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Carbene Chemistry

Rare-Earth-Metal Methylidene Complexes

Jochen Kratsch and Peter W. Roesky*

carbene · lanthanides · methylidene · rare-earth metals

Transition-metal carbene complexes have been known for about 50 years and widely applied as reagents and catalysts in organic transformations. In contrast, the carbene chemistry of the rare-earth metals is much less developed, but has attracted the research interest in the recent years. In this field rare-earth-metal alkylidene, especially methylidene, compounds are an emerging class of compounds with a high synthetic potential for organometallic chemistry and maybe in the future also for organic chemistry.

1. Introduction

The rare-earth elements consist of seventeen elements, the fifteen lanthanides, from lanthanum ($Z = 57$) to lutetium ($Z = 71$), and the elements of Group 3, scandium ($Z = 21$) and yttrium ($Z = 39$). In recent years, they attracted public notice owing to the export policy of the Chinese government. Inorganic and organometallic compounds of the rare-earth metals have been applied in magnetic[1] and luminescent[2] materials as well as catalysts. The catalytic applications comprise both heterogeneous, for example, CeO_2 in catalytic converters,[3] and homogeneous catalysis, for example, polymerization reactions,[4] and σ-bond metathesis.[5] Also Lewis acid catalysts which are mostly homogenous systems, for example, for aldol reactions, allylations, Diels–Alder reactions, and Friedel–Crafts acylations, have been reported.[6]

In comparison to the well-studied transition-metal carbene complexes,[7] the carbene chemistry of the rare-earth metals has been investigated far less. N-heterocyclic (NHC) carbene ligands were widely used in rare-earth metal chemistry and their complexes were applied in the activation of small, inert molecules and as homogeneous catalysts,[8] but rare-earth alkylidene species remain scarce. They were first described in 1979 by Schumann and Müller, who reported the formation of an anionic lutetium complex, $[Li(tmeda)_2]^+[Lu(CH_2SiMe_3)_2(CHSiMe_3)]^-$, and a neutral erbium complex, $[Er(CH_2SiMe_3)(CHSiMe_3)]_n$. The alkylidene species were obtained by slow decomposition of the homoleptic alkyl complexes $[Li(Et_2O)_4][Lu(CH_2SiMe_3)_4]$ and $[Er(CH_2SiMe_3)_3]$ in diethyl ether.[9] The first structurally characterized carbene-type rare-earth metal complex bearing a pincer-like bis(iminophosphorano) methandiide ligand, $[Sm\{C(Ph_2P{=}NSiMe_3)_2\}(NCy_2)(thf)]$, was reported in 2000.[10] The coordination chemistry of the bis(iminophosphorano) methandiide and related compounds was reviewed recently by Liddle et al. and is not addressed herein.[11]

Rare-earth-metal methylidene (CH_2^{2-}) complexes are an emerging class of compounds which have not been reviewed. For a comprehensive overview about complexes containing multiple bonds between lanthanides and main-group fragments see Ref. [12].

2. Syntheses and Structures of Rare-Earth-Metal Methylidene Complexes

In 2006 Anwander et al. postulated the formation of an "Y–methylidene–Y" fragment as an intermediate to the formation of a heterooctanuclear Y–Al methylidine complex.[13] In the same year, they also published the first structurally characterized rare-earth-metal methylidene complexes, $[Cp^*{}_3Ln_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}CH_2)(thf)_3]$ (Ln = Y (**1a**), La (**1b**), Cp* = pentamethylcyclopentadienyl).[14] They are formed by slow decomposition of $[Cp^*Ln\{Al(CH_3)_4\}_x(Cl)_y]_z$ (Ln = Y ($z = 2$, $y = x$), La ($z = 6$, $y = 2x$)) in toluene/THF at room temperature. Complexes **1a** and **1b** are isostructural in the solid state and the lanthanide ions are coordinated in a pseudo-octahedral geometry by one Cp* ligand, three bridging chloride atoms, one THF molecule, and one μ_3-CH_2 group. The cluster core forms a hexagonal bipyramid with alternating Ln ions and μ_2-Cl ions in the equatorial plane and one μ_3-Cl ion and one μ_3-CH_2 group in the apical positions (Scheme 1). The three Y–CH_2 distances in **1a** are nearly equal (2.424(2)–2.450(2) Å) whereas the La–CH_2 distances in **1b** differ from 2.537(3) to 2.635(3) Å.[14]

Anwander et al. also isolated a comparable compound by treating $[Y\{Al(CH_3)_4\}_3]$ with $KNSiMe_3Ar^{iPr}$ in *n*-hexane.[15] They obtained $[Y\{Al(CH_3)_4\}_2(NSiMe_3Ar^{iPr})]$ which decom-

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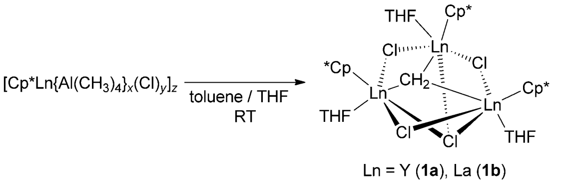
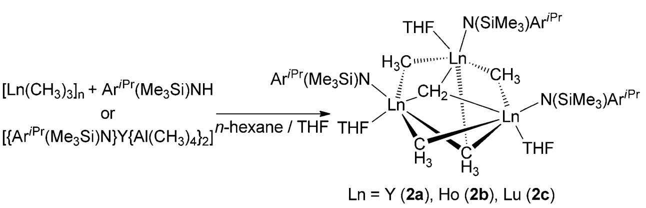
[*] Dr. J. Kratsch, Prof. Dr. P. W. Roesky
Institute of Inorganic Chemistry
Karlsruhe Institute of Technology (KIT)
Engesserstrasse 15, 76131 Karlsruhe (Germany)
E-mail: roesky@kit.edu

