

# A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

# **Accepted Article**

Title: Gallium Methylene

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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201902063 Angew. Chem. 10.1002/ange.201902063

Link to VoR: http://dx.doi.org/10.1002/anie.201902063 http://dx.doi.org/10.1002/ange.201902063

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# COMMUNICATION

# **Gallium Methylene**

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Abstract: Despite the eminent importance of metal alkylidene species for organic synthesis and industrial catalytic processes, molecular homoleptic metal methylene compounds [M(CH<sub>2</sub>)<sub>n</sub>] as the simplest representatives, have remained elusive. Reports on this topic date back to 1955 when polymeric  $[Li_2(CH_2)]_n$  and  $[Mg(CH_2)]_n$  were accessed by pyrolysis of methyllithium and dimethylmagnesium, respectively. However, the insoluble salt-like composition of these compounds has impeded their application as valuable reagents. We report that rare-earth metallocene methyl complexes [(C5Me5)2Ln({µ-Me<sub>2</sub>GaMe<sub>2</sub>)] (Ln = Lu, Y) trigger the formation of homoleptic gallium methylene [Ga<sub>8</sub>(µ-CH<sub>2</sub>)<sub>12</sub>] from trimethylgallium [GaMe<sub>3</sub>] (Me = methyl) via a cascade C-H bond activation with dodecametallic [(C5Me5)6Ln3(µ3-CH2)6Ga9(µ-CH2)9] as crucial intermediates. These gallium methylene compounds feature a reversible [Ga<sub>8</sub>(µ-CH<sub>2</sub>)<sub>12</sub>]/[Ga<sub>6</sub>(µ-CH<sub>2</sub>)<sub>9</sub>] oligomer switch in donor solvents and act as Schrock-type methylene transfer reagents.

Metal methylene/methylidene moieties display key components of carbonyl olefination reactions for natural product synthesis<sup>[1]</sup> and major industrial catalytic processes such as olefin metathesis<sup>[2]</sup> or Fischer-Tropsch synthesis alike.<sup>[3]</sup> In particular the discovery and structural elucidation of transition metal methylidene species has triggered immense research in these emerging fields<sup>[4]</sup>. Seminal works comprise Schrock's terminal methylidene Cp<sub>2</sub>Ta(=CH<sub>2</sub>)(CH<sub>3</sub>) (I, Figure 1),<sup>[4a,4b]</sup> Herrmann's bridging methylene Cp(CO)<sub>2</sub>Mn(µ-CH<sub>2</sub>)MnCp(CO)<sub>2</sub> (II),<sup>[4c,4d]</sup> and Tebbe's reagent Cp2Ti(µ-CH2)(µ-CI)AI(CH3)2 (II),[4e-g] having crucially contributed to a fundamental understanding of the processes involved as well as successful further development. d/f-Transition metal methylidene/alkylidene chemistry is still a current hot topic, e.g., unveiling terminal methylidene complexes of the group 4 metals, and more specifically complexes (PNP)M=CH<sub>2</sub>(OAr) (M = Zr, Hf, PNP = N[2-P(*i*Pr)<sub>2</sub>-4-CH<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>, Ar = C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)<sup>[5]</sup> and  $(PN)Ti=CH_2$   $(PN = N[2-P(iPr)_2-4-CH_3-C_6H_3]_2(C_6H_2Me_3-2,4,6)^{[6]}$ . The latter progress has been made possible mainly through tailormade ligand environments and the emergence of new synthesis strategies. In stark contrast, and despite the enormous importance of Wittig's reagent Ph<sub>3</sub>PCH<sub>2</sub> for olefination chemistry,[1, 7] main group metal methylene chemistry has remained underdeveloped. Remarkably, the syntheses of dilithiummethylene Li<sub>2</sub>CH<sub>2</sub> and magnesium methylene MgCH<sub>2</sub> were described by Ziegler already in 1955 via pyrolysis of the respective methyl compounds,<sup>[8]</sup> but it was only in 1990 that the solid-state structure of salt-like Li2CD2 was examined by X-ray

