds in **2-Tm** and **2-Lu** are 2.50(2) and 2.49(1) Å, respectively, which are much longer than those of the terminal Ln–CH₂SiMe₃ bonds in **1-Tm** [av 2.348(5) Å] and **1-Lu** [av 2.322(5) Å], respectively.^{10b} The overall structure of the trinuclear hexamethyl complexes **2-Tm** and **2-Lu** is similar to that of the C₅Me₅-ligated Y complex [(C₅Me₅)Y(μ-Me)₂]₃,^{6a} but it contrasts with those of the C₅Me₄SiMe₃-ligated Sc binuclear complex [(C₅Me₄SiMe₃)Sc(μ-Me)Me]₂^{11a} and the monomeric dimethyl complexes [(Tp^{tBu,Me})LnMe₂]₂^{11b} and [(nacnac)LnMe₂] (Ln = Sc, Y; nacnac = {(2,6-Pr₂C₆H₃N)C(^tBu)}₂CH).^{11c} These results demonstrate that the structure of the rare-earth dimethyl complexes is significantly dependent on the bulkiness of the ancillary ligands and the ionic radius of the central metal.

The trinuclear tetramethyl/methylidene complex **3-Tm** possesses three μ₂-Me groups, one μ₃-Me group, and one μ₃-CH₂ group, as shown by an X-ray diffraction study (Figure 1). The average bond length of the Tm–(μ₃-C2) (methyl) bonds [2.66(2) Å] is much longer than that [2.49(1) Å] of the Tm–(μ₂-C3) [av 2.493(6) Å], Tm–(μ₂-C4) [av 2.51(1) Å], and Tm–(μ₂-C5) [av 2.48(1) Å] (methyl) bonds. The latter is comparable with that of the Tm–(μ₂-CH₃) bonds in **2-Tm** [2.50(1) Å]. In contrast, the bond lengths of the Tm–(μ₃-C1) (methylidene) bonds in **3-Tm**, which range from 2.326(3) to 2.366(3) Å with an average value of 2.35(2) Å, are significantly shorter than those of the Tm–(μ₂-C3,4,5) (methyl) bonds [av 2.49(1) Å] and much shorter than those of the Tm–(μ₃-C2) (methyl) bonds [av 2.66(2) Å], suggesting that the C1 atom in **3-Tm** is distinctly different from the C2–C5 atoms and can be assigned as a methylidene carbon. In agreement with this assignment, only two hydrogen atoms were found on the C1 atom, while three hydrogen atoms are located on each of the atoms C2–C5 in the difference Fourier electron density map. The core structure of **3-Tm** is similar to those of mixed methyl/methylidene rare-earth complexes bearing non-Cp ligands, namely, [(2,6-PrC₆-

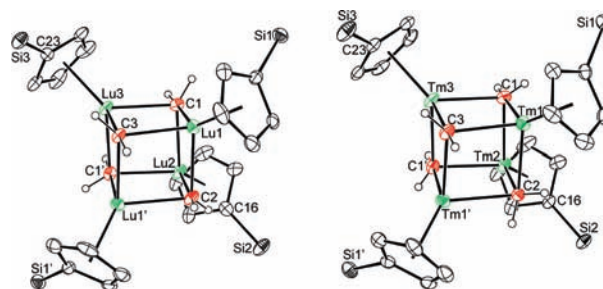


Figure 2. ORTEP drawings of (left) **4-Lu** and (right) **4-Tm** with 30% thermal ellipsoids. H atoms (except those on Ln–CH₂ units) and Me groups on Cp' rings and Si atoms have been omitted for clarity. Selected bond lengths (Å) in **4-Lu**: Lu(1)–C(1), 2.318(11); Lu(1)–C(2), 2.393(11); Lu(1)–C(3), 2.408(11); Lu(2)–C(1), 2.391(12); Lu(2)–C(2), 2.325(16); Lu(3)–C(1), 2.411(12); Lu(3)–C(3), 2.334(15); Lu(1)–Cp(av), 2.60(2); Lu(2)–Cp(av), 2.61(2); Lu(3)–Cp(av), 2.62(3). In **4-Tm**: Tm(1)–C(1), 2.319(5); Tm(2)–C(1), 2.410(5); Tm(3)–C(1), 2.424(5); Tm(1)–C(2), 2.409(4); Tm(2)–C(2), 2.324(6); Tm(1)–C(3), 2.405(4); Tm(3)–C(3), 2.337(7); Tm(1)–Cp(av), 2.60(2); Tm(2)–Cp(av), 2.60(2); Tm(3)–Cp(av), 2.60(1).

