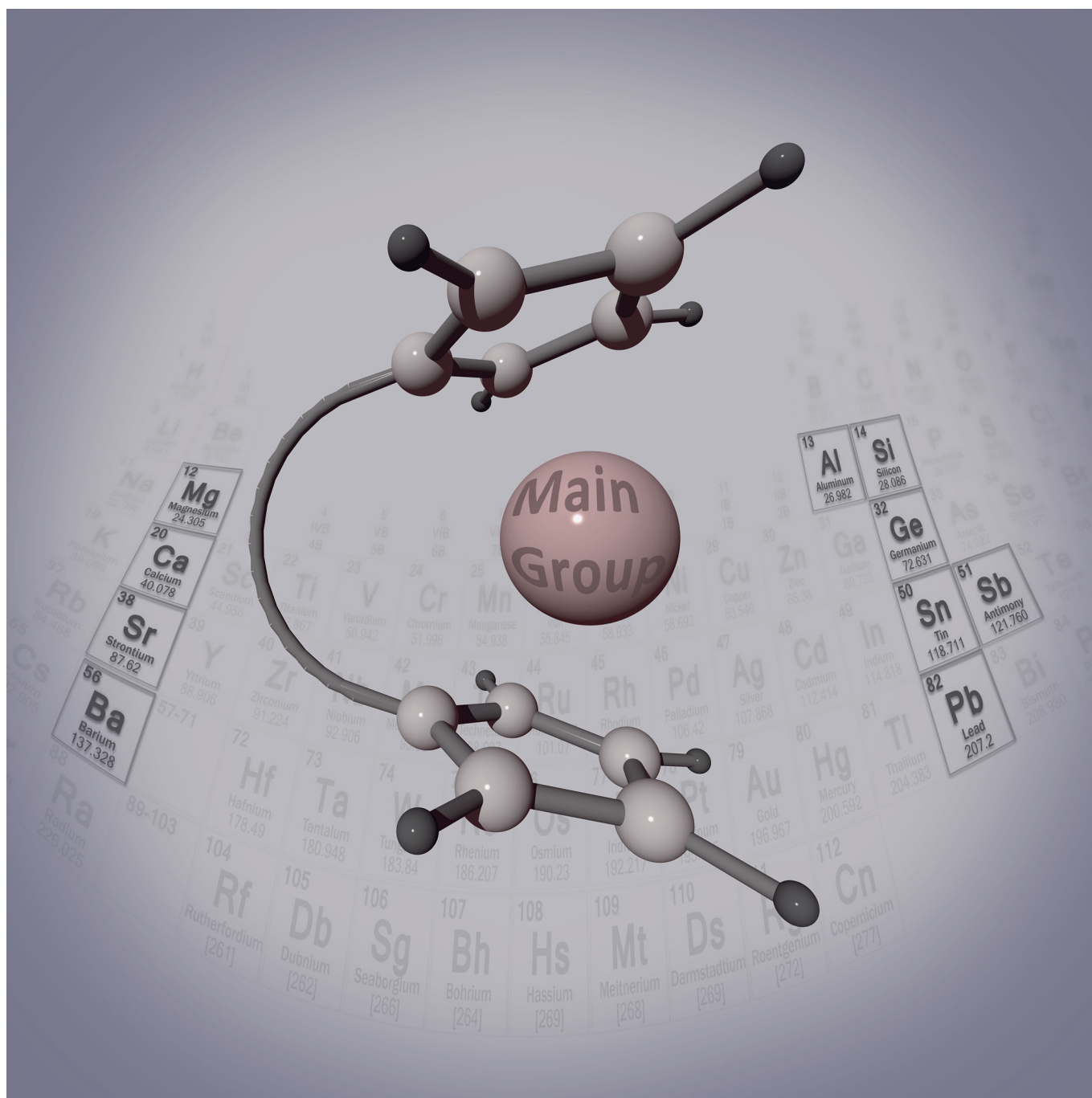


■ Inorganic Chemistry

Main-Group Metallocenophanes

Lisa Wirtz and André Schäfer*^[a]

Abstract: Metallocenes with interlinked cyclopentadienide ligands are commonly referred to as *ansa*-metallocenes or metallocenophanes. These can have drastically different properties than their unbridged parent compounds. While this concept is best known for transition metals such as iron,

it can also be adopted for many main-group elements. This review aims to summarize recent advances in the field of metallocenophanes based on main-group elements of group 2, group 13, group 14 and group 15, focusing on synthesis, structure and properties of these compounds.

Introduction

Following the discovery of ferrocene, **I**, and its structural elucidation,^[1–5] many isostructural or structurally related metallocenes of other transition metals have been reported ever since.^[6] Furthermore, it was quickly found that the concept of a sandwich type π -complex, with a metal bound to two cyclopentadienyl ligands in a η^5/η^5 fashion, is not limited to d-block elements, but can also be realized for many s- and p-block elements.^[7–10] The first example of such a main-group metallocene was magnesocene, **II**,^[11,12] an s-block metal based metallocene, which was quickly followed by the reports of stannocene, **III**, and plumbocene, **IV**,^[13,14] the first p-block metallocenes (Figure 1).

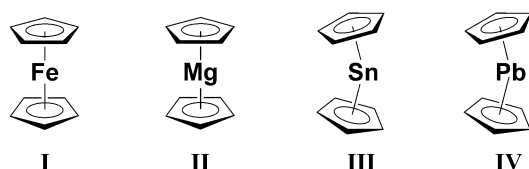


Figure 1. From left to right: ferrocene, **I**, magnesocene, **II**, stannocene, **III**, and plumbocene, **IV**.

In general, the cyclopentadienyl ligands in metallocene-type compounds can be functionalized in many different ways, modifying their steric and electronic properties. One such modification that has, in many cases, proven to greatly affect the overall reactivity of the corresponding compound, is interlinkage of the two cyclopentadienyl moieties, resulting in *ansa*-metallocenes, also referred to as metallocenophanes (Figure 2). This structural motif was first realized for iron, ferrocenophanes, respectively, but has since then been studied extensively for various transition metals for over 50 years.^[15–19] Different transition metal metallocenophanes have seen appli-

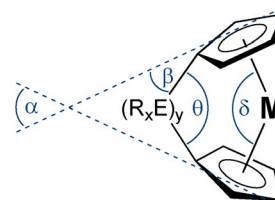


Figure 2. General representation of a metallocenophane with definition of relevant angles.

cations for example in homogenous catalysis^[20,21] and ring-opening polymerizations.^[22,23] Furthermore, it is worth mentioning that this concept has since also been applied to systems with other π ligands such as phenyl or cycloheptatrienyl.^[15,24,25]

On the other hand, while main-group metallocenes have been known for almost as long as their transition metal analogues, metallocenophanes of main-group elements are much younger and less explored.^[7–10,19] The first examples date back some decades, and several new p-block based metallocenophanes have only recently been reported. This review aims to provide an overview of this emerging research field, describing the synthesis, structure and properties of metallocenophanes based on group 2, group 13, group 14 and group 15 elements. *ansa*-Ligands metalated with group 1 metals, will not be discussed.


Metallocenophanes of Group 2 Elements


With magnesocene, **II**, being the first main-group metallocene,^[11,12] and metallocene-type compounds known for every alkaline earth metal,^[8–10] it comes as no surprise that there are numerous examples of group 2 based metallocenophanes. The earliest reports date back to the 1990s, which makes these compounds much younger than their unbridged parent compounds.

