

## RESEARCH ARTICLE


View Article Online

View Journal | View Issue



Cite this: *Inorg. Chem. Front.*, 2025, **12**, 4513

## Half-sandwich scandium methylidenes†

Gernot T. L. Zug, Sylvia A. Zeiner, Jonas Reuter, Hartmut Schubert, Cécilia Maichle-Mössmer and Reiner Anwander \*

$\text{AlMe}_3$  sticks,  $\text{GaMe}_3$  quits. A series of Lewis acid stabilized scandium methylidenes with commercially available cyclopentadienyl ligands  $\text{Cp}^R$  ( $\text{Cp}^R = \text{C}_5\text{Me}_5$  ( $\text{Cp}^*$ ),  $\text{C}_5\text{Me}_4\text{SiMe}_3$  ( $\text{Cp}^i$ )) were synthesized. The salt metathesis reaction of new half-sandwich dichloride precursors  $\text{Cp}^R\text{ScCl}_2(\mu\text{-Cl})\text{Li}(\text{thf})_3$  with  $\text{LiAlMe}_4$  and  $\text{AlMe}_3$  at ambient temperature yielded  $[\text{Cp}^R\text{Sc}(\text{AlMe}_4)\text{Cl}]_2$ .  $[\text{Cp}^R\text{Sc}(\text{AlMe}_4)\text{Cl}]_2$  was further methylated at ambient temperature to yield  $\text{Cp}^R\text{Sc}(\text{AlMe}_4)\text{Me}$ . At 70 °C, the reaction of  $\text{Cp}^R\text{ScCl}_2(\mu\text{-Cl})\text{Li}(\text{thf})_3$  with  $\text{LiAlMe}_4$  and  $\text{AlMe}_3$  led to the formation of Lewis acid stabilized  $\text{Sc}/\text{Al}_2$  methylidenes  $\text{Cp}^R\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$ . The new mixed  $\text{Sc}/\text{Al}/\text{Ga}$  methylidene  $\text{Cp}^R\text{Sc}(\text{CH}_2)(\text{AlMe}_3)(\text{GaMe}_3)$  was obtained from the reaction of  $\text{Cp}^R\text{Sc}(\text{AlMe}_4)\text{Me}$  with  $\text{GaMe}_3$ . When heated, complex  $\text{Cp}^R\text{Sc}(\text{CH}_2)(\text{AlMe}_3)(\text{GaMe}_3)$  converted into the  $\text{Sc}/\text{Al}$  methylidene  $[\text{Cp}^R\text{Sc}(\text{CH}_2)_2\text{AlMe}_3]$  via release of the comparatively weak Lewis acid  $\text{GaMe}_3$  and methane. The core of trimeric  $[\text{Cp}^R\text{Sc}(\text{CH}_2)_2\text{AlMe}_3]$  can be described as a triscandacyclohexane  $\{\text{Sc}(\text{CH}_2)_3\}$  stabilized by a trialacyclohexane  $\{\text{Al}(\text{CH}_2)_3\}$  via Pearson hard/hard matching. Complexes  $\text{Cp}^R\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  and  $[\text{Cp}^R\text{Sc}(\text{CH}_2)_2\text{AlMe}_3]$  differ in rigidity, thermal stability and reactivities toward ketones and Lewis bases. The isolated methylidenes were analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{45}\text{Sc}$ , and variable temperature  $^1\text{H}$  NMR spectroscopy, SC-XRD, IR spectroscopy, and elemental analysis. Complexes  $\text{Cp}^R\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  feature pronounced  $\text{Sc}\cdots\text{HC}$   $\alpha$ -agostic interactions. The reaction of  $\text{Cp}^R\text{ScCl}_2(\mu\text{-Cl})\text{Li}(\text{thf})_3$  with  $\text{LiAlMe}_4$  and  $\text{AlMe}_3$  was investigated via *in situ*  $^1\text{H}$  and  $^{45}\text{Sc}$  NMR spectroscopy.

Received 15th January 2025,  
Accepted 3rd April 2025

DOI: 10.1039/d5qi00152h

rsc.li/frontiers-inorganic

## Introduction

It is now 50 years since Schrock reported on the synthesis and structural characterization of tantalum methylidene  $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$  as the first isolable molecular metal-methylidene complex.<sup>1</sup> Soon after in 1978, Tebbe described the heterobimetallic titanium methylidene  $\text{Cp}_2\text{Ti}(\text{CH}_2)(\text{Cl})\text{AlMe}_2$ ,<sup>2</sup> which ever since advanced organic synthesis and, more specifically, excelled as Tebbe's reagent in functional group tolerant methylenation reactions.<sup>3</sup> Early mechanistic and structural investigations have also contributed to an in-depth understanding of the role of the organoaluminum component.<sup>4</sup> For example, while Schrock pointed out that  $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$  does reversibly form an adduct with  $\text{AlMe}_3$ ,<sup>1</sup> ideal performance of Tebbe's compound is achieved in the presence of a Lewis base like  $\text{NEt}_3$ , resulting in the displacement of "stabilizing"  $\text{Me}_2\text{AlCl}$  and the formation of transient  $[\text{Cp}_2\text{Ti}=\text{CH}_2]$ .<sup>5</sup> Not surprisingly, research into Tebbe-like nucleophilic carbene

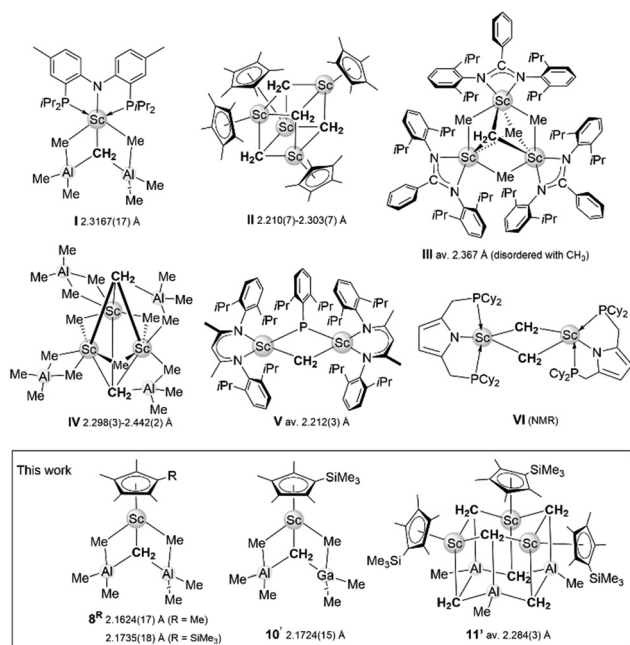
chemistry also triggered feasibility studies on discrete methylidene complexes of metals adjacent to titanium. More recent studies include the structural characterization of the first monometallic, terminal methylidenes of zirconium(IV) and vanadium(V),  $(\text{PNP})\text{Zr}(\text{OAr})(\text{CH}_2)$  and  $(\text{PNP})\text{V}(\text{NAr})(\text{CH}_2)$  ( $\text{PNP} = \text{N}[\text{2-P}(\text{iPr})_2\text{-4-methylphenyl}]_2$ ,  $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ) by the group of Mindiola.<sup>6,7</sup> The latter two synthesis protocols do not involve any organoaluminum components. In contrast, the first discrete scandium methylidene complex  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$ ,<sup>8</sup> also reported by the Mindiola group in 2008 draws not only on kinetic stabilization of the  $[\text{Sc}=\text{CH}_2]$  moiety via a sterically demanding PNP pincer but also Lewis acid/base interactions with  $\text{AlMe}_3$  (Chart 1, I).<sup>8–10</sup> We have previously shown that such multifaceted stabilization is also applicable for the larger rare-earth metals (Ln) when employing bulky hydrotris(3-*R'*-5-*R*-pyrazolyl)borato scorpionate ligands  $\text{Tp}^{R',R}$  and either  $\text{AlMe}_3$  or  $\text{GaMe}_3$ , e.g.,  $(\text{Tp}^{\text{tBu,Me}})\text{La}(\text{CH}_2)(\text{EMe}_3)_2$  ( $\text{E} = \text{Al, Ga}$ ) and  $(\text{Tp}^{\text{Me,Me}})\text{Sm}(\text{CH}_2)(\text{AlMe}_3)_2$ .<sup>9</sup> For these larger metals, the ubiquitous cyclopentadienyl ancillary ligand only led to trimetallic clusters of the type  $(\text{C}_5\text{Me}_5)_3\text{Ln}_3(\mu\text{-CH}_2)\text{X}_4$  ( $\text{X} = \text{Cl, Br}$ ).<sup>11,12</sup> Compared to d-transition-metal methylidenes, the bonding in rare-earth-metal methylidenes is increasingly ionic and stabilization of the highly polarized  $\text{Ln}-\text{C}(\text{methylidene})$  bond is achieved via cluster formation involving bridging  $\text{CH}_2^{2-}$  moieties. The cluster size is greatly impacted by the steric shielding of the ancillary ligand. It is also noteworthy

Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen,  
Auf der Morgenstelle 18, 72076 Tübingen, Germany.

E-mail: reiner.anwander@uni-tuebingen.de

†Electronic supplementary information (ESI) available: Supporting figures, detailed crystallographic data, spectroscopic data (NMR, IR), analytical details. CCDC 2410874–2410889. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5qi00152h>





**Chart 1** Known scandium methylidene complexes, including Sc–C (methylidene) distances.

that except for the cuboidal cluster  $[(C_5Me_5)Sc(\mu-CH_2)]_4$  (Chart 1, II, Cheng, 2021)<sup>13</sup> all previously reported methylidene complexes of the smallest rare-earth metal scandium feature non-cyclopentadienyl ancillary ligands (Chart 1, I and III–VI).<sup>13–18</sup> The formation of tetrametallic II *via* thermal treatment (90 °C) of  $[(C_5Me_5)Sc(CH_3)(\mu-CH_3)]_2$  clearly parallels the transformation of the Petasis reagent  $Cp_2Ti(CH_3)_2$ , which generates transient  $[Cp_2Ti=CH_2]$  upon heating at 60–80 °C.<sup>19</sup>

Many of the isolated nucleophilic metal methylidenes were probed in the methylenation of ketones and compared to Tebbe's reagent.

Given the feasibility of the half-sandwich complex  $(C_5Me_5)Sc(AlMe_2)_2$ ,<sup>18</sup> although decomposing at temperatures  $>-20$  °C, we wondered about the existence of discrete scandium methylidene complexes with the commercially available ligands  $Cp^*$  ( $C_5Me_5$ ) and  $Cp'$  ( $C_5Me_4SiMe_3$ ). This might bring us a step closer to a scandium analog of the cyclopentadienyl-supported Tebbe reagent. Further, fathoming any group 13 effect ( $AlMe_3$  versus  $GaMe_3$ ) might unveil distinct methylidene formations.<sup>9b,20</sup>

Here, we present discrete  $AlMe_3$ -stabilized half-sandwich scandium methylidenes of the known motif I. Additionally, we present a novel mixed scandium aluminum gallium methylidene complex of motif I. This trimetallic complex decomposes under the release of  $GaMe_3$  and  $CH_4$  granting access to a hexametallal  $\{Sc_3Al_3\}$  cluster motif which is new in rare-earth-metal chemistry.

