PAPER

Pentamethyl- and 1,2,4-tri(*tert*-butyl)cyclopentadienyl containing p-block complexes – differences and similarities†

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The sterically encumbered cyclopentadienyl ligand 1,2,4-$(Me_3C)_3C_5H_2$ (Cp‴) was used to stabilize efficiently the main group metals of Al, Ga, In, Ge and Sn, respectively. The σ-bonded gallium compounds $[\eta^1\text{-Cp‴Ga}(\mu\text{-X})X]_2$ (X = Cl, **2**; X = I, **3**) and indium compound $[\eta^1\text{-Cp‴In}(\mu\text{-Br})^n\text{Bu}]_2$ (**7**) exhibit dimers through halogen bridges. Reduction of **2** with 2 equivalents of KC_8 leads almost to the same amount of $\eta^1\text{-Cp‴Ga(THF)Cl}_2$ (**4**) and $\eta^5\text{-Cp‴Ga}$ (**5**), respectively. The exception is compound **5**, which is obtained by reducing **2** or **3** with 4 equivalents of KC_8. Compound **5** as Lewis base reacts with GaI_3 readily forming the Lewis acid–base adduct product $\eta^5\text{-Cp‴Ga} \rightarrow GaI_3$ (**6**). Moreover, compounds with the Cp‴ ligand stabilize heavier low-valent group 14 elements for example $[\eta^5\text{-Cp‴E}^{II}]^+[E^{II}Cl_3]^-$ (E = Ge **8**, Sn **9**), which are π-bonded ionic compounds that possess a low-valent cation and an anion. In the cation of $[\eta^5\text{-Cp‴E}^{II}]^+$, the Cp‴ ligand adopts an η⁵-coordination mode with germanium and tin, respectively, which present half-sandwich complexes. While the E^{II} fragment interacts with five π electrons from the Cp‴ unit to generate an electron-octet arrangement at the respective element. All new reported structures are comparing well with the corresponding compounds containing the pentamethylcyclopentadienyl (Cp*) ligand.

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Introduction

In 1951 the seminal discovery of ferrocene was reported,[1] with the η⁵,η⁵ sandwich structure containing two cyclopentadienyl ligands. This class of compounds plays more and more an important role in the development of organometallic chemistry.[2] The modification of the five-membered ring structure has been a topic of important research during the last 65 years. Especially the substitution of the hydrogen atoms by introducing more bulky substituents in the cyclopentadienyl ring resulted in mono-, di-, tri-, tetra-, and penta substituted cyclopentadienyl ring compounds $C_5H_{5-x}R_x$ (x = 1–5; R = Me, Et, ^{i}Pr, ^{t}Bu, benzyl), which can bind to a metal with different hapticity (η¹–η⁵).[3]

The first room-temperature stable Al(I) compound $[Cp*Al]_4$ (Cp* = C_5Me_5) was reported by Schnöckel *et al.* in 1991.[4] Two years later they reported the congener Cp*Ga.[5] The subsequent research found that it is a monomer in the gas phase and in solution but a hexamer in the solid state.[6] In 1993, Roesky *et al.*[7] reported an easy route to $[Cp*Al]_4$ in good yield that allowed to study the chemistry of this molecule on a broad scale.[8] Furthermore $[Cp*Al]_4$ and Cp*Ga were increasingly popular and extensively used by chemists.[9] In 2004, Jutzi *et al.*[10] isolated the first silylene cation $[Cp*Si:]^+[B(C_6F_5)_4]^-$, which is thermally stable but extremely air- and moisture sensitive. Subsequently, the $[Cp*Si:]^+$ ion became an important catalyst.[11] Very recently, Heitkemper *et al.* reported a neutral Silicon(II) half-sandwich compound. It is interesting that in this compound the five-membered ring of the ligand consists of four carbon and one boron atoms and the distance between Si and the five-membered ring is closer than that in Cp*.[12] Because of the excellent steric bulk, solubility, stability, and electron donor properties of Cp* ligand, it has been demonstrated versatility of the σ- (η^{3/2/1}) or π-bonding (η⁵) in main group element chemistry.[3,4,9–11,13]

However, the 1,2,4-$(Me_3C)_3C_5H_2$ (Cp‴) ligand with bulky substituents is rarely used for main group metals. Recently, Braunschweig *et al.* reported Cp‴AlBr₂, which was reduced by
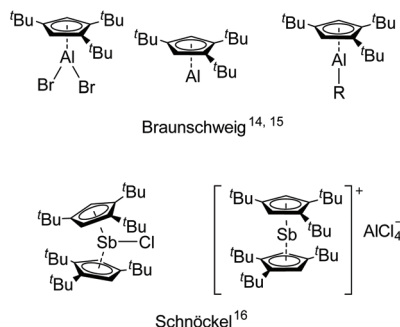
Fig. 1 The main group metals supported by Cp‴ ligand.