[\*] M. Bonath, Dr. C. Maichle-Mössmer, Dr. P. Sirsch, Prof. Dr. R. Anwander Institut für Anorganische Chemie Eberhard Karls Universität Tübingen Auf der Morgenstelle 18, 72076 Tübingen (Germany) E-mail: reiner.anwander@uni-tuebingen.de Supporting information for this article is given via a link at the end of the document. and neutron powder diffraction techniques.<sup>[9]</sup> Methylene-bridged aluminum centers of the type R<sub>2</sub>Al–CH<sub>2</sub>–AlR<sub>2</sub> (**IV**)<sup>[10]</sup> have been made accessible via derivatization of the halogenido derivatives X<sub>2</sub>Al–CH<sub>2</sub>–AlX<sub>2</sub> (available from Al and CH<sub>2</sub>X<sub>2</sub>)<sup>[11]</sup> and degradation/deprotonation of methyl and tetramethylaluminato ligands as found in, e.g., [(*t*Bu<sub>3</sub>PN)<sub>2</sub>TiAl<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>7</sub>]<sup>[12]</sup> or [La<sub>4</sub>Al<sub>8</sub>(C)(CH)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>22</sub>(toluene)].<sup>[13]</sup>



Figure 1. Milestones in metal methylene/methylidene chemistry.

Methane activation via solvent-free rare-earth metallocene derivatives  $[(C_5Me_5)_2LnMe]$  (Ln = Sc, Lu) features one of the major discoveries in organolanthanide chemistry.<sup>[14]</sup> We have shown that such highly reactive Ln-CH<sub>3</sub> moieties can engage in multiple C-H bond activation, preferably in the presence of AIMe<sub>3</sub> even at ambient temperature.<sup>[13]</sup> Crucially, such methyl group degradation can be controlled in the presence of sterically demanding ancillary ligands, affording, e.g., methylidene complex  $[(C_5Me_5)_3Y_3(\mu-Cl)_3(\mu_3-Cl)(\mu_3-CH_2)(thf)_3]^{[15]}$ and Tebbe-like  $[(Tp^{tBu,Me})La[(\mu-CH_2){(\mu-Me)AIMe_2}]]$  (Tp<sup>tBu,Me</sup> + hydrotris(3-tertbutyl-5-methylpyrazolyl)borato).[16] By studying the reactivity of  $[(C_5Me_5)_2LnMe]$  (Ln = Y, Lu) toward an excess of trimethylgallium we now obtained oligomeric gallium methylene [Ga<sub>8</sub>(µ-CH<sub>2</sub>)<sub>12</sub>]. Herein we describe this organorare-earth metal-promoted formation and full characterization of [Ga<sub>8</sub>(µ-CH<sub>2</sub>)<sub>12</sub>], displaying the first molecular homoleptic metal methylene complex.

Treatment of  $[(C_5Me_5)_2Ln(\{\mu-Me\}_2GaMe_2)]$  (Ln = Lu  $(1^{Lu})$ ,<sup>[17]</sup> Y  $(1^{Y})$ ;<sup>[18]</sup> *cf.*, supplementary material) with an eightfold excess of [GaMe<sub>3</sub>] at 130 °C in aromatic solvents like C<sub>6</sub>D<sub>6</sub> generates methane and provides access to [Ga<sub>8</sub>( $\mu$ -CH<sub>2</sub>)<sub>12</sub>] (**2**) as a pale yellow crystalline material in 80% yields (Scheme 1).<sup>[19]</sup> The solid-state structure of oligomeric compound **2** was determined by single-crystal X-ray diffraction (XRD) analysis (Scheme 1), revealing a cage-like structural motif closely related to silsesquioxanes of the general formula [Si<sub>8</sub>( $\mu$ -O)<sub>12</sub>]R<sub>8</sub>.<sup>[20]</sup> Each gallium atom of the "[Ga<sub>8</sub>] cube" binds to three methylene bridges ("edges"), thus adopting a trigonal planar geometry (sum of angles about Ga 359.2°) with bond lengths (1.960(2) Å, 1.961(1) Å, 1.972(2) Å) in the same range as reported for [GaMe<sub>3</sub>].<sup>[21]</sup>

# COMMUNICATION



Scheme 1. Synthesis of compounds 2, 3 and 6, including the crystal structures of gallium methylenes 2 and 3. Atomic displacement parameters set at 50% probability. Hydrogen atoms and the disorder in coordinated thf molecules in 3 have been omitted for clarity. For selected interatomic distances and angles, see supporting information.