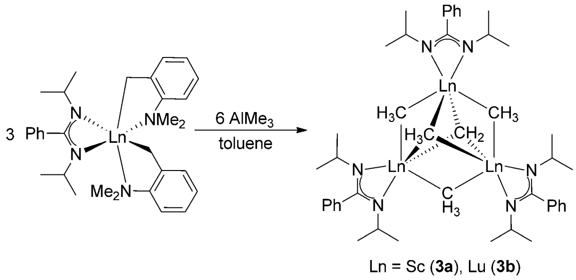


Scheme 1.

poses to $[(\text{Ar}^{i\text{Pr}}\{\text{SiMe}_3\}\text{N})_3\text{Y}_3(\mu_2\text{-CH}_3)_3(\mu_3\text{-CH}_3)(\mu_3\text{-CH}_2)(\text{thf})_3]$ (**2a**) after addition of THF. A second synthetic route is the treatment of $(\text{LnMe}_3)_n$ with $\text{Ar}^{i\text{Pr}}(\text{Me}_3\text{Si})\text{NH}$ in *n*-hexane/THF which leads to the formation of $[\{\text{Ar}^{i\text{Pr}}(\text{Me}_3\text{Si})\text{N}\}_3\text{Ln}_3(\mu_2\text{-CH}_3)_3(\mu_3\text{-CH}_3)(\mu_3\text{-CH}_2)(\text{thf})_3]$ (Ln = Y (**2a**), Ho (**2b**), Lu (**2c**); Scheme 2).[15] Compounds **2a**–**2c** are isostructural in the solid state. In the solid state, compounds **2** have a very similar structure to **1** in which the chloride ions are substituted by methyl groups. The lanthanide ions in **2** are coordinated by one amido ligand, one THF molecule, three bridging methyl groups and one bridging methylidene group leading to a distorted pseudooctahedral geometry. The core of the trinuclear compound builds a distorted hexagonal bipyramid with alternating Ln and μ_2-CH_3 groups in the equatorial and the μ_3-CH_3 group and the μ_3-CH_2 group in the apical positions. The Ln–CH_2 distances lie between 2.345(5) and 2.424(4) Å (Y-CH_2), and 2.310(5)–2.385(5) Å (Lu-CH_2), respectively.[15]



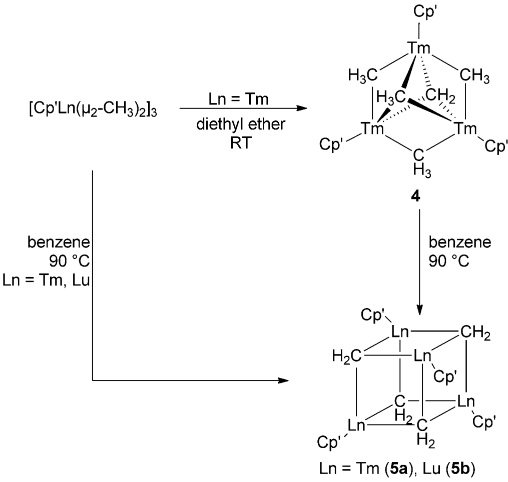
Scheme 2.



Scheme 3.

By using a different synthetic strategy, Zhou et al. synthesized trinuclear methylidene complexes, $[\{\text{LLn}(\mu_2\text{-CH}_3)\}_3(\mu_3\text{-CH}_3)(\mu_3\text{-CH}_2)]$ (L = *N*,*N*′-diisopropylbenzamidinate, Ln = Sc (**3a**), Lu (**3b**)). Complexes **3a**,**b** were obtained by adding two equivalents of AlMe_3 to the rare-earth-metal alkyl complexes $[\text{LLn}\{\text{CH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{-o}\}_2]$ (Scheme 3).[16] The isolated trinuclear complexes are thermally stable up to 210 °C (**3a**) and 180 °C (**3b**), respectively. They build a hexagonal bipyramid with alternating Ln atoms and μ_2-CH_3 groups in the equatorial plane and the μ_3-CH_3 and μ_3-CH_2 groups in the apical position. The metal ions bear an octahedral coordination geometry with average Ln–CH_2 distances of 2.367 Å (**3a**) and 2.376 Å (**3b**).[16]

A similar thulium complex, $[\{\text{Cp}'\text{Tm}(\mu_2\text{-CH}_3)\}_3(\mu_3\text{-CH}_3)(\mu_3\text{-CH}_2)]$, (Cp′ = trimethylsilylcyclopentadienyl, **4**) was obtained by the reaction of $[\{\text{Cp}'\text{Tm}(\text{CH}_3)_2\}_3]$ with one equivalent of AlMe_3 at room temperature (Scheme 4).[17] Com-



Scheme 4.

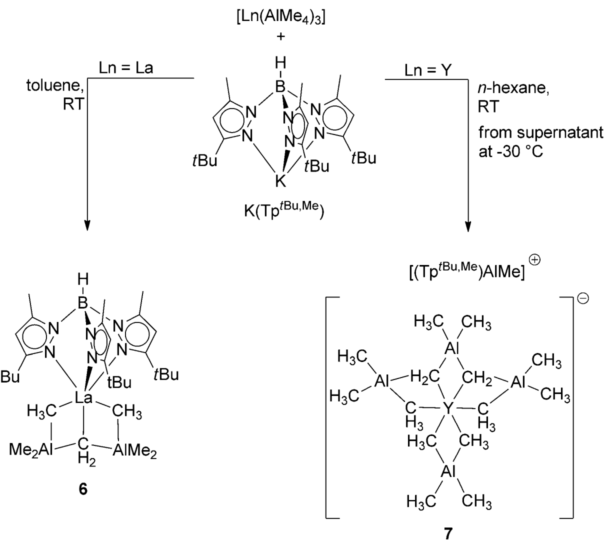
Jochen Kratsch studied chemistry at the University of Kaiserslautern and completed his diploma in 2009 with Prof. W. Thiel on immobilization of cationic catalysts. In 2012 he finished his PhD research with Prof. P. W. Roesky at the Karlsruhe Institute of Technology, exploring chiral amidines as ligands in the coordination chemistry of the lanthanides as well as N-donor ligands for selective extraction of actinides.