In case of magnesium, sila- and carba-bridged [1]- and [2]magnocenophanes, **1**, with a variety of substitution patterns have been reported (Figure 3).^[26–35] The synthesis usually follows the same route, which is the synthesis of the corresponding neutral *ansa*-ligand system, followed by treatment of this protonated ligand with a suitable magnesium base like di-*n*-butyl magnesium (Scheme 1). This synthetic route was first realized in 1997 by Burger et al. in the preparation of Me₂C[1]magnocenophane **1a**,^[26] and has since been adopted for several examples of [1]- and [2]magnocenophanes (Figure 3).

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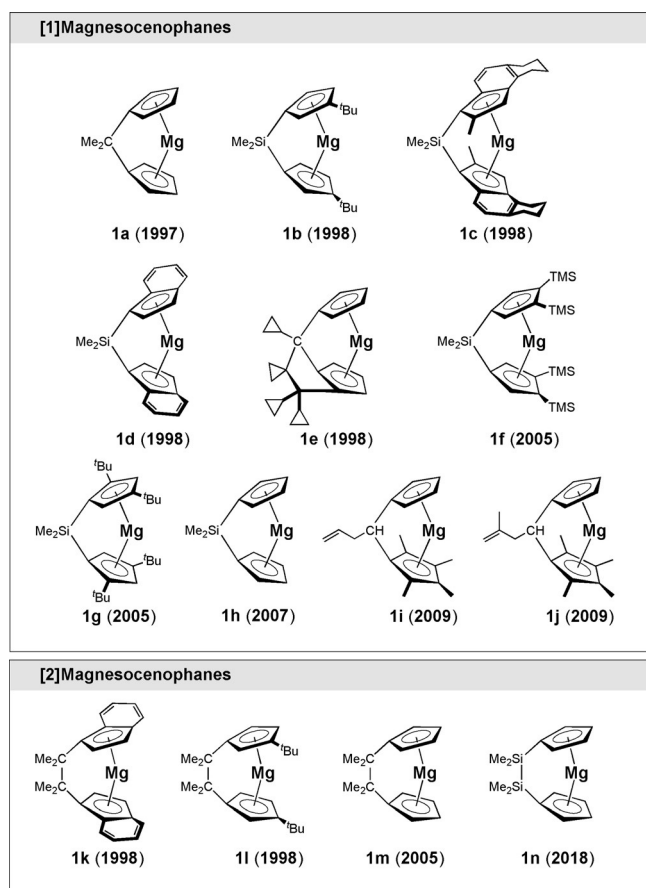
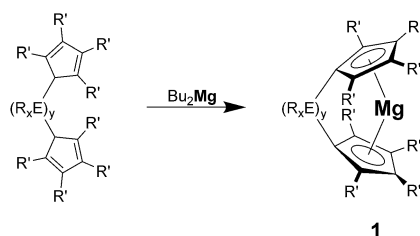


Figure 3. [n]Magnesocenophanes, 1.

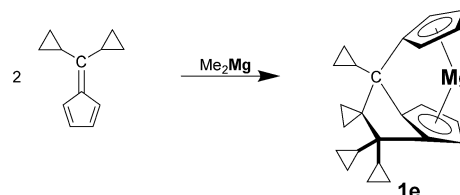


Scheme 1. Common synthetic routes to [n]magnesocenophanes, 1.

It is worth mentioning, that the carba[1] bridging motif is rarely found in transition metal metallocenophanes,^[15,17] as it makes the ligand system quite small and the resulting ring strain in such metallocenophanes is considered to be extremely high. For instance, this seems to be the reason that C[1]ferrocenophanes are unknown.^[15–17] An exception are metallocenophanes of group 4 metals with d^0 electron configuration, in which the d-orbitals that are raised in energy upon tilting, are unoccupied. Due to the high ionic character of the alkaline earth metal Cp bonds, the ring strain in C[1]metallocenophanes of group 2 metals is probably relatively small. In case of C[1]magnesocenophanes, very large dihedral angles α of the Cp plains (Figure 2) can be observed for some solvent complexes. For instance, in **1a**-(dme) an α angle of around

80° is observed, which is the second largest in any metallocenophane, only surpassed by the α angle in bariocenophane **4c**-(thf)₃ (vide infra). To put this into perspective with transition metal based metallocenophanes, the largest α angle in a [1]ferrocenophane is just 32.4° ,^[16] the α angle in a Me₂C[1]titanocenophane is 66.9° .^[20]

In addition to the deprotonation/metalation route utilizing dibutyl magnesium, it was demonstrated by Westerhausen et al. that treatment of 6,6-dicyclopropylfulvene with dimethylmagnesium results in the formation of a [1,2]magnesocenophane via nucleophilic addition and C–C coupling reaction (Scheme 2).^[30]



Scheme 2. Synthesis of C[1,2]magnesocenophane 1e.

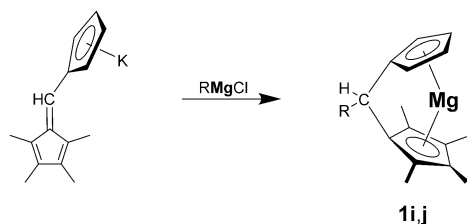
This is quite surprising, as reactions of fulvenes with magnesiumorganyls usually yield magnesocenes via oxidative addition to the exocyclic double bond.^[30] This uncommon reaction route has not been employed further for the preparation of other magnesocenophanes. However, in 2009, it was recognized by Antiñolo et al. that treatment of a potassium fulvenyl-

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André Schäfer studied chemistry at the Carl von Ossietzky University of Oldenburg, where he graduated in 2009. He joined the group of Prof. Dr. Thomas Müller for his doctoral research and received his Ph.D. in 2013. After a two-year postdoctoral stay in the group of Prof. Dr. Ian Manners at the University of Bristol, he began his independent career at Saarland University where he was awarded an Emmy Noether grant in 2016. His research focuses on main-group element cyclopentadienyl compounds, with a particular interest in main-group metallocenophanes.





Scheme 3. Synthesis of C[1]magnesocenophane **1 i,j** (i: R=CH₂CH=CH₂; j: R=CH₂CMe=CH₂).

cyclopentadienide with a Grignard reagent would result in the formation of C[1]magnesocenophanes, via nucleophilic addition to the exocyclic double bond and elimination of KCl (Scheme 3).^[33] Only two examples of magnesocenophanes were prepared via this route.