For comparison, galloxane clusters like  $[Ga_{12}tBu_{12}(\mu_3-O)_8(\mu-O)_2(\mu-OH)_4]$  obtained via alkyl hydrolysis tend to adopt an icosahedral arrangement of the alkylgallium(III) moieties,  $^{[22]}$  while silicon methylene derivatives favor ring structures.  $^{[23]}$ 

Analysis of 2 by means of nuclear magnetic resonance (NMR) spectroscopy at ambient temperature in  $d_{\theta}$ -thf solutions provided data consistent with homoleptic gallium methylene 2. The <sup>1</sup>H NMR spectrum of **2** shows a singlet resonance at  $\delta$  0.19 ppm assignable to equivalent methylene protons. However, at ambient temperature in *d*<sub>8</sub>-thf solutions compound 2 converted within 24 to the smaller gallium methylene oligomer hours [Ga<sub>6</sub>(µ-CH<sub>2</sub>)<sub>9</sub>(thf)<sub>6</sub>] (**3**), giving rise to a set of signals at 0.12 ppm (d,  ${}^{2}J_{H,H}$  = 9.1 Hz, 6H), 0.10 ppm (s, 6H), and -0.49 ppm (d,  ${}^{2}J_{H,H}$ = 8.8 Hz, 6H) consistent with three magnetically inequivalent protons. Tracking this process at variable temperatures by NMR spectroscopy revealed that the [Ga8(µ-CH2)12]/[Ga6(µ-CH2)9] oligomer switch in thf solutions is suppressed at temperatures below -40 °C and pushed back at temperatures above 80 °C [Figures S2 and S3]. Single crystals of compound 3 could be harvested from saturated thf solutions at -40 °C and were subjected to XRD analysis. The solid-state structure of hexagallium methylene 3 (Scheme 1) features two six-membered [Ga<sub>3</sub>(µ-CH<sub>2</sub>)<sub>3</sub>] rings in chair conformation. The two [Ga<sub>3</sub>(µ-CH<sub>2</sub>)<sub>3</sub>] subunits are co-facially oriented and connected by three Ga-CH2-Ga bridges, overall being reminiscent of silsesquioxanes of the general formula [Si<sub>6</sub>(µ-O)<sub>9</sub>]R<sub>6</sub>.<sup>[24]</sup> All gallium atoms in compound 3 are coordinated additionally by a thf molecule and therefore display distorted tetrahedral geometry with slightly elongated average Ga-C bond lengths (av. 1.982 Å) compared to 2

Crystallization of gallium methylene **2** from thf solutions at ambient temperature by slowly condensing *n*-pentane into the solution triggers the rearrangement of the  $[Ga_8(\mu-CH_2)_{12}]$  cage as

confirmed by <sup>1</sup>H NMR spectroscopy. Single-crystal XRD analysis corroborates a rather weak Ga–thf interaction since the solid-state structures of  $[Ga_8(\mu-CH_2)_{12}(thf)_4]$  (4) and  $[Ga_8(\mu-CH_2)_{12}(thf)_5]$  (5) display only partial thf coordination (Figure 2).



Figure 2. Crystal structures 4 (A) and 5 (B). Atomic displacement parameters set at 50% probability. Hydrogen atoms and the disorder in coordinated thf molecules have been omitted for clarity. For selected interatomic distances and angles, see supporting information.

# COMMUNICATION

Thf coordination leads to structural distortions of the cage motif disclosed for unsolvated compound **2**. The coordinated thf molecules in **3**, **4**, and **5** get slowly displaced at glovebox atmosphere and can be evaporated completely under reduced pressure [Figure S13].

