Cyclic polyenes of heavy group 14 elements: new generation ligands for transition-metal complexes

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Cyclic polyenes, such as benzene, cyclopentadienyl and cyclobutadiene, are widely used as key ligands for a variety of transition-metal complexes. The heavy versions of these compounds, in which the skeletal carbon atoms are fully (or partially) replaced with heavy group 14 elements (Si, Ge, Sn and Pb) were not synthetically accessible until quite recently. However, they are now readily available following the pioneering discoveries of derivatives of sila- and germabenzenes, sila- and germacyclopentadienide ions and tetrasila- and disiladigermacyclobutadiene dianions. Apart from their undoubted structural and synthetic interest, such organometallic compounds are particularly important as the precursors of novel ligands for new-generation transition-metal complexes, and this is covered in this *critical review* (124 references).

1. Introduction

Carbocyclic polyenes of the type *cyclo*-C_nR_n (n = 3–8), namely, cyclopropenyls η^3-C_3R_3, cyclobutadienes η^4-C_4R_4, cyclopentadienyls η^5-C_5R_5, arenes η^6-C_6R_6, cycloheptatrienyls η^7-C_7R_7 and cyclooctatetraenes η^8-C_8R_8, are among the most commonly encountered ligands that are widely utilized for the preparation of a vast number of transition-metal complexes.[1] The most famous examples of this class of compounds include such 18-electron complexes as (cyclobutadiene)tricarbonyliron [(η^4-H_4C_4)Fe(CO)$_3$] (Pettit, 1965),[2] bis(cyclopentadienyl)iron(II), ferrocene, [(η^5-H_5C_5)$_2$Fe] (Pauson, 1951)[3] and bis(benzene)chromium [(η^6-H_6C_6)$_2$Cr] (Fisher, 1955).[4] Their undoubted structural appeal, along with their three-dimensional aromaticity and nonclassical bonding modes, caused an exponentially growing interest among the organometallic community. To date, more than half a century after these pioneering discoveries, the structural and bonding peculiarities of the transition-metal complexes featuring carbocyclic polyene ligands are well understood, and their synthetic chemistry is greatly developed. On the other hand, because of the high technological demands for the production of new advanced materials for various aspects of our modern life, the application of transition-metal complexes in the materials science field has become increasingly important. Among the most representative examples, one should mention the metallocenes (including the milestone ferrocene) that have found widespread practical application: in catalysis (chiral ferrocene as a ligand scaffold), supramolecular chemistry (metallocene-containing host macroheterocycles able to recognize charged and neutral species), medicine (anticancer drugs based on ferrocenium salts), nanotechnology (preparation of carbon nanotubes), polymer science (vinyl ferrocene polymer as a ferrocenyl version of polystyrene), the car industry (fuel antiknock agents for petrol

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engines), molecular magnets (decamethylferrocenium ion-radical as a donor in charge-transfer complexes), *etc.*[5]

The heavy analogues of the carbocyclic polyene ligands, in which the skeletal carbons are fully (or partially) replaced with Si, Ge, Sn or Pb atoms, were completely unknown until the first transition-metal complexes featuring the sila- and germacyclopentadienyl ligands were reported by Tilley *et al.* in the mid-1990s. The major problem in the synthesis of such complexes with heavy cyclic polyene ligands was definitely associated with the synthetic inaccessibility of the corresponding ligand precursors. The first 6π-electron heavy analogues of benzene, cyclopentadienyl anion and cyclobutadiene dianion, formally obeying Hückel's $(4n + 2)$ π-electron rule, have been synthesized only very recently.[6] This breakthrough brought about the successful syntheses of new-generation transition-metal complexes, featuring heavy cyclic polyene ligands of the type *cyclo*-$E_nC_mR_{n+m}$ (E = Si, Ge, Sn; $n + m = 4$–6). In the present review, we will deal with the most recent fundamental developments in this field, discussing the synthesis of the heavy analogues of 6π-electron species and their utilization as novel ligands for transition-metal complexes.