Overall, at least 14 magnesocenophanes, **1 a–n**, have been reported since 1997 (Figure 3), with eight of them being structurally characterized in form of solvent adducts (Table 1). In many cases, the magnesocenophanes, **1**, were not the prime target of the study, but were merely generated and used in situ as Cp-transfer reagents in the preparation of transition metal metallocenophanes. The fact that the magnesocenophanes, **1**, were only isolated and structurally characterized in form of donor-solvent adducts, results from their rather poor solubility in unpolar solvents and the high Lewis acidity of the central atom. It must be taken into consideration that the solvent coordination can have a strong influence on the overall

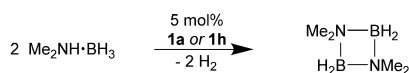
geometry. For instance, in case of the aforementioned C[1]magnesocenophane **1 a**, dme coordination to the magnesium atom results in an increased dihedral angle of the Cp planes, α , compared to what is predicted for the solvent-free form, by DFT calculations.^[28] Furthermore, thf and acetonitrile coordination to C[1]magnesocenophane **1 a** result in ring slippage of one of the Cp ligands in the solid state structure, as η^1/η^5 coordination is found in **1 a**·(thf)₂ and η^2/η^5 coordination is found in **1 a**·(NCMe)(thf).^[26] Structural features like this are a result of the highly ionic Mg–Cp bonds and are found throughout many crystal structures of magnesocenophanes, **1** (Table 1), but are usually not reflected by NMR spectroscopy in solution. For convenience, all structures of magnesocenophanes, **1**, in Figure 3 are presented in a general form without solvent molecules and with η^5/η^5 coordination mode. The details of the solid-state structures are given in Table 1.

In contrast to transition metal chemistry, where metallocenophanes have seen a lot of application in homogenous catalysis, for example in olefin polymerization,^[21] utilization of main-group metallocenophanes in any kind of catalytic bond activation process is very rare. The predominant application for these compounds are transmetalation reactions for the preparation of transition metal metallocenophanes, and in some cases also p-block metallocenophanes. However, in 2020, Schäfer et al. reported the use of magnesocenophanes as catalysts in dehydrocoupling reactions of amine boranes. In particular [1]magnesocenophanes were found to be very potent catalysts in the dehydrocoupling of dimethylamine borane (Scheme 4), outperforming many other group 2 compounds.^[28]

Table 1. Selected structural parameters and references of group 2 metallocenophanes, **1**, **2**, **4** (if more than one crystal structure of a compound exists, more than one molecule is found in the asymmetric unit, and/or bond lengths/angles are found more than once in the molecule, all values are given. Angles α and δ are only given for η^5/η^5 geometries).

Compound	M–Cp ^[a] [pm]	Cp hapticity	α ^[b] [°]	δ ^[b] [°]
1 a ·(thf) ₂ ^[27]	215.4; 231.4	η^1/η^5	–	–
1 a ·(dme) ^[28]	223.3; 225.4; 230.4	η^5/η^5	77.9; 80.1	119.9; 121.7
1 b ·(thf) ₂ ^[29]	221.0; 236.2	η^1/η^5	–	–
1 c ·(thf) ₂ ^[29]	222.7 ^[d] ; 223.1 ^[d] ; 222.6 ^[d] ; 225.0 ^[d]	η^3/η^3	–	–
1 e ·(thf) ₂ ^[30]	211.5; 213.0; 227.2	η^1/η^5	–	–
1 h ·(thf) ₂ ^[32]	216.6; 235.7	η^2/η^5	–	–
1 k ·(thf) ₂ ^[29]	227.7; 230.0; 231.8; 231.9	η^3/η^3	–	–
1 l ·(thf) ₂ ^[29]	208.6; 216.9	η^2/η^5	53.3	130.5
1 n ·(dme) ^[35]	226.6; 230.8	η^5/η^5	52.7	133.4
2 a ·(thf) ₃ ^[36]	253.0; 271.4 ^[d]	η^3/η^3	–	–
2 b ^[37]	247.7; 250.1	η^5/η^5	68.8	118.2
2 c ·((^t BuNCH) ₂) ^[38]	228.7; 237.7; 239.1; 239.6; 242.8	η^5/η^5	59.2; 61.0; 61.2	119.0; 119.2; 121.5
2 d ·(thf) ₂ ^[39,40]	239.1; 239.5; 240.6; 241.2; 241.9 ^[c]	η^5/η^5	61.3; 63.3 ^[c]	119.8; 120.4 ^[c]
2 g ·(thf) ₂ ^[43]	244.0; 245.2; 245.3; 247.7	η^5/η^5	66.0; 66.3	118.5; 118.8
2 j ·(dme) ^[46]	238.1	η^5/η^5	59.7	121.4
2 k ·(thf) ₂ ^[48]	243.7; 243.8; 244.6; 244.7	η^5/η^5	61.2; 61.7	118.8; 119.1
2 l ·(dme) ^[49]	234.9; 235.4; 235.7; 238.1	η^5/η^5	59.5; 63.5	117.4; 119.3
2 l ·(dme) ₂ ^[49]	239.7; 242.8	η^2/η^5	65.7	114.1
2 n ·(thf) ₂ ^[51]	240.6; 241.8	η^5/η^5	58.3	120.2
2 o ·(thf) ₂ ^[52]	244.9; 248.7	η^2/η^5	65.3	119.1
4 a ·(thf) ₄ ^[36]	296.9 ^[d] ; 297.9 ^[d]	η^3/η^3	–	–
4 c ·(thf) ₃ ^[53]	297.1 ^[d] ; 308.1	η^3/η^5	–	–
	283.1; 283.4	η^2/η^5	94.3	103.8

[a] Bond length given with respect to the corresponding hapticity. [b] See Figure 2 for definition of angle. [c] Isomers with *cis* and *trans* configuration of the substituents of the *ansa*-bridge. [d] Exocyclic coordination to indenyl/fluorenyl ligands.



Scheme 4. Dehydrocoupling of dimethylamine borane catalyzed by magnesocenophanes **1a** or **1h**.

In this context, it was shown that different bridging motifs in magnesocenophanes, **1**, can have an important influence on their electronic properties. The global electrophilicity indices and fluoride ion affinities of [1]- and [2]magnesocenophanes **1a**, **1h**, **1m** and **1n** were probed by DFT calculations and found to increase as a function of tilt of the cyclopentadienide ligands, thus are larger in case of [1]magnesocenophanes and smaller in case of [2]magnesocenophanes. This seems to have an effect on the reactivity of these compounds, as C[1]- and Si[1]magnesocenophanes **1a** and **1h** perform much better in the catalytic dehydrocoupling of dimethylamine borane than the related C[2]- and Si[2]magnesocenophanes **1m** and **1n**.