The ease of donor-mediated interconversion of Ga6 and Ga8 methylene cages involving Ga-C bond disruption and formation, respectively, seems remarkable. To gain further insights into this process and the relative stabilities of the different oligomers in dependence of donor solvent coordination, density functional theory (DFT) calculations were carried out. They revealed that in the absence of thf, the larger Ga<sub>8</sub> oligomers are clearly more stable than the Ga<sub>6</sub> cages:  $\Delta E$  = +226 kJ/mol and  $\Delta G(298 \text{ K})$  = +175 kJ/mol for the conversion of three Ga8 into four Ga6 oligomers. However, the smaller cages should become more favorable in the case of thf coordination, as more donor molecules in total can now be bound by gallium atoms: Whereas in 3 all gallium atoms were coordinated by thf, only partial coordination was observed for the larger cages 4 and 5. Interestingly, the additional bonds formed and the concomitant loss in entropy balance each other out, and the computed value of  $\Delta G$  (+4 kJ/mol at 298 K) for the conversion of 5 into 3 (for comparison,  $\Delta E = -400$ kJ/mol) points to an equilibrium at room temperature. At lower temperature, the equilibrium shifts towards the smaller cage (e.g.,  $\Delta G = -129$  kJ/mol at 200 K), which is in-line with the lowtemperature NMR results. Replacing thf by the stronger donor pyridine renders the Ga6 cage the preferred species at room temperature (cf., NMR spectra and solid-state structures of the pyridine adduct  $[Ga_6(\mu-CH_2)_9(pyr)_6]$  (7) and its partial decomposition product  $[Ga_5(\mu-CH_2)_7(CH_3)(pyr)_5]$  (8) in the supplementary material). It is noteworthy, that the calculated thermochemical data ( $\Delta E = -464$  kJ/mol,  $\Delta G(298$  K) = -111 kJ/mol) suggest, that this is only partly due to stronger bonds forming between the solvent molecules and the gallium atoms. To a larger extent, it is a consequence of a lower entropy contribution of the free pyridine ligands, which are more rigid than their thf counterparts. Finally, in order to understand the observed partial coordination of the Ga<sub>8</sub> oligomer, we computed the changes in energy and free enthalpy for the successive coordination of 2 by thf. The values for  $\Delta E$  range from -70 to -45 kJ/mol (coordination of the first and last thf, respectively). Due to entropy losses, the differences in free energy at 298 K, however, are considerably lower (-27 and +11 kJ/mol, respectively).  $\Delta G$  for binding a sixth or seventh thf donor are less than -5 kJ/mol and explain the partial coordination pattern observed for the crystal structures of 4 and 5. Packing effects can therefore be ruled out as a potential cause and partial coordination might also be prevalent in solution.

Treating the supernatant of the initial reaction mixture with another eight equivalents of [GaMe<sub>3</sub>] at 130 °C generated additional **2** in about the same yields. Since this procedure can be repeated several times, an elusive intermediate capable of promoting the "pseudocatalytic" transformation of [GaMe<sub>3</sub>] into **2** persists after each cycle. Fortunately, prolonged thermal treatment of the supernatant without addition of [GaMe<sub>3</sub>] afforded reproducibly colorless crystals of the bimetallic rare-earth metallocene gallium methylene complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>6</sub>Ln<sub>3</sub>(µ<sub>3</sub>-CH<sub>2</sub>)<sub>6</sub>Ga<sub>9</sub>(µ-CH<sub>2</sub>)<sub>9</sub>] (Ln = Lu (**6**<sup>Lu</sup>); Y (**6**<sup>Y</sup>); Figure 3; compound **6**<sup>Y</sup> behaves in complete analogy to **6**<sup>Lu</sup>, *cf.*, supplementary material).

Compound 6<sup>Lu</sup> was identified as a crucial intermediate in the formation of 2, since it converts excessive [GaMe3] to 2 at 130 °C within 3 days (87%, Scheme 1). Even at ambient temperature compound 6<sup>Lu</sup> slowly extrudes 2 in the presence of [GaMe<sub>3</sub>], release accompanied by the of starting material  $[(C_5Me_5)_2Lu(\{\mu-Me\}_2GaMe_2)]$  (1<sup>Lu</sup>), as evidenced by NMR spectroscopy [Figure S6]. Monitoring compound 6<sup>Lu</sup> in the presence of excessive [GaMe<sub>3</sub>] by NMR spectroscopy revealed spectral data very similar to those achieved when examining the transformation of [GaMe3] to compound 2 promoted by  $[(C_5Me_5)_2Lu(\{\mu-Me\}_2GaMe_2)]$  (1<sup>Lu</sup>). This suggests that the reactive intermediate is in fact an addition product of 6<sup>Lu</sup> and [GaMe<sub>3</sub>] (Scheme 1).

