

## Sandwich Complexes | Hot Paper |

## Stack by Stack: From the Free Cyclopentadienylgermanium Cation Via Heterobimetallic Main-Group Sandwiches to Main-Group Sandwich Coordination Polymers

Marcel Schorpp and Ingo Krossing\*<sup>[a]</sup>

**Abstract:** Heterobimetallic cationic sandwich complexes  $[M(\mu\text{-Cp})M'\text{Cp}]^+$  of group 13 ( $M = \text{Ga}, \text{In}$ ) and group 14 ( $M' = \text{Ge}, \text{Sn}$ ) elements have been prepared as  $[\text{WCA}]^-$  salts ( $\text{WCA} = \text{Al}(\text{OR}^f)_4$ ;  $\text{OR}^f = \text{OC}(\text{CF}_3)_3$ ). Their molecular structures include free apical gallium or indium atoms. The sandwich complexes were formed in the reactions of  $[\text{M}(\text{HMB})]^+$   $[\text{WCA}]^-$  ( $\text{HMB} = \text{C}_6\text{Me}_6$ ) with the free metallocenes  $[\text{M}'\text{Cp}_2]$ . Their structures are related to known stannocene and stannocenium salts; the unprecedented germanium analogues,

namely the free germanocenium cation  $[\text{GeCp}]^+$  and the corresponding triple-decker complex cation  $[\text{CpGe}(\mu\text{-Cp})\text{GeCp}]^+$ , are described herein. By variation of the reaction conditions, these sandwich complexes can be transformed into the group 13/14 mixed cationic coordination polymer  $[\{\text{In}(\text{HMB})(\mu\text{-SnCp}_2)\}_n][\text{WCA}]_n$ . This polymeric chain motif was also successfully replicated by the synthesis of complexes  $[\{\text{Ga}/\text{In}(\text{HMB})(\mu\text{-FeCp}_2)\}_n][\text{WCA}]_n$  containing  $\text{FeCp}_2$  as a bridging ligand.

## Introduction

The stabilisation of highly reactive and subvalent main-group compounds is a topic of great current interest, often realised by kinetic stabilisation imparted by sterically demanding ligand frameworks. Yet, the complexity of the employed ligand system is often proportional to the novelty of the aimed-for compound.<sup>[1]</sup> The cyclopentadienide ( $\text{Cp}^-$ ) ligand and the more electron-rich alkyl-substituted  $\text{Cp}^x$  derivatives represent exceptions to this generalised observation. As anionic  $6\pi$  aromatics, they allow for the isolation of a plethora of subvalent neutral<sup>[2]</sup> and cationic<sup>[3]</sup> p-block compounds with often undisturbed  $\eta^5$ -coordination modes. Due to their rich coordination chemistry, the following will focus on the most prominent archetypes of this ligand system, that is, the parent  $\text{Cp}^-$  and permethylated cyclopentadienide  $\text{Cp}^{*-}$ , although sterically more demanding  $\text{Cp}^{\text{R}-}$  residues bearing, for example, phenyl, isopropyl, *tert*-butyl moieties, have attracted increasing attention.<sup>[4]</sup> An overview of the known examples of homoleptic neutral and cation-

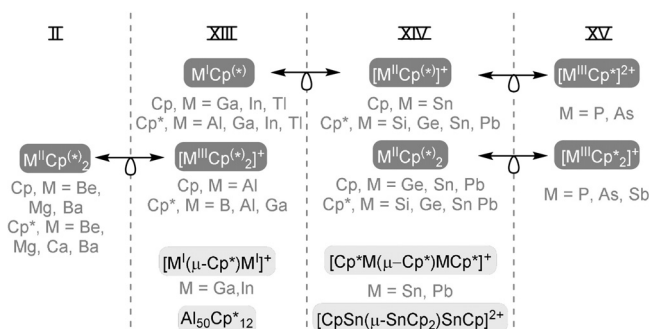
ic  $\text{Cp}^-$  and  $\text{Cp}^{*-}$  compounds involving elements from groups 13–15 is shown in Scheme 1.

By using a specialised reactor, Schnepf and Schnöckel generated the first structurally authenticated subvalent Al and Ga halide complexes, which were used in the synthesis of subvalent clusters.<sup>[5]</sup> With  $\text{Cp}^-$  and especially  $\text{Cp}^{*-}$ , the subvalent metal–metal-bonded clusters  $[\text{M}(\text{Cp}^x)]_n$  ( $M = \text{Al}$ ,  $n = 4$ ;  $M = \text{Ga}$ ,  $n = 6$ )<sup>[6]</sup> were accessed for the first time, culminating in the unique metalloid cluster  $\text{Al}_{50}(\text{Cp}^*)_{20}$ .<sup>[7]</sup> The compound  $\text{InCp}$  includes a polymeric solid-state structure, and its reactivity and coordination behaviour have rarely been reported.<sup>[8]</sup> In contrast to the related metal alkyls, silyls and amides, the  $[\text{M}(\text{Cp}^x)]_n$  oligomers are in equilibrium with their monomer  $\text{M}(\text{Cp}^x)$ .<sup>[9]</sup> Thus,  $[\text{Ga}(\text{Cp}^*)]_6$  is used as a precursor for the introduction of monomeric  $\text{GaCp}^*$  moieties. Therefore, simpler routes to the corresponding  $[\text{MCp}^*]_n$  aggregates needed to be developed.<sup>[10,11]</sup> Group 13 metallocenes were subsequently used to generate many transition-metal or main-group coordination com-

[a] Dr. M. Schorpp, Prof. Dr. I. Krossing  
Institut für Anorganische und Analytische Chemie and  
Freiburger Materialforschungszentrum (FMF)  
Albert-Ludwigs-Universität Freiburg  
Albertstr. 21, 79104 Freiburg (Germany)  
E-mail: krossing@uni-freiburg.de

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**Scheme 1.** Schematic overview of a selection of known homoleptic neutral and cationic  $\text{Cp}^-$  and  $\text{Cp}^{*-}$  compounds of the p-block elements and the global group 2 analogues.

pounds, as well as small clusters, including  $\text{MCp}^*$  as a ligand.<sup>[12]</sup> Cyclopentadienides also stabilise the highly Lewis acidic cations  $[\text{M}^{\text{III}}\text{Cp}^{(*)}_2]^+$  ( $\text{M} = \text{B}, \text{Al}, \text{Ga}$ ) with varying binding modes from  $\eta^1, \eta^3/\eta^5$  ( $\text{M} = \text{B}, \text{Ga}$ ) to  $\eta^5, \eta^5$  ( $\text{M} = \text{Al}$ ).<sup>[13]</sup> The isolobal neutral alkaline-earth metal analogues  $[\text{MCp}^{(*)}_2]$  ( $\text{Cp}$ :  $\text{M} = \text{Be}$ ,<sup>[14]</sup>  $\text{Mg}$ ,<sup>[15]</sup>  $\text{Ba}$ ,<sup>[16]</sup>  $\text{Cp}^*$ :  $\text{M} = \text{Be}$ ,<sup>[17]</sup>  $\text{Mg}$ ,<sup>[18]</sup>  $\text{Ca}$ ,  $\text{Ba}$ <sup>[19]</sup>) are also known and show an increasing tendency for oligomerisation when descending the group.<sup>[20]</sup> For group 14 elements, neutral metallocenes ( $[\text{MCp}^{(*)}_2]$ :  $\text{M} = \text{Si}$ ,<sup>[21]</sup>  $\text{Ge}$ ,<sup>[22,23]</sup>  $\text{Sn}$ ,<sup>[23]</sup>  $\text{Pb}$ <sup>[24]</sup>), metallocenium cations ( $[\text{MCp}^{(*)}]^+$ :  $\text{M} = \text{Si}$ ,<sup>[25]</sup>  $\text{Ge}$ ,<sup>[26]</sup>  $\text{Sn}$ ,  $\text{Pb}$ <sup>[27]</sup>) and even homometallic triple-decker metallocenium cations ( $[\text{Cp}^*\text{M}(\mu, \eta^5: \eta^5\text{-Cp}^*)\text{MCp}^{(*)}]^+$ :  $\text{M} = \text{Sn}, \text{Pb}$ <sup>[27]</sup>) are known. For the parent unsubstituted  $\text{Cp}^-$  ligand, the coordination chemistry is generally much less developed, as both the electronic as well as the steric stabilisation provided by this ligand are inferior, which makes  $\text{Cp}^-$ -substituted compounds much more reactive. For group 14 elements, apart from the neutral metallocenes ( $[\text{MCp}_2]$ :  $\text{M} = \text{Ge}$ ,<sup>[28]</sup>  $\text{Sn}$ ,<sup>[24]</sup>  $\text{Pb}$ <sup>[29]</sup>), only  $[\text{SnCp}]^+$  and the corresponding quadruple-decker complex  $[\text{Sn}_3\text{Cp}_4]^{2+}$  are known.<sup>[30]</sup> For group 15 elements, only the  $\text{Cp}^{*-}$ -substituted highly Lewis acidic metallocenium monocations ( $[\text{MCp}^{(*)}_2]^+$ :  $\text{M} = \text{P}$ ,<sup>[31]</sup>  $\text{As}$ ,  $\text{Sb}$ <sup>[32]</sup>) and dications ( $[\text{MCp}^{(*)}]^{2+}$ :  $\text{M} = \text{P}$ ,<sup>[33]</sup>  $\text{As}$ <sup>[34]</sup>) have been reported, whereas the  $\text{Cp}^-$ -substituted congeners are unknown.