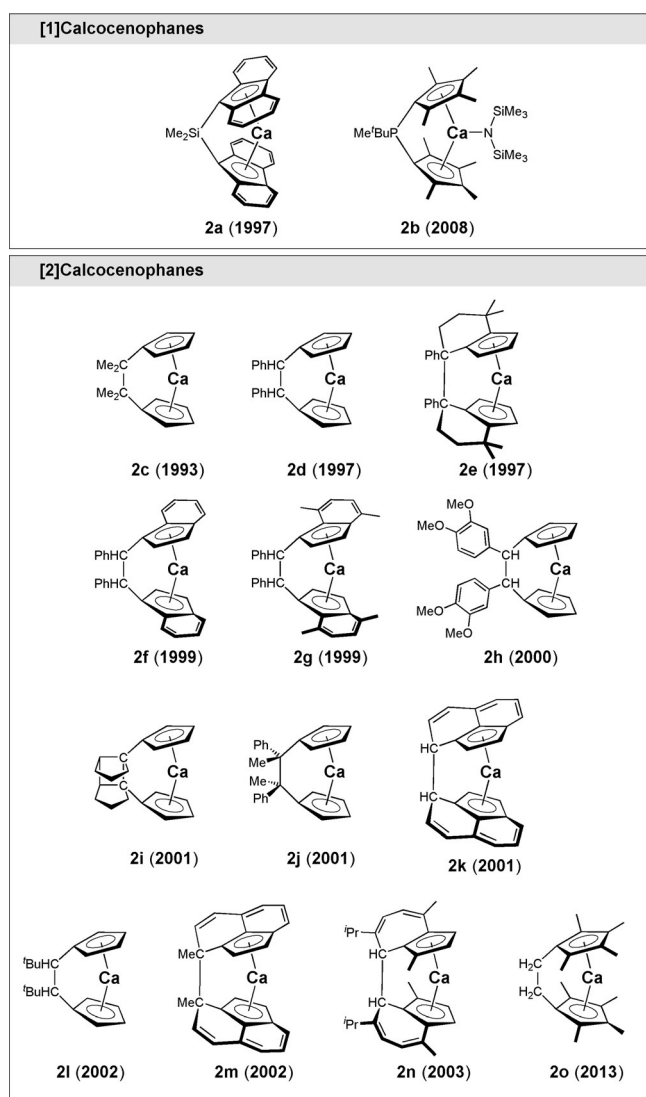
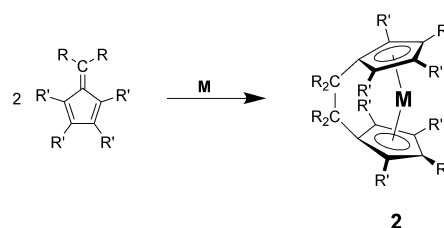


Figure 4. [n]Calcocenophanes, **2** (in case of **2n** different isomers were reported).

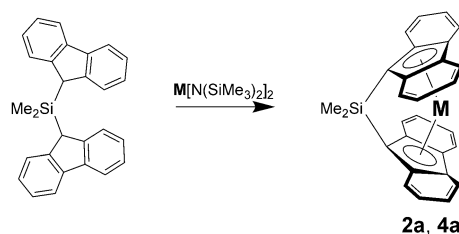
In addition to metallocenophanes of magnesium, there are several examples of metallocenophanes of the heavier alkaline earth metals calcium, strontium and barium, with the majority being calcocenophanes, **2** (Figure 4).^[36–53] In contrast to magnesocenophanes, **1**, where the synthesis commonly involves metalation of an *ansa*-ligand system by deprotonation with di-*n*-butyl magnesium (Scheme 1), calcocenophanes, **2**, and strontiocenophane, **3**, are often prepared by oxidative coupling starting from the corresponding alkaline earth metal and a suitable fulvene.^[38–52]



Scheme 5. Synthetic routes to C[2]calcocenophanes, **2**, and C[2]strontiocenophane, **3** (M = Ca, Sr).

Activated calcium or strontium metal reacts with a suitable fulvene in a donor solvent, such as thf, and gives the corresponding C[2]metallocenophane, as first demonstrated by Edlmann et al. in 1993.^[38] Since then, this synthetic route has been widely applied, giving rise to many C[2]calcocenophanes (Figure 4). Since this approach is naturally limited to C[2] bridging-motives, which might be the reason why [1]metallocenophanes of calcium and the related heavier group 2 elements are much less explored. Furthermore, this reaction route can suffer from mediocre yields, which is due to the fact that the Cp radicals, which are formed as intermediates in the initial single electron transfer step, can abstract a hydrogen atom from the solvent before undergoing recombination, which results in formation of a metallocene, rather than a metallocenophane. This was for example shown for the reaction of 6,6-dimethylfulvene with calcium, yielding calcocenophane **2a** and also 1,1'-diisopropylcalcocene.^[39] Interestingly, the treatment of 6,6'-dimethylfulvene with barium metal was reported to give no reaction.^[39]

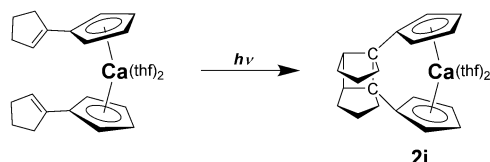
In addition, it was established by Harder et al. in 1997 that deprotonation and metalation of a sila[1]-bridged bis(fluorenyl) *ansa*-ligand system can be achieved by treatment with calcium and barium bis(trimethylsilyl)amide (Scheme 6).^[36] This route



Scheme 6. Synthesis of Si[1]calcocenophane, **2a** and Si[1]bariocenophane, **4a** (M = Ca, Ba).

gives access to the corresponding Si[1]calcocenophane, **2a** and Si[1]bariocenophane, **4a**. In case of the Si[1]calcocenophane, **2a**, this is one of only two examples of [1]metallocenophanes of calcium (Figure 4).

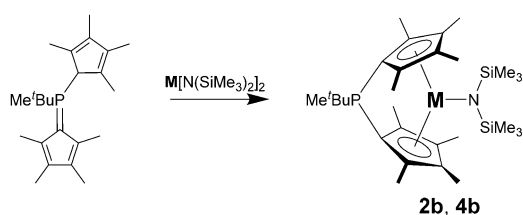
Additionally, it was demonstrated by Shapiro et al. in 2001 that a ring closing reaction on a calcocene can be realized to prepare a corresponding calcocenophane (Scheme 7).^[45]



Scheme 7. Synthesis of C[2]calcocenophane, **2i**.

When a 1,1'-dicyclopentenylcalcocene is photolyzed for a prolonged duration, [2+2] cycloaddition takes place, which gives calcocenophane **2i**. This route does not present a viable synthetic pathway, as it requires very long reaction times while giving only poor yields. For instance, the authors reported that 90% conversion of the starting material was observed after 10 days of continuous irradiation, with an isolated yield of calcocenophane **2i** of just 20%.

Furthermore, a P[1]calcocenophane, **2b**, was obtained from the reaction of a cyclopentadienylphosphafulvene with calcium bis(trimethylsilyl)amide in low yields (Scheme 8), as reported by Hanusa et al. in 2008.^[37] Since this phosphafulvene *ansa*-ligand system is formally a single negatively charged ligand, with two anionic cyclopentadienyl moieties and a cationic phosphorous atom, P[1]calcocenophane **2b** exhibits a trivalent calcium(II) atom, which retains a bis(trimethylsilyl)amide ligand for charge balance. In a similar manner, Brintzinger et al. reported the synthesis of P[1]bariocenophanes, **4b–d**, in 1998, by treatment of a phosphonium iodide *ansa*-ligand with barium bis(trimethylsilyl)-amide (Scheme 8).



Scheme 8. Synthesis of P[1]calcocenophane, **2b**, and P[1]bariocenophane, **4b** (M = Ca, Ba).

Depending on stoichiometry and reaction conditions, they were able to isolate the bariocenophane bis(trimethylsilyl)-amide complex, **4b** and additionally the corresponding cationic bariocenophane **4c** and spiro bariocenophane **4d**, carrying two *ansa*-ligands (Figure 5).