## Results and discussion

### Half-sandwich scandium chloride precursors

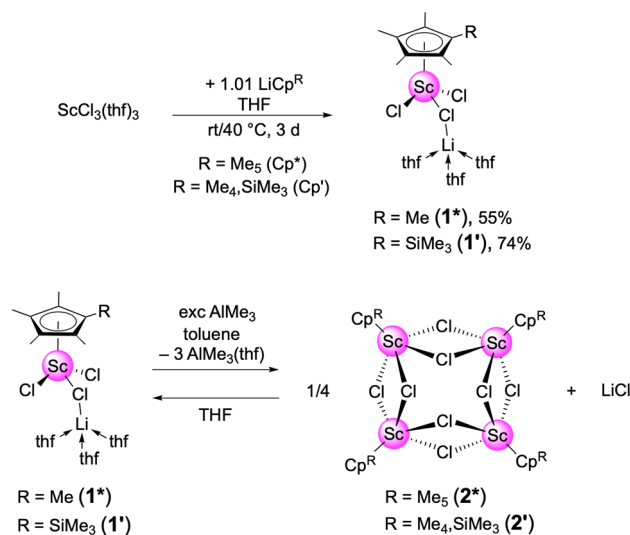
Initial investigations bore on the known metathesis reaction of  $ScCl_3(thf)_3$  and  $Cp^*Li$  ( $Cp^* = C_5Me_5$ ) to yield  $Cp^*$

$ScCl_2(thf)_2$ <sup>21</sup> as well on Okuda's work on half-sandwich methyl scandium complexes (*vide infra*).<sup>22</sup> In our hands, the metathesis reactions of  $ScCl_3(thf)_3$  and  $Cp^R Li$  ( $Cp^R = C_5Me_5$ ,  $C_5Me_4SiMe_3$ ) yielded repeatedly crystals of ate complexes  $Cp^R ScCl_2(\mu-Cl)Li(thf)_3$  (**1<sup>R</sup>**) (Scheme 1). While **1'** was obtained in 74% yield, the initial low yield of **1\*** could be increased from 31% to 55% by raising the reaction temperature to 40 °C and additional toluene extraction. Complexes **1'** and **1\*** are isostructural exhibiting a piano stool configuration, and were further analyzed by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>7</sup>Li, and <sup>45</sup>Sc NMR spectroscopy in  $C_6D_6$ , as well as elemental analysis. Compound **1\*** loses THF at prolonged exposure to vacuum.

Targeting a potential Tebbe-like reactivity, the dichlorido precursors were treated with 5.2 (**1'**) or 5.5 (**1\***) equivalents of  $AlMe_3$ . Not unexpectedly, addition of  $AlMe_3$  to **1<sup>R</sup>** did not afford alkylation but displacement/precipitation of  $LiCl$  only,<sup>23</sup> along with the formation of white  $[Cp^R ScCl_2]_4$  (**2<sup>R</sup>**). The reaction mixture was heated to 130 °C for one day, yielding a pale-yellow solution. Upon cooling to ambient temperature, complexes **2<sup>R</sup>** crystallized and were analyzed by single-crystal X-ray diffraction (SC-XRD). Tetrameric **2<sup>R</sup>** are isostructural to other half-sandwich rare-earth-metal dihalides including  $[Cp^R ScI_2]_4$ .<sup>21b,24</sup> Although  $LiCl$  is not included in the crystal structure, **2<sup>R</sup>** showed a <sup>7</sup>Li NMR signal even after crystalline isolation. Treatment of **2<sup>R</sup>** with THF yielded **1<sup>R</sup>** (Scheme 1).

### Metathesis reactions of $Cp^R ScCl_2(\mu-Cl)Li(thf)_3$ with $LiAlMe_4$

In 2008, the group of Okuda reported on metathesis reactions of  $Cp^*ScCl_2(thf)_2$  with two equivalents of  $LiAlMe_4$ . This led to the successful isolation of  $[Cp^*ScMe_2]_2$ .<sup>22</sup> When  $AlMe_3$  was added in the metathesis reaction, an "orange oil" was obtained at ambient temperature, then depicted as  $[Cp^*Sc(AlMe_2)_2]$ . The orange oil could not be identified unequivocally. The actual congener  $Cp^*Sc(AlMe_2)_2$  was isolated by our group in 2019,

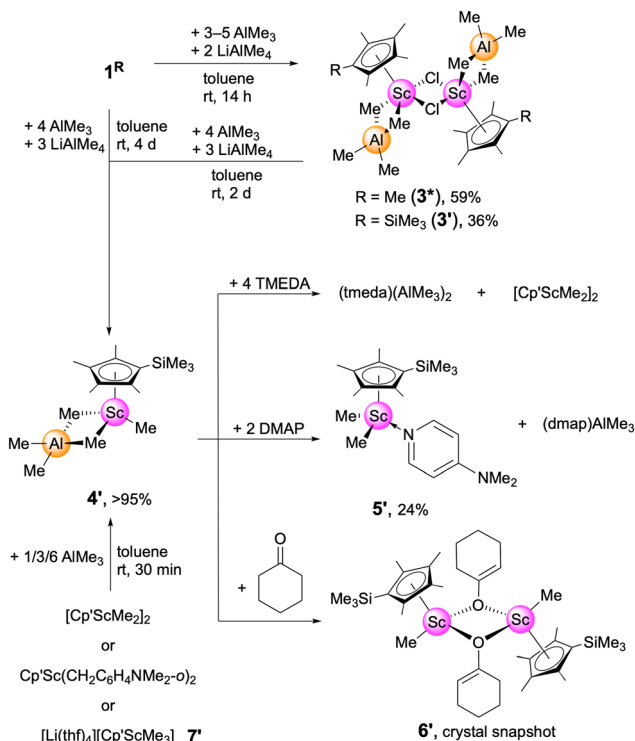


**Scheme 1** Synthesis of scandium chloride precursors  $Cp^R ScCl_2(\mu-Cl)Li(thf)_3$  (**1<sup>R</sup>**) and their reactions with  $AlMe_3$  to yield  $[Cp^R ScCl_2]_4$  (**2<sup>R</sup>**).



showing high sensitivity toward temperatures above  $-20\text{ }^{\circ}\text{C}$ .<sup>18</sup> This sparked our interest in re-investigating Okuda's orange oil. Accordingly, complexes  $1^{\text{R}}$  were reacted with 3 equiv.  $\text{LiAlMe}_4$  and 4 equiv.  $\text{AlMe}_3$  in toluene at ambient temperature overnight. This resulted in the isolation of mixed chlorido tetramethylaluminato complexes  $[\text{Cp}^{\text{R}}\text{Sc}(\text{AlMe}_4)\text{Cl}]_2$  ( $3^{\text{R}}$ ), which were analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$  and toluene- $d_8$ , SC-XRD, as well as elemental analysis. Complexes  $3^{\text{R}}$  crystallized as chlorido-bridged dimers.<sup>11b,25</sup> The  $^{45}\text{Sc}$  NMR spectra displayed three signals (*cf.* ESI†). The  $^1\text{H}$  NMR spectra, however, did not indicate multiple species. Therefore, we assumed that  $3^{\text{R}}$  are subject to monomer-dimer equilibria or to the formation of even larger aggregates in solution which is only seen in the  $^{45}\text{Sc}$  NMR spectra. A variable temperature (VT) NMR study in toluene- $d_8$  lent support to this hypothesis (*cf.* ESI†). The spectrum at  $60\text{ }^{\circ}\text{C}$  revealed only one broad peak in the methyl region. At  $-80\text{ }^{\circ}\text{C}$ , four sharp peaks appeared, assignable to the monomer and the dimer. The VT  $^{45}\text{Sc}$  NMR spectra show that the peak at about 210 ppm increases with lower temperatures, whereas the peak at about 400 ppm gets bigger with higher temperatures. We were hoping that these mixed chlorido/tetramethylaluminato complexes  $3^{\text{R}}$  may directly lead to methylidene complexes, since the congeners of the larger rare-earth metals form trinuclear methylidenes when reacted with THF.<sup>11</sup> In the case of the small scandium however, treatment of  $3^{\text{R}}$  with THF did not form such methylidenes. Instead, undefined decomposition occurred, and, on one occasion, the extremely sensitive aluminate cleavage product  $[\text{Cp}^*\text{ScMeCl}(\text{thf})]_2$  could be identified *via* a crystal snapshot.

Prolonging the reaction of  $1^{\text{R}}$  with 3 equiv.  $\text{LiAlMe}_4$  and 4 equiv.  $\text{AlMe}_3$  in toluene for at least two days led to the isolation of  $[\text{Cp}^*\text{Sc}(\text{AlMe}_4)\text{Me}]$  ( $4'$ ) (Scheme 2). Compound  $4'$  features the orange oil reported by Okuda (*vide supra*),<sup>22</sup> also in our hands opposing successful crystallization. To prove its identity,  $4'$  was analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$ . The  $^1\text{H}$  NMR signal of the  $\text{Sc}-\text{CH}_3$  protons of  $4'$  appeared as one broad peak, suggesting a high fluxionality, as known for tetramethylaluminato and methyl ligands. Moreover, this broad peak showed integrals between 15 and 22 which is less than the expected 24 for putative  $[\text{Cp}^*\text{Sc}(\text{AlMe}_4)_2]$ . The higher integral numbers (compared to 15 in  $4'$ ) originate from residual  $\text{AlMe}_3(\text{thf})$  as the oil had to be evacuated and co-evaporated with toluene extensively in order to get rid of all  $\text{AlMe}_3(\text{thf})$ . The  $^{45}\text{Sc}$  NMR resonance of  $4'$  was detected at 404.2 ppm, shifted considerably to lower field compared to  $\text{Cp}^*\text{Sc}(\text{AlMe}_4)_2$  (245.1 ppm).<sup>18</sup> This downfield shift of  $4'$  suggests that it indeed is not putative  $[\text{Cp}^*\text{Sc}(\text{AlMe}_4)_2]$ . To strengthen our hypothesis and without a crystal structure on hand, we envisaged derivatization reactions to further prove the identity of  $4'$  (Scheme 2). First, we reacted  $[\text{Cp}^*\text{ScMe}_2]_2$  with 1 equiv.  $\text{AlMe}_3$  which led to the sole quantitative formation of  $4'$ . Compound  $4'$  reacted with TMEDA according to a donor-induced aluminate cleavage yielding single crystals of  $(\text{tmeda})(\text{AlMe}_3)_2$ ,<sup>26</sup> verified by a unit cell check. The  $^1\text{H}$  and  $^{45}\text{Sc}$  NMR spectra of this reaction identified  $[\text{Cp}^*\text{ScMe}_2]_2$  as the coproduct



**Scheme 2** Syntheses of  $\text{Cp}^*\text{Sc}(\text{AlMe}_4)\text{Me}$  ( $4'$ ) using various precursors, and reactivities of  $\text{Cp}^*\text{Sc}(\text{AlMe}_4)\text{Me}$  ( $4'$ ).