[Cp*Al]$_4$ and then treated with cAAC to isolate the liquid low-valent monomer aluminum [η^5-Cp‴Al],[14] which was studied for a number of interesting reactions under mild conditions.[15] The main group metals supported by Cp‴ ligand are depicted in Fig. 1.[14–16] Encouraged by [η^5-Cp‴Al], we have initiated a research program based on other main group metals with the bulky Cp‴ ligand.
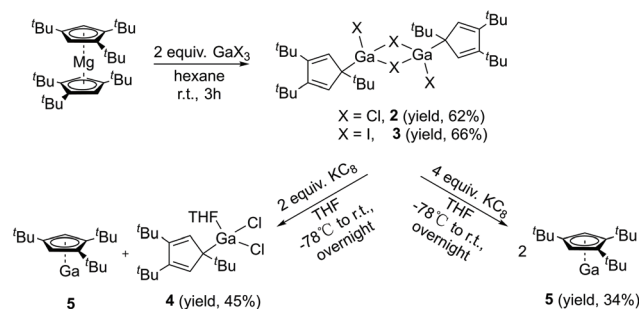
Herein, we report on σ-bonded gallium and indium, π-bonded gallium, germanium, and tin metals stabilized by Cp‴ ligand. The σ-bonded gallium and indium are μ$_2$-bridging halogen dimers. The π-bonded Cp‴Ga as Lewis base to afford Lewis acid–base adduct of composition (Ga^I → Ga^{III}). While the π-bonded germanium and tin have both the cationic [η^5-Cp‴E^{II}]$^+$ (E = Ge, Sn) as well as the anionic [M^{II}Cl$_3$]$^-$ (E = Ge, Sn) species of their respective low-valent group 14 elements. To the best of our knowledge, these are the first X-ray structures of ionic compounds with low-valent group 14 elements of Cp‴, when compared with those containing the ionic feature of Cp species. We also discuss the differences and similarities between the Cp‴ and Cp* metal compounds.

Results and discussion

Compound **1** is easily synthesized (Scheme 1) and characterized by NMR. In the ^{1}H NMR spectrum, there is a resonance at δ 6.60 ppm for the two aromatic protons and two resonances at δ 1.39 and 1.20 ppm in a ratio of 18 to 9 protons of the ^{t}Bu groups. The ^{27}Al NMR spectrum exhibits a sharp singlet at δ = −27.09 ppm, which is considerably downfield shifted compared to that of [Cp*AlCl$_2$]$_2$ (δ = −51 ppm)[17] and Cp‴AlBr$_2$ (δ = −42 ppm).[14] The spectroscopic method strongly confirms compound **1**. Regrettably, we were not able to obtain suitable single crystals for measurement. Reduction of **1** with 2.2
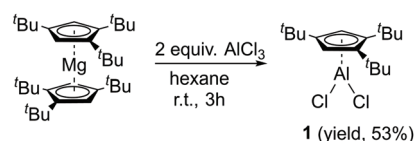
Scheme 1 Synthesis of aluminum compound **1**.

equivalents of KC$_8$ was successful. However, according to the complicated ^{1}H NMR spectrum of Cp‴Al, it cannot be traced. This is exactly the same result as that reported by Braunschweig and co-workers.[14]

Halogen bridged compound [η^1-Cp‴Ga(μ-X)X]$_2$ (X = Cl, **2**; X = I, **3**) was synthesized according to Scheme 2. The reaction proceeded quickly within 3 h at ambient temperature, due to the high solubility of the magnesium precursor in hexane. The ^{1}H NMR spectrum at δ 6.54 ppm exhibits a resonance for the aromatic protons, while for the ^{t}Bu groups in [η^1-Cp‴Ga(μ-Cl)Cl]$_2$ (**2**) two resonances are observed at δ 1.34 and 1.20 ppm. However, in [η^1-Cp‴Ga(μ-I)I]$_2$ (**3**) the less electronegative iodine caused upfield shifts to δ 6.32, 1.30, and 1.17 ppm in the ^{1}H NMR spectrum. Single crystals suitable for X-ray diffraction analysis are obtained by cooling a saturated n-hexane solution at −32 °C for 12 h. Molecular structures of **2** and **3** are presented in Fig. 2 and 3.

The structures of **2** and **3** show isostructural dimeric arrangements with two bridging halogen atoms, which connect two gallium to constitute a planar four-membered Ga$_2$X$_2$ ring. While the asymmetric unit of **2** contains two halves of the molecule, with the other half generated by an inversion center, the asymmetric unit of **3** consists of a single complete molecule. Two Cp‴ ligands and terminal halogen atoms residing alternately at both sides of the symmetric Ga$_2$X$_2$ ring. These are similar to the corresponding compounds

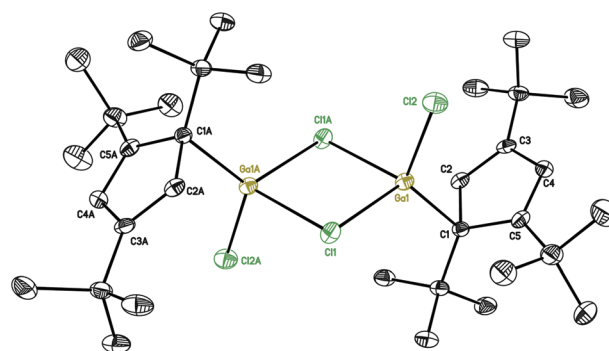**Scheme 2** Synthesis of gallium compounds **2**–**5**.

Fig. 2 Molecular structure of **2**. Anisotropic displacement parameters are depicted at 50% probability level. The hydrogen atoms as well as the second molecule within the asymmetric unit are omitted for clarity.
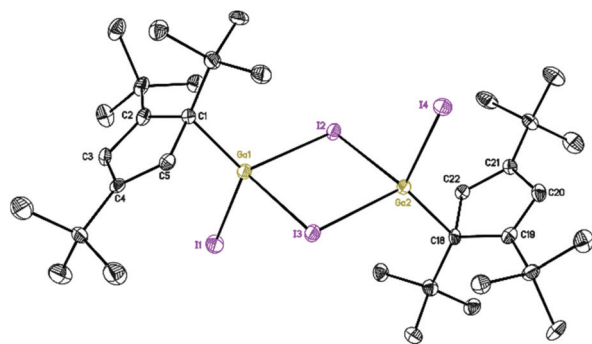
Fig. 3 Molecular structure of **3**. Anisotropic displacement parameters are depicted at 50% probability level. The hydrogen atoms are omitted for clarity.