H₃)(Me₃Si)N]₃Ln₃(μ₂-Me)₃(μ₃-Me)(μ₃-CH₂)(THF)₃] (Ln = Y, Ho, Lu)^{9a} and [(NCN)₃Ln₃(μ₂-Me)₃(μ₃-Me)(μ₃-CH₂)] [Ln = Sc, Lu; NCN = PhC(NC₆H₄^tPr₂,2,6)₂].^{9b}

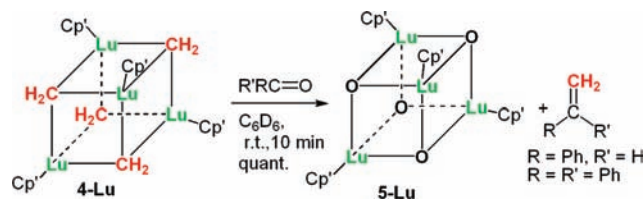
X-ray diffraction studies of the methylidene complexes **4-Tm** and **4-Lu** revealed that these complexes adopt a tetranuclear cubane-like Ln₄(CH₂)₄ core structure formed by four “Cp'Ln–(μ₃-CH₂)” units (Figure 2). These two complexes are isomorphous. There is a crystallographic mirror plane in which two metal atoms (Ln1 and Ln3), two methylidene carbon atoms (C2 and C3), two Si atoms (Si2 and Si3), and two Cp-ring carbon atoms (C16 and C23) are located. The C₅Me₄SiMe₃ ligands on the Ln2 and Ln3 metal atoms are bisected by the mirror plane. The methyl groups of SiMe₃ in a C₅Me₄SiMe₃ ligand in **4-Tm** and **4-Lu** are disordered because of the crystallographic mirror symmetry. The Tm–(μ₃-C) methylidene bond lengths in **4-Tm**, ranging from 2.319(5) to 2.424(5) Å with an average value of 2.38(4) Å, are comparable to the Lu–(μ₃-C) bond lengths in **4-Lu** [av 2.37(3) Å] and the Tm–(μ₃-C1) (methylidene) bond distances found in **3-Tm** [av 2.35(2) Å]. The hydrogen atoms in the methylidene units were also easily located. As far as we are aware, **4-Tm** and **4-Lu** represent the first examples of structurally characterized rare-earth polymethylidene complexes consisting solely of simple “LLnCH₂” units and also the first examples of M₄(CH₂)₄ cubane-type methylidene complexes of any metal.

It is also noteworthy that the selective formation of the Al-free multimethyl or methylidene complexes such as **2-Ln**, **3-Tm**, and **4-Ln** in the present reactions of **1-Ln** with AlMe₃ (Scheme 1) is in sharp contrast with the previously reported reactions of lanthanide dialkyl or diamido complexes with AlMe₃, which often yield Al-containing heterometallic complexes.^{8,12}

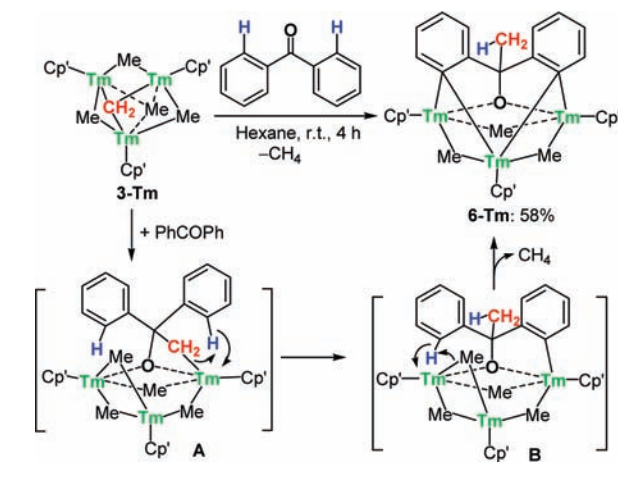
The diamagnetic Lu complexes **2-Lu** and **4-Lu** showed well-resolved ¹H and ¹³C NMR spectra in C₆D₆. The “Lu–Me” groups in **2-Lu** gave a singlet at 0.19 ppm in the ¹H NMR spectrum and a singlet at 37.2 ppm in the ¹³C NMR spectrum. The ¹H and ¹³C NMR spectra of **4-Lu** showed a singlets at 1.72 and 115.89 ppm, respectively, which can be unambiguously assigned to the “Lu–CH₂” methylidene units. A DEPT experiment also confirmed the presence of CH₂ units in **4-Lu**.

The reactions of the methylidene complexes **4-Tm** and **4-Lu** with benzaldehyde or benzophenone took place rapidly at room

Scheme 2. Reactions of Methylidene Complex 4-Lu with Benzophenone and Benzaldehyde



Scheme 3. Reaction of Methyl/Methylidene Complex 3-Tm with Benzophenone



temperature in benzene. ^1H NMR monitoring of the reaction of 4-Lu with benzaldehyde or benzophenone in C_6D_6 showed quantitative formation of the tetraoxo complex $\text{Cp}'_4\text{Lu}_4\text{O}_4$ (5-Lu)¹³ and the alkene $\text{CH}_2=\text{CRR}'$ ($\text{R}, \text{R}' = \text{Ph}, \text{H}$ or Ph, Ph) (Scheme 2). In contrast, the polymethyl complex 2-Lu did not react with benzophenone at room temperature over several hours. These results clearly demonstrate that a methylidene species is much more reactive than a methyl group.