### Isolobal analogies

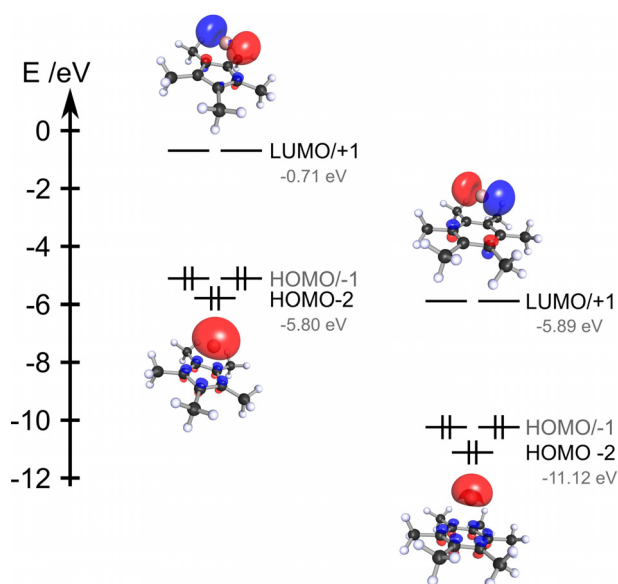
The  $\text{Cp}^-$  ligand is isoelectronic with benzene, and hexamethylbenzene (HMB) corresponds to  $\text{Cp}^{*-}$ . Similarly to  $[\text{M}(\eta^5\text{-Cp}^{(*)})]^{(n-1)+}$  ( $\text{M} = \text{main-group element}$ ,  $n = \text{formal oxidation state}$ ), the corresponding  $[\text{M}(\eta^6\text{-C}_6\text{R}_6)]^{(n-1)+}$  units ( $\text{R} = \text{H}, \text{Me}$ ) are *nido* clusters, sharing an isolobal relationship.<sup>[35]</sup> Yet, such compounds formally exchanging  $\text{Cp}^{(*)-}$  for an arene are scarce. The cationic group 2 arene complexes of Harder and Hill and co-workers represent one example.<sup>[36]</sup> Our recently developed dicationic complexes  $[\text{M}(\text{HMB})]^{2+}$  ( $\text{M} = \text{Ca}, \text{Sr}$ ) as *o*-difluorobenzene (*o*DFB) solvates can be directly compared with the corresponding  $\text{Cp}^{*-}$  complexes.<sup>[37]</sup> However, the arene/ $\text{Cp}^{(*)-}$  structural relationships are most evident when comparing neutral group 13  $\text{Cp}^{*-}$  complexes with the cationic arene complexes, for example,  $[\text{Ga}(\eta^5\text{-Cp}^*)]$  versus  $[\text{Ga}(\eta^6\text{-HMB})]^+$ . The first group-13 arene complexes were reported by Schmidbaur et al., formed by the reaction between mixed-valence  $\text{Ga}[\text{Ga}^{\text{III}}\text{X}_4]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and neutral arenes.<sup>[38]</sup> However, these always showed close contact with the respective tetrahalogallate counterion.<sup>[39]</sup> Only recently we isolated the first subvalent, truly free monoarene complexes as WCA ( $\text{WCA} = \text{Al}(\text{OR}^{\text{F}})_4$ ;  $\text{OR}^{\text{F}} = \text{OC}(\text{CF}_3)_3$ ) salts,  $[\text{M}(\text{HMB})][\text{Al}(\text{OR}^{\text{F}})_4]$  ( $\text{M} = \text{Ga}$  (**1**),  $\text{In}$  (**2**)), by direct oxidation of the elemental metals with stable  $[\text{arene}]^+$  radical-cation solutions.<sup>[40]</sup> With these in hand, we were interested in exploring the coordination chemistry of  $[\text{M}(\text{HMB})]^+$ , that is, comparing the similarities and differences with the group 13  $\text{Cp}^{*-}$  compounds. For  $[\text{MCp}^*]$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ), widespread applications as Lewis bases<sup>[41–43]</sup> with coordination modes comparable to CO but with  $\sigma$ -donating capabilities exceeding even those of the carbonyl ligand have been reported. Because the  $[\text{M}(\text{HMB})]^+$  cations represent their cationic equivalent, we reasoned that they could potentially act as cationic

Lewis bases related to  $\text{NO}^+$ , which is isolobal with CO. Similar relations have been reported for N-heterocyclic phosphonium ions, isolobal with N-heterocyclic carbenes and with a coordination behaviour closely related to  $\text{NO}^+$ .<sup>[44]</sup>

## Results and Discussion

### Orienting reactions to use $[\text{M}(\text{HMB})]^+$ as $\text{NO}^+$ -like Ligands

To probe the potential Lewis basicity of the complex cations  $[\text{Ga}(\text{HMB})]^+$  in **1** and  $[\text{In}(\text{HMB})]^+$  in **2**, the salts were treated with a variety of common Lewis acids **A** (e.g.,  $\text{B}(\text{C}_6\text{F}_5)_3$ ) or in situ generated Lewis acidic transition-metal fragments (e.g.,  $[\square\text{-Fe}(\text{CO})_4]$ ,  $[\square\text{-W}(\text{CO})_5]$ ). All of the reagents **A** employed have shown precedence for the formation of  $\text{A-MCp}^*$  Lewis acid–base adducts.<sup>[41–43]</sup> However, in all the reactions between **1** or **2** and **A**, the starting materials were re-isolated, as proven by NMR and single-crystal XRD (scXRD) analyses. Comparison of the frontier orbital energies of the donor sites in cationic  $[\text{Ga}(\text{HMB})]^+$  and neutral  $\text{GaCp}^*$  underlined this experimental finding: All the frontier orbitals of the former are lower in energy than those of the latter, due to the positive charge. Thus, the metal-centred lone-pair donor orbital (HOMO–2) is 5.3 eV lower in energy in  $[\text{Ga}(\text{HMB})]^+$  than in  $\text{GaCp}^*$ , and confirms its observed negligible Lewis basicity. By contrast, the orbital energies and spatial projections shown in Figure 1 indicate favourable acceptor properties of  $[\text{M}(\text{HMB})]^+$ . We therefore set out to synthesise so far unknown heteroleptic group 13 complex salts.