2. Heavy analogues of arenes

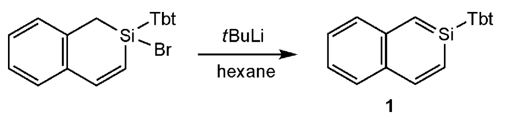
2.1 Theoretical studies

The experimental accomplishments in the field were preceded by numerous computational studies recently comprehensively covered by Apeloig and Karni,[7] the most important of which are discussed below. Thus, silabenzene, extensively studied by many research groups, was found to be markedly aromatic. This conclusion was based on its structural features: a planar six-membered ring with a Si–C bond length of 1.760 Å (3-21G*)[8] and 1.771 Å (B3LYP/6-311 + G**),[9] intermediate between those of the typical Si–C and Si=C bond lengths. Energetic considerations were taken as the other manifestation of π-delocalization in silabenzene, giving a value for its aromaticity *ca.* 70–85% that of benzene, depending on the reference compounds and computational level.[8,10,11] Magnetic criterion also pointed to the aromaticity of silabenzene, providing a nucleus independent chemical shift (NICS) value of −9.1, which was virtually identical to that of benzene (−9.7).[9] A comprehensive computational study of the electronic structure and aromaticity of the series of silabenzenes $Si_nC_{6-n}H_6$ (n = 1–6) was recently reported by Baldridge *et al.*[12] The aromatic stabilization of the heavier germabenzene was predicted to be of the same level as that of silabenzene, 17.97 *vs.* 16.75 kcal mol^{-1}, albeit such stabilization sharply decreased on going from germabenzene to stannabenzene, 16.75 *vs.* 12.20 kcal mol^{-1}.[8]

All three possible isomers of disilabenzene (1,2-, 1,3- and 1,4-disilabenzenes) were calculated to have a planar geometry at the B3LYP/3-21G*[7] and HF/STO-2G[13] levels. The most stable isomer was 1,3-disilabenzene, while the other two, 1,2- and 1,4-disilabenzenes, were destabilized by 6.1 and 11.1 kcal mol^{-1}, respectively.[7] The aromaticity levels of 1,3-, 1,4- and 1,2-disilabenzenes, based on the aromatic stabilization energy calculations, were estimated as 80, 62 and 38% of the benzene aromaticity, respectively.[13]

The planar aromatic D_{3h} structure of 1,3,5-trisilabenzene was found to be a minimum on the potential energy surface by Gordon and co-workers at the RHF and MP2 levels (6-31G(d) and 6-311G(d,p) basis sets),[14,15] Schaefer and co-workers at the HF/TZ2P and CCSD(T)/DZP//CISD/DZP,[16] and Apeloig *et al.* at the MP2/6-31G**[7] levels of theory. A comparison of the resonance energies of 1,3,5-trisilabenzene and benzene allowed the estimation of the aromaticity of 1,3,5-trisilabenzene: *ca.* 83% of the benzene aromaticity.[16]