supported by Cp* ligand. The gallium centers have distorted tetrahedral environments. The angles between the planes of the Cp‴ ring and the Ga_2X_2 ring are 33.23(6)° and 33.29(6)° in **2** and 29.30(7)° and 28.61(7)° in **3**. The angles between the Ga–C bond and the plane of the Cp‴ rings reach 99.1° and 98.0° in **2** and 101.0° and 101.2° in **3**, while the angles to Ga_2X_2 reach the values of 131.3° and 130.6° for the two molecules in the asymmetric unit in compound **2**, and 128.0° and 130.1° in compound **3**. For a similar series of dimeric halogen bridged molecules, regular changes in bond distances and bond angles as well as in distances between similar but nonbonded atoms in the four-membered rings are shown in Table 1. In the structure of **2** the Ga–Cl bridging bond distances [2.3497(10) to 2.3817(9) Å] are longer than the Ga–Cl terminal bond distance [2.1520(8) and 2.1518(8) Å]. In $[Cp*Ga(\mu\text{-}Cl)Cl]_2$,[18] $[Cp*Ga(\mu\text{-}I)I]_2$,[19] and **3**, the arrangements are also the same when compared with **2**. It is obvious that for both chlorine and iodine bridging bonds are longer than the terminal Ga–X bonds where the sterically more demanding ligand is involved.

Similarly, Cp* and Cp‴ ligands with the same structure center, reveal the bond lengths in the compound with more sterically hindered Cp‴ ligand to be slightly longer.

Inspired by $[\eta^1\text{-}Cp*_2GaCl]_2$,[18] we tried to react with equivalent amounts of $GaCl_3$ with $Cp‴_2Mg$ to get the dimeric compound of composition $[\eta^1\text{-}Cp‴_2GaCl]_2$. Unfortunately, the crystals we obtained were still compound **2**. Presumably, the bulk of Cp‴ was the reason we failed to get $[\eta^1\text{-}Cp‴_2GaCl]_2$.

With σ-bonded compound $[\eta^1\text{-}Cp‴Ga(\mu\text{-}Cl)Cl]_2$ (**2**) in hand, we next tried to synthesize $[\eta^1\text{-}Cp‴Ga(\mu\text{-}Cl)]_2$ and Cp‴Ga (**5**), respectively, which are accessible via direct reductive dehalogenation with KC_8. First of all, **2** reacts with two equivalents of KC_8 in THF, after the reaction the solvent THF was removed in a vacuum, and the product was extracted with *n*-hexane. We obtained colorless crystals of composition of two η^1-Cp‴Ga $(THF)Cl_2$ (**4**), with a THF molecule strongly coordinated to the gallium per asymmetric unit. However, after isolating the crystals from the mother liquor, the liquid residue is treated in a vacuum to get a yellow-green liquid. The ^1H NMR spectrum of the yellow-green liquid exhibits an aromatic proton signal at δ 5.93 ppm and two ^tBu groups resonate at δ 1.37 and 1.20 ppm. This pattern is very similar to monomeric Cp‴Al reported by Braunschweig *et al.*[14] The reduction of **2** with two equivalents of KC_8 produces η^1-Cp‴Ga$(THF)Cl_2$ (**4**) as well as η^5-Cp‴Ga (**5**). In the structure of **4** (Fig. 4), the Ga–Cl bond distances [2.1869(9), 2.1886(9), 2.1891(9), and 2.1863(9) Å] are considerably longer than Ga–Cl terminal distance [2.1520(8) Å] in compound **2**, however, shorter than Ga–Cl bridging distances [2.3497(10) to 2.3817(9) Å].

Therefore, a reduction of **2** or **3** with four equivalents of KC_8 has tried again in toluene, and pure compound **5** can be obtained in high yield as a yellow-green liquid. This is in contrast to the reduction of $Cp‴AlBr_2$ with KC_8 that does not yield Cp‴Al. The ^{71}Ga NMR spectrum of **5** exhibits a resonance at δ −676.06 ppm, this value is observed between the CpGa[20]

Table 1 Comparison of distances (Å) and angles (°) between $[Cp*GaCl_2]_2$, $[Cp*GaI_2]_2$, **2**, **3**, and **4**

	$[Cp*GaCl_2]_2$	**2**	$[Cp*GaI_2]_2$	**3**	**4**
Ga⋯Ga	3.382	3.4338(10)[c] 3.4215(10)[d]	3.745	3.8672(7)	—
Ga–C	1.97(1)	2.005(2)[c] 2.003(2)[d]	2.008(6)	2.034(3) 2.030(3)	2.021(3)[c] 2.021(3)[d]
Ga–X_t[a]	2.124(4)	2.1520(8)[c] 2.1518(8)[d]	2.4895(11)	2.5197(6) 2.5186(6)	2.1869(9)[c] 2.1886(9)[c] 2.1863(9)[d] 2.1891(9)[d]
Ga–X_b[b]	2.352(3); 2.373(3)	2.3497(10)[c] 2.3817(9)[c] 2.3486(9)[d] 2.3753(10)[d]	2.7150(11); 2.7131(10)	2.7039(6) 2.7103(6) 2.7610(5) 2.7736(5)	
X_b⋯X_b	3.300	3.2552(13)[c] 3.2572(13)[d]	3.931	3.8749(6)	
X_b–Ga–X_b	88.6(1)	86.94(3)[c] 87.18(3)[d]	92.78(2)	90.042(17) 90.176(16)	
Ga–X_b–Ga	91.4(1)	93.06(3)[c] 92.82(3)[d]	87.23(2)	90.081(17) 89.684(16)	