**Figure 1.** Comparison of the frontier orbitals of  $\text{GaCp}^*$  and  $[\text{Ga}(\text{HMB})]^+$  calculated at the BP86-D3(BJ)/def-SV(P) level of theory.

## Using $M^+$ in $[M(\text{HMB})]^+$ ( $M = \text{Ga}, \text{In}$ ) as $\pi$ acceptors for metallocene ligands

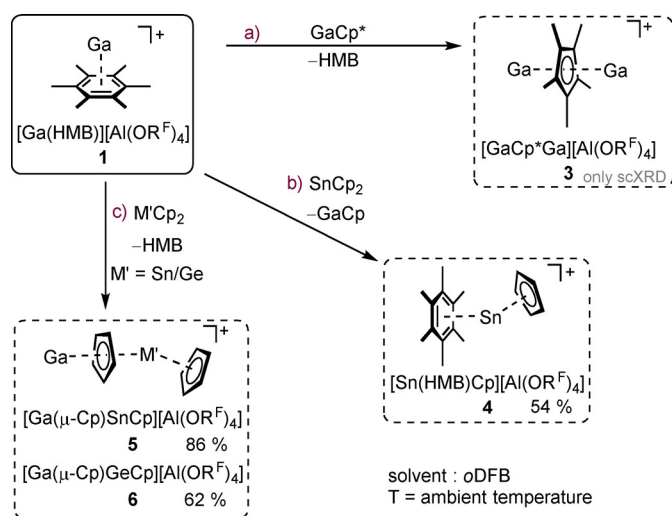
### Syntheses

As a first attempt, **1** was combined with  $\text{GaCp}^*$  to potentially yield a Ga–Ga-bonded Lewis acid–base adduct (Scheme 2a).  $\text{GaCp}^*$  was generated in situ by the reaction of  $[\text{Ga}(\text{PhF})_n][\text{Al}(\text{OR}^F)_4]$  ( $n = 2, 3$ ) with  $\text{LiCp}^*$  followed by filtration to separate the product from the sparingly soluble  $\text{Li}[\text{Al}(\text{OR}^F)_4]$ . However, both, experimental and DFT studies showed that  $\text{GaCp}^*$  coordination by the Lewis basic Ga atom is less favoured than coordination by the negatively polarised aromatic  $\text{Cp}^*$  moiety. Thus, the reaction with  $[\text{Ga}(\text{HMB})]^+$  proceeded by substitution of the neutral HMB to yield the inverse sandwich cation  $[\text{GaCp}^*\text{Ga}][\text{Al}(\text{OR}^F)_4]$  (**3**; see Scheme 2a). The same cation is part of the  $[\text{B}(\text{Ar}^F)_4]^-$  ( $\text{Ar}^F = \text{C}_6\text{H}_3(\text{CF}_3)_2$ ) salt developed by Fischer and co-workers.<sup>[45]</sup> Following these findings, we started to investigate the underdeveloped coordination chemistry of  $M^+/[M(\text{HMB})]^+$  ( $M = \text{Ga}, \text{In}$ ) with unsubstituted Cp units in other metallocenes, specifically the neutral group 14 metallocenes  $[\text{GeCp}_2]$  and  $[\text{SnCp}_2]$ , because they exhibit a  $\sigma$ -donor-type lone pair and a  $\pi$ -donor-type  $\text{Cp}^-$  moiety. Depending on the conditions, two reaction products, **4** and **5**, were isolated from the reaction between **1** and  $[\text{SnCp}_2]$ . Firstly, the HMB-stabilised stannocenium cation salt  $[\text{Sn}(\text{HMB})\text{Cp}][\text{Al}(\text{OR}^F)_4]$  (**4**) was isolated from the in vacuo concentrated reaction mixture in oDFB (see Scheme 2b). Apparently, salt **4** is formed by the abstraction of a  $\text{Cp}^-$  ring by  $\text{Ga}^+$  followed by evaporation of the formed monomeric  $\text{GaCp}$ , which is known to be rather volatile.<sup>[6]</sup> In the absence of a vacuum and by layering of the reaction mixture with apolar pentane, the heterobimetallic sandwich cation salt  $[\text{Ga}(\mu\text{-Cp})\text{SnCp}][\text{Al}(\text{OR}^F)_4]$  (**5**) formed (Scheme 2c).

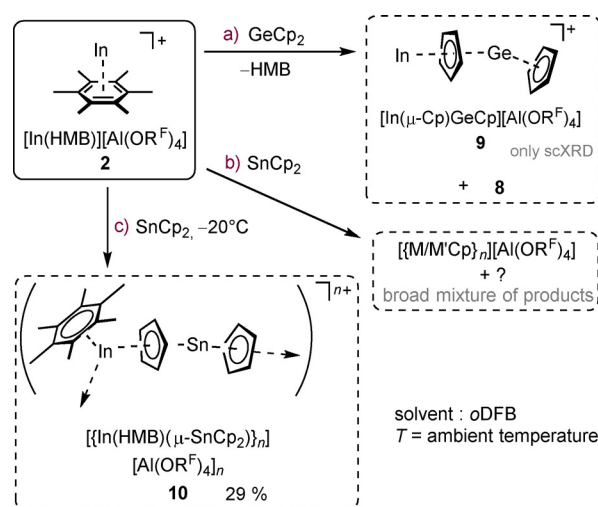
Thus, in direct competition, unexpectedly,  $\text{GaCp}$  appears to be a better  $\pi$ -donor ligand towards  $[\text{Sn}(\text{Cp})]^+$  than free HMB. The analogous reaction with **1** and  $[\text{GeCp}_2]$  resulted in the iso-

lation of the salt  $[\text{Ga}(\mu\text{-Cp})\text{GeCp}][\text{Al}(\text{OR}^F)_4]$  (**6**; Scheme 2c). The structural data suggest considerable distortion of the neutral  $M'\text{Cp}_2$  ( $M' = \text{Ge}, \text{Sn}$ ) moiety in **5** and **6** as a result of the coordination to  $\text{Ga}^+$ . By changing to the corresponding indium salt **2** as the starting material, we expected much less distortion and possibly the formation of higher aggregates. In addition, indium salt **2** was expected to be less likely to abstract a  $\text{Cp}^-$  moiety from the parent group 14 metallocene, while possibly retaining both HMB and the metallocene in the coordination sphere as weakly bound ligands. However, the reaction between **2** and  $[\text{M}'\text{Cp}_2]$  at ambient temperature revealed widely different reactivity patterns compared with **1**. For example, the reaction between **2** and  $[\text{GeCp}_2]$  gave a product mixture in which the only identifiable indium-containing product was the sandwich cation  $[\text{In}(\mu\text{-Cp})\text{GeCp}][\text{Al}(\text{OR}^F)_4]$  (**9**) from (Scheme 3a). By contrast, the reaction between **2** and  $[\text{SnCp}_2]$  at  $-20^\circ\text{C}$  followed by crystallisation at low temperature (Scheme 3c) gave a defined reaction product, the cationic multi-decker sandwich coordination polymer  $[\{\text{In}(\text{HMB})(\mu\text{-SnCp}_2)\}_n][\text{Al}(\text{OR}^F)_4]_n$  (**10**), which served as inspiration for the work discussed later below.