Hexasilabenzene, Si_6H_6, is the most comprehensively studied heavy arene representative. The early calculations at the HF/3-21G level described Si_6H_6 as a D_{6h} structure with identical Si–Si bond lengths of *ca.* 2.220 Å.[17–19] However, subsequent higher-level computations found a chair-like puckered D_{3d} geometry for Si_6H_6 as the true minimum structure.[15,20–23] However, at all computational levels, the Si–Si bond distances in both the D_{6h} and D_{3d} structures were found to be intermediate between the typical Si=Si (2.15 Å) and Si–Si (2.34 Å) bond lengths, implying the presence of the cyclic electron delocalization. The value of the aromatic stabilization energy for the planar D_{6h} hexasilabenzene was reported to be *ca.* 50–80% that of benzene (depending on the theoretical method used).[14,17,18,23] This agreed well with the magnetic considerations: NICS$(Si_6H_6) = -14.1$ *vs.* NICS$(C_6H_6) = -16.8$.[23] The most stable Si_6H_6 structural isomer is hexasilaprismane, which is more favorable than the planar D_{6h} hexasilabenzene, puckered D_{3d} hexasilabenzene, hexasila(Dewar)benzene and hexasilabenzvalene by 11.9, 7.7, 10.5 and 5.9 kcal mol^{-1}, respectively.[24] This situation is completely opposite to that of organic C_6H_6 isomers, of which benzene is by far the most stable isomer followed by prismane (+117.5), Dewar(benzene) (+81.0) and benzvalene (+74.8 kcal mol^{-1}).[24] A study on the influence of substituents on the structure and aromaticity of R_6Si_6 isomers showed that the strongly σ-accepting groups (F) impose the largest deviation from planarity and stretching of the Si–Si bonds, whereas σ-donating (SiH_3) and π-accepting (BH_2) substituents exhibited completely opposite effect, resulting in overall aromatic stabilization and flattening of the R_6Si_6 molecule.[22] The departure of the heavy arenes E_6H_6 (E = Ge, Sn, Pb) from planarity becomes more prominent going down group 14: the puckering angles for Ge_6H_6, Sn_6H_6 and Pb_6H_6 are 38.0, 50.8 and 58.0°, respectively. In the same direction, the planar D_{6h} structure of E_6H_6 is progressively destabilized compared with the puckered D_{3d} structure: 9.1 (Ge_6H_6), 23.1 (Sn_6H_6) and 63.3 (Pb_6H_6) kcal mol^{-1}.[21] Subsequent calculations showed that the D_{3d} structure of Ge_6H_6 is 14.5 kcal mol^{-1} more stable than its planar D_{6h} isomer, and the aromaticity of hexagermabenzene in its D_{6h} form is comparable to that of hexasilabenzene: NICS$(Ge_6H_6) = -14.4$ *vs.* NICS$(Si_6H_6) = -14.1$ (NICS $(C_6H_6) = -16.8$).[23] Similar to the case of Si_6H_6, the prismane was found to be the most stable E_6H_6 system, which was explained by the reluctance of the heavy group 14 elements to form double bonds, as well as their ability to release the strain of polycyclic compounds.[21] Accordingly, the synthesis of hexasilaprismane (Ar_6Si_6, Ar = 2,6-diisopropylphenyl) and its low-temperature photochemical isomerization to hexasila-Dewar(benzene) were reported.[25,26]



Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl

Scheme 1

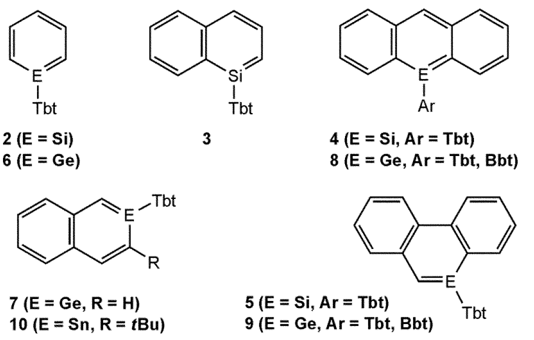
2.2 Experimental accomplishments

The first silaaromatic compound stable at room temperature, 2-silanaphthalene **1**, was prepared by Tokitoh *et al.* in 1997 by the dehydrohalogenative reduction of the bromosilane precursor with *t*BuLi in hexane[9,27,28] (Scheme 1).

Utilizing the same synthetic procedure and taking advantage of the protective power of Tbt and Bbt (2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) groups, the same authors prepared the most fundamental silabenzene **2**,[29,30] as well as 1-silanaphthalene **3**[31,32] and 9-silaanthracene **4**[33] and 9-silaphenanthrene **5**[34] (Scheme 2).

The problem of kinetic stabilization of heavy aromatics becomes increasingly important descending group 14 because of the general tendency of reluctance of the heavier elements (particularly, Sn and Pb) for s,p-hybridization and formation of multiple bonds. Consequently, while several stable germaaromatic derivatives have been synthesized, including germabenzene **6**,[35] 2-germanaphthalene **7**,[36,37] 9-germaanthracene **8**[38] and 9-germaphenanthrene **9**[38] (Scheme 2), only one stable stannaaromatic compound has been reported, namely, 2-stannanaphthalene **10**[39] (Scheme 2). The synthesis of a stable stannabenzene derivative has not been accomplished yet, whereas the 9-stannaphenanthrene generated at −78 °C produced its head-to-tail dimer as a final product.[40] No stable representatives of plumbaaromatic compounds have been reported thus far.