[a] X_t = terminal halogen atom. [b] X_b = bridging halogen atom. [c] First molecule in asymmetric unit. [d] Second molecule in asymmetric unit.
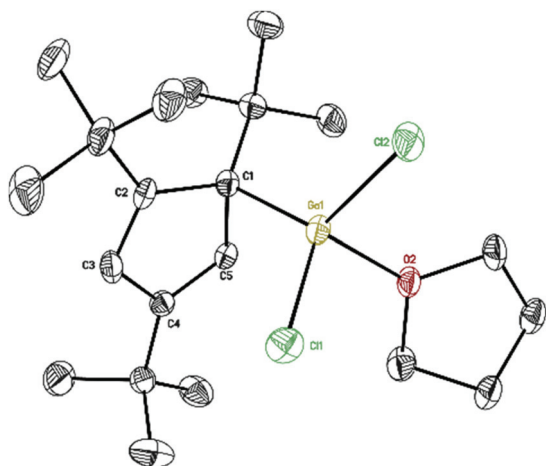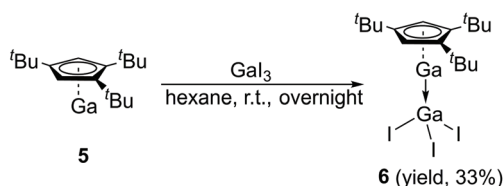
Fig. 4 Molecular structure of **4**. Anisotropic displacement parameters are depicted at 50% probability level. The hydrogen atoms are omitted for clarity.
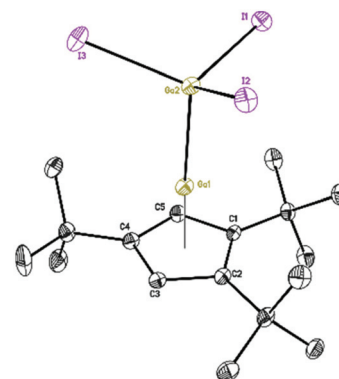

Fig. 5 Molecular structure of **6**. Anisotropic displacement parameters are depicted at 50% probability level. The hydrogen atoms are omitted for clarity.

(−714 ppm) and Cp*Ga[5] (−653 ppm) reported by Schnöckel *et al.* The slight shift indicates that **5** also exists in the monomeric [η^5-Cp'''Ga] form in solution.[21]

The Lewis acid GaI$_3$ was reacted smoothly with **5** to afford the Lewis acid–base adduct product **6** (Scheme 3). However, the Lewis base PPh$_3$ did not react with **5** according to the ^{1}H NMR spectroscopy. This indicated that compound **5**, like Cp''' Al and other monovalent Ga(I) species, is a Lewis base. The ^{1}H NMR spectrum of **6** shows an aromatic proton signal at δ 6.12 ppm, two ^{t}Bu group resonances at δ 1.19 and 1.09 ppm. Compared with **5**, the aromatic proton shifted downfield, but the ^{t}Bu group shifted upfield. The ^{71}Ga NMR spectrum of **6** exhibits a resonance at δ −279.55 ppm. Surprisingly, the ^{71}Ga NMR signal of **6** (at *ca.* −240 to −320 ppm) is broader than that of **5** (at *ca.* −650 to −700 ppm) and strongly downfield shifted. This ^{71}Ga resonance is for the tetracoordinate Ga(III) fragment while the signal of the Ga(I) center was not detected. This observation is in good agreement to that of ^{27}Al NMR spectrum, reported for its Al analogue.[14] The Ga(I)–Ga(III) distance (Fig. 5) in the structure of **6** is 2.4563(9) Å, which is very similar with that of [Li(THF)$_4$][GaI$_3$-GaI(P^{i}Pr$_2$CH$_2$)$_2$BPh$_2$] (2.4521(11) Å)[22] and corresponds to the Ga–Ga coordination bond. Remarkably, these distances fall into the range of covalent Ga–Ga bond distances in complex (dpp-Bian)Ga–Ga (dpp-Bian) (2.3598(3) Å) (dpp-Bian = 1,2-bis[(2,6-diisopropyl-phenyl)imino]-acenaphthene),[23] [RGaCl]$_2$ (2.445(9) Å) (R = [(Me$_3$Si)$_2$C(Ph)C(Me$_3$Si)N]),[24] and the following compounds:

[(^{t}BuN=CH)$_2$]IGa–GaI[(^{t}BuN=CH)$_2$] (2.4232(7) Å),[25] (dpp-Bian) IGa–GaI(dpp-Bian) (2.4655(5) Å),[26] [(ArN=CH)$_2$]IGa–GaI [(ArN=CH)$_2$] (2.5755(16) Å),[27] [(Me$_3$Si)$_3$SiGaCl]$_4$ (2.509(12) Å),[28] [((Me$_3$Si)$_2$CH)$_2$Ga]$_2$ (2.541(1) Å),[29] [(2,4,6-i-Pr$_3$C$_6$H$_2$)$_2$ Ga]$_2$ (2.513(3) Å),[30] [2,4,6-t-Bu$_3$C$_6$H$_2$GaCl]$_2$ (2.438(6) Å),[31] and [(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)$_2$Ga]$_2$ (2.479(1) Å).[32] After the success with Cp'''Ga we became interested in the corresponding Cp'''In compound. InBr$_3$ was treated with 0.5 equivalents of Cp'''$_2$Mg in hexane at ambient temperature for 6 h. However, we were not able to isolate any pure product. Next, we tried a one-pot reaction with Cp'''$_2$Mg, InBr$_3$ and ^{n}BuLi. First, Cp'''$_2$Mg was treated with 2.2 equivalents of InBr$_3$ in hexane at ambient temperature for 6 h. Then 2.2 equivalents of ^{n}BuLi were added to react at −78 °C. Finally, the mixture was warmed to room temperature and stirring was continued for 6 h. The filtered solution was stored at −32 °C in a freezer for 3 days (Scheme 4).