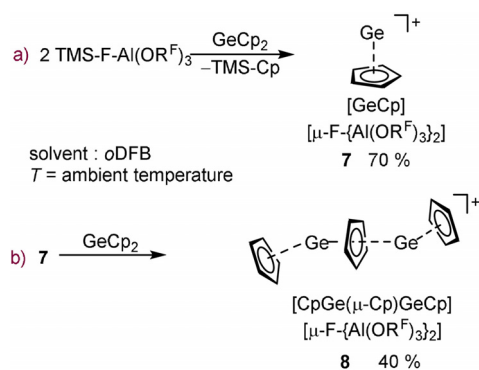
The reaction with  $[\text{GeCp}_2]$  (Scheme 3a) also furnished the unprecedented triple-decker cation  $[\text{CpGe}(\mu\text{-Cp})\text{GeCp}][\mu\text{-F}\{\text{Al}(\text{OR}^F)_3\}_2]$  (**8**) as an inseparable side product. We therefore set out to selectively synthesise **8**, since  $[\text{GeCp}_2]$  currently represents the only structurally characterised compound that includes the  $\text{GeCp}$  unit. For this, the unprecedented free cation  $[\text{GeCp}]^+$  was accessed by the reaction of 2 equivalents of the strong silylium “ion-like” Lewis acid  $\text{TMS-F-Al}(\text{OR}^F)_3$  ( $\text{TMS} = \text{Me}_3\text{Si}$ ) with  $[\text{GeCp}_2]$ , which resulted in the separation of  $\text{TMS-Cp}$  and the formation of  $[\text{GeCp}][\mu\text{-F}\{\text{Al}(\text{OR}^F)_3\}_2]$  (**7**) as the major product (Scheme 4a).<sup>[46]</sup> Further reaction of **7** with  $[\text{GeCp}_2]$  (Scheme 4b) afforded the corresponding triple-decker cation  $[\text{CpGe}(\mu\text{-Cp})\text{GeCp}][\mu\text{-F}\{\text{Al}(\text{OR}^F)_3\}_2]$  (**8**).



**Scheme 2.** Reactivity of **1** towards  $\text{GaCp}^*$  (a),  $[\text{SnCp}_2]$  (b,c) and  $[\text{GeCp}_2]$  (c). Unless explicitly stated otherwise, all reactions were performed at ambient temperature with oDFB as solvent.



**Scheme 3.** Reactivity of **2** towards  $[\text{GeCp}_2]$  (a) and  $[\text{SnCp}_2]$  (b,c). Unless explicitly stated otherwise, all reactions were performed at ambient temperature with oDFB as solvent.

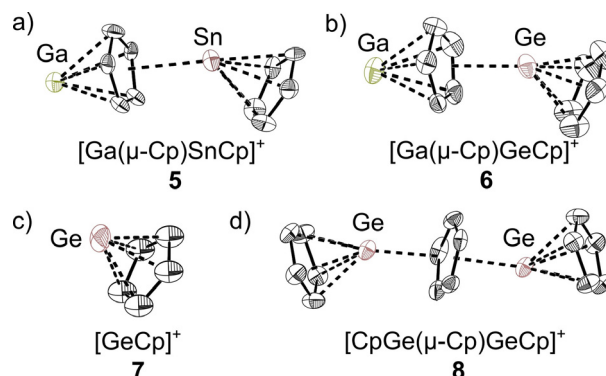


**Scheme 4.** Synthesis of the unprecedented germanocenium cation  $[\text{GeCp}]^{\text{T}+}$  (a) and triple-decker germanium sandwich cation  $[\text{CpGe}(\mu\text{-Cp)GeCp}]^{\text{T}+}$  (b). Unless explicitly stated otherwise, all reactions were performed at ambient temperature with oDFB as solvent.

### Molecular structures of 3–9

The structure of the inverse sandwich cation  $[\text{GaCp}^*\text{Ga}][\text{Al(OR}^{\text{F}}\text{)}_4]$  (**3**) is closely related to the known  $[\text{B(Ar}^{\text{F}}\text{)}_4]^-$  ( $\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3(\text{CF}_3)_2$ ) salt<sup>[45]</sup> and is reported only in the Supporting Information (Figure S16 and Table S1). Crystals from the in vacuo concentrated reaction mixture of **1** and  $(\text{SnCp}_2)$  (Scheme 2b) revealed the HMB-stabilised stannocenium cation salt  $[\text{SnCp}(\text{HMB})][\text{Al(OR}^{\text{F}}\text{)}_4]$  (**4**; cf. the known toluene adduct  $[\text{SnCp}(\text{C}_7\text{H}_8)][\text{Al(OR}^{\text{F}}\text{)}_4]$ <sup>[30]</sup>). Because all crystals showed an inherent superstructure at 100 K, data had to be collected at 170 K, which induced strong disorder such that the refinement stopped at  $wR2 = 0.32$ . Thus, the data on **4** is only included in the Supporting Information (Figure S17 and Table S2). Layering the reaction mixture containing **1** and  $[\text{SnCp}_2]$  with pentane yielded crystals of  $[\text{Ga}(\mu\text{-Cp)SnCp}][\text{Al(OR}^{\text{F}}\text{)}_4]$  (**5**), with coordination of  $\text{Ga}^+$  by a  $\text{Cp}^-$  moiety of  $\text{SnCp}_2$  and an apical free Ga atom (see Figure 2a and Scheme 2c). Such a structural motif is rare and only found in transition-metal-Cp fragments, for example, in  $[\text{Tl}(\mu\text{-Cp)FeCp}]^+$  or  $[\text{Tl}(\mu\text{-Cp}^{\text{B}})\text{CoCp}]$  ( $[\text{Cp}^{\text{B}}]^{2-} = [\text{C}_3\text{B}_2\text{Me}_3]^{2-}$ , pentamethylidiboroly).<sup>[47]</sup>

The cation structures can be described either as  $\text{Ga}^+$  coordinated by a neutral  $\text{SnCp}_2$  unit or as a stannocenium cation  $[\text{SnCp}]^+$  coordinated by the  $\text{Cp}^-$  moiety of  $\text{GaCp}$ . Both descriptions are viable and partly represent the nature of the obtained cation. Calculation of the partial charges by using the population analytical methods QTAIM,<sup>[48]</sup> NBO<sup>[49]</sup> or PABOON<sup>[50]</sup>



**Figure 2.** Molecular structures of the cations in a)  $[\text{Ga}(\mu\text{-Cp)SnCp}][\text{Al(OR}^{\text{F}}\text{)}_4]$  (**5**), b)  $[\text{Ga}(\mu\text{-Cp)GeCp}][\text{Al(OR}^{\text{F}}\text{)}_4]$  (**6**), c)  $[\text{GeCp}][\mu\text{-F}\{\text{Al(OR}^{\text{F}}\text{)}_3\}_2]$  (**7**) and d)  $[\text{CpGe}(\mu\text{-Cp)GeCp}][\mu\text{-F}\{\text{Al(OR}^{\text{F}}\text{)}_3\}_2]$  (**8**). Counterions and hydrogen atoms have been omitted for clarity. The thermal displacement ellipsoids were set at the 50% probability level. For **5** and **7**, only the majority component of the disordered cations is shown.