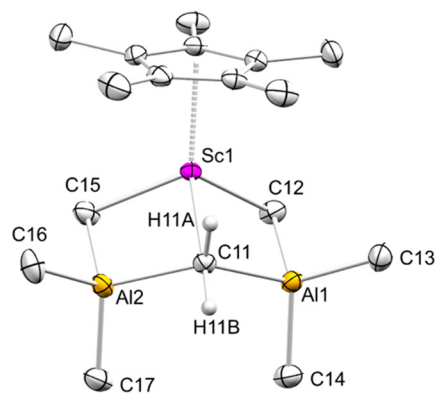
(*cf.*, ESI†).<sup>22</sup> Reacting  $4'$  with the donor DMAP afforded the monomeric adduct  $\text{Cp}^*\text{ScMe}_2(\text{dmap})$  ( $5'$ ), which was analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{45}\text{Sc}$  NMR spectroscopy, SC-XRD, and elemental analysis. The  $^1\text{H}$  NMR spectrum of  $5'$  in  $\text{C}_6\text{D}_6$  revealed that coproduct  $(\text{dmap})\text{AlMe}_3$  could not be removed entirely by crystallization.  $(\text{dmap})\text{AlMe}_3$  itself was crystallized from the supernatant and identified by a unit cell check.<sup>27</sup> To rule out that the orange oil itself is a methylidene complex,  $4'$  was treated with cyclohexanone. This led to the identification of dimeric cyclohexenolate complex  $[\text{Cp}^*\text{ScMe}(\text{OC}_6\text{H}_9)]_2$  ( $6'$ ) *via* a crystal snapshot (*cf.*, ESI†). The small quantity of  $6'$  was also analyzed by  $^1\text{H}$  and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$ .

In order to skip the isolation of  $1^{\text{R}}$ , we probed a one-pot reaction of  $\text{ScCl}_3(\text{thf})_3$ , 1.1 equiv.  $\text{Cp}^*\text{H}$  and 5 equiv.  $\text{MeLi}$  in THF. This led to the new half-sandwich scandium trimethylate complex  $[\text{Li}(\text{thf})_4][\text{Cp}^*\text{ScMe}_3]$  ( $7'$ ), which was analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^7\text{Li}$ , and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$ , SC-XRD, and elemental analysis. Complex  $7'$  is isostructural with  $[\text{Li}(\text{tmeda})_2][\text{Cp}^*\text{LuMe}_3]$ , which was obtained from a one-pot reaction of  $\text{LuCl}_3$ ,  $\text{NaCp}^*$ , and  $\text{MeLi}$ .<sup>28</sup> When treated with 6 equiv.  $\text{AlMe}_3$ , complex  $7'$  gave  $4'$  in essentially quantitative yield. Compound  $4'$  was also obtained from the reaction of half-sandwich dibenzyl complex  $\text{Cp}^*\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_2$  with trimethylaluminum, further proving the orange oil  $4'$  to exhibit the connectivity  $[\text{Cp}^*\text{Sc}(\text{AlMe}_4)\text{Me}]$ . Compound  $4'$  could not be isolated in pure form. It contained at least 5% impurities such as  $8'$  (*vide infra*) or  $\text{Me}_2\text{Al}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})$ .



### Monomeric methylidenes $\text{Cp}^{\text{R}}\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$

The thermal behavior of **4'** at temperatures  $>70$  °C indicated release of methane but yielded a red oil containing an undefined mixture of products. Similarly, performing the metathesis reaction of **1<sup>R</sup>** with 3 equiv.  $\text{LiAlMe}_4$  and 4 equiv.  $\text{AlMe}_3$  at an increased temperature of 70 °C led to methane formation, yielding a red oil as well. However, now repeated recrystallization of that red oil from an *n*-hexane solution gave methylidenes  $\text{Cp}^{\text{R}}\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**8<sup>R</sup>**) as colorless crystals in moderate yields of 66% ( $\text{R} = \text{Cp}^*$ ) and 47% ( $\text{R} = \text{Cp}'$ ) (Scheme 3, Fig. 1 and Fig. S74†). Complexes **8<sup>R</sup>** were analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$  and toluene- $d_8$ , SC-XRD, DRIFTS, and elemental analysis. Compounds **8<sup>R</sup>** feature Lewis acid stabilized methylidenes with the recurring structural motif  $[\text{Ln}(\text{CH}_2)(\text{EMe}_3)_2]^+$  ( $\text{Ln} = \text{rare-earth metal}$ ,  $\text{E} = \text{Al, Ga}$ ) as detected for  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**I**) and  $\text{Tp}^{\text{tBu,Me}}\text{Ln}(\text{CH}_2)(\text{EMe}_3)_2$  ( $\text{Ln} = \text{La, Ce, Nd}$ ;  $\text{E} = \text{Al, Ga}$ ;  $\text{Ln} = \text{Sm}$ ;  $\text{E} = \text{Ga}$ ).<sup>8–10</sup> The  $^1\text{H}$  NMR spectrum of **8<sup>R</sup>** at ambient temperature displayed the methylidene protons as two broad signals (Table 1:  $\delta = 0.95$ ,  $-0.01$  ppm for **8'**,  $\delta = 0.84$ ,  $-0.13$  ppm for **8\***). The slight upfield shift of one methylidene proton points to  $\text{Sc}\cdots\text{HC}$   $\alpha$ -agostic interactions. The methyl groups appeared as one singlet ( $\delta = -0.33$  ppm for **8'**,  $\delta = -0.43$  ppm for **8\***), accounting for a rapid exchange of bridging and terminal methyl groups at ambient temperature. To further elucidate this fluxional behavior in solution, a variable temperature  $^1\text{H}$  NMR study was conducted between  $-80$  and  $+80$  °C (*cf.*, ESI†). At low temperatures, the methylidene signals get sharper and geminal coupling of the two inequivalent protons is detected. The bridging and the two terminal methyl groups split into three signals at  $-80$  °C. At 80 °C, the methylidene signals coalesce into one very broad peak. Crucially, the

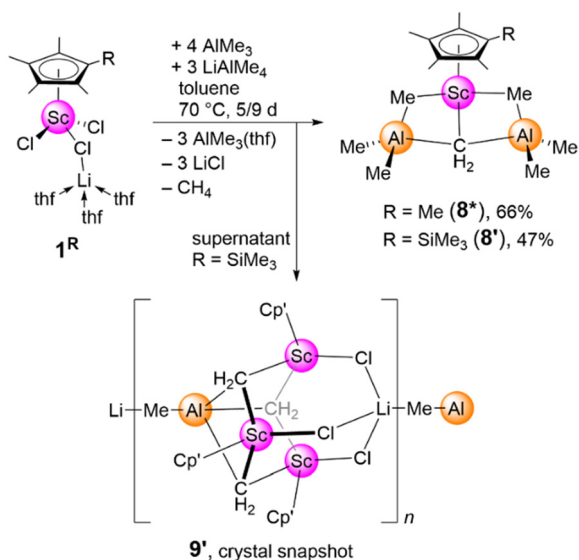


**Fig. 1** Crystal structure of **8\***. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms except methylidene hydrogen atoms omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sc1–C11 2.1624(17), Al1–C11 2.0914(18), Al2–C11 2.0647(17), Sc1–H11A 2.17(2), Sc1–C11–H11A 77.2(13) (ESI†). Complex **8'** is isostructural (Fig. S74†).

spectroscopic signature of the methylidene moiety is distinct from that reported for  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**I**), which showed a singlet at 0.69 ppm at ambient temperature shifting to 0.75 ppm at  $-50$  °C.<sup>8</sup>

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **8<sup>R</sup>** at ambient temperature show peaks at 53.2 (**8\***) and 53.0 ppm (**8'**) for the methylidene carbon atoms (Table 1), rather comparable to the respective shift of  $\text{Tp}^{\text{tBu,Me}}\text{La}(\text{CH}_2)(\text{AlMe}_3)_2$  ( $\delta = 50.9$  ppm)<sup>9a</sup> than of  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**I**, 28.8 ppm). The signals of the methylidene carbon atoms are broadened due to  $^1J$  coupling to 7/2 and 5/2 nuclei of  $^{45}\text{Sc}$  and  $^{27}\text{Al}$ , respectively. The peaks were assigned to the methylidene carbon atom by  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR coupling with the methylidene protons. The  $\text{Sc}\cdots\text{HC}$   $\alpha$ -agostic interaction is also seen in the SC-XRD analysis with short  $\text{Sc}\cdots\text{H}$  (agostic) distances of 2.17(2) Å (**8\***) and 2.14(3) Å (**8'**). The  $\text{Sc}\cdots\text{C}$  (methylidene)–H(agostic) angles are 77.2(13)° (**8\***) and 75.1(16)° (**8'**). The  $\text{Sc}\cdots\text{C}$  (methylidene) distances are 2.1624(17) Å (**8\***) and 2.1735(18) Å (**8'**) (Table 1 and Fig. 1). To the best of our knowledge, these are the shortest distances of scandium to a methylidene carbon atom detected so far. In accordance with the NMR spectroscopic signatures, the  $\text{Sc}\cdots\text{C}$  (methylidene) distance is markedly shorter than the 2.3167(17) Å detected for  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**I**).<sup>8</sup> The short  $\text{Sc}\cdots\text{C}$  (methylidene) distance and the  $^1J$  coupling hint to comparatively strong  $\text{Sc}$ –methylidene interactions in **8<sup>R</sup>**. The Al–C (methylidene) distances of **8\*** are 2.0647(17) Å and 2.0914(18) Å, and of **8'** are 2.0898(18) Å and 2.0879(18) Å. Compared to  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**I**, 2.0387(18) Å and 2.0369(18) Å), the longer Al–C (methylidene) distances in **8<sup>R</sup>** support the assumption of a stronger  $\text{Sc}\cdots\text{C}$  (methylidene) interaction in **8<sup>R</sup>** compared to  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$ .

The complexes **8<sup>R</sup>** and  $\text{Tp}^{\text{tBu,Me}}\text{La}(\text{CH}_2)(\text{AlMe}_3)_2$  show  $\alpha$ -agostic interactions, fluxionality at ambient temperature, geminal coupling of the methylidene protons at  $-80$  °C and a similar  $^{13}\text{C}\{^1\text{H}\}$  NMR shift of the methylidene carbon atom (*vide supra*). Thus, one could draw the comparison of the frag-



**Scheme 3** Synthesis of  $\text{AlMe}_3$ -stabilized methylidenes  $\text{Cp}^{\text{R}}\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**8<sup>R</sup>**) via tandem metathesis/thermally induced methyl deprotonation.