The molecular structure of **7** is presented in Fig. 6, while selected bond distances can be found in the figure caption. We obtained colorless crystals of compound **7** (Fig. 6), reminiscent of the halogen bridged gallium compound [η^1-Cp'''Ga(μ-X)X]$_2$. The dimeric molecule of **7** has two bridging bromine atoms, forming together with the indium atoms a planar four-membered In$_2$Br$_2$ ring with a center of symmetry. The two Cp''' ligands and the two *n*-butyl substituents reside alternately above and below the In$_2$Br$_2$ ring.

After group 13 metals supported by Cp''' ligand, we extended the Cp''' chemistry to stabilize group 14 metals. Germanium [Cp*Ge]$^+$[X]$^-$ (X = AlCl$_4$,[33] BF$_4$,[34] C$_5$(CO$_2$Me)$_5$,[35] GeCl$_3$,[36] SnCl$_3$,[37]) and tin [Cp*Sn]$^+$[X]$^-$ (X = AlCl$_4$,[38] B(C$_6$F$_5$)$_4$,[39] BF$_4$,[36,38,40] CF$_3$SO$_3$.[38]) ionic compounds supported by the Cp* ligand have been reported successively since 1980. Most of

Scheme 3 Synthesis of Lewis acid–base adduct gallium compound **6**.
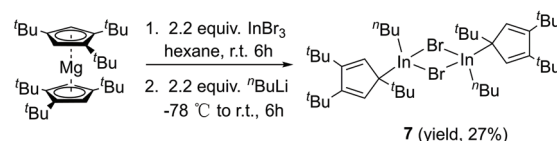
Scheme 4 Synthesis of indium compound **7**.

them were characterized by NMR and mass spectrometry. However, single-crystal X-ray structural analysis of ionic compounds of group 14 metals are rare.

The simple salt elimination reaction of Cp'''Li with ECl_2 (E = Ge, Sn) resulted in a poor conversion of the products. However, compounds **8** (E = Ge) and **9** (E = Sn) were isolated in good yields by reacting Cp'''$_2$Mg in Et_2O solution (Scheme 5).
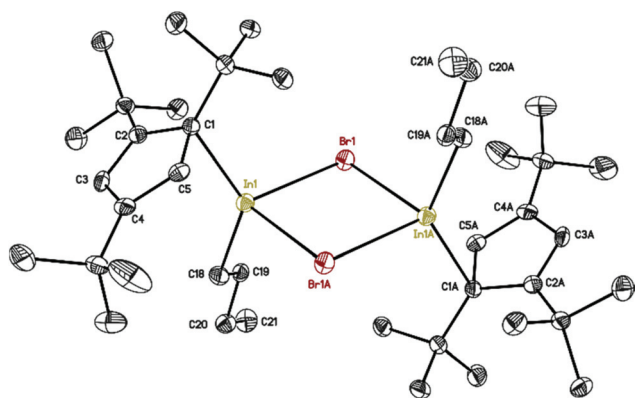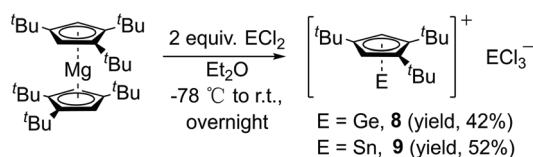

Fig. 6 Molecular structure of **7**. Anisotropic displacement parameters are depicted at 50% probability level. The hydrogen atoms are omitted for clarity. In–In 4.0476(14) Å; In–C18: 2.158(3) Å.

Scheme 5 Synthesis of germanium and tin compounds **8** and **9**.

The same reactions were also carried out with Cp'''$_2$Mg and $SiCl_4$ as well with $SiHCl_3$. However, with silicon chlorides no reaction was observed. The reactions were monitored by ^1H

NMR spectroscopy. The corresponding ionic compound of $[\eta^5\text{-}Cp'''E^{II}]^+[E^{II}Cl_3]^-$ was obtained when Cp'''$_2$Mg was reacted with $GeCl_2$·dioxane or $SnCl_2$ in a ratio of 1 : 2 and 1 : 4, respectively.

The ^1H NMR the spectrum of compounds **8** and **9** exhibit resonances for the aromatic protons at δ 6.03 and 6.07 ppm and two resonances for the ^tBu groups at δ 1.14, 1.09 and 1.25, 1.17 ppm, respectively. Compounds **8** and **9** each possess a cationic charge. The electrophilicity of the metals is higher than those in neutral compounds. Due to this, the protons of Cp''' ligands of compounds **8** and **9** are shifted upfield in the ^1H NMR, when compared with the corresponding resonances of compounds **2**–**4**. However, this observation is similar to that of compound **5**, which also indicates that **5** exhibits an η^5-coordination mode.