Single-crystal XRD analysis of complex 6<sup>Lu</sup> disclosed its solidstate structure (Figure 3), which can be described as a highly aggregated anionic [(µ<sub>3</sub>-CH<sub>2</sub>)<sub>6</sub>Ga<sub>9</sub>(µ-CH<sub>2</sub>)<sub>9</sub>]<sup>3-</sup> core stabilized by three cationic [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Lu]<sup>+</sup> entities. The [(µ<sub>3</sub>-CH<sub>2</sub>)<sub>6</sub>Ga<sub>9</sub>(µ-CH<sub>2</sub>)<sub>9</sub>]<sup>3-</sup> core unit comprises three staggered six membered [Ga<sub>3</sub>(µ-CH<sub>2</sub>)<sub>3</sub>] rings interconnected by µ3-Ga2Lu-bridging methylene units involving the flanking rare-earth metallocene units. Comparably to 3, the outer rings adopt a chair conformation with gallium atoms in distorted trigonal planar geometry. In contrast, the central ring system exhibits a planar arrangement with gallium atoms in a distorted tetrahedral coordination environment. Consequently, the 3-coordinate gallium atoms display Ga-C bond lengths (1.961(6), 1.973(6), 1.972(6) Å) comparable to compound 2 whereas all 4coordinate gallium atoms exhibit longer Ga-C distances (Ga-(µ-CH<sub>2</sub>) = 2.008(7), Ga-(µ<sub>3</sub>-CH<sub>2</sub>) = 2.125(6) Å) similar to those reported for [GaMe<sub>4</sub>]<sup>-</sup> entities.<sup>[25]</sup> The Lu-(methylene) distances of 2.510(6) Å are considerably shorter than the Lu–Me bond lengths of the starting material  $[(C_5Me_5)_2Lu(\{\mu-Me\}_2GaMe_2)]$  (1<sup>Lu</sup>) (av. 2.614 Å) [Figure S35] which is attributable to the increased negative charge at the methylene carbon atoms.



**Figure 3.** Crystal structure of  $6^{Lu}$ . Atomic displacement parameters set at 50% probability in metal methylene/methylidene chemistry. For selected interatomic distances and angles, see supporting information.

# COMMUNICATION

In contrast to homoleptic gallium methylene 2, compound 6<sup>Lu</sup> is insoluble in  $d_{\theta}$ -thf but dissolved to a minor extent when adding 4-dimethylaminopyridine (DMAP) to the corresponding suspension in  $d_{8}$ -thf. The data achieved by NMR spectroscopy analysis of  $6^{Lu}$  in  $d_{\beta}$ -thf are consistent with the composition in the solid state [Figure S14]. The [(µ<sub>3</sub>-CH<sub>2</sub>)<sub>6</sub>Ga<sub>9</sub>(µ-CH<sub>2</sub>)<sub>9</sub>] core structure of  $6^{Lu}$  is evidenced by <sup>1</sup>H NMR resonances at  $\delta$  0.25 (d,  ${}^{2}J_{H,H}$  = 9.3 Hz, 6H), -0.75 (d,  ${}^{2}J_{H,H}$  = 9.3 Hz, 6H), -0.99 (s, 12H) and -1.35 ppm (s, 6H). Similarly as found for compound 2, the equatorial and axial arrangements of the protons at C13 give rise to doublet resonance signals while the protons at C14 and C15 perceive a symmetrical environment and show singlet resonance signals. However, compound  $\mathbf{6}^{Lu}$  is not stable in solution and decomposes slowly by forming 3 and other products [Figure S15]. Further analysis of compounds 2 and 6<sup>Lu</sup> in the solid state was performed by means of cross polarization magic angle spinning (CP-MAS) NMR spectroscopy. The <sup>13</sup>C CP/MAS NMR spectrum of **2** exhibits a very broad singlet at  $\delta$  28 ppm assigned to the methylene carbon atoms [Figure S12]. The line broadening may originate from a strong quadrupolar coupling caused by both NMR-active isotopes of gallium (69Ga and 71Ga).[26] In a similar vein, the <sup>13</sup>C CP-MAS NMR spectrum of 6<sup>Lu</sup> revealed very broad methylene resonances at  $\delta$  18 ppm and –4 ppm in addition to the signals of the C<sub>5</sub>Me<sub>5</sub> ligands at δ 116 ppm and 12 ppm [Figure S16]. The absence of gallium methyl moieties was verified by deuterolysis experiments of compounds 2 and 6<sup>Lu</sup> [Figure S28].