**Table 1** Scandium–C(methylidene) distances and selected NMR spectroscopic signatures ( $\delta$ )

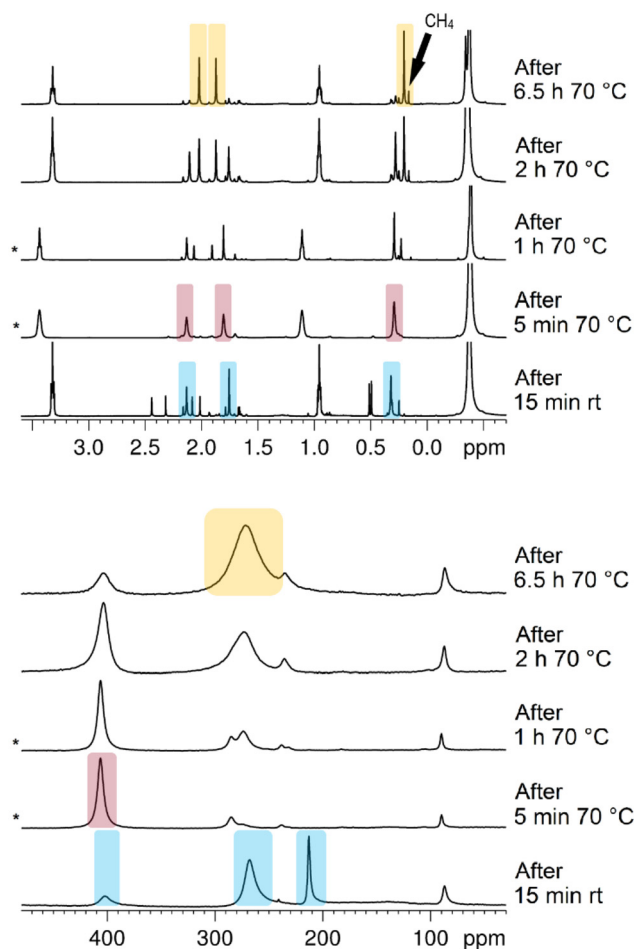
Compound	CN	Sc–C [Å]	$^{13}\text{C}\{^1\text{H}\}$ [ppm]	$^1\text{H}$ [ppm]	Ref.
$\text{Cp}^*\text{Sc}(\mu_3\text{-CH}_2)(\text{AlMe}_3)_2$ ( <b>8*</b> )	6	2.1624(17)	53.2	0.84(br)/–0.13(br)	This work
$\text{Cp}^*\text{Sc}(\mu_3\text{-CH}_2)(\text{AlMe}_3)_2$ ( <b>8'</b> )	6	2.1735(18)	53.0	0.95(br)/–0.01(br)	This work
$\text{Cp}^*\text{Sc}(\mu_3\text{-CH}_2)(\text{AlMe}_3)(\text{GaMe}_3)$ ( <b>10'</b> )	6	2.1724(15)	53.1	0.94(br)/0.10(br)	This work
$[\text{Cp}^*\text{Sc}(\mu_3\text{-CH}_2)(\text{Al}(\mu_3\text{-CH}_2)\text{Me})_3]$ ( <b>11'</b> )	6	2.245(3)–2.3338(18)	81.2/35.0	0.73(d)/–0.13(s)/–1.37(d)	This work
$(\text{PNP})\text{Sc}(\mu_3\text{-CH}_2)(\text{AlMe}_3)_2$ ( <b>I</b> )	6	2.3167(17)	28.8	0.69(s)	8
$[\text{Cp}^*\text{Sc}(\mu_3\text{-CH}_2)]_4$ ( <b>II</b> )	6	2.210(7)–2.303(7)	—	1.71(s)	13
$\text{L}^1\text{Sc}_3(\mu_3\text{-CH}_2)(\text{CH}_3)_4$ ( <b>III</b> )	6	2.367	123.9	3.32(s)	15
$\text{Sc}_3(\mu_4\text{-CH}_2)_2(\mu_2\text{-CH}_3)_3(\text{AlMe}_4)_2(\text{AlMe}_3)_2$ ( <b>IV</b> )	6	2.298(3)–2.442(2)	78.9	2.06(s)	18
$\text{L}^2\text{Sc}_2(\mu_2\text{-CH}_2)(\mu_2\text{-PC}_6\text{H}_3\text{iPr}_2\text{-2,6})$ ( <b>V</b> )	5	2.193(3)/2.232(3)	—	5.62(d, $^3J_{\text{PH}}$ )	17
$[\text{L}^3\text{Sc}(\mu_2\text{-CH}_2)]_2$ ( <b>VI</b> )	5	—	—	1.51/1.48/1.13/1.09	16
$(\text{NN}^{\text{Fc}})\text{Sc}(\mu_3\text{-CH}_2)(\text{AlMe}_3)_2$	5	2.6921(18)	–4.7	–1.42(d)	35

$\text{L}^1 = \text{PhC}(\text{NC}_6\text{H}_4\text{iPr}_2\text{-2,6})$ .  $\text{L}^2 = \text{N}_2\text{C}_3\text{HAR}^{\text{iPr}}\text{-2-1,5-Me}_2\text{-2,4}$ .  $\text{L}^3 = \text{NC}_4\text{H}_2(\text{CH}_2\text{PCy}_2)_2\text{-2,5}$ .  $\text{NN}^{\text{Fc}} = 1,1'\text{-fc}(\text{NSi}t\text{BuMe}_2)_2$ . Structures of **I–VI** are depicted in Chart 1.

ments  $[\text{Cp}^*\text{Sc}]^{2+}$  and  $[\text{Tp}^{\text{tBu,Me}}\text{La}]^{2+}$ . The congener with the smaller yttrium,  $[\text{Tp}^{\text{tBu,Me}}\text{Y}(\text{CH}_2)(\text{AlMe}_3)_2]$ , is elusive since the reaction comes to a halt at  $\text{Tp}^{\text{tBu,Me}}\text{YMe}(\text{AlMe}_4)$ .<sup>9a</sup> It seems that the steric bulk of the ancillary ligand (L) has to match the size of the rare-earth-metal cation (Ln) in order to obtain methylidene complexes from the intermediary formed  $[\text{LLn}(\text{AlMe}_4)_2]$ . Such size match is the case for the fragments  $[\text{Cp}^*\text{Sc}]^{2+}$  and  $[\text{Tp}^{\text{tBu,Me}}\text{La}]^{2+}$ . In **8<sup>R</sup>**, the steric requirement is achieved with the commercially available ligands  $\text{C}_5\text{Me}_5$  and  $\text{C}_5\text{Me}_4\text{SiMe}_3$ .

To gain more insight into the formation mechanism of **8'**, the reaction of **1'** with 3 equiv.  $\text{LiAlMe}_4$  and 4 equiv.  $\text{AlMe}_3$  was monitored by  $^1\text{H}$  and  $^{45}\text{Sc}$  NMR spectroscopy without agitation of the reaction mixture (Fig. 2 and Scheme 4). At initial ambient temperature, the chlorido-bridged dimer **3'** is detected as the main species along with different unidentified species, maybe differently sized clusters of  $[\text{Cp}^*\text{ScCl}_2]$  (**2**). Upon heating to 70 °C, full conversion into the mixed methyl/tetramethylaluminato complex **4'** evolved within 5 minutes. Over the course of two hours at 70 °C, methylidene complex **8'** emerged as the main product. Relating to the  $^{45}\text{Sc}$  NMR spectra, at the beginning, the peak pattern of **3'** appeared in the range between 200 and 420 ppm. Then, after 5 minutes at 70 °C, complex **4'** ( $\delta = 404.2$  ppm) emerged as the main intermediate (Scheme 4). During prolonged heating at 70 °C, **8'** became the main product already after 2 h ( $\delta = 272.6$  ppm). Consequently, **8'** could be obtained according to another reaction path by treating isolated **4'** in *n*-hexane with excess  $\text{AlMe}_3$  at 70 °C.

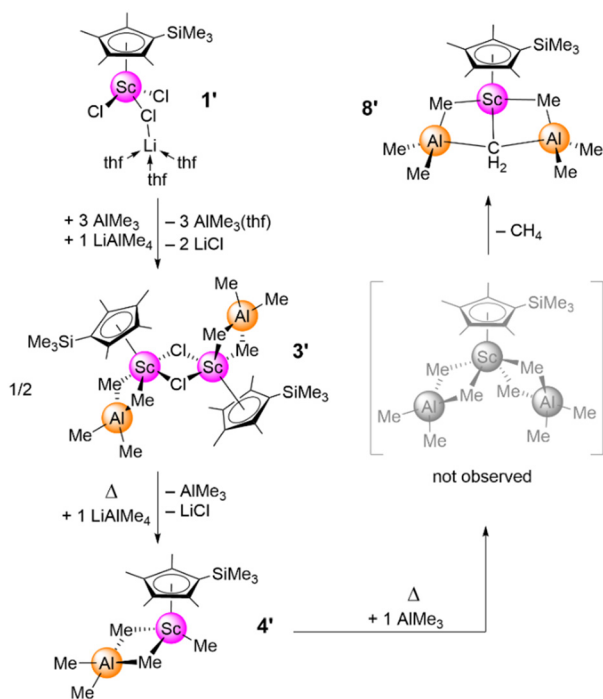
On one occasion, the red supernatant of precipitated **8'** yielded very few colorless crystals of another methylidene complex,  $[(\text{Cp}^*\text{ScCH}_2)_3\text{LiAlMeCl}_3]_n$  (**9'**). The obtained small quantity of **9'** was analyzed by  $^1\text{H}$  and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$ , and SC-XRD. Compound **9'** consists of three  $[\text{Cp}^*\text{ScCH}_2]$  units which are linked to a one-dimensional coordination polymer *via*  $\text{LiAlMeCl}_3$  moieties (*cf.*, ESI<sup>†</sup>). The  $^1\text{H}$  NMR spectrum of **9'** shows two very broad signals at 0.97 ppm and 1.36 ppm attributable to the methylidene protons. Compound **9'** revealed a very broad  $^{45}\text{Sc}$  NMR signal at 429.2 ppm being in stark contrast to the chemical shift of **8'** ( $\delta = 272.6$  ppm), and more in the range of cluster  $\text{Sc}_3(\mu_4\text{-CH}_2)_2(\mu_2\text{-}$



**Fig. 2** Monitoring of the reaction of **1'** with 3 equiv.  $\text{LiAlMe}_4$  and 4 equiv.  $\text{AlMe}_3$  in a J. Young-valved NMR tube without agitation *via in situ*  $^1\text{H}$  (top) and  $^{45}\text{Sc}$  (bottom) NMR spectroscopy in  $\text{C}_6\text{D}_6$ , beginning with **3'** (blue), then intermediate **4'** (red), and final product **8'** (yellow). Unmarked spectra were measured (after cooling) at 26 °C. Spectra marked with an asterisk (\*) were measured at 70 °C.

$\text{CH}_3)_3(\text{AlMe}_4)_2(\text{AlMe}_3)_2$  (Chart 1, **IV**,  $\delta = 388.3/331(2:1)$  ppm). However, the amount of pure isolated **9'** was not sufficient for further analytics and various attempts failed to reproduce **9'**.





**Scheme 4** Mechanism of reaction of **1'** with  $\text{LiAlMe}_4$  and  $\text{AlMe}_3$  with intermediates **3'** and **4'** to yield the final product **8'**.