The sila- and germabenzene (as well as their homologues) are aromatic, which was reliably demonstrated by a consideration of structural, energetic and magnetic criteria of aromaticity. Thus, all of them feature nearly planar six-membered rings with a trigonal-planar geometry around the Si, Ge and Sn atoms and cyclic C–C bonds very similar to those in benzene (1.39–1.40 Å). Moreover, in silabenzene **2** both adjacent Si–C bond lengths are nearly identical (1.765(4) and 1.770(4) Å), being intermediate between those of the typical Si–C single and Si=C double bonds (Fig. 1).



Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl

Scheme 2

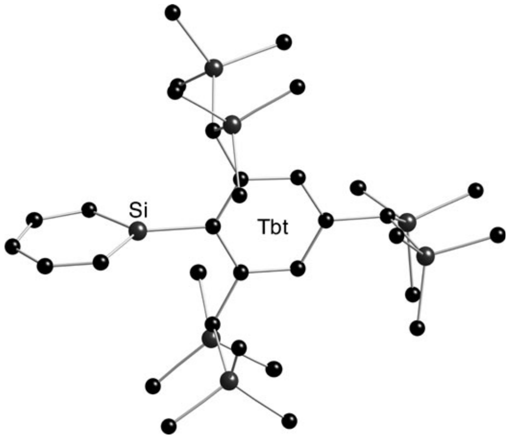


Fig. 1 Crystal Maker view of silabenzene **2** (hydrogen atoms are not shown).

As expected, the heavy group 14 element atoms were diagnostically deshielded, as can be seen in their ^{29}Si and ^{119}Sn NMR resonances: 93.6 (silabenzene **2**),[29] 91.7 (1-silanaphthalene **3**),[31] 87.3 (2-silanaphthalene **1**),[9] 87.2 (9-silaanthracene **4**),[33] 86.9 (9-silaphenanthrene **5**),[34] and 264 (2-stannanaphthalene **10**)[39] ppm (Scheme 2). Accordingly, the resonances of the ring proton and carbon atoms were observed in the region diagnostic of aromatic compounds, indicating the presence of a diamagnetic ring current. Such a magnetic manifestation of aromaticity was well supported by the NICS computations, providing negative values for all heavy aromatics (Table 1, the values for the parent organic derivatives are given in parentheses).[41,42]

Calculations on the diamagnetic susceptibility exaltation also provided large negative values for germabenzene and 2-germanaphthalene (−19.5 and −27.9), reasonably comparable with those of the parent benzene and naphthalene (−22.7 and −30.4).[42] Accordingly, the values of the aromatic stabilization energies for sila- and germabenzene were estimated to be almost identical to those of the parent benzene: 34.0 and 33.8 kcal mol^{-1} *vs.* 34.1 kcal mol^{-1}.[41] Finally, it was concluded that benzene, naphthalene, anthracene and phenanthrene analogues of the heavy group 14 elements (Si, Ge, Sn) are aromatic to a large extent, implying that the introduction of heavy elements in the six-membered rings does not interrupt the aromatic cyclic π-delocalization.[41,42]

Only a couple of stable benzene analogues, where the two cyclic carbon atoms were replaced with their heavy group 14 element congeners, have been synthesized starting from the heavy alkyne analogues. The first compound, heavy pyrazine analogue **11**, was prepared by Power *et al.* by the reaction of the digermyne analogue Ar′GeGeAr′ (Ar′ = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) with PhCN in hexane (Scheme 3).[43,44] Although **11**, incorporating two Ge atoms in the ring, formally obeys Hückel's 6π-electron rule, it in fact lacks the cyclic delocalization of its π-electrons. Indeed, the six-membered ring of **11** was markedly puckered and both Ge atoms were highly pyramidalized (the sum of the bond angles *ca.* 326°). Moreover, the Ge–Ge bond (2.4963(4) Å) in **11** was slightly longer than that in elemental Ge (2.44 Å), whereas Ge–N (av. 1.803(3) Å) were best described as single bonds, N–C

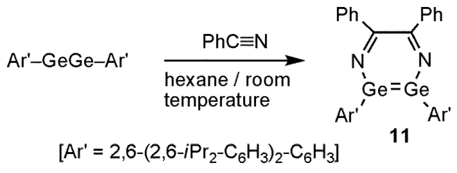
Table 1 NICS(1) values calculated for the model unsubstituted heavy aromatics (values for the parent organic derivatives are given in parentheses)