Peter W. Roesky obtained his diploma in 1992 from the University of Würzburg and his doctoral degree from the Technical University of Munich (with Prof. W. A. Herrmann) in 1994. He was as a postdoc with Prof. T. J. Marks at Northwestern University (1995–1996). In 1999 he completed his Habilitation at the University of Karlsruhe. As a full professor he joined the faculty of the Freie Universität Berlin in 2001. Since 2008 he has held the chair for inorganic functional materials at the University of Karlsruhe. In 1996 he received a Liebig scholarship, in 1999 a Heisenberg scholarship, and in 2000 a Karl-Winnacker scholarship.

pound **4** is similar to **3a** and **3b** with a hexagonal bipyramidal cluster core. The average Tm–CH_2 distance is 2.35(2) Å. Heating of **4** in benzene at 90 °C led to the formation of the tetranuclear complex $[\{Cp'Tm(\mu_3\text{-}CH_2)\}_4]$ (**5a**). Complex **5a** and the isomorphic lutetium complex **5b** can also be obtained from $[\{Cp'Ln(\mu_2\text{-}CH_3)_2\}_3]$ by methane elimination in benzene at 90 °C. Complexes **5** consist of four $Cp'LnCH_2$ units which build up a heterocubane-like core $[Ln_4(CH_2)_4]$ with average Ln–CH_2 distances of 2.38(4) Å (**5a**) and 2.37(4) Å (**5b**). These are the only known methylidene complexes which consists only of "$LLnCH_2$" units.[17]

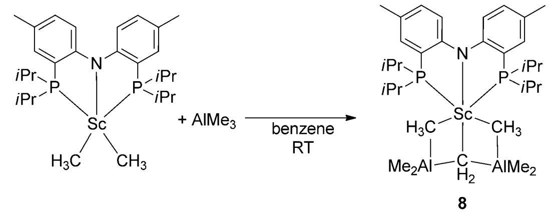
Since most of the methylidene complexes were obtained by using methyl aluminum compounds, it is not surprising that a number of mixed rare-earth-metal aluminum methylidene complexes are known. All these complexes have in common that the methylidene unit is bridging between an aluminum and a rare-earth-metal atom.

Anwander et al. showed that the reaction of $[La(AlMe_4)_3]$ with $K(Tp^{tBu,Me})$ ($Tp^{tBu,Me}$ = tris(3-*tert*-butyl-5-methylpyrazolyl)borate) in toluene leads to the formation of the trinuclear $LnAl_2$ species $[(Tp^{tBu,Me})La((\mu_3\text{-}CH_2)\{(\mu_2\text{-}CH_3)Al(CH_3)_2\}_2)]$ (**6**, Scheme 5).[18] In compound **6**, the κ^3-coordinating $Tp^{tBu,Me}$ ligand, the two μ_2-bridging methyl groups, and the μ_3-bridging methylene group build up a distorted octahedron around the lanthanum center. The Tebbe-like unit, $[(\mu_3\text{-}CH_2)\{(\mu_2\text{-}CH_3)Al(CH_3)_2\}_2]^{2-}$, has a butterfly structure and forms a short La–CH_2 bond (2.519(2) Å). Additionally, an α-agostic interaction between the lanthanum atom and one of the methylidene protons is observed (La–H 2.60(3) Å). In contrast, on treating $[Ln\{Al(CH_3)_4\}_3]$ (Ln = Y, Lu) with $K(Tp^{tBu,Me})$ in *n*-hexane, $[(Tp^{tBu,Me})Ln\{Al(CH_3)_4\}(CH_3)]$ precipitates.[19] Cooling the supernatant solution to −30 °C resulted in the crystallization of the byproduct $[(Tp^{tBu,Me})Al(CH_3)]^+$ $[Y\{Al(CH_3)_4\}\{(\mu_3\text{-}CH_2)(\mu_2\text{-}CH_3)AlMe_2\}_2(AlMe_2)]^-$ (**7**; Scheme 5). The yttrium atom has an octahedral coordination geometry and Y–CH_2 distances are relatively short (2.378(9) Å).[19]



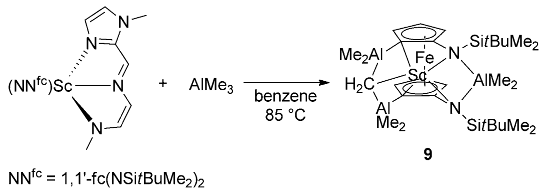
Scheme 5.