The Cp\*-analog compound  $[\text{Cp}^*\text{Sc}(\text{AlMe}_4)\text{Me}]$  (**4\***) was not encountered. Prolonged reaction times of **1\*** with 3 equiv.  $\text{LiAlMe}_4$  and 4 equiv.  $\text{AlMe}_3$  at ambient temperature only led to the isolation of  $[\text{Cp}^*\text{Sc}(\text{AlMe}_4)\text{Cl}]_2$  (**3\***), alongside small amounts of **8\***. A reaction of  $\text{Cp}^*\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$  with 3 equiv.  $\text{AlMe}_3$  at ambient temperature did not yield a distinct product nor  $^1\text{H}$  and  $^{45}\text{Sc}$  NMR spectra similar to **4'**.

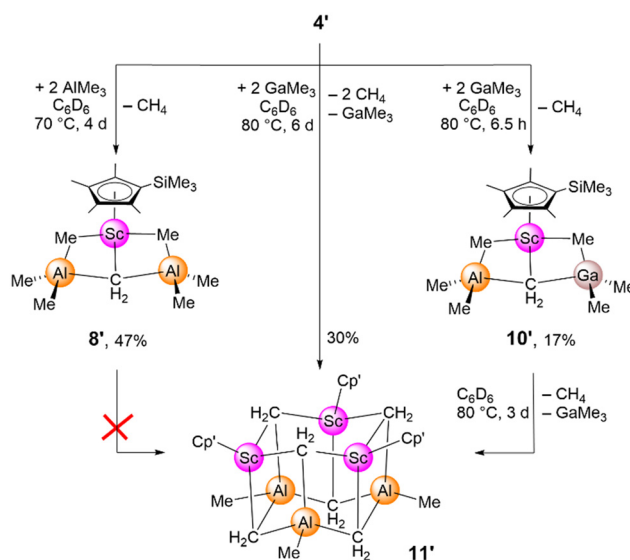
### GaMe<sub>3</sub> in place of AlMe<sub>3</sub>: formation of a trimeric Lewis acid stabilized scandium methylidene

$\text{GaMe}_3$  is a weaker Lewis acid than  $\text{AlMe}_3$ , according to Pearson's HSAB concept.<sup>29</sup> This was key to the isolation of otherwise elusive compounds by our group. For example,  $\text{GaMe}_3$  gets easily displaced in imido complexes  $\text{Tp}^{t\text{Bu},\text{Me}}\text{Ln}(\text{NAr})(\text{GaMe}_3)$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $\text{Ar} = \text{C}_6\text{H}_3\text{iPr}_2\text{-}2,6$ ) *via* treatment with THF to yield the terminal imides.<sup>9b</sup> The  $\text{AlMe}_3$ -containing congener did not show the same reactivity. In another case,  $\text{GaMe}_3$  was released under reduced pressure from  $\text{Tp}^{t\text{Bu},\text{Me}}\text{Ln}(\text{Me})(\text{GaMe}_4)$  to yield the terminal methyl complex  $\text{Tp}^{t\text{Bu},\text{Me}}\text{LnMe}_2$ .<sup>30</sup> Thus, we envisaged organogallium instead of organoaluminum-stabilized scandium methylidenes. The initial reactions of  $\text{Cp}'\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$  with 3 or 4 equiv.  $\text{GaMe}_3$  at ambient temperature yielded a mixture of ill-defined products. Since the instability of elusive  $[\text{Cp}'\text{Sc}(\text{GaMe}_4)_2]$  was safe to assume or any subsequently evolved methylidene complex might also be unstable, we targeted a mixed aluminum/gallium compound.

Given the formation of  $\text{Sc}/\text{Al}_2$  methylidene **8'** in a reaction of **4'** with  $\text{AlMe}_3$  at 70 °C, **4'** was treated with  $\text{GaMe}_3$  in a

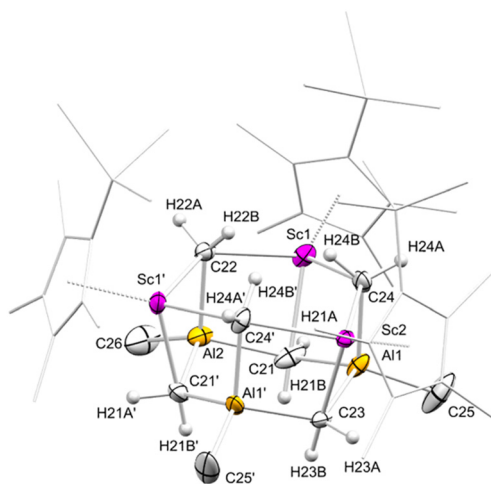
$\text{J. Young}$ -valved NMR tube and heated to 70 °C (Scheme 5). After 6.5 h, the heterotrimetallic methylidene  $\text{Cp}'\text{Sc}(\text{CH}_2)(\text{AlMe}_3)(\text{GaMe}_3)$  (**10'**) was evidenced as the main product through a  $^{45}\text{Sc}$  NMR chemical shift similar to **8'** (275.3 vs. 272.6 ppm). Compound **10'** was (re-)crystallized from a saturated *n*-hexane solution several times, and analyzed by  $^1\text{H}$ ,  $^{13}\text{C}$   $\{^1\text{H}\}$ , and  $^{45}\text{Sc}$  NMR spectroscopy in toluene- $d_8$ , SC-XRD, and elemental analysis. Compound **10'** is isotopic to **8'** and features a very similar Sc–C(methylidene) distance (2.1724(15) vs. 2.1735(18) Å). The  $^1\text{H}$  NMR spectrum of **10'** shows a broad peak for each  $\text{AlMe}_3$  and  $\text{GaMe}_3$  moiety. While the shift of the  $\text{AlMe}_3$  moiety equals that of **8'**, the  $\text{GaMe}_3$  signal appeared at lower field (−0.17 ppm). The  $^1\text{H}$  NMR spectroscopic monitoring also revealed that **10'** decomposes slowly at ambient temperature *via* methane evolution. This lack of stability may be due to  $\text{GaMe}_3$  being a softer Lewis acid compared to  $\text{AlMe}_3$ ,<sup>29</sup> once more underpinning the limited coordination capability of  $\text{GaMe}_3$  in Pearson-type hard/hard metal–ligand pairs. Following this trend,  $\text{AlMe}_3$  instantly replaces  $\text{GaMe}_3$  when  $\text{AlMe}_3$  was added to **10'** to form **8'**.

The decomposition of **10'** is complete after 3 days at 80 °C. During this time, **10'** releases  $\text{GaMe}_3$  and another equivalent of  $\text{CH}_4$ . Afterwards, crystals of the new  $\text{Sc}/\text{Al}$  methylidene  $[\text{Cp}'\text{Sc}(\text{CH}_2)_2\text{AlMe}_3]$  (**11'**) could be isolated, devoid of any gallium component (Scheme 5). Thus, the decomposition pathway of **10'** favors the formation of a second methylidene over the formation of a methylidyne.<sup>13,31</sup> Compound **11'** was analyzed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{45}\text{Sc}$  NMR spectroscopy in  $\text{C}_6\text{D}_6$ , SC-XRD, DRIFTS, and elemental analysis. The molecular structure of **11'** can be described as a trimer of a half-sandwich scandium methylidene stabilized by a trimeric aluminum methyl methylidene (Fig. 3).



**Scheme 5** Reactions of  $\text{Cp}'\text{Sc}(\text{AlMe}_4)\text{Me}$  (**4'**) with  $\text{AlMe}_3$  or  $\text{GaMe}_3$  to form  $\text{Sc}/\text{Al}_2$  methylidene **8'** or mixed  $\text{Sc}/\text{Al}/\text{Ga}$  methylidene **10'** and its reaction to  $[\text{Cp}'\text{Sc}(\text{CH}_2)_2\text{AlMe}_3]$  (**11'**).





**Fig. 3** Crystal structure of **11'**. Atomic displacement ellipsoids were set at 50% probability. Hydrogen atoms except methylidene hydrogen atoms omitted for clarity. Selected interatomic distances (Å) and angles [°]: Sc1–C21 2.246(3), Sc1–C24 2.322(3), Al1–C21 2.054(3), Al1–C24 2.015(3), Sc1–H21A 2.29(3), Sc1–H24B 2.41(3), Sc1–C21–H21A 79.6(17) (ESI<sup>†</sup>).

Overall, **11'** features a  $\text{Sc}_3\text{Al}_3(\text{CH}_2)_6$  distorted hexagonal prismatic core, or in other words a triscandacyclohexane ring  $\{\text{Sc}_3(\text{CH}_2)_3\}$  faced with a trialuminum ring  $\{\text{Al}_3(\text{CH}_2)_3\}$  through Pearson-type hard/hard matching. In terms of nuclearity, **11'** ranges between the homometallic parent methylidene complex  $[\text{Cp}^*\text{Sc}(\text{CH}_2)_4]$  (**II**)<sup>13</sup> and dodecameric  $[\text{MeAl}(\text{CH}_2)]_{12}$ .<sup>32</sup> The core structure of **11'** with two chair-like six-membered rings is a common motif for aluminum imides.<sup>33</sup> For rare-earth-metal chemistry, it has been rarely observed. A crystal snapshot of homometallic  $\text{Cp}^*\text{Y}_6(\text{CH}_2)_4\text{Me}_4$ , which was obtained *via* thermolysis of  $[\text{Cp}^*\text{YMe}_2]_3$ , comes close,<sup>34</sup> but organo-heterobimetallic Ln/Al clusters exhibiting this structural motif have not been encountered to this date.

The  $^1\text{H}$  NMR spectrum of **11'** shows one signal set for the three Cp' ligands and one signal set for the three methyl groups, accounting for a  $\text{C}_3$  symmetry in solution. The methylidene moieties show three signals. The methylidene protons of the  $\{\text{Sc}_3(\text{CH}_2)_3\}$  ring appeared as a singlet at  $-0.13$  ppm at ambient temperature. In contrast, the  $^1\text{H}$  NMR signal of the methylidene protons of the  $\{\text{Al}_3(\text{CH}_2)_3\}$  ring is split at 0.73 and  $-1.37$  ppm, mainly due to the distinct axial and equatorial ring positions. This splitting might also involve weak  $\alpha$ -agostic interactions of one methylidene proton with scandium. In contrast to the rather fluxional methylidene moieties in **8<sup>R</sup>** and **10'**, the  $^1\text{H}$  NMR methylidene signals in **11'** do not coalesce into one signal even at  $120$  °C. Instead, the methylidene protons of the  $\{\text{Al}_3(\text{CH}_2)_3\}$  ring show geminal coupling at ambient temperature and at low temperatures, arising from the rigid chair conformation.