revealed consistent results for all variations of the obtained heterobimetallic sandwich cations  $[\text{M}(\mu\text{-Cp)M}^{\text{C}}\text{Cp}]^+$  ( $\text{M} = \text{Ga, In}$ ;  $\text{M}^{\text{C}} = \text{Ge, Sn}$ ; for details of the population analyses, see the Supporting Information). In **5**, for example, the splitting into formal  $\text{Ga}^+$  and  $\text{SnCp}_2$  gives atoms-in-molecules (AIM) charges of +0.60 and +0.40, whereas the alternative separation into  $\text{GaCp}$  and  $[\text{SnCp}]^+$  fragments gives AIM charges of +0.22 and +0.78, respectively. Therefore, the positive charge is delocalised over the entire molecular ion. The asymmetric unit of **5** contains two cations, both of which are disordered over two positions by a  $180^\circ$  rotation of the  $[\text{Ga}(\mu\text{-Cp)SnCp}]^+$  moiety perpendicular to the  $\text{M}-\text{M}^{\text{C}}$  axis resulting in lower precision of the bond distances. The central Sn atom closely interacts with the terminal  $\eta^5\text{-Cp}^-$  moiety with  $d_{\text{Sn-C}_{\text{avg}}} = 2.482(15) \text{ \AA}$  ( $d_{\text{Sn-C}_{\text{range}}} = 2.414(16)\text{--}2.577(11) \text{ \AA}$ ) and a Sn-centroid (ct) distance of  $d_{\text{Sn-ct,avg}} = 2.176(9) \text{ \AA}$  ( $d_{\text{Sn-ct,range}} = 2.144(8)\text{--}2.204(8) \text{ \AA}$ ; Table 1). This is  $0.23 \text{ \AA}$  shorter than the corresponding distance in neutral  $[\text{SnCp}_2]$  with  $d_{\text{Sn-ct,avg}} = 2.406 \text{ \AA}$ ,<sup>[24]</sup> only slightly longer than that in free  $[\text{SnCp}]^+$  ( $d_{\text{Sn-ct,avg}} = 2.122 \text{ \AA}$ <sup>[30]</sup>) and virtually identical to the related outer distances in  $[\text{Sn}_3\text{Cp}_4]^{2+}$  ( $d_{\text{Sn-ct,avg}} = 2.180 \text{ \AA}$ <sup>[30]</sup>). The distance between the gallium atom and the ring centroid of the bridging  $\text{Cp}^-$  moiety is, with  $d_{\text{Ga-ct2,avg}} = 2.160(8) \text{ \AA}$  ( $d_{\text{Ga-ct2,range}} = 2.162(6)\text{--}2.177(10) \text{ \AA}$ ;  $d_{\text{Ga-C}_{\text{avg}}} = 2.470(14) \text{ \AA}$ ,  $d_{\text{Ga-C}_{\text{range}}} = 2.43(2)\text{--}2.53(2) \text{ \AA}$ ), notably longer than that in the corresponding Lewis acid–base adducts formed be-

**Table 1.** Selected interatomic distances in the cations of **5–8**.

Distance [Å]		<b>5</b> $[\text{Ga}(\mu\text{-Cp)SnCp}]^+$	<b>6</b> $[\text{Ga}(\mu\text{-Cp)GeCp}]^+$	<b>7</b> $[\text{GeCp}]^+$	<b>8</b> $[\text{CpGe}(\mu\text{-Cp)GeCp}]^+$
terminal Cp	Ge/Sn- $C_{\text{range}}$	2.414(16)–2.577(11)	2.237(17)–2.360(14)	2.162(12)–2.284(10)	2.292(2)–2.424(2)
	Ge/Sn- $C_{\text{avg}}$	2.482(15)	2.290(15)	2.227(9)	2.378(2)
	Ge/Sn-ct1	2.176(9)	1.949(8)	1.884(5)	2.037(1)
bridging Cp	Ge/Sn-pl2	2.784(6)	2.646(7)	–	2.534(4)
	Ga- $C_{\text{range}}$	2.43(2)–2.53(2)	2.469(12)–2.477(12)	–	–
	Ga- $C_{\text{avg}}$	2.47(1)	2.472(13)	–	–
	Ga-ct2	2.160(8)	2.161(6)	–	–



tween GaCp and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [Cr(CO)<sub>5</sub>] ( $d_{\text{Ga-ct}} = 1.884^{[11]}$  and 1.946 Å,<sup>[51]</sup> respectively). Note that structures including GaCp without coordination of the gallium atom are unknown. Finally, the distance between the ring plane (pl) of the bridging Cp<sup>-</sup> moiety and Sn is, with  $d_{\text{Sn-pl2,avg.}} = 2.767(7)$  Å ( $d_{\text{Sn-pl2,range}} = 2.7596(9)–2.784(6)$  Å), shorter by 0.1 Å than that in the comparable [Sn<sub>3</sub>Cp<sub>4</sub>]<sup>2+</sup>.<sup>[30]</sup> Note that here the coordination deviates slightly from perfect η<sup>5</sup> coordination, hence the distance between the group 14 element and the ring plane of the bridging Cp<sup>-</sup> was chosen for discussion here and later. The two Cp<sup>-</sup> rings of the central SnCp<sub>2</sub> unit are tilted against each other by 54°, which is less acute than in free [SnCp<sub>2</sub>] (46.7°).

The same structural motif was obtained when layering the reaction mixture of **1** and [GeCp<sub>2</sub>] with pentane at ambient temperature. The molecular structure is shown in Figure 2b) and shows the coordination of Ga<sup>+</sup> by a Cp<sup>-</sup> moiety of GeCp<sub>2</sub> to give [Ga(μ-Cp)GeCp][Al(OR<sup>F</sup>)<sub>4</sub>] (**6**). The asymmetric unit of **6** contains one cation, which is located at a special position with a mirror plane. The central Ge atom in **6** again shows close interactions with the η<sup>5</sup>-bound terminal Cp<sup>-</sup>. With  $d_{\text{Ge-C,avg.}} = 2.290(15)$  Å ( $d_{\text{Ge-C,range}} = 2.237(17)–2.360(14)$  Å), they are on average 0.15 Å shorter than that in neutral [GeCp<sub>2</sub>] ( $d_{\text{Ge-C,avg.}} = 2.517(7)$  Å,  $d_{\text{Ge-C,range}} = 2.347(7)–2.730(7)$  Å).

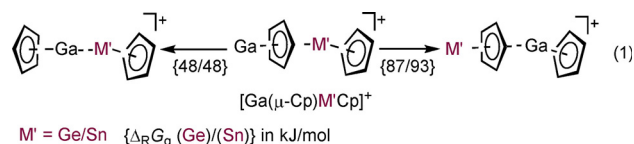
Crystals of [GeCp][μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}] (**7**) and [CpGe(μ-Cp)GeCp][μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}] (**8**) were obtained by layering the respective reaction mixtures with pentane. The cationic part of **7** is disordered over two positions. The apical Ge atom falls almost in the Cp ring plane of the second part (major orientation of the molecular structure is shown in Figure 2c; for the cation disorder, see Figure S47 in the Supporting Information), similarly to the reported molecular structure of [SnCp][μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}]<sup>[30]</sup>. Attempts to generate a quadruple-decker dication [CpGe(μ-Cp)GeCp]<sup>2+</sup> by the reaction of **7** with [GeCp<sub>2</sub>] proved unfruitful and yielded the triple-decker monocation [CpGe(μ-Cp)GeCp][μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}] (**8**; see Figure 2d). Cation **8** represents the first multi-decker germanocenium cation. Access to a quadruple-decker dication might have been futile due to crystal packing/lattice energy effects induced by the use of the larger counterion [μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}]<sup>-</sup> instead of [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup>. Comparison of the distance between Ge and the ring centroid of the terminal Cp<sup>-</sup> in **6** ( $d_{\text{Ge-ct1}} = 1.949(8)$  Å) with those for **7** ( $d_{\text{Ge-ct}} = 1.884(5)$  Å) and **8** ( $d_{\text{Ge-ct1}} = 2.037(1)$  Å) shows similar shifts to those noted above for the corresponding Sn analogues. The distances of Ga to the bridging Cp<sup>-</sup> of  $d_{\text{Ga-C,avg.}} = 2.472(13)$  ( $d_{\text{Ga-C,range}} = 2.469(12)–2.477(12)$  Å,  $d_{\text{Ga-ct2}} = 2.161(6)$  Å) in **6** are identical to those found in **5**, and the distance of Ge to the ring plane of the bridging Cp<sup>-</sup> moiety is, with  $d_{\text{Ge-pl2}} = 2.646(7)$  Å, longer by 0.1 Å than that in **8**. The tilt angle between the two Cp<sup>-</sup> moieties in **6** (44.3°) lies between those of neutral [GeCp<sub>2</sub>] (50.4°) and **8** (41.2°).