Suitable single crystals of **8** were obtained from saturated toluene solution at −32 °C and those of **9** were formed in a mixture of toluene and Et_2O at 4 °C. The structures of **8** (Fig. 7 left) and **9** (Fig. 7 right) contain each a half-sandwich cationic $[\eta^5\text{-}Cp'''E^{II}]^+$ (E = Ge, Sn) unit and their respective low-valent element of anionic $[E^{II}Cl_3]^-$ species are located in the same crystal lattice. In the cationic $[\eta^5\text{-}Cp'''E^{II}]^+$ E(II) coordinates through η^5-coordination to a Cp''' ligand. In the solid-state structure of compound **8**, the Ge^{II} is coordinated by the three chlorine atoms of $GeCl_3^-$, which in turn points to the Cp''' moiety with a distance of 3.8706(13) Å (see Fig. S15†). In contrast, the solid-state structure of **9** does not exhibit this ordering in one-dimensional chains. The distance between the two metals in cation and anion is 3.8265(8) Å in compound **8** and 4.5920(6) Å in compound **9**. These exceed the single bond length of Ge–Ge and Sn–Sn.[41] The distances of the Ge and Sn atom to the center of the Cp''' ring are 1.9336(8) and 2.2056(10) Å; the Ge–C(Cp''') distances are 2.2529(16) to 2.3233(16) Å as well as Sn–C(Cp''') distances are 2.4759(14) to 2.5856(14) Å. The Cp''' rings are planar and exhibit η^5-coordination to germanium and tin as shown by the C_{ring}–C_{ring} bond length patterns within each Cp''' ring. In the anion $[E^{II}Cl_3]^-$, three chlorine atoms (Cl1, Cl2, and Cl3) are attached to the metal ion E^{II}, resulting in a trigonal pyramidal shape of the anion.
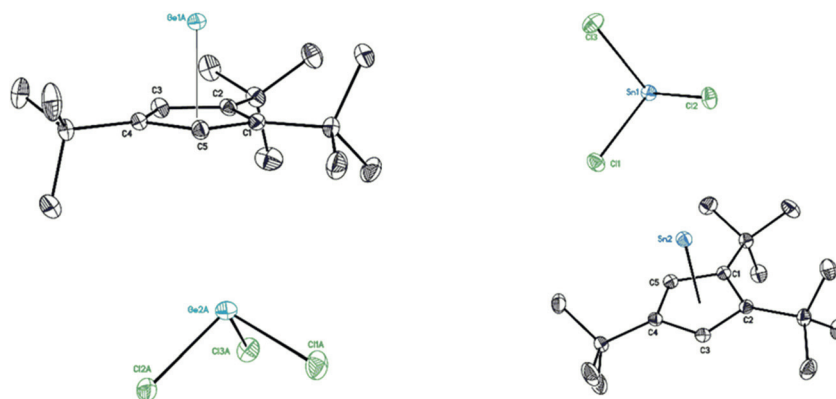

Fig. 7 Molecular structure of **8** (left) and **9** (right). Anisotropic displacement parameters are depicted at 50% probability level. The hydrogen atoms and the smaller disordered faction are omitted for clarity.

Conclusions

In summary, we report halogen bridged σ-bonded dimers of gallium and indium, π-bonded aluminum, gallium, germanium, and tin compounds supported by the bulky 1,2,4-tri (*tert*-butyl)cyclopentadienyl ligand. Reducing the halogen bridged σ-bonded dimers of gallium with KC$_8$ to afford the π-bonded Cp′′′Ga, which exhibits a Lewis base that forms an acid–base Ga(ɪ)/Ga(ɪɪɪ) adduct of Cp′′′Ga → GaI$_3$. The ionic compounds contain half-sandwich cationic $[\eta^5\text{-Cp}'''\text{E}^{II}]^+$ as well as trigonal pyramidal anionic $[\text{E}^{II}\text{Cl}_3]^-$ with the same elements. Due to the larger steric hindrance and poor solubility, Cp′′′ ligand is difficult to form metallocene-type molecules of main group metals. Comparing the Cp* substituted main group metal compounds with those containing Cp′′′ ligands, the latter are much more difficult to synthesize. For metallocenes, the Cp* ligand is a very good choice, however, for ionic compounds the Cp′′′ ligand is the preferable ligand.

Experimental section

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high purity dinitrogen. THF, hexane, and toluene, respectively, were distilled over Na/K alloy (25 : 75), while diethyl ether was distilled over potassium mirror. Deuterated NMR solvent C$_6$D$_6$ was dried by stirring for 2 days over Na/K alloy followed by distillation in a vacuum and degassed. ^{1}H, ^{13}C{^{1}H}, ^{27}Al and ^{71}Ga NMR spectra were recorded on Bruker Avance 400 or 500 MHz NMR spectrometer and were referenced to the resonances of the solvent used. Microanalyses were performed by the Analytisches Labor für Anorganische Chemie der Universität Göttingen. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting material Cp′′′$_2$Mg was synthesized by following literature procedure,[42] and Cp′′′Li was prepared by reaction of Cp′′′H with ^{n}BuLi in hexane at 85 °C overnight. All other reagents were used as received.

General synthesis of $[\eta^1\text{-Cp}'''\text{M}(\mu\text{-X})\text{X}]_2$

A mixture of Cp′′′$_2$Mg (490 mg, 1 mmol) and of two millimoles of MX$_3$ was taken in a 100 mL round bottom flask and 40 mL of hexane were added at ambient temperature. The reaction mixture was stirred for 3 h to give corresponding compounds. After filtration of insoluble residue, the solvent was concentrated to 10 mL under vacuum. The solution was stored at −32 °C for 12 h in a freezer to get solid of **1** and X-ray quality crystals of **2**, and **3**, respectively.

η^1-Cp′′′AlCl$_2$ (1). Light yellow solid **1** (yield: 348 mg, 53%). ^{1}H NMR (C$_6$D$_6$): δ 6.60 (s, 2 H, C$_5$H$_2$(^{t}Bu)$_3$), 1.39 (s, 18 H, ^{t}Bu), 1.20 (s, 9 H, ^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 129.42 (Ar), 126.49 (Ar), 112.59 (Ar), 33.95 (C(CH$_3$)$_3$), 32.32 (C(CH$_3$)$_3$), 31.84 (C(CH$_3$)$_3$), 30.68 (C(CH$_3$)$_3$) ppm. ^{27}Al NMR (C$_6$D$_6$): δ −27.09 ppm. Mp: 132–134 °C to an orange liquid. Anal (%).

calcd for C$_{17}$H$_{29}$AlCl$_2$ (330.15): C, 61.63; H, 8.82 Found: C, 62.08; H, 9.02.