Considering the  $^{45}\text{Sc}$  NMR chemical shifts, that of **11'** ( $\delta = 396.7$  ppm) is shifted downfield compared to **8'** ( $\delta = 272.6$  ppm), and hence similar to **9'** ( $\delta = 429.2$  ppm). Like observed for **9'**, the  $^{45}\text{Sc}$  NMR signal of **11'** is much broader

than that of **8'** (FWHM: 5566 Hz vs. 2715 Hz, *cf.*, ESI<sup>†</sup>). The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **11'** at ambient temperature shows two broadened signals for the methylidene carbon atoms of each  $\{\text{M}_3(\text{CH}_2)_3\}$  ring (M = Sc:  $\delta = 81.2$  ppm, Al:  $\delta = 35.0$  ppm). Similarly, compound  $\text{Sc}_3(\mu_4\text{-CH}_2)_2(\mu_2\text{-CH}_3)_3(\text{AlMe}_4)_2(\text{AlMe}_3)_2$  (Chart 1, **IV**) featuring two  $\text{Sc}_3\text{Al}(\mu_4\text{-CH}_2)$  coordination environments revealed a  $^{13}\text{C}\{^1\text{H}\}$  (methylidene) resonance at 78.9 ppm.<sup>18</sup> Apparently, the  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts of the methylidene carbon atoms are strongly influenced by the number of adjacent rare-earth-metal and aluminum centers. For example,  $[\text{Ln}_3(\mu_3\text{-CH}_2)]$  moieties revealed the largest downfield shifts (*e.g.*  $(\text{NSiMe}_3\text{Ar}^{\text{iPr}})_3\text{Y}_3(\mu_2\text{-Me})_3(\mu_3\text{-Me})(\mu_3\text{-CH}_2)(\text{thf})_3$ ,  $\delta = 100.2$  ppm).<sup>12a</sup> Changing the ratio of coordinating metal centers from  $\text{Sc}_2\text{Al}$  in **11'** ( $\delta = 81.2$  ppm) to  $\text{ScAl}_2$  in **8'** with a very short Sc–C(methylidene) distance (2.1735(18) Å) causes a significant shift to higher field ( $\delta = 53.0$  ppm). The signal of the methylidene carbon atom  $[\text{ScAl}_2(\mu_3\text{-CH}_2)]$  in **11'** ( $\delta = 35.0$  ppm) featuring a longer Sc–C(methylidene) distance (2.246(3) Å) is similar to the methylidene shifts in  $(\text{PNP})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  (**I**,  $\delta = 28.77$  ppm)<sup>8</sup> and  $(\text{TiPTAC})\text{Y}(\text{Me}_3\text{AlCH}_2\text{AlMe}_3)(\mu\text{-MeAlMe}_3)$  ( $\delta = 34.2$  ppm).<sup>10c</sup> An even higher upfield chemical shift was observed by the group of Diaconescu for the moiety  $[\text{ScAl}_2(\mu_3\text{-CH}_2)]$  in  $(\text{NN}^{\text{Fc}})\text{Sc}(\text{CH}_2)(\text{AlMe}_3)_2$  ( $\delta = -4.7$  ppm;  $\text{NN}^{\text{Fc}} = 1,1'\text{-fc}(\text{NSi}t\text{BuMe}_2)_2$ ), in accordance with a very long Sc–C(methylidene) distance of 2.6921(18) Å.<sup>35</sup> The latter chemical shift is very close to the  $^{13}\text{C}\{^1\text{H}\}$  NMR shift of the methylidene carbon atoms in  $[\text{MeAl}(\text{CH}_2)]_{12}$  ( $\delta = -5.1$  ppm).<sup>32</sup>

The Sc–C(methylidene) distances in **11'** (2.245(3)–2.3338(15) Å) are elongated compared to the monomeric structures of **8<sup>R</sup>** (2.1624(17)/2.1735(18) Å) and **10'** (2.1724(15) Å) (Fig. 3). Consequently, the Sc–H(agostic) distances in **11'** (2.24(4) Å/2.29(3) Å) are longer than those in **8<sup>R</sup>** (2.17(2) Å/2.14(3) Å), but the Sc–C(methylidene)–H(agostic) angles (79.6(17)°/76(2)°) are similar to those in **8<sup>R</sup>** (77.2(13)° for **8\***, 75.1(16)° for **8'**). The  $\{\text{Al}_3(\text{CH}_2)_3\}$  ring shows a chair-like conformation with methylidene protons in distinct axial or equatorial positions, whereas the  $\{\text{Sc}_3(\text{CH}_2)_3\}$  ring is distorted due to the steric pressure of the Cp' ligands. Here, the methylidene protons don't assume the classical axial or equatorial positions. This may go hand-in-hand with a high mobility of the increasingly ionic methylidene moiety, resulting in only one signal for the two methylidene protons in the  $^1\text{H}$  NMR spectrum (*vide supra*). A strategy for reducing the ratio of stabilizing aluminum moieties per rare-earth-metal center to 1 : 1 was described for the Sc/Al silylalkylidene complex  $(\text{PNP})\text{Sc}(\mu_2\text{-CHSiMe}_3)(\mu_2\text{-Me})[\text{Al}(\text{Me})(\text{CH}_2\text{SiMe}_3)]$  by the group of Mindiola.<sup>36</sup> There, the chemical shift of the methylidene carbon atom was noted as a broad signal at 137 ppm, corresponding to a very short Sc–CHSiMe<sub>3</sub> distance of 2.0845(14) Å. The heterobimetallic complex  $\text{Cp}^*\text{Ir}(\mu_2\text{-CHSiMe}_3)(\mu_2\text{-N}t\text{Bu})\text{Sc}(\text{Cp}')(\text{py})_x$  displayed similar spectroscopic and structural signatures ( $x = 0$ :  $^{13}\text{C}\{^1\text{H}\}$ , 114.4 ppm;  $x = 1$ : Sc–C, 2.139(9) Å).<sup>37</sup> For further comparison, scandium complexes bearing dianionic  $[\text{C}(\text{PPh}_2\text{S})_2]$  carbene pincer-type ligands revealed Sc–C distances as short as 2.200(3) Å,<sup>38</sup> and non-chelated phosphoniomethylidene complex  $(\text{PNP})\text{Sc}(\mu_2\text{-$



CPPPh<sub>3</sub>(AlMe<sub>3</sub>) feature the shortest Sc–C distance (2.036(5) Å) recorded to date.<sup>36,39</sup>

### Reactivity studies of methylidenes Cp<sup>R</sup>Sc(CH<sub>2</sub>)(AlMe<sub>3</sub>)<sub>2</sub> and [Cp<sup>R</sup>Sc(CH<sub>2</sub>)<sub>2</sub>AlMe<sub>3</sub>]

Monomeric methylidenes **8<sup>R</sup>** eliminate methane at 80 °C, yielding unidentified products. Trimeric **11'**, in contrast, is stable at 100 °C. Compounds **8<sup>R</sup>** methylenate fluorenone instantly at ambient temperature, whereas the reaction of **11'** with fluorenone takes 3 h at 80 °C until completion (*cf.*, ESI†). Full conversion of methylidene complexes **8<sup>R</sup>** is indicated by <sup>45</sup>Sc NMR spectroscopy, revealing chemical shifts to higher field by *ca.* 50 ppm, likely ascribed to the symmetric oxo species Cp<sup>R</sup>Sc(O)(AlMe<sub>3</sub>)<sub>2</sub> (*cf.*, ESI†). Since the reactions were conducted with two equivalents of fluorenone, methylenation is competing with or followed by methylation.<sup>9c,12c</sup> Hence, comparatively low yields of dibenzofulvene were obtained (**8\***, 45%; **8'**, 46%; **11'**, 19%). It should be noted that DFT calculations on the methylenation of ketones by the trinuclear cluster [PhC(NC<sub>6</sub>H<sub>3</sub>iPr<sub>2</sub>-2,6)<sub>2</sub>]<sub>3</sub>Sc<sub>3</sub>(μ<sub>3</sub>-CH<sub>2</sub>)(μ<sub>2</sub>-Me)(μ<sub>2</sub>-Me)<sub>3</sub> showed that methylene transfer rather than methyl transfer applies.<sup>40</sup> Reactivities of the methylidenes toward multiple donors were tested as well. Compound **8\*** was treated with pyridine, leading to an immediate color change from colorless to yellow. After two hours at ambient temperature, a dark-brown solution had evolved. From this dark-brown solution, colorless crystals of AlMe<sub>3</sub>(pyr) could be obtained at –40 °C (*cf.*, ESI†). Compound **11'** does not react with pyridine, THF nor diethyl ether even at 100 °C. Compounds **8<sup>R</sup>** and **11'** oligomerize δ-valerolactone instead of promoting methylenation (*cf.*, ESI†). This suits the known reactivities of rare-earth-metal methylidenes in contrast to Tebbe's reagent.<sup>11</sup> A preliminary evaluation of the oligomerization/polymerization performance of complexes **8<sup>R</sup>** reveal an activity comparable to [Cp<sup>R</sup>ScMe<sub>2</sub>]<sub>2</sub> (ref. 22) but significantly higher than Cp<sup>\*</sup><sub>2</sub>YMe(thf) or commercially available yttrium isopropoxide (conditions: toluene as a solvent, ambient temperature, 1 h; Table S5†).

## Conclusions

Cyclopentadienyl-supported discrete methylidenes Cp<sup>R</sup>Sc(CH<sub>2</sub>)(AlMe<sub>3</sub>)<sub>2</sub> (Cp<sup>R</sup> = C<sub>5</sub>Me<sub>5</sub>, C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>) are accessible directly by a tandem metathesis reaction/thermally induced methane elimination by treatment of Cp<sup>R</sup>ScCl<sub>2</sub>(μ-Cl)Li(thf)<sub>3</sub> with the alkylating mix LiAlMe<sub>4</sub>/AlMe<sub>3</sub>. These reactions proceed *via* isolable intermediates as evidenced for [Cp<sup>R</sup>Sc(AlMe<sub>4</sub>)Cl]<sub>2</sub> and [Cp<sup>R</sup>Sc(AlMe<sub>4</sub>)Me]. Here, *in situ* <sup>45</sup>Sc NMR spectroscopy provides a valuable tool to assess the progress of such one-pot reactions. The mixed methyl/tetramethylaluminato complex [Cp<sup>R</sup>Sc(AlMe<sub>4</sub>)Me] reacts with GaMe<sub>3</sub> to yield the first example of a mixed Sc/Al/Ga methylidene, Cp<sup>R</sup>Sc(CH<sub>2</sub>)(AlMe<sub>3</sub>)(GaMe<sub>3</sub>). Thermal treatment of Cp<sup>R</sup>Sc(CH<sub>2</sub>)(AlMe<sub>3</sub>)(GaMe<sub>3</sub>) generates the new trimeric scandium aluminum bis(methylidene) cluster [Cp<sup>R</sup>Sc(CH<sub>2</sub>)<sub>2</sub>AlMe<sub>3</sub>]<sub>3</sub>, under release of GaMe<sub>3</sub> and CH<sub>4</sub>. The {Sc<sub>3</sub>Al<sub>3</sub>} hexametallc cluster is closing the gap between

methylidenes solely bound to rare-earth-metal centers of the {Sc<sub>4</sub>} cubane-type, [Cp<sup>\*</sup>Sc(CH<sub>2</sub>)<sub>4</sub>] (ref. 13), and {ScAl<sub>2</sub>}-type methylidenes bound to only one rare-earth-metal center and two stabilizing Lewis acids, like Cp<sup>R</sup>Sc(CH<sub>2</sub>)(AlMe<sub>3</sub>)<sub>2</sub>. X-ray diffraction and NMR analyses revealed enhanced rigidity of the thermally quite stable {Sc<sub>3</sub>Al<sub>3</sub>} cluster in contrast to the fluxional methylidenes Cp<sup>R</sup>Sc(CH<sub>2</sub>)(AlMe<sub>3</sub>)<sub>2</sub>. Distinct reactivity of the {ScAl<sub>2</sub>} and {Sc<sub>3</sub>Al<sub>3</sub>} methylidenes is found toward donors and for ketone methylenation. The {ScAl<sub>2</sub>}-type methylidene converts fluorenone immediately at ambient temperature, whereas the {Sc<sub>3</sub>Al<sub>3</sub>} cluster needs prolonged reaction time at elevated temperatures. Finally, taking the earlier reported orange oil, putative [Cp<sup>R</sup>Sc(AlMe<sub>4</sub>)<sub>2</sub>], under close scrutiny led to the development of this new line of methylidenes with commercially available ligands Cp<sup>\*</sup> and Cp<sup>†</sup>.