Within the mixed rare-earth metal aluminum methylidene complex the Tebbe-like unit, $[(\mu_3\text{-}CH_2)\{(\mu_2\text{-}CH_3)Al(CH_3)_2\}_2]^{2-}$, seems to be one of the preferred structural motives. An isomorphous compound to **6** with this unit, $[(\mu_3\text{-}CH_2)\{\mu_2\text{-}CH_3)Al(CH_3)_2\}_2]^{2-}$, was published by Mindiola et al. in 2008.[20] They treated $[(PNP)Sc(CH_3)_2]$ (PNP = N[2-P-(*i*Pr)$_2$-4-methylphenyl]$_2$) with two equivalents of trimethyl aluminum and obtained $[(PNP)Sc[(\mu_3\text{-}CH_2)\{(\mu_2\text{-}CH_3)Al(CH_3)_2\}_2]]$ (**8**, Scheme 6).[20] The scandium atom in **8** is coordinated by the tridentate PNP ligand, two μ_2-CH_3 groups, and one μ_3-CH_2 group. The six ligands are arranged in a distorted octahedral geometry. As in **6**, there is an α-agostic interaction between the scandium atom and one proton of the methylidene group (Sc–H 2.33(2) Å). The Sc–CH_2 distance is significantly shorter (2.317(2) Å) than the La–CH_2 distance in **3**, a result of the smaller ionic radius of Sc.[20]



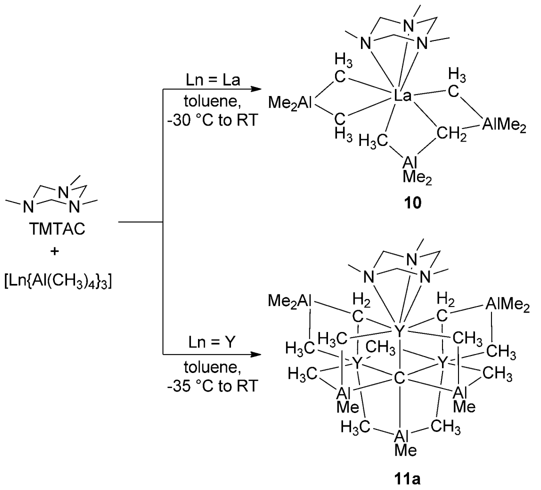
Scheme 6.

A similar unit was also observed in the Sc complex **9**, which is supported by a ferrocene diamide ligand. Complex **9** was obtained by the reaction of $[(NN^{fc})Sc(L)]$ (L = *N*-methyl((((1-methylimidazol-2-yl)methylene)amino)vinyl)-amide) with an excess of $AlMe_3$ in benzene (Scheme 7). The coordination sphere at the scandium atom is built up by two amido groups of the ferrocene derivative, two deprotonated cyclopentadienyl carbon atoms, and the methylidene unit. In comparison to **8** the Sc–CH_2 distance in **9** is significantly longer (Sc–CH_2 2.692(2) Å).[21]

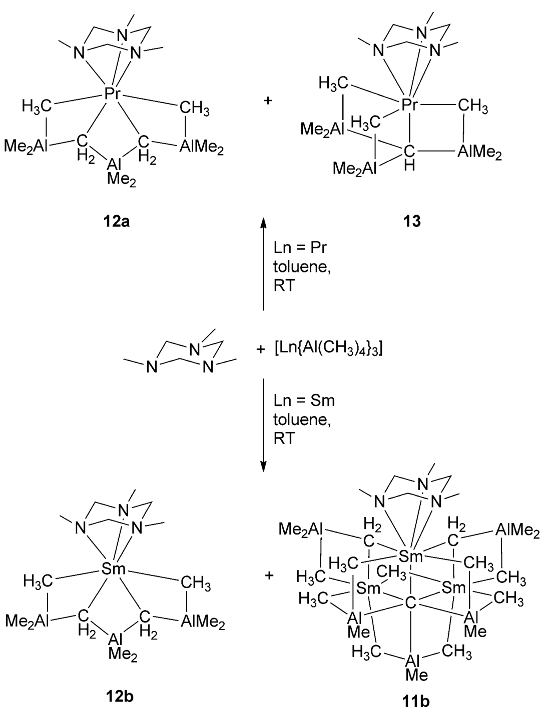


Scheme 7.

Another lanthanum complex with the Tebbe-like bis(aluminate) ion $[(\mu_3\text{-}CH_2)\{\mu_2\text{-}CH_3)Al(CH_3)_2\}_2]^{2-}$ was obtained by Mitzel et al. in 2009. Compound **10**, $[(TMTAC)La\{(\mu_2\text{-}CH_3)_2Al(CH_3)_2\}[(\mu_3\text{-}CH_2)\{\mu_2\text{-}CH_3)Al(CH_3)_2\}_2]$ (TMTAC = 1,3,5-trimethyl-1,3,5-triazacyclohexane), was obtained from the reaction of TMTAC with $[La\{Al(CH_3)_4\}_3]$ (Scheme 8). The lanthanum center is coordinated in a distorted pseudo-octahedral fashion with a La–CH_2 distance of 2.549(2) Å. One of the methylidene protons points in the direction of the La indicating an α-agostic interaction (La–H 2.55(2) Å).[22]



Scheme 8.



Scheme 9.