Similarly, to the afore-discussed magnesocenophanes, **1**, most calcocenophanes, **2**, strontiocenophane, **3**, and barioce-

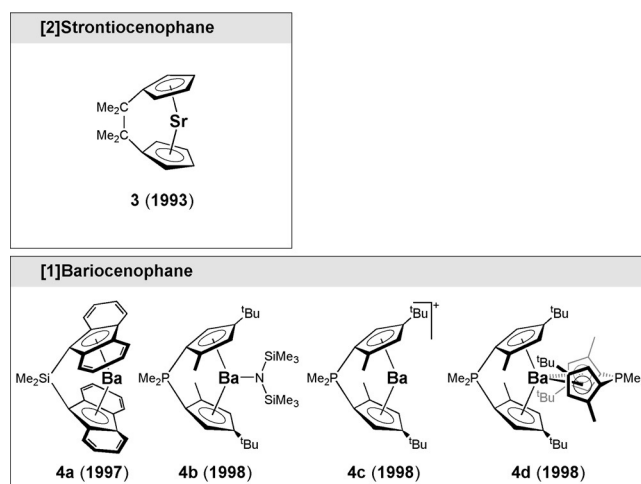


Figure 5. [2]Strontiocenophane, **3**, and [1]bariocenophanes, **4**.

nophanes, **4**, possess a rather poor solubility in unpolar solvents and thus are usually synthesized and handled in donor solvents such as thf. Therefore, almost all reported crystal structures of these compounds exhibit solvent coordination to the central atom, but in contrast to magnesocenophanes, **1**, this solvent coordination only rarely results in ring slippage in the solid state (Table 1).

As before, for convenience, all structures in Figure 4 and Figure 5 are presented in a general form with η^5/η^5 coordination mode and without solvent coordination, while the details of the solid-state structures are given in Table 1. The single strontiocenophane, **3**, is unfortunately not structurally characterized, and only limited analytical data is available for this compound.

Similar to [1]magnesocenophanes, the dihedral angle α of the Cp planes in the structurally characterized [1]calcocenophane **2b**-(thf)₃ and [1]bariocenophane **4c**-(thf)₃ are extreme large (Table 1), compared to [1]metallocenophanes of transition metals.^[16,20] In particular, it is worth noting that P[1]bariocenophane **4c**-(thf)₃ exhibits the largest α angle (94.3°) reported for any [1]metallocenophane so far.

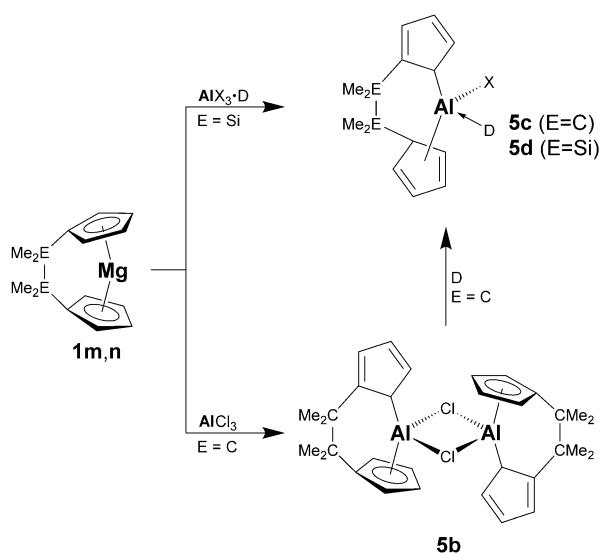
In summary, at least 15 calcocenophanes, one strontiocenophane and four bariocenophanes have been reported, not all of which have been structurally characterized, as some were only generated in situ.

In addition, dimethylplatinum complexes of diphosphanyl-substituted calcocenes, strontiocenes and bariocenes have also been reported and structurally characterized in form of thf adducts, and could in principle be regarded as P-Pt-P[3]-metallocenophanes of these group 2 metals,^[54] but will not be discussed further in this review.

Metallocenophanes of Group 13 Elements

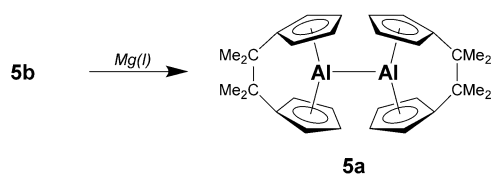
There are several bis(cyclopentadienyl)compounds of group 13 elements, in many cases exhibiting $\eta^1 \sigma$ bonded cyclopentadienyl groups. η^5 bonded cyclopentadienide ligands on the other hand are often observed in case of divalent cationic

compounds, with the aluminocenium cations being isostructural to ferrocene.^[8,10,55] However, metallocenophane-type compounds of group 13 elements are rather rare and limited to aluminum. In 2005 Shapiro et al. reported the transmetalation of C[2]magnocenophane **1m** with aluminum(III) chloride to give the corresponding aluminocenophane chloride dimer **5b** (Scheme 9).^[34] Addition of a donor molecule such as thf or an isonitrile yielded the corresponding monomeric adducts **5c**. In 2018 Schäfer et al. showed that such donor-stabilized bis(cyclopentadienyl)alanes with interlinked cyclopentadienyl ligands, could also be obtained directly by transmetalation of Si[2]magnocenophane **1n** with aluminum(III) halide donor complexes (AlX₃·D), with donors such as thf, carbenes and thions (Scheme 9).^[35]



Scheme 9. Synthetic routes to [2]aluminocenophane donor complexes, **5b–d**.

Although these aluminum compounds, **5b–d**, are structurally closely related to metallocenophanes, none of these compounds exhibited two η^5 bonded Cp groups in the solid state (**5b**: η^1/η^5 ; **5c**: η^1/η^{1-3} ; **5d**: η^1/η^1), which raises the question whether they can be considered metallocenophanes. The quest for a “true” group 13 metallocenophane was successful, when in 2019 Schäfer et al. reported that the C[2]aluminocenophane chloride dimer, initially reported by Shapiro et al., could be reduced using a 1,3-diketiminato magnesium(I) reagent, to give the corresponding dialane **5a** (Scheme 10).^[56]



Scheme 10. Synthesis of bis(C[2]aluminocenophane) **5a** (Mg(I) = {Nac-NacMg₂}).

Compound **5a** is noteworthy in several regards, as it exhibits two η^5 -bonded cyclopentadienyl groups, making it the only neutral aluminum compound with this structural feature (Al–Cp^{cent}: 204.3–234.1 pm; α : 72.3–73.9°; δ : 143.7–144.9°). To that effect, the formal coordination number of each aluminum atom is eleven. The aluminum-aluminum single bond was found to be the shortest of all acyclic dialanes and was studied in-depth by DFT calculations involving NBO and EDA techniques. The shortness of the bond was found to be a result of the high ionic character of the Al–Cp bonds, giving the Al–Al bond an unusually large *s*-character of more than 66%. Even though the bond is so short, it was demonstrated that it can easily be oxidatively cleaved by treatment of dialane **5a** with different reagents, such as element chlorides of isonitriles.

Overall, the field of metallocenophanes of group 13 elements is rather limited, with just a handful of examples of aluminum compounds, **5**, and only **5a** being a “true” metallocenophane (Figure 6).