The reaction of the [In(HMB)]<sup>+</sup> complex salt **2** with [GeCp<sub>2</sub>] (Scheme 3a) led, after layering with pentane, to the above described triple-decker cation salt **8**, accompanied by the known decomposition of the [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> anion to the fluoride-bridged [μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}]<sup>-</sup> counterion,<sup>[52]</sup> and [In(μ-Cp)GeCp][Al(OR<sup>F</sup>)<sub>4</sub>] (**9**). The latter showed a superstructure and prevented refinement of the data at  $wR_2 > 0.45$  (cf. Figure S53 and Table S7 in the

Supporting Information). However, the constitution of the cationic part can clearly be assigned to the proposed species (due to the inferior quality of the data, the structural features are presented only in the Supporting Information). Similar reactivity was observed in the reaction between **2** and [SnCp<sub>2</sub>]. Crystallisation of the reaction mixture by layering with pentane resulted in at least three crystallographically inequivalent species, all of which showed heavy superstructures prohibiting generation of a satisfactory structure model, thereby allowing for only minor structural information on the analysed crystalline material. However, all of the characterised species are salts showing the presence of either [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> or [μ-F-{Al(OR<sup>F</sup>)<sub>3</sub>}]<sup>-</sup> and contain heavy-element MCp fragments in ring or chain motifs in which In and Sn are indistinguishable. Furthermore, no coordination of HMB was observed. As both free [M'Cp]<sup>+</sup> cations are stable towards the counterion, the degradation of [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>-</sup> is presumably mediated by In<sup>+</sup> in solution. This might be seen in analogy with the increased Lewis acidity of the heavier InX<sub>3</sub> compared with the lighter GaX<sub>3</sub> [ $\Delta FIA = 5$  (X = F), 24 (Cl), 34 (Br), 24 kJ mol<sup>-1</sup> (I);  $FIA = \text{fluoride ion affinity}$ ];<sup>[53]</sup> only the heavier In<sup>+</sup>/metallocene couple induces decomposition, and not the lighter couple with Ga<sup>+</sup>.

### Rationalising the observed structures by DFT methods

The structural motifs found in the heterobimetallic sandwich cations in **5**, **6** and **9** with free apical group 13 elements are unprecedented. In particular, GaCp is known as an exceptionally good σ donor, and solid-state structures including GaCp or GaCp\* without coordination at the Ga atom are scarce. Therefore, coordination of GaCp through the Ga lone-pair orbital to the group 14 element to form the M–M'-bonded species [CpGa–M'Cp]<sup>+</sup> seemed viable. However, DFT studies at the BP86-D3(BJ)/def-SV(P) level of theory showed that both M–M'-bonded (M = Ga; M' = Ge/Sn) molecular ions as well as the inverse-constituted sandwich cations [M'(μ-Cp)MCp]<sup>+</sup> are unfavourable, respectively, by a moderate  $\Delta_{\text{R}}G_{\text{gas}} = +48/48$  kJ mol<sup>-1</sup> and a much clearer  $\Delta_{\text{R}}G_{\text{gas}} = +87/+93$  kJ mol<sup>-1</sup> [see Eqn. (1)], which supports the experimental findings for this structural motif.



### NMR spectroscopic characterisation in oDFB and solution thermodynamics study by DFT

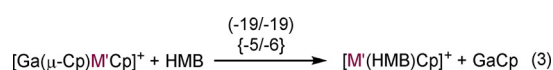
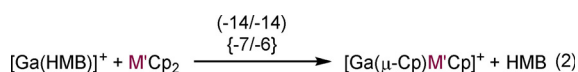
#### NMR spectra of 4–6

NMR investigation of a solution of crystalline **4** (Scheme 2b) revealed a <sup>119</sup>Sn chemical shift of  $\delta = -2380$  ppm, just between the chemical shift of a free stannocenium cation ( $\delta = -2430$  ppm)<sup>[30]</sup> and neutral stannocene ( $\delta = -2199$  ppm).<sup>[54]</sup>

The  $^1\text{H}$  NMR spectrum showed the expected 1:1 ratio between HMB and  $\text{Cp}^-$ . The NMR spectra of a reaction mixture of **1** and  $[\text{SnCp}_2]$  revealed a different species to be present in solution: the considerable downfield shift of the  $^{119}\text{Sn}$  NMR resonance to  $\delta = -2308$  ppm, comparable to that of the quadruple-decker  $[\text{Sn}_3\text{Cp}_4][\text{Al}(\text{OR}^f)_4]_2$  ( $\delta = -2318$  ppm<sup>[30]</sup>), together with the  $^{71}\text{Ga}$  NMR signal at  $\delta = -540$  ppm (cf. the signals for free GaCp,  $\delta = -708$  ppm<sup>[11]</sup> and **1**,  $\delta = -712$  ppm<sup>[40]</sup>) suggest that the sought-after coordination of  $\text{Ga}^+$  to  $[\text{SnCp}_2]$  is present in solution. However, in all the spectra, and also for the following related compounds, only one resonance corresponding to both  $\text{Cp}^-$  units was observed, which indicates the highly fluxional nature of the compounds in solution [cf. Eqn. (1) as one path for exchange]. Thus, the initially isolated **4** was presumably formed upon concentration of the reaction mixture under reduced pressure with removal of volatile GaCp. This is also supported by the NMR spectra of a dried and redissolved reaction mixture that suggested partial removal of a Cp-containing moiety (ratio  $\text{Cp}^-/\text{HMB} = 1.5:1$ ), no detectable  $^{71}\text{Ga}$  NMR resonance and an intermediate  $^{119}\text{Sn}$  NMR resonance at  $\delta = -2340$  ppm. Layering of this reaction mixture with pentane led to a mixture of crystals of **4** and **5** (SCXRD). Isolated **4** did not react with another equivalent of **1** to abstract the second Cp ring with the formation of the hypothetical dication  $[\text{Sn}(\text{HMB})_2]^{2+}$ . Furthermore, redissolved pure **5** did not liberate GaCp under reduced pressure, further supporting the nature of the GaCp moiety as bound to the  $[\text{SnCp}]^+$  subunit in solution. The experimental data for the reaction of **1** and  $[\text{SnCp}_2]$ , with the two reaction products **4** and **5**, suggest that this reaction is close to the thermodynamic equilibrium. Similar reactivity was observed for the reaction of **1** with  $[\text{GeCp}_2]$  (Scheme 2c). NMR investigation of the reaction mixture containing **6** showed a singlet resonance in the  $^{71}\text{Ga}$  NMR spectrum at  $\delta = -670$  ppm, which is in the low-field region of reported GaCp shifts. However, this is upfield-shifted by 100 ppm compared with the resonance observed from the reaction mixture of **1** with  $[\text{SnCp}_2]$ .

### Reaction energetics for 4–6 by DFT calculations

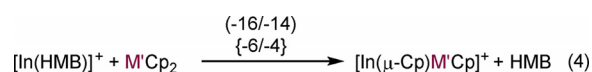
The calculated reaction thermodynamics, including the solvation energies (at the BP86-D3(BJ)/def-SV(P) level, COSMO solvation), support these conclusions. The conversions of **1** and  $[\text{M}'\text{Cp}_2]$  ( $\text{M} = \text{Ge}/\text{Sn}$ ) into the corresponding sandwich cations  $[\text{Ga}(\mu\text{-Cp})\text{M}'\text{Cp}]^+$  are exergonic by only  $\Delta_{\text{R}}G_{\text{sol}} = -7/-6$  kJ mol $^{-1}$  for the two metallocenes [Eqn. (2)], whereas the subsequent generation of the HMB-stabilised metallocenium cation is favourable by  $\Delta_{\text{R}}G_{\text{sol}} = -5/-6$  kJ mol $^{-1}$  [Eqn. (3)].



Therefore, when working under reduced pressure, GaCp is displaced by HMB and readily removed from the reaction mixture, resulting in the formation of **4**. In contrast, upon layering with pentane, the increasingly apolar reaction medium induces the crystallisation of **5**.

### NMR data and DFT energetics towards 9

Although the calculated thermodynamics (at the BP86-D3(BJ)/def-SV(P) level, COSMO solvation) for the reactions of **2** in Equation (4) are essentially identical to those for Equation (2), owing to its polymeric nature, InCp is much less volatile and is not easily removed from the reaction mixture under reduced pressure.