$[\eta^1$-Cp′′′Ga(μ-Cl)Cl]$_2$ (2). Colorless block-shaped crystals of **2** (yield: 462 mg, 62%). ^{1}H NMR (C$_6$D$_6$): δ 6.54 (s, 2 H, C$_5$H$_2$(^{t}Bu)$_3$), 1.34 (s, 18 H, ^{t}Bu), 1.20 (s, 9 H, ^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 149.60 (Ar), 125.14 (Ar), 123.13 (Ar), 35.19 (C(CH$_3$)$_3$), 32.39 (C(CH$_3$)$_3$), 31.66 (C(CH$_3$)$_3$), 29.65 (C(CH$_3$)$_3$) ppm. Mp: 149–150 °C to a yellowish liquid. Anal (%). calcd for C$_{34}$H$_{58}$Cl$_4$Ga$_2$ (744.18): C, 54.59; H, 7.82 Found: C, 55.02; H, 7.95.

$[\eta^1$-Cp′′′Ga(μ-I)I]$_2$ (3). Orange-red block-shaped crystals of **3** (yield: 733 mg, 66%). ^{1}H NMR (C$_6$D$_6$): δ 6.32 (s, 2 H, C$_5$H$_2$(^{t}Bu)$_3$), 1.30 (s, 18 H, ^{t}Bu), 1.17 (s, 9 H, ^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 156.57 (Ar), 128.79 (Ar), 117.62 (Ar), 34.85 (C(CH$_3$)$_3$), 32.65 (C(CH$_3$)$_3$), 32.32 (C(CH$_3$)$_3$), 30.71 (C(CH$_3$)$_3$) ppm. Mp: 117–118 °C to a yellowish liquid. Anal (%). calcd for C$_{34}$H$_{58}$Ga$_2$I$_4$ (1111.92): C, 36.66; H, 5.25 Found: C, 37.12; H, 5.95.

η^1-Cp′′′Ga(THF)Cl$_2$ (4). A mixture of **2** (750 mg, 1 mmol) and KC$_8$ (270 mg, 2 mmol) were taken in a 100 mL round bottom flask and 40 mL of tetrahydrofuran was added at −78 °C. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight to give a solution mixture of compounds **4** and η^5-Cp′′′Ga (**5**). The solvent was removed under a high vacuum and the product was extracted with 50 mL of hexane. After filtration of insoluble residue, the solvent was concentrated to 15 mL under vacuum. The colorless solution was stored at −32 °C for 12 h to get X-ray quality block-shaped crystals of **4** (yield: 200 mg, 45%). ^{1}H NMR (C$_6$D$_6$): δ 6.45 (s, 2 H, C$_5$H$_2$(^{t}Bu)$_3$), 3.75–3.70 (q, 4 H, THF), 1.45 (s, 18 H, ^{t}Bu), 1.23 (s, 9 H, ^{t}Bu), 1.07–1.03 (q, 4 H, THF) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 131.4 (Ar), 130.2 (Ar), 103.8 (Ar), 34.4 (C(CH$_3$)$_3$), 32.8 (C(CH$_3$)$_3$), 32.4 (C(CH$_3$)$_3$), 30.9 (C(CH$_3$)$_3$) ppm. Mp: 126–127 °C to a colorless liquid. Anal (%). calcd for C$_{21}$H$_{37}$Cl$_2$GaO (444.15): C, 56.54; H, 8.36 Found: C, 57.22; H, 8.64.

η^5-Cp′′′Ga (5). A mixture of **2** (750 mg, 1 mmol) or **3** (1112 mg, 1 mmol) and KC$_8$ (540 mg, 4 mmol) were placed in a 100 mL round bottom flask and 40 mL of tetrahydrofuran was added at −78 °C. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight to give a solution of compound **5**. After filtration of insoluble residue, the solvent was removed under vacuum to give the green-yellow liquid **5** (yield: 410 mg, 34%). ^{1}H NMR (C$_6$D$_6$): δ 5.93 (s, 2 H, C$_5$H$_2$(^{t}Bu)$_3$), 1.37 (s, 18 H, ^{t}Bu), 1.20 (s, 9 H, ^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 131.42 (Ar), 130.34 (Ar), 103.31 (Ar), 34.57 (C(CH$_3$)$_3$), 32.61 (C(CH$_3$)$_3$), 32.39 (C(CH$_3$)$_3$), 30.48 (C(CH$_3$)$_3$) ppm. ^{71}Ga NMR (C$_6$D$_6$): δ −676.06 ppm.

η^5-Cp′′′Ga → GaI$_3$ (6). A mixture of **5** (61 mg, 0.2 mmol) and GaI$_3$ (90 mg, 0.2 mmol) were placed in a 50 mL round bottom flask and 15 mL of hexane was added at room temperature. The mixture was stirred overnight to form a white precipitate. The solvent was removed in vacuum and the product was extracted with 10 mL of toluene. After filtration, the solvent was concentrated to 5 mL under vacuum. The light yellow solution was stored in a freezer at −32 °C overnight to get X-ray quality colorless block shaped crystals of **6** (yield: 50 mg,

33%). ^{1}H NMR (C_6D_6): δ 6.12 (s, 2 H, $C_5H_2(^tBu)_3$), 1.19 (s, 18 H, ^tBu), 1.09 (s, 9 H, ^tBu) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 133.87 (Ar), 132.74 (Ar), 102.83 (Ar), 33.48 ($C(CH_3)_3$), 33.38 ($C(CH_3)_3$), 31.48 ($C(CH_3)_3$), 31.43 ($C(CH_3)_3$) ppm. ^{71}Ga NMR (C_6D_6): δ −279.55 ppm. Mp: 189 °C (dec). Anal (%). calcd for $C_{17}H_{29}Ga_2I_3$ (753.58): C, 27.10; H, 3.88 Found: C, 26.22; H, 3.74.