## Author contributions

GTLZ, synthesis and characterization of compounds, writing and editing original draft; SAZ, synthesis and characterization of compound **11'**; JR, synthesis and characterization of compound **8\***; HS, crystallography of compound **8'**; CM-M, crystallography, editing original draft; RA, conceptualization, supervision, writing and editing original draft, project administration, funding acquisition.

## Data availability

Experimental, spectroscopic and structural data supporting this article have been uploaded as part of the ESI.† Crystallographic data for all compounds have been deposited at the CCDC under 2410874–2410889,† and can be obtained from <https://www.ccdc.cam.ac.uk/structures/>.

## Conflicts of interest

There are no conflicts to declare.

## References

- (a) R. Schrock, The First Isolable Transition Metal Methylene Complex and Analogs. Characterization, Mode of Decomposition, and Some Simple Reactions, *J. Am. Chem. Soc.*, 1975, **97**, 6577–6578; (b) R. R. Schrock, Alkyldiene Complexes of Niobium and Tantalum, *Acc. Chem. Res.*, 1979, **12**, 98–104.
- F. N. Tebbe, G. W. Parshall and G. S. Reddy, Olefin Homologation with Titanium Methylene-Compounds, *J. Am. Chem. Soc.*, 1978, **100**, 3611–3613.
- Olefination: (a) S. H. Pine, G. S. Shen and H. Hoang, Ketone Methylenation Using the Tebbe and Wittig Reagents - A Comparison, *Synthesis*, 1991, 165–167;



- (b) *Modern Carbonyl Olefination*, ed. T. Takeda, Wiley-VCH, 2004.
- 4 (a) T. R. Howard, J. B. Lee and R. H. Grubbs, Titanium metallacarbene-metallacyclobutane reactions: stepwise metathesis, *J. Am. Chem. Soc.*, 1980, **102**, 6876–6878; (b) K. C. Ott, E. J. M. De Boer and R. H. Grubbs, An investigation of the reaction of bis(cyclopentadienyl)titanium dichlorides with trimethylaluminum. Mechanism of an  $\alpha$ -hydrogen abstraction reaction, *Organometallics*, 1984, **3**, 223–230; (c) J. D. Meinhart, E. V. Anslyn and R. H. Grubbs, Synthesis, reactivity and kinetic studies of bis( $\eta^5$ -cyclopentadienyl)titanium methylidene phosphine complexes, *Organometallics*, 1989, **8**, 583–589; (d) R. Thompson, E. Nakamaru-Ogiso, C.-H. Chen, M. Pink and D. J. Mindiola, Structural Elucidation of the Illustrious Tebbe Reagent, *Organometallics*, 2013, **33**, 429–432.
- 5 J. Scott and D. J. Mindiola, A tribute to Frederick Nye Tebbe. Lewis acid stabilized alkylidyne, alkylidene, and imides of 3d early transition metals, *Dalton Trans.*, 2009, 8463–8472 and references therein.
- 6 M. Kamitani, B. Pinter, C.-H. Chen, M. Pink and D. J. Mindiola, Mononuclear and Terminal Zirconium and Hafnium Methylidenes, *Angew. Chem., Int. Ed.*, 2014, **53**, 10913–10915.
- 7 S. Senthil, D. Fehn, M. R. Gau, A. M. Bacon, P. J. Carroll, K. Meyer and D. J. Mindiola, A Vanadium Methylidene, *J. Am. Chem. Soc.*, 2024, **146**, 15666–15671.
- 8 J. Scott, H. J. Fan, B. F. Wicker, A. R. Fout, M.-H. Baik and D. J. Mindiola, Lewis Acid Stabilized Methylidene and Oxoscandium Complexes, *J. Am. Chem. Soc.*, 2008, **130**, 14438–14439.
- 9 (a) R. Litlabø, M. Zimmermann, K. Saliu, J. Takats, K. W. Törnroos and R. Anwender, A Rare-Earth Metal Variant of the Tebbe Reagent, *Angew. Chem., Int. Ed.*, 2008, **47**, 9560–9564; (b) T. E. Rieser, R. Thim-Spöring, D. Schädle, P. Sirsch, R. Litlabø, K. W. Törnroos, C. Maichle-Mössmer and R. Anwender, Open-Shell Early Lanthanide Terminal Imides, *J. Am. Chem. Soc.*, 2022, **144**, 4102–4113; (c) D. Schädle, R. Litlabø, M. Meermann-Zimmermann, R. Thim-Spöring, C. Schädle, C. Maichle-Mössmer, K. W. Törnroos and R. Anwender, Rare-Earth-Metal Methyl and Methylidene Complexes Stabilized by TpR,R'-Scorpionato Ligands—Size Matters, *Inorg. Chem.*, 2024, **63**, 9624–9637.
- 10 Similar Lewis acid stabilized complexes were obtained by introducing neutral donors to homoleptic tris(tetramethyl)aluminates  $\text{Ln}(\text{AlMe}_4)_3$ : (a) L. C. H. Gerber, E. LeRoux, K. W. Törnroos and R. Anwender, Elusive trimethyl-lanthanum: snapshots of extensive methyl group degradation in La–Al heterobimetallic complexes, *Chem. – Eur. J.*, 2008, **14**, 9555–9564; (b) A. Venugopal, I. Kamps, D. Bojer, R. J. F. Berger, A. Mix, A. Willner, B. Neumann, H.-G. Stammer and N. W. Mitzel, Neutral ligand induced methane elimination from rare-earth metal tetramethyl-aluminates up to the six-coordinate carbide state, *Dalton Trans.*, 2009, 5755–5765; (c) D. Bojer, A. Venugopal, A. Mix, B. Neumann, H.-G. Stammer and N. W. Mitzel, C–H Activation versus Yttrium–Methyl Cation Formation from  $[\text{Y}(\text{AlMe}_4)_3]$  Induced by Cyclic Polynitrogen Bases: Solvent and Substituent-Size Effects, *Chem. – Eur. J.*, 2011, **17**, 6248–6255.
- 11 (a) H. M. Dietrich, K. W. Törnroos and R. Anwender, “Ionic carbenes”: Synthesis, structural characterization, and reactivity of rare-earth metal methylidene complexes, *J. Am. Chem. Soc.*, 2006, **128**, 9298–9299; (b) V. M. Birkelbach, F. Kracht, H. M. Dietrich, C. Stuhl, C. Maichle-Mössmer and R. Anwender, A Rare-Earth-Metal Ensemble of the Tebbe Reagent: Scope of Coligands and Carbonyl Olefination, *Organometallics*, 2020, **39**, 3490–3504; (c) D. A. Buschmann, L. Schumacher and R. Anwender, Rare-earth-metal half-sandwich complexes incorporating methyl, methylidene, and hydrido ligands, *Chem. Commun.*, 2022, **58**, 9132–9135.
- 12 Motif III is the most frequently one encountered for rare-earth-metal methylidenes: (a) M. Zimmermann, D. Rauschmaier, K. Eichele, K. W. Törnroos and R. Anwender, Amido-stabilized rare-earth metal mixed methyl methylidene complexes, *Chem. Commun.*, 2010, **46**, 5346–5348; (b) J. Kratsch and P. W. Roesky, Rare-Earth-metal methylidene complexes, *Angew. Chem., Int. Ed.*, 2014, **53**, 376–383; (c) D. Schädle, M. Meermann-Zimmermann, C. Maichle-Mössmer, C. Schädle, K. W. Törnroos and R. Anwender, Rare-earth metal methylidene complexes with  $\text{Ln}_3(\mu_3\text{-CH}_2)(\mu_3\text{-Me})(\mu_2\text{-Me})_3$  core structure, *Dalton Trans.*, 2015, **44**, 18101–18110; (d) J. Hong, Z. Li, Z. Chen, L. Weng, X. Zhou and L. Zhang, Small molecule activation by mixed methyl/methylidene rare earth metal complexes, *Dalton Trans.*, 2016, **45**, 6641–6649.
- 13 P. Deng, X. Shi, X. Gong and J. Cheng, Trinuclear scandium methylidyne complexes stabilized by pentamethyl-cyclopentadienyl ligands, *Chem. Commun.*, 2021, **57**, 6436–6439.
- 14 W.-X. Zhang, Z. Wang, M. Nishiura, Z. Xi and Z. Hou,  $\text{Ln}_4(\text{CH}_2)_4$  Cubane-Type Rare-Earth Methylidene Complexes Consisting of “ $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{LnCH}_2$ ” Units (Ln = Tm, Lu), *J. Am. Chem. Soc.*, 2011, **133**, 5712–5715.
- 15 J. Hong, L. Zhang, X. Yu, M. Li, Z. Zhang, P. Zheng, M. Nishiura, Z. Hou and X. Zhou, Syntheses, Structures, and Reactivities of Homometallic Rare-Earth-Metal Multimethyl Methylidene and Oxo Complexes, *Chem. – Eur. J.*, 2011, **17**, 2130–2137.
- 16 D. S. Levine, T. D. Tilley and R. A. Andersen, Evidence for the Existence of Group 3 Terminal Methylidene Complexes, *Organometallics*, 2017, **36**, 80–88.
- 17 J. Zhou, T. Li, L. Maron, X. Leng and Y. Chen, A Scandium Complex Bearing Both Methylidene and Phosphinidene Ligands: Synthesis, Structure, and Reactivity, *Organometallics*, 2015, **34**, 470–476.
- 18 D. Barisic, D. Diether, C. Maichle-Mössmer and R. Anwender, Trimethylscandium, *J. Am. Chem. Soc.*, 2019, **141**, 13931–13940.
- 19 N. A. Petasis and E. I. Bzowej, Titanium-mediated carbonyl olefinations. 1. Methyleneations of carbonyl compounds