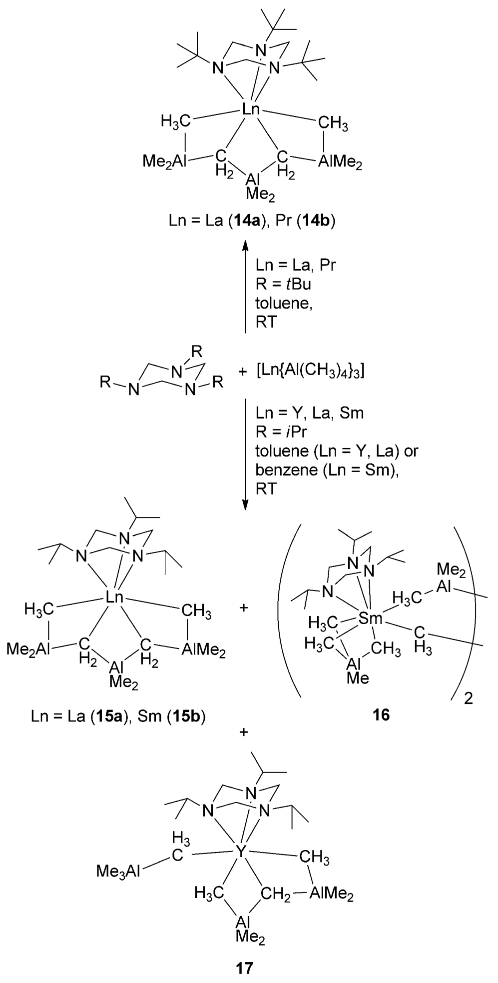
In contrast, $[\mathrm{Y\{Al(CH_3)_4\}_3}]$ and $[\mathrm{Sm\{Al(CH_3)_4\}_3}]$ reacted with TMTAC under the formation of $[\{(\mathrm{TMTAC})\mathrm{Ln}\}\{\mathrm{Ln_2}(\mu_2\text{-}\mathrm{CH_3})\}\{\mu_6\text{-}\mathrm{C}\}[\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})_2(\mathrm{CH_3})]_3\}\{(\mu_3\text{-}\mathrm{CH_2})(\mu_2\text{-}\mathrm{CH_3})\mathrm{Al}(\mathrm{CH_3})_2\}_2]$ (Ln = Y (**11a**, Scheme 8), Sm (**11b**, Scheme 9)), and two equivalents of $[(\mathrm{TMTAC})\{\mathrm{Al(CH_3)_3}\}_2]$. The center of compounds **11** is a carbide ion which is coordinated by three lanthanide and three aluminum atoms in *fac*-octahedral coordination mode. Two methylene groups are linking one aluminum and two lanthanide atoms. The Y–$\mathrm{CH_2}$ distances are 2.452(5) and 2.367(5) Å, the Sm–$\mathrm{CH_2}$ distances are 2.515(4) and 2.408(4) Å, respectively. The structure of compound **11a** was also verified by DFT analysis.[22]

From the reaction of $[\mathrm{Ln\{Al(CH_3)_4\}_3}]$ with TMTAC, a third product, $[(\mathrm{TMTAC})\mathrm{Ln}[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]]$ (Ln = Pr (**12a**), Sm (**12b**), was also isolated (Scheme 9). The Ln^{3+} has a sevenfold coordination with the tridentate TMTAC and the $[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]^{3-}$ trianion. This trianion, which consists of two methylidene groups, can be considered as a larger analogue of the Tebbe-like unit, $[(\mu_3\text{-}\mathrm{CH_2})\{\mu_2\text{-}\mathrm{CH_3})\mathrm{Al}(\mathrm{CH_3})_2\}_2]^{2-}$, which was observed in the previously described compounds. The two methylidene units of the $[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]^{3-}$ trianion in **12a,b** bridge the lanthanide center and two aluminum atoms. The Ln–$\mathrm{CH_2}$ distances are 2.456(6) and 2.489(5) Å (Ln = Pr (**12a**)) as well as 2.426(5) and 2.441(5) Å (Ln = Sm (**12b**)).[23]

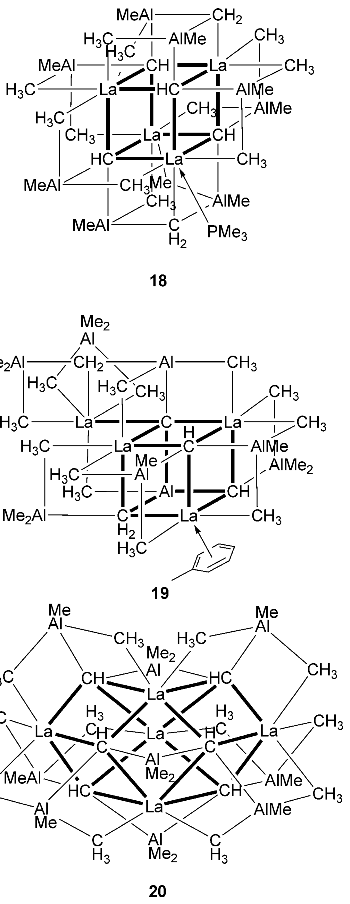
In the reaction of $[\mathrm{Pr\{Al(CH_3)_4\}_3}]$ with TMTAC, two equivalents of $[(\mathrm{TMTAC})\mathrm{Pr}\{(\mu_4\text{-}\mathrm{CH})((\mu_2\text{-}\mathrm{CH_3})\mathrm{Al}(\mathrm{CH_3})_2)_3\}]$ (**13**) cocrystallize with compound **12a**. Compound **13** crystallizes in two different structures, in both the praseodymium atom is coordinated by one methylidyne carbon atom, three methyl groups, and the TMTAC ligand, arranged in a pseudo-trigonal bipyramidal structure.[23] Analogous compounds to the complexes **12a** and **12b** were obtained by changing the alkyl substituents at the 1,3,5-triazacyclohexane ligand. $[\mathrm{Ln\{Al(CH_3)_4\}_3}]$ (Ln = La, Pr) reacted with 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane (T*t*BuTAC) to give $[(\mathrm{T}t\mathrm{BuTAC})\mathrm{Ln}[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]]$ (Ln = La (**14a**), Pr (**14b**)). A second reaction product was not observed (Scheme 10). Complexes **14** also contain the dimethylidene $[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]^{3-}$ trianion. The Ln–$\mathrm{CH_2}$ distances are 2.491(3) and 2.502(3) Å (**14a**) as well as 2.436(3) and 2.459(3) Å (**14b**).[23]