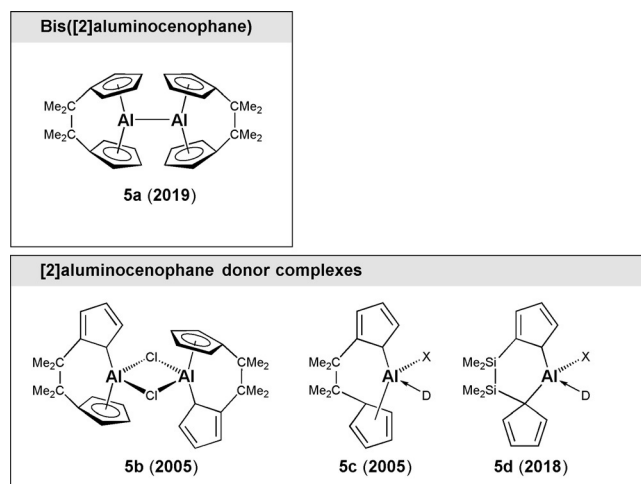


Figure 6. Bis([2]aluminocenophane), **5a**, and related bridged bis(cyclopentadienyl)aluminum halide complexes, **5b–d**.

Metallocenophanes of Group 14 Elements: Tetrelocenophanes

In the field of main-group metallocenophanes, group 14 based metallocenophanes present the group with the oldest examples, dating back to a report of Zuckerman et al. from 1984 about xyllyl-bridged stannocenophanes, **8a** (Figure 7). As seen before in case of group 2, this is again several decades after the first report of the group 14 metallocenes parent compounds.^[13,14] Since this first report, many more examples of metallocenophanes of all heavier group 14 elements (Si–Pb) have been described.^[57–66] Thus nowadays, this group hold many examples and a trivial name for group 14 based metallocenophanes would be appropriate and useful. In this regard, it has been suggested by Schäfer et al. that the metallocenes of group 14 elements could be referred to as “tetrelocenes”, a term constructed from Tetrrels—the group 14 elements—and metallocenes. Following this concept, the corresponding met-

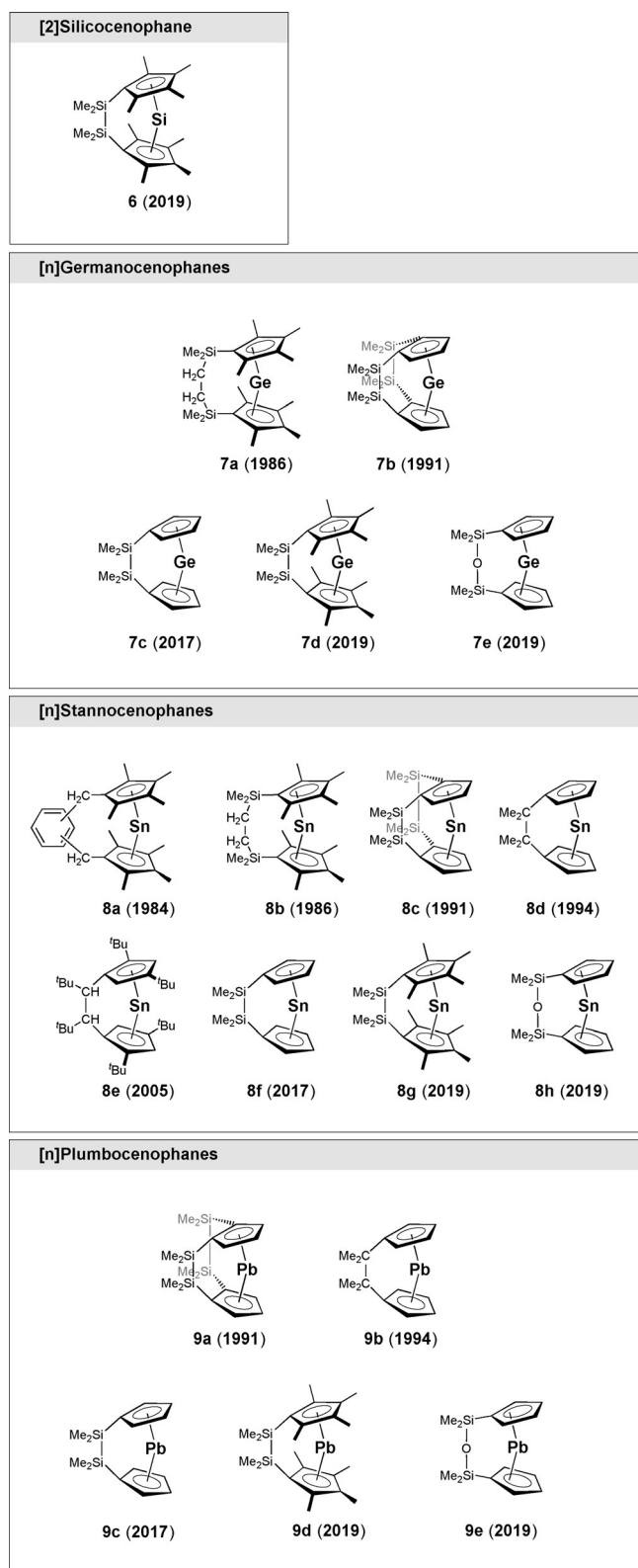
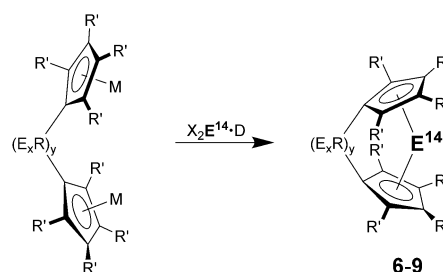


Figure 7. [n]Tetrelocenophanes, 6–9.

alocenophanes of group 14 elements could be referred to as “tetrelocenophanes”. This naming concept also circumvents the dilemma that not all group 14 elements are metals and

therefore the term metallocenophane is formally not correct for silicocenophanes and germanocenophanes.

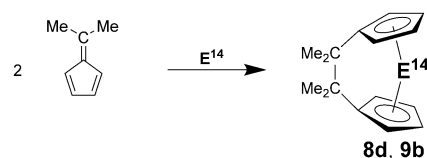
The majority of tetrelocenophanes, 6–9, has been prepared via the salt-elimination route that starts from a dimethylated *ansa*-ligand and a corresponding element dihalide (Scheme 11), often utilized for the synthesis of transition metal based metallocenophanes as well and sometimes referred to as “flytrap-approach”.



Scheme 11. Common synthetic route to [n]tetrelocenophanes, 6–9 ($E^{14} = \text{Si-Pb}$).

While for the heavy group 14 elements like germanium, tin and lead, the necessary dichlorides are stable and commercially available compounds, this is not the case for silicon dichloride. Therefore, in the synthesis of silicocenophane, 6, a dichloro-silylene carbene adduct was used as the silicon(II) precursor,^[57] following a report about the analogues synthesis of decamethyl silicocene by Filippou et al.^[67]

Furthermore, in 1994 Tacke reported that C[2]stannocenophane 8d and C[2]plumbocenophane 9b can be obtained by the reaction of the corresponding metal with 6,6-dimethylfulvene (Scheme 12),^[63] similar to the synthesis of C[2]calcocenophanes 2c–o and C[2]strontiocenophane 3 (vide supra).



Scheme 12. Synthesis of C[2]tetrelocenophanes 8d and 9b ($E^{14} = \text{Sn, Pb}$).

Although the first reports of tetrelocenophanes date back to 1984, it was not until 2005 that the first crystal structure was published by Balaich et al., which was of C[2]stannocenophane 8e.^[64] Since then, several crystal structures of tetrelocenophanes of silicon, germanium, tin and lead have been reported (Figure 7). Among these, silicocenophane 6 and germanocenophanes 7 are the only examples of “metalloidocenophanes”, hence metallocenophanes formally based on metalloids and not metals.