- with dimethyltitanocene, *J. Am. Chem. Soc.*, 1990, **112**, 6392–6394.
- 20 A. Mortis, C. Maichle-Mössmer and R. Anwander, Distinct Reactivity of Trimethylytterbium toward  $\text{AlMe}_3$  and  $\text{GaMe}_3$ . Synthesis of Donor-Stabilized Dimethylytterbium, *Chem. – Eur. J.*, 2023, **29**, e202203824.
- 21 (a) J. Hitzbleck, K. Beckerle and J. Okuda, Half-sandwich dibenzyl complexes of scandium: Synthesis, structure, and styrene polymerization activity, *J. Organomet. Chem.*, 2007, **692**, 4702–4707; (b) A. Fridrichová, A. Růžička, M. Lamač and M. Horáček, Structural differences of half-sandwich complexes of scandium and yttrium containing bulky substituents, *Inorg. Chem. Commun.*, 2017, **76**, 62–66.
- 22 D. Robert, T. P. Spaniol and J. Okuda, Neutral and monocationic half-sandwich methyl rare-earth metal complexes: Synthesis, structure, and 1,3-butadiene polymerization catalysis, *Eur. J. Inorg. Chem.*, 2008, 2801–2809.
- 23 P. L. Watson, Ziegler-Natta Polymerization: The Lanthanide Model, *J. Am. Chem. Soc.*, 1982, **104**, 337–339.
- 24 K. A. Tupper and T. D. Tilley, Synthesis and characterization of scandium complexes with reduced ligands: Crystal structures of  $\text{Cp}^*\text{ScI}_2$ ,  $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$ , and  $[\text{Cp}^*\text{ScCl}(\text{bpy})]_2$ , *J. Organomet. Chem.*, 2005, **690**, 1689–1698.
- 25 H. M. Dietrich, O. Schuster, C. Maichle-Mössmer and R. Anwander, Heterobimetallic Half-lanthanidocene Clusters: Novel Mixed Tetramethylaluminato Chloro Coordination, *Angew. Chem., Int. Ed.*, 2006, **45**, 4858–4863.
- 26 J. J. Byers, W. T. Pennington and G. H. Robinson, Bis-Adducts of Trimethylaluminum and Trimethylgallium with  $\text{N,N,N',N'}$ -Tetramethylethylenediamine, *Acta Crystallogr.*, 1992, **C48**, 2023–2025.
- 27 F. Thomas, T. Bauer, S. Schulz and M. Nieger, Comparative structural studies on 4-dimethylaminopyridine-adducts, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2018–2027.
- 28 H. Schumann, I. Albrecht, J. Pickardt and E. Hahn, Metallorganische Verbindungen der Lanthanoide. XXIII. Synthese und Struktur von  $[\text{Li}(\text{tmed})_2][\text{C}_5\text{Me}_5\text{Lu}(\text{CH}_3)_3]$ , *J. Organomet. Chem.*, 1984, **276**, C5–C9.
- 29 R. G. Pearson, Hard and Soft Acids and Bases, *J. Am. Chem. Soc.*, 1963, **85**, 3533–3539.
- 30 M. Zimmermann, R. Litlabø, K. W. Törnroos and R. Anwander, “Metastable”  $\text{Lu}(\text{GaMe}_4)_3$  Reacts Like Masked  $[\text{LuMe}_3]$ : Synthesis of an Unsolvated Lanthanide Dimethyl Complex, *Organometallics*, 2009, **28**, 6646–6649.
- 31 H. M. Dietrich, H. Drove, K. W. Törnroos and R. Anwander, Multiple C–H Bond Activation in Group 3 Chemistry: Synthesis, structural characterization of an Yttrium–Aluminum–Methine Cluster, *J. Am. Chem. Soc.*, 2006, **128**, 1458–1459.
- 32 G. Spiridopoulos, M. Kramer, F. Kracht, C. Maichle-Mössmer and R. Anwander,  $[(\text{CH}_3)\text{Al}(\text{CH}_2)]_{12}$ : Methylaluminumomethylene (MAM-12), *Chem. – Eur. J.*, 2022, **28**, e202200823.
- 33 (a) M. Cesari, G. Perego, G. Delpiero, S. Cucinella and E. Cernia, Chemistry and Stereochemistry of Poly(*N*-Alkyl-iminoalanes): II. Crystal and Molecular Structure of Hexamer,  $(\text{HAlN-}i\text{-Pr})_6$ , *Organomet. Chem.*, 1974, **78**, 203–213; (b) G. Delpiero, M. Cesari, G. Perego, S. Cucinella and E. Cernia, Chemistry and Stereochemistry of Poly(*N*-Alkyliminoalanes): XI. Crystal and Molecular Structure of Hexamer  $(\text{HAlN-}n\text{-Pr})_6$  and Octamer  $(\text{HAlN-}n\text{-Pr})_8$ , *J. Organomet. Chem.*, 1977, **129**, 289–298; (c) G. Delpiero, S. Cucinella and M. Cesari, Chemistry and the Stereochemistry of Poly(*N*-Alkyliminoalanes): XVI. Crystal and Molecular Structure of the Compound  $[\text{HAlNCH}(\text{CH}_3)\text{C}_6\text{H}_5]_6 \cdot 1/3 \text{C}_6\text{H}_{14}$ , *J. Organomet. Chem.*, 1979, **173**, 263–268; (d) A. A. I. Alwassil, P. B. Hitchcock, S. Sarisaban, J. D. Smith and C. L. Wilson, Complexes of Organoaluminium Compounds. Part 13. Preparation and Nuclear Magnetic Resonance Spectra of the Arylamido-Compounds  $\text{AlMe}_2(\text{NHR}')(\text{R}' = \text{Ph}, \text{C}_6\text{H}_4\text{Me-}o, \text{C}_6\text{H}_4\text{Me-}p, \text{C}_6\text{H}_3\text{Me}_2\text{-}2,6)$  and the Imido-Compounds  $\text{AlMe}(\text{NR}')$ . Crystal and Molecular Structures of  $[\{\text{AlMe}_2(\text{NHC}_6\text{H}_4\text{Me-}o)\}_2]$  and  $[\{\text{AlMe}(\text{NPh})\}_6]$ , *J. Chem. Soc., Dalton Trans.*, 1985, 1929–1934; (e) C. Schnitter, S. D. Waezsada, H. W. Roesky, M. Teichert, I. Uson and E. Parisini, Synthesis and characterization of (4-fluorophenyl)amino-based amino- and iminometallanes of group 13. Crystal structures of  $(\text{MeAlNR}_f)_4$ ,  $(\text{MeMNR}_f)_6 \cdot n\text{THF}$  ( $\text{M} = \text{Al}, n = 2; \text{M} = \text{Ga}, n = 7$ ), and  $(\text{MeIn}(\text{THF})\text{NR}_f)_4$  ( $\text{R}_f = 4\text{-C}_6\text{H}_4\text{F}$ ), *Organometallics*, 1997, **16**, 1197–1202; (f) J. E. Park, B.-J. Bae, Y. Kim, J. T. Park and I.-H. Suh, Reactions of  $\text{AlR}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) with  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ : Synthesis and characterization of amido- and imidoalanes, *Organometallics*, 1999, **18**, 1059–1067; (g) N. D. Reddy, H. W. Roesky, M. Noltemeyer and H. G. Schmidt, Reactions of  $\text{AlH}_3 \cdot \text{NMe}_3$  with nitriles: Structural characterization and substitution reactions of hexameric aluminum imides, *Inorg. Chem.*, 2002, **41**, 2374–2378; (h) E. K. Styron, C. H. Lake, D. H. Powell, L. K. Krannich and C. L. Watkins, Reactivity of  $\text{Me}_3\text{M}$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ) with benzylamine to form the dimers,  $[\text{Me}_2\text{MN}(\text{H})\text{CH}_2\text{Ph}]_2$ , and the hexamers,  $[\text{MeAlNCH}_2\text{Ph}]_6$  and  $[\text{MeGaNCH}_2\text{Ph}]_6$ : molecular structures of *trans*- $[\text{Me}_2\text{MN}(\text{H})\text{CH}_2\text{Ph}]_2$  and  $[\text{MeAlNCH}_2\text{Ph}]_6$ , *J. Organomet. Chem.*, 2002, **649**, 78–85; (i) N. D. Reddy, S. S. Kumar, H. W. Roesky, D. Vidovic, J. Magull, M. Noltemeyer and H. G. Schmidt, Synthesis of a hexadentate hexameric aluminum imide and its metathesis reactions, *Eur. J. Inorg. Chem.*, 2003, 442–448.
- 34 C. O. Hollfelder, L. N. Jende, H. M. Dietrich, K. Eichele, C. Maichle-Mössmer and R. Anwander, 1,3-Diene Polymerization Promoted by Half-Sandwich Rare-Earth-Metal Dimethyl Complexes: Active Species Clustering and Cationization/Deactivation Processes, *Chem. – Eur. J.*, 2019, **25**, 7298–7302.
- 35 W. Huang, C. T. Carver and P. L. Diaconescu, Transmetalation Reactions of a Scandium Complex Supported by a Ferrocene Diamide Ligand, *Inorg. Chem.*, 2011, **50**, 978–984.
- 36 P. Zatsepin, E. Lee, J. Gu, M. R. Gau, P. J. Carroll, M.-H. Baik and D. J. Mindiola, Tebbe-like and Phosphonioalkylidene and -alkylidyne Complexes of Scandium, *J. Am. Chem. Soc.*, 2020, **142**, 10143–10152.



- 37 T. Shima, T. Yanagi and Z. Hou, Rare-earth-iridium hetero-bimetallic complexes with bridging imido and silylmethyl ligands: synthesis, structure and reactivity, *New J. Chem.*, 2015, **39**, 7608–7616.
- 38 (a) M. Fustier, X. F. Le Goff, P. Le Floch and N. Mézailles, Nucleophilic Scandium Carbene Complexes, *J. Am. Chem. Soc.*, 2010, **132**, 13108–13110; (b) M. Fustier, X. F. Le Goff, M. Lutz, J. C. Slootweg and N. Mézailles, Scandium Carbene Complexes: Synthesis of Mixed Alkyl, Amido, and Phosphido Derivatives, *Organometallics*, 2015, **34**, 63–72.
- 39 (a) C. Wang, J. Zhou, X. Zhao, L. Maron, X. Leng and Y. Chen, Non-Pincer-Type Mononuclear Scandium Alkylidene Complexes: Synthesis, Bonding, and Reactivity, *Chem. – Eur. J.*, 2016, **22**, 1258–1261; (b) W. Mao, L. Xiang, C. A. Lamsfus, L. Maron, X. Leng and Y. Chen, Highly Reactive Scandium Phosphinoalkylidene Complex: C–H and H–H Bonds Activation, *J. Am. Chem. Soc.*, 2017, **139**, 1081–1084; (c) W. Mao, L. Xiang, L. Maron, X. Leng and Y. Chen, Nonchelated Phosphinomethylidene Complexes of Scandium and Lutetium, *J. Am. Chem. Soc.*, 2017, **139**, 17759–17762.
- 40 G. Luo, Y. Luo, J. Qu and Z. Hou, Mechanistic Insights into the Methylenation of Ketone by a Trinuclear Rare-Earth-Metal Methylidene Complex, *Organometallics*, 2015, **34**, 366–372.