$\text{M}' = \text{Ge}/\text{Sn}$  ( $\Delta_{\text{R}}G_{\text{g}}(\text{Ge})/(\text{Sn})$ ) and  $\{\Delta_{\text{R}}G_{\text{sol}}(\text{Ge})/(\text{Sn})\}$  in kJ/mol

Thus, the reaction between **2** and  $[\text{GeCp}_2]$  revealed a strikingly different reactivity. NMR spectroscopic investigation of the reaction mixture disclosed in the  $^{19}\text{F}$  and  $^{27}\text{Al}$  NMR spectra, the partial degradation of the counterion  $[\text{Al}(\text{OR}^f)_4]^-$  through the formation of 25% of  $[\mu\text{-F}\{\text{Al}(\text{OR}^f)_3\}_2]^-$  and an estimated 5% of  $[\text{F}\text{-Al}(\text{OR}^f)_3]^-$  with respect to  $[\text{Al}(\text{OR}^f)_4]^-$  and a strong downfield shift of the resonance in the  $^{115}\text{In}$  NMR spectrum to  $\delta = -1099$  ppm (cf.  $\delta = -1302$  ppm for **2**<sup>[40]</sup>). Similar behaviour was observed for the reaction between **2** and  $[\text{SnCp}_2]$ . Here, the NMR spectroscopic investigation again showed anion decomposition through the formation of the fluoride-bridged anion as well as the  $[\text{F}\text{-Al}(\text{OR}^f)_3]^-$  anion. The  $^{119}\text{Sn}$  NMR spectrum showed a single resonance at  $\delta = -2179$  ppm, close to the chemical shift of undisturbed  $[\text{SnCp}_2]$ , and an  $^{115}\text{In}$  NMR resonance at  $\delta = -1105$  ppm, close to that observed for the reaction with  $[\text{GeCp}_2]$ , which indicates a similar reactivity of **2** with the two group 14 metallocenes.

Overall, the DFT calculations and experimental observations suggest that the  $\pi$ -donating capabilities of the  $\text{MCp}$  ( $\text{M} = \text{Ga}, \text{In}$ ) fragment and HMB are rather similar. No heteroleptic complexes of  $\text{Ga}^+$  or clustering to multi-decker sandwich units were observed. HMB was readily liberated in all cases. The high volatility of GaCp also creates difficulties as it can be easily removed from the reaction mixture, but only in the presence of HMB.

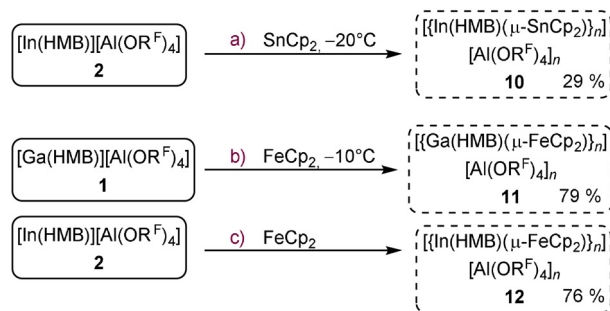
### From isolated sandwich cations to coordination polymers

When repeating the reaction between **2** and  $[\text{SnCp}_2]$  at  $-20^\circ\text{C}$ , subsequent crystallisation of the in vacuo concentrated solution at  $-30^\circ\text{C}$  led to crystals again showing a superstructure in the solid state. Fortunately, the collected data could be refined to a satisfactory level, and the molecular structure disclosed coordination of  $[\text{SnCp}_2]$  as a bridging ligand for intact  $[\text{In}(\text{HMB})]^+$  fragments to form the all- $\pi$  coordination polymer

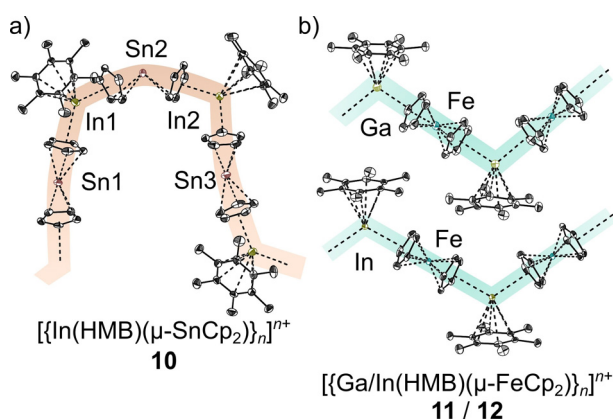
cation  $[\{\text{In}(\text{HMB})(\mu\text{-SnCp}_2)\}_n][\text{Al}(\text{OR}^F)_4]_n$  (**10**), as shown in Scheme 5a and Figure 3a. To extend the structural motif of these cationic coordination polymers and to investigate whether similar structures would also be formed when using a prototype transition-metal metallocene, the group 13 HMB complex salts **1** and **2** were also treated with ferrocene  $[\text{FeCp}_2]$ . Indeed, the reactions proceeded well and allowed isolation of zig-zag-type coordination polymers in the solid state for both Ga and In in the form  $[\{\text{M}(\text{HMB})(\mu\text{-FeCp}_2)\}_n][\text{Al}(\text{OR}^F)_4]_n$  ( $\text{M} = \text{Ga}$  (**11**),  $\text{In}$  (**12**); Scheme 5b,c and Figure 3b).

### Molecular structures of 10–12

The distances between the Sn and  $\text{Cp}^-$  moieties in **10** are, with  $d_{\text{Sn-ct}} = 2.396(17)$  Å ( $d_{\text{Sn-C,avg.}} = 2.662(16)$  Å,  $d_{\text{Sn-C,range}} = 2.583(16)$ – $2.783(13)$  Å; Table 2), almost identical to those in free  $[\text{SnCp}_2]$ , which is in agreement with the observed  $^{119}\text{Sn}$  NMR resonance described below. Furthermore, the angle between the ring planes of the two  $\text{Cp}^-$  moieties in the  $\text{SnCp}_2$  subunits ( $45.7^\circ$ ) closely resembles that in free  $[\text{SnCp}_2]$  ( $46.7^\circ$ ). The distance between indium and the ring centroid of the  $\eta^6$ -bound HMB is, with  $d_{\text{In-ct(HMB)}} = 2.807(11)$  Å, longer by 0.3 Å than that in



**Scheme 5.** Overview of reactions yielding cationic coordination polymers **10–12**. Unless explicitly stated otherwise, all reactions were performed at ambient temperature with oDFB as solvent.



**Figure 3.** Molecular structures of the infinite coordination polymers with  $n = \infty$ : a)  $[\{\text{In}(\text{HMB})(\mu\text{-SnCp}_2)\}_n][\text{Al}(\text{OR}^F)_4]_n$  (**10**, shown  $n = 3$ ) and b)  $[\{\text{M}(\text{HMB})(\mu\text{-FeCp}_2)\}_n][\text{Al}(\text{OR}^F)_4]_n$  ( $\text{M} = \text{Ga}$  (**11**),  $\text{In}$  (**12**); shown  $n = 2$ ). Counterions have been omitted for clarity. Thermal displacement ellipsoids are drawn at the 50% probability level.

free **2** (cf.  $d_{\text{In-ct(HMB)}} = 2.509(5)$  Å<sup>[40]</sup>, but 0.1 Å shorter than the distance to the ring centroid of the coordinated  $\text{Cp}^-$  moieties of  $\text{SnCp}_2$  ( $d_{\text{In-ct(Cp)}} = 2.90(2)$  Å). Note that the rather tight coordination of the  $[\text{GaCl}_4]^-$  counterion reported by Schmidbauer<sup>[55]</sup> for  $[\text{Ga}(\text{HMB})][\text{GaCl}_4]$  (2.522 Å) elongates the Ga–HMB ring centroid distance by a similar amount of roughly 0.3 Å compared with the non-interacting **1** (2.262 Å). It thus appears reasonable to propose that polymer formation is only possible by using the large and very weakly coordinating  $[\text{Al}(\text{OR}^F)_4]^-$  anion employed throughout this study,<sup>[56]</sup> otherwise coordination of the counterion, as in the case of  $[\text{GaCl}_4]^-$ , appears to be more favourable.