[η^1-Cp′″In(µ-Br)^{n}Bu]$_2$ (7). A mixture of Cp′″$_2$Mg (490 mg, 1 mmol) and InBr$_3$ (387 mg, 2.2 mmol) were placed in a 100 mL round bottom flask and 40 mL of toluene was added at ambient temperature. The reaction mixture was stirred 6 h and then ^{n}BuLi (2.5 M in hexane, 0.88 mL, 2.2 mmol) was added at −78 °C. The reaction mixture was allowed to warm to room temperature slowly and stirred 6 h to give a solution of compound 7. After filtration of insoluble residue, the solvent was concentrated to 10 mL under vacuum. The colorless solution was stored in a freezer at −32 °C for 12 h to get X-ray quality colorless block-shaped crystals of 7 (yield: 465 mg, 27%). ^{1}H NMR (C_6D_6): δ 6.61 (s, 2 H, $C_5H_2(^tBu)_3$), 1.79–1.62 (m, 4 H, In–CH$_2$CH_2CH$_2$CH$_3$), 1.49 (s, 18 H, ^tBu), 1.37–1.35 (m, 4 H, In–CH$_2$CH$_2$CH_2CH$_3$), 1.30 (s, 9 H, ^tBu) 1.04–0.98 (br q, 4 H, In–CH_2CH$_2$CH$_2$CH$_3$), 0.95–0.90 (m, 6 H, In–CH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 144.25 (Ar), 126.10 (Ar), 118.91 (Ar), 34.87 ($C(CH_3)_3$), 32.95 ($C(CH_3)_3$), 32.72 ($C(CH_3)_3$), 31.87 (In–CH$_2$CH$_2$CH$_2$CH_3), 30.65 ($C(CH_3)_3$), 29.41 (In–CH$_2$CH$_2$CH_2CH$_3$), 27.55 (In–CH$_2$CH$_2$CH$_2$CH$_3$), 13.35 (In–CH$_2$CH_2CH$_2$CH$_3$) ppm. Mp: 121–123 °C to a light yellow liquid. Anal (%). calcd for $C_{42}H_{76}Br_2In_2$ (970.48): C, 51.98; H, 7.89 Found: C, 52.42; H, 7.99.

[η^5-Cp′″Ge]$^+$[GeCl$_3$]$^−$ (8). A mixture of Cp′″$_2$Mg (245 mg, 0.5 mmol) and GeCl$_2$·dioxane (232 mg, 1 mmol) were placed in a 100 mL round bottom flask and 40 mL of Et$_2$O was added at −78 °C. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight to give a yellow solution of compound 8. The solvent was removed under high vacuum and the residue was extracted with 50 mL of toluene. After filtration of insoluble residue, the solvent was concentrated to 10 mL under vacuum. The yellow solution was stored at −32 °C in a freezer for 2 days to give X-ray quality colorless block-shaped crystals of 8 (yield: 204 mg, 42%). ^{1}H NMR (C_6D_6): δ 6.03 (s, 2 H, $C_5H_2(^tBu)_3$), 1.14 (s, 18 H, ^tBu), 1.09 (s, 9 H, ^tBu) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 138.85 (Ar), 136.71 (Ar), 108.96 (Ar), 33.24 ($C(CH_3)_3$), 33.09 ($C(CH_3)_3$), 31.36 ($C(CH_3)_3$), 31.10 ($C(CH_3)_3$) ppm. Mp: 107 °C (dec). Anal (%). calcd for $C_{17}H_{29}Cl_3Ge_2$ (485.98): C, 42.10; H, 6.03 Found: C, 41.89; H, 5.97.

[η^5-Cp′″Sn]$^+$[SnCl$_3$]$^−$ (9). A mixture of Cp′″$_2$Mg (245 mg, 0.5 mmol) and SnCl$_2$ (190 mg, 1 mmol) were placed in a 100 mL round bottom flask and 40 mL of Et$_2$O was added at −78 °C. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight to give a yellowish solution of compound 9. After filtration of insoluble residue, the solvent was concentrated to 5 mL under vacuum and then was added 5 mL of toluene. The solution was stored at 4 °C for 12 h in a freezer to get X-ray quality colorless block-shaped crystals of 9 (yield: 300 mg, 52%). ^{1}H NMR (C_6D_6): δ 6.07 (s, 2 H, $C_5H_2(^tBu)_3$), 1.25 (s, 18 H, ^tBu), 1.17 (s, 9 H, ^tBu) ppm. ^{13}C {^{1}H} NMR (C_6D_6): δ 137.61 (Ar), 135.98 (Ar), 107.83 (Ar), 34.10

$(C(CH_3)_3)$, 33.09 ($C(CH_3)_3$), 32.35 ($C(CH_3)_3$), 31.15 ($C(CH_3)_3$) ppm. Mp: 146 °C (dec). Anal (%). calcd for $C_{17}H_{29}Cl_3Sn_2$ (577.94): C, 35.38; H, 5.06 Found: C, 34.67; H, 5.03.

Conflicts of interest

There are no conflicts to declare.

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