All structurally characterized tetrelocenophanes, 6–9, exhibit η^5/η^5 bonded Cp groups, which is typical for metallocene-type compounds of heavier group 14 elements in oxidation state +II.

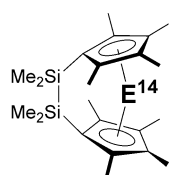
Table 2. Selected structural parameters and references of group 14 tetrelcenophanes, **6–9** (if more than one molecule is found in the asymmetric unit, and/or bond lengths/angles are found more than once in the molecule, all values are given).

Compound	E ¹⁴ –Cp ^[a] [pm]	Cp hapticity	α ^[a] [°]	δ ^[a] [°]
6 ^[57]	216.8; 217.6	η ⁵ /η ⁵	48.3	163.1
7c ^[60]	224.2; 226.4	η ⁵ /η ⁵	40.5; 42.4	156.9; 157.4
7d ^[57]	220.9; 222.5	η ⁵ /η ⁵	41.9	158.8
7e ^[61]	222.1; 236.7	η ⁵ /η ⁵	44.9	157.1
8e ^[61]	238.5	η ⁵ /η ⁵	75.0	129.4
8f ^[60]	239.4; 242.4	η ⁵ /η ⁵	47.3; 47.5	146.9; 147.4
8g ^[57]	240.9; 241.2	η ⁵ /η ⁵	52.2	148.9
8h ^[61]	239.2; 241.6	η ⁵ /η ⁵	49.8	147.7
9c ^[60]	245.7; 262.3	η ⁵ /η ⁵	48.8; 54.9	131.1; 134.6
9d ^[57]	248.0; 248.6	η ⁵ /η ⁵	51.7	145.4
9e ^[61]	243.0; 256.0	η ⁵ /η ⁵	36.3; 54.2	137.1; 147.5
8f ·NHC ^[b] ^[65]	206.5; 266.3	η ⁵ /η ⁵	57.4	132.7
8f ·NHC ^[c] ^[66]	260.2; 261.9	η ⁵ /η ⁵	56.8	132.7
8f ·NHC ^[d] ^[66]	263.5; 264.7	η ⁵ /η ⁵	62.4	128.8
8h ·NHC ^[b] ^[61]	257.0	η ⁵ /η ⁵	37.6	140.9
9e ·NHC ^[b] ^[61]	260.5	η ⁵ /η ⁵	37.0	140.5
9e ·NHC ^[d] ^[65]	256.0; 258.9	η ⁵ /η ⁵	44.8	135.2

[a] See Figure 2 for definition of angle. [b] NHC: 1,3,4,5-tetramethylimidazolin-2-ylidene. [c] NHC: 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene. [d] NHC: 1,3-dimesitylimidazolin-2-ylidene.

Compared to the group 2 metallocenophanes, **1–4**, the central atoms in tetrelcenophanes, **6–9**, exhibit a much less Lewis acidic character, which means that no solvent complexes, such as thf adducts, are known. The observed E¹⁴–Cp^{cent} bonds are generally a bit shorter than what is observed in the group 2 metallocenophanes, owing to a stronger and more covalent bond. Interestingly, the dihedral angles α in [2]tetrelcenophanes are in the range of 40–55° (Table 2), which is larger than in [1]ferrocenophanes, where the largest α angle is 32.4°,^[16] but similar to [2]metallocenophanes of group 4 metals.^[20] It must be taken into consideration however that this is not just a result of the *ansa*-bridge, but that tetrelcenophanes in general possess a stereochemically active lone pair on the central atom and that consequently the unbridged tetrelcenophanes are also bend.^[7,8,10]

In one case, **6**, **7d**, **8g**, **9d**, the exact same *ansa*-ligand has been employed to the complete series of heavy group 14 elements (Si–Pb), which allows for a direct comparison of the effect of the group 14 element on the structural properties of the tetrelcenophanes. For instance, in case of Si[2]silicocenophane **6**, Si[2]germanocenophane **7d**, Si[2]stannocenophane **8g**, and Si[2]plumbocenophane **9d**, the effect of the increasing size of the central atom to the structure can be observed (Figure 8).



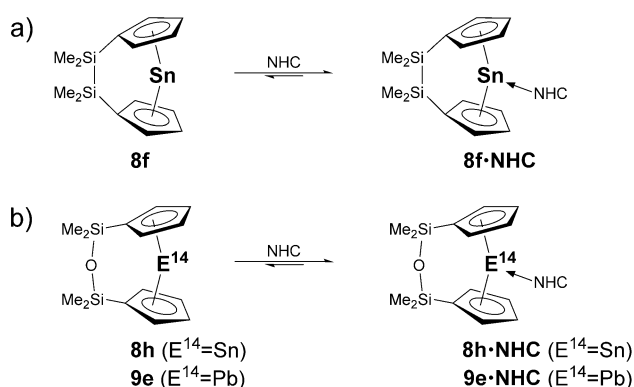
compound	α	E ¹⁴ –Cp ^{cent}
6 (E ¹⁴ = Si)	48.3°	216.8–217.6 pm
7d (E ¹⁴ = Ge)	41.9°	220.9–222.5 pm
8g (E ¹⁴ = Sn)	52.2°	240.9–241.2 pm
9d (E ¹⁴ = Pb)	51.7°	248.0–248.6 pm

Figure 8. Selected structural properties of Si[2]tetrelcenophanes **6**, **7d**, **8g** and **9d**.

Interestingly, while the increasing size of the group 14 element is of course accompanied by an elongation of the E¹⁴–Cp bonds, there is no linear trend for the dihedral angle α of the Cp planes. Silicocenophane **6** exhibits a significantly larger dihedral angle α than germanocenophane **7d**. Stannocenophane **8g** and plumbocenophane **9d** possess very similar α angles, only slightly larger than angle α in silicocenophane **6**. Aside from packing effects in the crystal that can have an important effect on the molecular geometry, the stereochemically active lone pair on the group 14 element will almost certainly also have a strong influence, and is believed to have higher p character in case of silicon and increasingly high s character when going down the group, thus has less impact on the bending in case of the heavier elements. Therefore, the bend geometry of silicocenophane **6** could be in larger part attributed to the lone pair on the silicon atom than the *ansa*-bridge, while in case of plumbocenophane **9d**, the importance of the effects are probably reversed, with the *ansa*-bridge playing a more important role than the lone pair on the lead atom.