For both polymers **11** and **12**, the bridging  $[\text{FeCp}_2]$  is undistorted when compared with free  $[\text{FeCp}_2]$ , with  $d_{\text{Fe-ct(Cp)}} = 1.645(2)$  and  $1.644(2)$  Å, respectively. The distances between the group 13 element and the coordinated  $\text{Cp}^-$  moieties are, for both Ga and In, despite the larger radius of the latter, almost identical, with  $d_{\text{Ga/In-ct(Cp)}} = 3.083(2)/3.064(2)$  Å, even being slightly shorter by 0.02 Å for the heavier indium in **12**. Only one related coordination polymer has been reported in the past, generated by the reaction of  $\text{GaCl}_3$  with excess  $[\text{FeCp}_2]$  to form  $[\{\text{Ga}(\mu\text{-FeCp}_2)\}_n][\text{GaCl}_4]_n$  among other products. Here, the subvalent gallium is also coordinated by the counterion  $[\text{GaCl}_4]^-$  forming 3D networks.<sup>[57]</sup> In this coordination polymer, the gallium–centroid distances are, with  $d_{\text{Ga-ct(Cp)}} = 2.999$  Å, in good agreement with the distances in **11**.

### Solution reactivity and NMR spectra of 11 and 12

An NMR spectroscopic investigation of solutions of isolated crystalline material of **11** and **12** showed the presence of HMB and Cp in a 1:2 ratio in the respective  $^1\text{H}$  NMR spectra. The  $^{71}\text{Ga}$  and  $^{115}\text{In}$  NMR spectra showed singlet resonances at  $\delta = -700$  and  $-1244$  ppm, which are slightly shifted downfield compared with those in free **1** ( $\delta_{\text{Ga}} = -711$  ppm) and **2** ( $\delta_{\text{In}} = -1302$  ppm). The NMR resonances corresponding to  $\text{Cp}^-$  differed greatly between the two samples: for the In complex **12**, the respective resonances appeared as sharp singlets at  $\delta_{\text{H}} = 4.19$  ppm and  $\delta_{\text{C}} = 69.4$  ppm, whereas the Ga complex **11** showed broad resonances for both the proton ( $\delta_{\text{H}} = 9.60$  ppm,  $\omega^{1/2} = 200$  Hz) and carbon resonances ( $\delta_{\text{C}} = 78.9$  ppm), which suggests partial electron transfer to form a paramagnetic  $\text{Fe}^{\text{III}}$  species. This reactivity was also observed when the more electron-deficient salt  $[\text{Ga}(\text{PhF})_n][\text{Al}(\text{OR}^F)_4]$  ( $n = 2, 3$ ) was treated with  $[\text{FeCp}_2]$ : this resulted in a redox reaction and the formation of the ferrocenium salt  $[\text{FeCp}_2][\text{Al}(\text{OR}^F)_4]$  together with elemental  $\text{Ga}^0$ . Upon reaction of **1** with  $[\text{FeCp}_2]$  at  $-10^\circ\text{C}$ , no change in colour was observed. However, upon warming the reaction mixture to  $50^\circ\text{C}$ , a grey precipitate (possibly  $\text{Ga}^0$ ) formed over time. Both  $[\text{FeCp}_2][\text{Al}(\text{OR}^F)_4]$  and **11** crystallised from this reaction mixture.

### Comparing $\pi$ -donor strength of HMB and $[\text{M}^+\text{Cp}_2]$

With the reactivity described above and by comparison of the interatomic distances between the group 13 elements and bound aromatics in the molecular structures, a rough estimate

**Table 2.** Selected interatomic distances in the cations **10–12**.

	<b>10</b> M = In, M' = Sn	<b>11</b> M = Ga, M' = Fe	<b>12</b> M = In, M' = Fe
$[(M(HMB)(\mu-M'Cp_2))_n]^{19+}$			
M'–C <sub>range</sub> [Å]	2.583(16)–2.783(13)	2.036(3)–2.046(3)	2.030(4)–2.051(4)
M'–C <sub>avg.</sub> [Å]	2.662(16)	2.041(3)	2.039(3)
M'–ct(Cp) [Å]	2.396(17)	1.645(2)	1.644(2)
M'–pl(Cp) [Å]	2.376(24)	–	–
M–ct(Cp) [Å]	2.897(20)	3.083(2)	3.064(2)
M–C(HMB) <sub>range</sub> [Å]	3.045(10)–3.203(14)	2.797(3)–2.838(3)	3.006(3)–3.051(3)
M–C(HMB) <sub>avg.</sub> [Å]	3.138(15)	2.814(3)	3.025(3)
M–ct(HMB) <sub>avg.</sub> [Å]	2.807(11)	2.438(1)	2.678(1)

of the  $\pi$ -donor strength of HMB and  $[M'Cp_2]$  ( $M' = Ge, Sn, Fe$ ) can be obtained. HMB and the group 14 metallocenes seem to be similar in coordination strength, as seen in the generation of either the HMB-stabilised stannocenium salt **4** or the heterobimetallic sandwich cations **5**, **6** and **9**. The distance between the group 13 element and the ring centroid of HMB can be used as a probe for the coordinative strength of the bound metallocene in the isolated heteroleptic polymeric complexes **10** and **12**. The longer In–ct<sub>HMB</sub> distance (by 0.12 Å) observed in **10** in comparison with **12** suggests increased donor capabilities of  $[SnCp_2]$  compared with  $[FeCp_2]$ .

## Conclusions

The coordination behaviour of the subvalent  $[Ga(HMB)]^+$  and  $[In(HMB)]^+$  cations in the salts  $[M(HMB)][Al(OR^F)_4]$  has been explored. The isolobal analogy between  $[M(HMB)]^+$  and the corresponding neutral  $MCp^*$  is not mirrored in their reactivity. No coordination of the lone-pair orbital to Lewis acidic main-group and transition-metal fragments was observed. DFT calculations suggested that M–M' bound species might be relevant for fast exchange processes on the NMR timescale. By contrast, the  $\pi$ -accepting ability of these cations was investigated through reactions with the group 14 metallocenes  $[M'Cp_2]$  ( $M' = Ge, Sn$ ), which yielded a series of novel heterobimetallic sandwich complexes. Compound **1** cleanly formed sandwich cations  $[Ga(\mu-Cp)M'Cp]^+$  ( $M' = Sn$  (**5**),  $Ge$  (**6**)) with apical *exo* Ga atoms. These heterometallic sandwich cations might serve as precursors for the simultaneous introduction of  $\sigma$ -donating group 13 Cp fragments and highly Lewis acidic group 14 metallocenium cations to generate heterometallic main-group or transition-metal push–pull complexes, which will be investigated in the future. Compound **2** exhibits strikingly different reactivities: upon pairing with the two group 14 metallocenes, partial decomposition of the counterion was observed at ambient temperature. Thus, only at reduced temperature was the unprecedented main-group coordination polymer  $[(In(HMB)(\mu-SnCp_2))_n][Al(OR^F)_4]_n$  (**10**) accessible, this polymer showing coordination of In by both HMB and an essentially undisturbed  $SnCp_2$ . This structural motif was extended to the transition-metal metallocene  $[FeCp_2]$ , which formed the related coordination polymers  $[(M(HMB)(\mu-FeCp_2))_n][Al(OR^F)_4]_n$  ( $M = Ga$  (**11**),  $In$  (**12**)).

## Experimental Section

Full details of the experimental procedures and DFT calculations can be found in the Supporting Information.

Deposition numbers 2000267, 2000268, 2000269, 2000270, 2000271, 2000272, 2000273, 2000274 and 2000275 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of interest

The authors declare no conflict of interest.

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