The reaction of $[\mathrm{Ln\{Al(CH_3)_4\}_3}]$ (Ln = La, Sm) with 1,3,5-tri-*iso*-propyl-1,3,5-triazacyclohexane (T*i*PTAC) led to $[(\mathrm{T}i\mathrm{PTAC})\mathrm{Ln}[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]]$ (Ln = La (**15a**), Sm (**15b**), Scheme 10).[23,24] For the reaction of $[\mathrm{La\{Al(CH_3)_4\}_3}]$ with T*i*PTAC no further products were obtained,[23] whereas in the reaction of $[\mathrm{Sm\{Al(CH_3)_4\}_3}]$ with T*i*PTAC a second product, the divalent species $[(\mathrm{T}i\mathrm{PTAC})\mathrm{Sm}\{\mathrm{Al(CH_3)_4}\}\{\mu_2\text{-}\mathrm{Al(CH_3)_4}\}]_2$ (**16**), was formed (Scheme 10).[24] In compounds **15**, the Ln–$\mathrm{CH_2}$ distances are 2.542(4) and 2.521(4) Å (**15a**), as well as 2.464(8) and 2.455(8) Å (**15b**). Running the same reaction with $[\mathrm{Y\{Al(CH_3)_4\}_3}]$ leads to $[(\mathrm{T}i\mathrm{PTAC})\mathrm{Y}[(\mu_3\text{-}\mathrm{CH_2})\{\mu_2\text{-}\mathrm{CH_3})\mathrm{Al}(\mathrm{CH_3})_2\}_2]\text{-}\{(\mu\text{-}\mathrm{CH_3})\mathrm{Al}(\mathrm{CH_3})_3\}]$ (**17**). Complex **17** again contains a Tebbe-like bis(aluminate) ion as well as a η^1-coordinating $[\mathrm{AlMe_4}]^-$ ion. The change in the hapticity of the coordinating tetraaluminate anion is rare and is in contrast to the η^2-coordination mode of $[\mathrm{AlMe_4}]^-$ in the related complex **10**, due to the larger ionic radius of the lanthanum ion (1.040 Å (Y) vs. 1.172 Å (La)). The Y–$\mathrm{CH_2}$ distance is 2.376(3) Å which is comparable to the distance in the yttrium methylidene complex **7**.[25] Reactions of $[\mathrm{Ln\{Al(CH_3)_4\}_3}]$ (Ln = Y, Sm) with other 1,3,5-trialkyl-1,3,5-triazacyclohexanes (alkyl = ethyl, *tert*-butyl, cyclohexyl) did not led to the formation of methylidene complexes.[24–26]

The formation of the $[\{(\mathrm{CH_3})_2\mathrm{Al}(\mu_2\text{-}\mathrm{CH_3})(\mu_3\text{-}\mathrm{CH_2})\}_2\mathrm{Al}(\mathrm{CH_3})_2]^{3-}$ trianion which is commonly observed in 1,3,5-triazacyclohexane compounds seems to take place only when no other anionic ligands are coordinated to the rare-earth



Scheme 10.



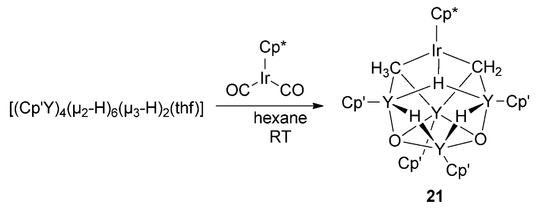
Scheme 11.

metal. The formation of polynuclear rare-earth-metal compounds ligated by this anion is thus not observed. Consequently, in the presence of one other anionic ligand only the dianionic Tebbe-like unit, $[(\mu_3\text{-CH}_2)\{\mu_2\text{-CH}_3)\text{Al(CH}_3)_2\}_2]^{2-}$, is formed, based on the current state of knowledge

Large rare-earth-metal aluminum methylidene clusters were obtained by Anwander et al. In an effort to synthesize $[(\text{LaMe}_3)_n]$, $[\text{La}\{\text{Al(CH}_3)_4\}_3]$ was treated with trimethylphosphine. The reaction of $[\text{La}\{\text{Al(CH}_3)_4\}_3]$ with one equivalent of trimethylphosphine led to two La_4Al_8 clusters (**18**, and **19**) and one La_5Al_9 cluster (**20**) with methylene, methine, and carbide groups (Scheme 11), which can be regarded as snapshots of degradation of $[\text{Ln(AlMe}_4)_3]$ towards $[\text{Ln(Me)}_3]_n$.[27] Compound **18** ($[\text{La}_4\text{Al}_8(\mu\text{-CH})_4(\mu\text{-CH}_2)_2(\mu\text{-CH}_3)_{20}(\text{PMe}_3)]$) has a cubic cluster core, which is built from four lanthanum ions and four methine groups. The cluster core is stabilized by coordinating methylaluminum ligands and trimethylphosphine. There are three distinct lanthanum sites. The La–CH_2 distances are 2.588(4) Å (six-coordinate) and 2.629(4) Å (seven-coordinate).[27] Compound **19**, $[\text{La}_4\text{Al}_8(\mu\text{-C})(\mu\text{-CH})_2(\mu\text{-CH}_2)_2(\mu\text{-CH}_3)_{22}(\text{toluene})]$, has a distorted cubic cluster core which is built by three lanthanum and one aluminum cation which are connected by one carbide, two methine groups, and one methylidene group. The La–CH_2 distances are 2.623(7) and 2.889(7) Å in the cluster core, and 2.549(7) Å.[27]

In the third cluster $[\text{La}_5\text{Al}_9(\mu\text{-CH}_6)(\mu\text{-CH}_3)_{30}]$ (**20**), the core unit is built by five lanthanum ions, which are arranged in a trigonal bipyramidal fashion, and six methine groups, each capping a trigonal bipyramidal face. Methylidene groups are not present in lanthanum methyl/methine cluster **20**.[27]