The reaction of the tetramethyl/methylidene complex 3-Tm with 1 equiv of benzophenone at room temperature gave the trinuclear complex $[\text{Cp}'_3\text{Tm}_3(\mu_2\text{-Me})_3\{(\text{C}_6\text{H}_4)_2\text{C}(\text{O})\text{Me}\}]$ (6-Tm), which contains three Me groups and one unprecedented pincerlike bis(benzo-1,2-diyl)ethoxy trianion unit (Scheme 3 and Figure 3).¹⁴ Because a methylidene unit is obviously more reactive than a methyl group, complex 6-Tm could be formed by nucleophilic addition of the methylidene unit of 3-Tm to the carbonyl group of benzophenone (to give A) and subsequent activation of an ortho C–H bond of a phenyl group (to give B), followed by ortho C–H activation of the other phenyl group by a Me group and release of CH_4 .¹⁵ The C–H activation of benzophenone by an yttrium carbene complex was reported recently.^{5a}

In summary, we have demonstrated that the reaction of half-sandwich rare-earth dialkyl complexes such as 1-Ln with 1 equiv of AlMe_3 can serve as an excellent route to rare-earth methylidene complexes that has afforded for the first time well-defined $\text{Ln}_4(\text{CH}_2)_4$ cubane-type methylidene complexes such as 4-Ln. The isolation and structural characterization of the polymethyl precursors 2-Ln and a methyl/methylidene complex 3-Tm have also been achieved, thus providing clear evidence for understanding the methylidene formation process. The reaction of the

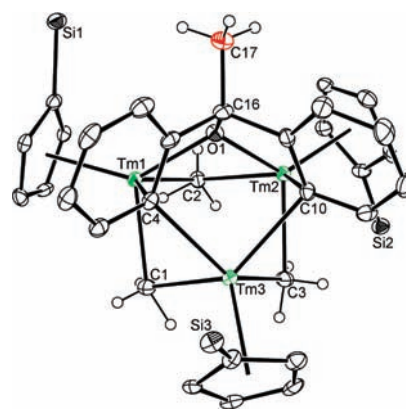


Figure 3. ORTEP drawing of 6-Tm with 30% thermal ellipsoids. H atoms (except those on Tm–Me units) and Me groups on Cp' rings and Si atoms have been omitted for clarity. Selected bond lengths (Å): C(16)–O(1), 1.464(6); C(16)–C(17), 1.536(7); Tm(1)–C(1), 2.482(5); Tm(3)–C(1), 2.513(6); Tm(1)–C(2), 2.516(6); Tm(2)–C(2), 2.502(6); Tm(2)–C(3), 2.451(6); Tm(3)–C(3), 2.522(6); Tm(1)–C(4), 2.536(5); Tm(3)–C(4), 2.570(5); Tm(2)–C(10), 2.521(5); Tm(3)–C(10), 2.549(6); Tm(1)–O(1), 2.197(4); Tm(2)–O(1), 2.211(4); Tm(1)–Cp(av), 2.66(2); Tm(2)–Cp(av), 2.65(2); Tm(3)–Cp(av), 2.69(4).

cubane-type methylidene complex 4-Lu with a carbonyl compound such as benzophenone leads to deoxygenation and C=C bond formation, giving the tetraoxo complex 5-Lu and an alkene (1,1-diphenylethylene), while the methyl/methylidene complex 3-Tm undergoes methylidene addition and C–H activation reactions with benzophenone to yield the bis(benzo-1,2-diyl)ethoxy-chelated complex 6-Tm. The results presented in this work suggest that the reactivity (or stability) of rare-earth methylidene species could be fine-tuned by changing the metal size in the rare-earth series. Further studies of the synthesis and reactivity of the analogous methylidene complexes with other rare-earth metals and related ancillary ligands are in progress.¹⁶

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details and X-ray data (CIF) for 2-Tm, 2-Lu, 3-Tm, 4-Tm, 4-Lu, and 6-Tm. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Structural characterization of the same tetraoxo Lu complex has been reported previously. See: Shima, T.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 8124–8125.

(14) The reaction of **3-Tm** with PhCOMe or PhCHO gave a complicated product mixture from which a characterizable species could not be obtained.

(15) Attempts to detect possible deuterated methanes such as CH₃D from the reaction of **3-Tm** with benzophenone-*d*₁₀ by ¹H or ²H NMR spectroscopy were not successful, probably because of the low concentration of the gas in the solution and the influence of the paramagnetic Tm(III) species. Hydrolysis of the reaction mixture caused dehydration to give a product mixture containing 1,1-diphenylethylene, which made it difficult to obtain a decisive H/D ratio in the hydrolysis products.

(16) The cubane-type scandium methylidene complex [Cp[′]Sc(μ₃-CH₂)₄] was also obtained. Crystallographic data: monoclinic; *P*2₁/*m*; *a* = 12.0943(12) Å, *b* = 23.114(2) Å, *c* = 13.1802(13) Å, β = 115.690(2)°; *V* = 3320.3(6) Å³; *Z* = 2; *D*_{calcd} = 1.166 g cm⁻³; *R* (*R*_w) = 0.052 (0.138).