Even though the central atom in tetrelcenophanes is much less Lewis acidic than in group 2 metallocenophanes, it maintains enough Lewis acidity to coordinate strong σ donors such as N-heterocyclic carbenes (Scheme 13). This is in line with tetrelcenophanes and tetrelcenophanes being tetrylene-type compounds and that many tetrylene carbene adducts are known.^[68,69]

N-heterocyclic carbene complexes of tetrelcenophanes of tin and lead, as well as for their unbridged parent compounds, have been studied by Schäfer et al.,^[61,65,66] and several examples of stannocenophane and plumbocenophane carbene adducts have been structurally characterized. A side-on coordination of the NHC ligand to the tetrelcenophane framework is found, which can be explained by the stereochemically active lone pair on the central atom and the shape of the LUMO, which is essentially a vacant p-orbital on the central atom. It



Scheme 13. a) Reaction of stannocenophane **8f** with NHCs (NHC: 1,3,4,5-tetramethylimidazolin-2-ylidene, 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene, 1,3-dimesitylimidazolin-2-ylidene). b) Reaction of stannocenophane **8h** and plumbocenophane **9e** with NHCs (NHC: 1,3,4,5-tetramethylimidazolin-2-ylidene, 1,3-dimesitylimidazolin-2-ylidene).

was recognized early on that these complexes are extremely reactive and only marginally stable at room temperature, which is very surprising considering that tetrelcenenes and tetrelcenophanes in general are thermally quite robust compounds. This feature has been attributed to the fact that the LUMO of the tetrelcenophanes is antibonding in nature with respect to the $E^{14}\text{--Cp}$ bond (Figure 9). Therefore, donation of a σ donor such as a NHC into the LUMO of a tetrelcenophane results in a weakening of the $E^{14}\text{--Cp}$ bond.

This is also evident from the crystal structures, as the $E^{14}\text{--Cp}$ bonds in these tetrelcenophane carbene complexes are significantly elongated compared to the corresponding tetrelcenophanes. For example, the $\text{Sn}\text{--Cp}^{\text{cent}}$ bond in stannocenophane **8f** is 239.4–242.4 pm, while bond length of up to 266.3 pm are found in the carbene complexes **8f·NHC**. A similar bonding situation is found in plumbocenophane carbene complexes **9e·NHC**, with $\text{Pb}\text{--Cp}^{\text{cent}}$ bond length of up to 260.5 pm, while $\text{Pb}\text{--Cp}^{\text{cent}}$ bond lengths of just 243.0 pm and 256.0 pm are found in plumbocenophane **9e** (Table 2). It has been suggested that this activation/weakening of the $E^{14}\text{--Cp}$ bond by coordination of a donor molecule could be utilized in a ring-opening reaction, but so far, no ring-open form of a tetrelcenophane has been reported. An in-depth study of the $E^{14}\text{--NHC}$ bonding by DFT calculations found that the bond is comparably weak and that a significant percentage of the complexation energy can be attributed to attractive dispersion

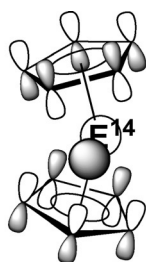


Figure 9. Schematic illustration of the LUMO of tetrelcenenes.

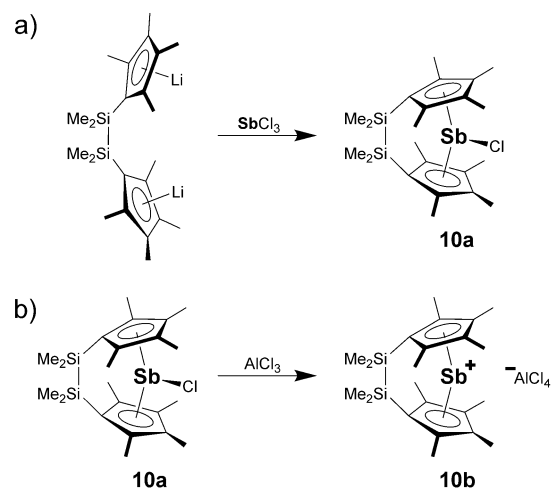
interactions, rather than classical σ bonding.^[65] In addition, it was found experimentally that these complexes most likely exist in a dissociative equilibrium in solution at room temperature,^[61] which is in agreement with the rather small binding energies, that were calculated.

Metallophenanes of Group 15 Elements

Even though there are several metallocene-type compounds of the heavy group 15 elements, phosphorous, arsenic, antimony, and bismuth, metallophenanes of group 15 elements are almost unexplored, with just one example of antimony.^[57]

Following the naming concept that was introduced for metallocenes and metallophenanes of group 14 elements, metallocene-type compounds of group 15 elements—pnictogenocenes—could be referred to as pnictogenocenes and the corresponding metallophenanes may be referred to as pnictogenocenophanes. This name might become more useful if more examples of pnictogenocenophanes are reported.

The synthesis of stibocenophane **10a** followed a similar route to tetrelcenophanes and many transition metal based metallophenanes. Treatment of a dilithiated Si[2] *ansa*-ligand system with antimony trichloride resulted in the formation of chloro stibocenophane **10a** (Scheme 14).



Scheme 14. a) Synthesis of chloro stibocenophane, **10a**. b) synthesis of stibocenophanium cation **10b**.

It is worth noting that the same route was reported to be unsuccessful for other group 15 trihalides.^[57] Compound **10a** exhibits a trivalent central atom with η^5/η^5 bonded Cp groups. Treatment of **10a** with aluminum trichloride or sodium tetraphenylborate resulted in chloride abstraction and formation of the corresponding stibocenophanium cation **10b** (Scheme 14), with only the tetrachloroaluminate salt being structurally characterized. This compound is formally isoelectronic to the neutral stannocenophane **8g**, and both **10a** and **10b** exhibit some similar structural feature as **8g** (Figure 10).

In comparison, chloro stibocenophane **10a** and stibocenophanium cation **10b** possess dihedral angles α of 51.4°

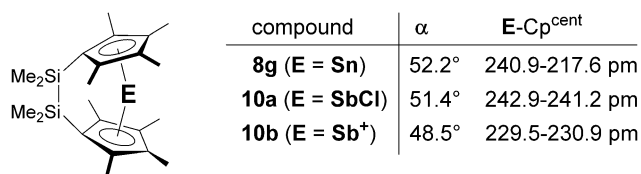


Figure 10. Selected structural properties of Si[2]stannocenophane **8g**, Si[2]-chloro stibocenophane **10a**, and Si[2]stibocenophanium **10b**.

(**10a**) and 48.5° (**10b**), δ angles of 136.9° (**10a**) and 154.1° (**10b**), which is similar to what is found in stannocenophane **8g** (Table 2). The Sb–Cp^{cent} bond lengths on the other hand are 242.9–246.8 pm (**10a**) and 229.5–230.9 pm (**10b**), thus 10–15 pm shorter in the cationic stibocenophanium **10b** than in chloro stibocenophane **10a** or stannocenophane **8g**, owing to an increased ionic Sb–Cp interaction in cationic compound **10b**.

Summary and Outlook

The area of metallocenophanes in general is a very active research field, since these compounds have been used with great success in homogenous catalysis and as monomers in ring-opening reactions, although mostly limited to transition metal derivatives. Metallocenophanes of main-group elements are often overlooked, since their primary application so far, if any, has been as Cp transfer reagents in transmetalation reactions for the synthesis of transition metal based metallocenophanes. However, in recent years, metallocenophanes of main-group elements, in particular of group 2 and group 14 elements have been the focus of in-depth studies. In particular magnesocenophanes have seen the first application in homogenous catalysis and the coordination chemistry of metallocenophanes of group 14 elements—tetrelocenophanes—has been more closely studied, for instance with regards to NHC complexes. Even though to date no ring-opening polymerization reactions of main-group metallocenophanes have been successfully performed, and the exact amount of ring-strain in these systems is unknown, this remains an important and auspicious target for future research.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: *ansa*-metallocenes · cyclopentadienyl compounds · main-group elements · metallocenes · metallocenophanes

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