The olefination of carbonyl moieties is a characteristic reaction of Schrock-type metal alkylidene compounds. This prompted us to study the reactivity of gallium methylene compounds **2** and **6**<sup>Lu</sup> toward 9-fluorenone. Treating **2** with two equivalents 9-fluorenone at ambient temperatures in *d*<sub>8</sub>-thf solutions resulted in complete conversion to 9-methylidene-fluorene within 5 days [Figure S29], while upon heating to 80 °C the reaction was nearly complete after two hours [Figure S30]. Due to the insolubility of compound **6**<sup>Lu</sup> in *d*<sub>8</sub>-thf olefination of 9-fluorenone required more forcing conditions. Hence, 9-methylidene-fluorene could be detected in the corresponding <sup>1</sup>H NMR spectra only after heating the sample to 130 °C for three days, besides other products [Figure S31]. Clearly, gallium methylene compounds are prone to olefination reactions.

Encouraged by the existence of 2 we wondered whether the original pyrolysis protocol described by Ziegler et al.<sup>[8]</sup> would also be viable to transfer [GaMe<sub>3</sub>] into 2. Indeed, heating neat [GaMe<sub>3</sub>] to 280 °C for 42 hours led to the formation of trackable amounts of 2 (~1%) next to unreacted [GaMe3], according to <sup>1</sup>H NMR measurements [Figure S4]. In contrast, Ziegler et al. could not isolate the analogous aluminum compound upon heating [AIMe3]2 to temperatures up to 235 °C. Instead mixed aluminum [methylmethylene-methine-carbide] compounds or aluminum carbide [Al<sub>4</sub>C<sub>3</sub>] were achieved.<sup>[27]</sup> Certainly, [Al<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>]<sub>n</sub> would be a reasonable intermediate but is prone to further degradation under that harsh conditions.<sup>[28]</sup> Since gallium carbide is presumed to be thermodynamically unstable  $^{[29]}$  pyrolysis of  $[Ga_8(\mu\text{-}CH_2)_{12}]$  is, therefore, much more disfavored. Additionally, formation of 2 may benefit from the increased covalent character of the Ga-C bond compared to the AI-C bond owing to a decreased difference of the electronegativities.

The present findings on oligomeric gallium methylenes show that rare-earth metal alkyl complexes display efficient promotors for methyl group deprotonation being capable of both stabilizing and transferring methylene moieties. The ease of Ga–C(methylene) bond disruption and formation might contribute to a better understanding of the occurrence of multiple methylene insertions on gallium-rich GaAs(100) surfaces and open new avenues for gallium as a promotor metal in Fischer-Tropsch catalysis.<sup>[30]</sup>

#### Acknowledgements

We thank the German Science Foundation (Grant AN 238/15-2) for funding.

#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords**: gallium • methylidene • C–H bond activation • lutetium • yttrium

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# COMMUNICATION

#### Entry for the Table of Contents

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Rare-earth metal-mediated cascade C–H bond activation of trimethylgallium gives access to the first molecular homoleptic metal methylene complex, engaging in a reversible  $[Ga_8(\mu-CH_2)_{12}]/[Ga_6(\mu-CH_2)_9]$  oligomer switch.

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Page No. – Page No.

Gallium Methylene