In 2009 Hou et al. presented the only mixed rare-earth-metal transition-metal methylidene complex. They used an yttrium polyhydride to reduce CO ligands of transition-metal complexes of the Groups 6, 7, and 9.[28] The reaction led to different methyl and oxymethyl complexes. In the reaction between $[\text{Cp*Ir(CO)}_2]$ with $[(\text{Cp}'\text{Y})_4(\mu_2\text{-H})_6(\mu_3\text{-H})_2(\text{thf})]$ the oxycarbene complex $[(\text{Cp}'\text{Y})_4(\text{Cp*Ir})(\mu_2\text{-H})_2(\mu_3\text{-H})(\mu_3\text{-CH}_3)(\mu_3\text{-CH}_2)(\mu_3\text{-O})_2]$ (**21**) was obtained (Scheme 12). The meth-

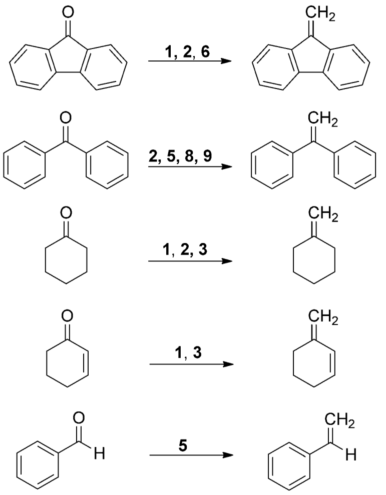


Scheme 12.

ylidene group bridges two yttrium atoms and the iridium atom. The Y–CH_2 distances are 2.5206(13) and 2.5673(13) Å.[28]

3. Reactivity of Rare-Earth Methylidene Complexes

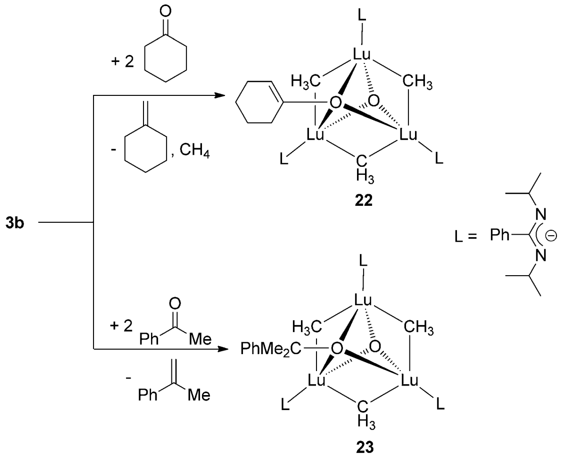
The reactivity of the rare-earth methylidene complexes is mainly dominated by the highly nucleophilic character of the CH_2^{2-} unit. The complexes show a unique reactivity towards carbonyl compounds, comparable to transition-metal Schrock carbene complexes. Thus, comparable to Tebbe's reagent, compounds **1**, **2**, **3**, **5**, **6**, **8**, and **9** react as methylidene transfer agents with carbonyl compounds (Scheme 13) leading to alkenes and rare-earth-metal oxo complexes.[14–18,20,21]



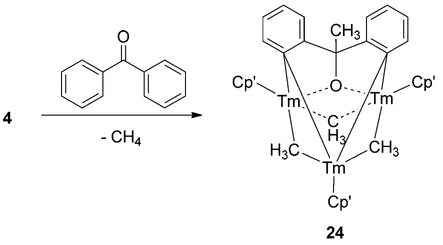
Scheme 13.

With mixed rare-earth-metal methyl/methylidene complexes, subsequent methylenation/methylation and methylenation/deprotonation reactions are possible. Thus, complexes **2** react with five equivalents of the carbonylic substrate as a methylenation and methylation reagent giving rare-earth-metal oxo/methyl alkoxo compounds, which could not be characterized by single-crystal X-ray diffraction.[15] It was shown for complex **3b** that the reactivity strongly depends on the nature of the ketone. The reaction with two equivalents of cyclohexanone instead results in the deprotonation of the second equivalent of ketone and a rare-earth-metal oxo/methyl enolate cluster **22** is obtained (Scheme 14). Treating **3b** with two equivalents of acetophenone led also to a rare-earth-metal oxo/methyl alkoxo compound (**23**).[16]

The conversion of **4** with one equivalent of benzophenone led to $[Cp'_3Tm_3(\mu_2\text{-}CH_3)_3\{(C_6H_4)_2C(O)CH_3\}]$ (**24**) which contains a pincer-like bis(benzo-1,2-diyl)ethoxy trianion (Scheme 15). It is believed that the reaction occurs by a nuleophilic addition of the methylidene group at the carbonyl group. One *ortho* C–H bond is activated by the methylidene, followed by a second *ortho* C–H activation by a methyl group.[17]

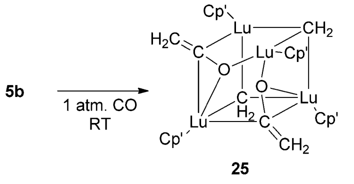


Scheme 14.



Scheme 15.

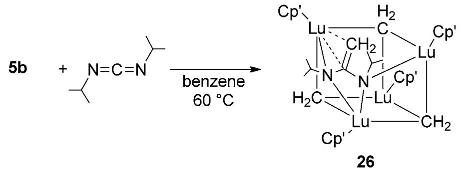
A more detailed reactivity study was carried out by Hou et al. with compound **5b**. They investigated the reactivity of this methylidene cluster towards C–O, C–N, and C–S multiple bonds. Carbon monoxide inserts at room temperature in two of the four Lu–CH_2 bonds of **5b** giving a bis(ketene dianion)/dimethylidene complex $[Cp'_4Lu_4(\mu_3\text{-}CH_2)_2(\mu_3,\eta^2\text{-}O\text{-}C{=}CH_2)_2]$ (**25**, Scheme 16).[29]



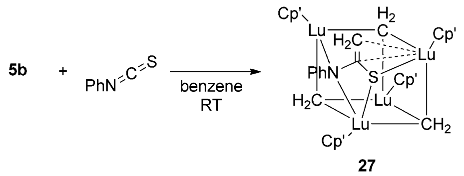
Scheme 16.

Complex **5b** reacts with only one equivalent *N*,*N*-diisopropylcarbodiimide forming an ethylene diamido/dimethylidene complex, $[Cp'_4Lu_4(\mu_3\text{-}CH_2)_3\{(i\text{PrN})_2C{=}CH_2\}]$ (**26**, Scheme 17). With a second equivalent of the carbodiimide no reaction occurs, because of steric hindrance. The ethylene diamido ligand is formed by a nucleophilic attack of the methylidene group on the carbodiimide, followed by an isomerization.[29]

The reaction of **5b** with phenyl isothiocyanate led to an ethylene amido thiolate/methylidene complex ($[Cp'_4Lu_4(\mu_3\text{-}CH_2)_3\{\mu_3,\eta^3\text{-}PhNC(S){=}CH_2\}]$ (**27**, Scheme 18). Compound **27**



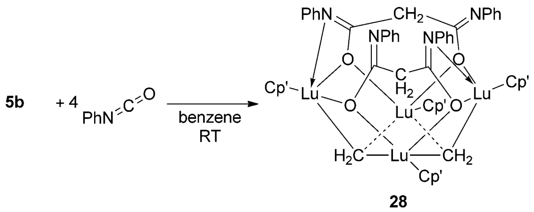
Scheme 17.



Scheme 18.

decomposes after 30 min at room temperature, but is stable at lower temperature. The ethylene diamido thiolate ligand binds to three lutetium atoms in a η^3-(CH$_2$=C–S) fashion. Further reaction of **27** with PhN=C=S was proposed but no derivatives could be characterized.[29]

In contrast to the formation of **26** and **27** in which only one equivalent of the C–N and C–S reagent reacted with **5b**, the reaction of phenyl isocyanate with **5b** is different. With four equivalents of phenyl isocyanate a malonodiimidate/methylidene complex, $[Cp'_4Lu_4(\mu_3\text{-}CH_2)_2\{(PhN{=}C(O))_2CH_2\}_2]$ (**28**), was formed (Scheme 19). During the reaction, two of the methylidene groups added to two C=O bonds of the phenyl isocyanate giving a malonodiimidate.[29]



Scheme 19.

4. DFT Calculations

To study the bonding situation in the cationic $LnCH_2^+$ species (Ln = Sc, Y, La–Lu), quasi-relativistic Douglas–Kroll–Hess CASPT2 calculations were performed by Pyykkö et al. in 2010.[30] Shortly after, Schwarz et al. expanded these studies for the whole series of MCH_2^+ cations (M = K–La and Hf–Rn) to identify periodic trends.[31] Pyykkö et al. predicted that in principle all lanthanides can form a double bond to the methylene group. The double bond is mainly formed by the 5d orbitals with just a small occupation of the 6s orbitals. The bond length decreases with ionic radius from 2.11 (La) to 1.96 Å (Yb). A significant variance in the bond energies from 4.54 (La) to −1.17 eV (Yb), which is mostly influenced by the promotion energy of the lanthanide cation, is observed.[30] In comparison, in [H$_2$CAnFCl] (An = Th, U) the An–C double bond is formed by 6d and 5f orbitals with bond energies of 5.16 (Th) and 4.56 eV (U).[32]

Some of the ions can also form single bonds. Ho and Er have similar binding energies for the single ($D_e = 2.30$ eV (Ho) and 2.81 eV (Er)) and double bond ($D_e = 2.02$ eV (Ho) and 2.15 eV (Er)) leading to a double-well potential. A more stable single bond is formed with Ln = Eu (2.67 vs. −0.67 eV), Tm (3.19 vs. 0.84 eV), and Yb (3.13 vs. −1.17 eV). The Ln–C single-bond length ranges from 2.332 (Eu) to 2.254 Å (Yb). The single bond is formed between a 6s5d hybrid orbital and the σ radical orbital on methylene.[30] In the case of cerium the calculation of the vibrational frequencies of the double bonded $CeCH_2^+$ identified an imaginary frequency. This vibration belongs to an in-plane wagging of the CH$_2$ group. Re-optimization of the $CeCH_2^+$ molecule without symmetry restrictions showed an agostic interaction between the lanthanide and one of the hydrogen atoms,[30] as was observed in compounds **6**, **8**, and **10**.[18,20,22] This situation is in agreement with previous DFT and matrix IR studies of uranium and thorium methylidene complexes, which also show an agostic interaction between the metal center and one hydrogen atom of the methylidene group.[32,33]

5. Conclusion

Although rare-earth-metal alkylidene complexes were reported for the first time in 1979, they were only intensively investigated in the last decade. By considering that Schrock-type carbene complexes of the transition metals are a well-established class of compounds for some decades now, the new developments in rare-earth chemistry come relatively late. However, the chemistry of rare-earth-metal methylidene complexes shown herein clearly shows that this is an emerging class of compounds which form spectacular solid-state structures. The reactivity of these methylidene complexes is mainly influenced by the nucleophilic CH_2^{2-} unit and can be compared to early-transition-metal Schrock carbene complexes. However, their synthetic potential in organometallic and organic chemistry is underdeveloped. Whereas, the rare-earth-metal methylidene complexes are shown to be reactive in carbonyl olefination, the scope of the possible substrates and tolerated functional groups has not been examined in detail. Also, their reactivity in olefin reactions, such as metathesis or cyclopropanation which are known from early-transition-metal alkylidenes, has not been studied to date.

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