Heavy aromatic (aromatic)	NICS(1)
Silabenzene **2**	−9.1
(benzene)	(−11.1)
Germabenzene **6**	−9.0
(benzene)	(−11.1)
1-Silanaphthalene **3** (Si-containing ring)	−9.1
(naphthalene)	(−11.5)
2-Silanaphthalene **1** (Si-containing ring)	−9.4
(naphthalene)	(−11.5)
2-Germanaphthalene **7** (Ge-containing ring)	−9.3
(naphthalene)	(−11.5)
9-Silaanthracene **4** (Si-containing ring)	−11.0
(anthracene)	(−13.7)

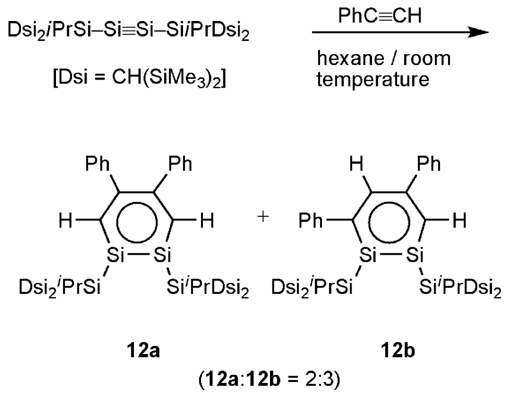
(av. 1.281(3) Å) as double bonds and C–C (1.517(3) Å) as a single bond. That is, the Ge–Ge bond in **11**, with the bond order less than one, is actually a weakened single bond rather than a double bond, which is reasonable taking into account the fact that the bond between the two Ge atoms in the starting Ar′GeGeAr′ is not a triple bond but approximate double bond instead. This reaction, involving the change in the formal oxidation state of Ge from +1 to +2, may proceed as the one-electron reduction of the two benzonitrile molecules by one molecule of Ar′GeGeAr′ to form a 1,6-biradical intermediate, followed by its ring closure accompanied with the C–C bond formation. Overall, this points to an important contribution of the biradical resonance form Ar′–Ge•=Ge•–Ar′ to the structure of Ar′GeGeAr′.

In contrast to digermabenzene **11**, its silicon analogue, 1,2-disilabenzene **12**, was found to be somewhat aromatic. **12** was prepared as a mixture of two regioisomers (**12a** : **12b** = 2 : 3) by the reaction of disilyne Dsi_2iPrSi–Si≡Si–SiiPrDsi$_2$ (Dsi = $CH(SiMe_3)_2$) with PhC≡CH in hexane (Scheme 4).[45]

As was expected for a silaaromatic compound, the resonances of the skeletal Si atoms were observed in the low-field region at 99.2 ppm for **12a** and 99.4 and 106.8 ppm for **12b**, whereas those of the ring protons and carbons were found in the typical aromatic region. The disilabenzene ring in the structurally characterized isomer **12a** was almost flat with nearly trigonal-planar geometries around the cyclic Si atoms (the sum of the bond angles *ca.* 360°). The Si–Si bond length of 2.2018(18) Å was just in between those of the typical Si–Si and Si=Si bonds, and the endocyclic Si–C bonds of 1.804(4) and 1.799(5) Å were also intermediate between those of typical single and double bonds. Evidently, 1,2-disilabenzene **12a** is still able to benefit (at least, in part) from the 6π-electron aromatic delocalization, similar to the prototypical benzene and silabenzene. The NICS values for the model **12a** and **12b** (Me_3Si instead of Dsi_2iPrSi groups) were calculated to be negative: −8.0 and −8.1, respectively.



Scheme 3



Scheme 4

It is also worth mentioning a transient 1,4-dimethyl-2,3,5,6-tetrakis(trimethylsilyl)-1,4-disilabenzene, which was believed to be formed upon the photolysis of its valence isomer 1,4-dimethyl-2,3,5,6-tetrakis(trimethylsilyl)-1,4-disila(Dewar)benzene, and whose intermediacy was proved by the [4 + 2] cycloaddition with either 2,3-dimethylbuta-1,3-diene or C_6D_6.[46]

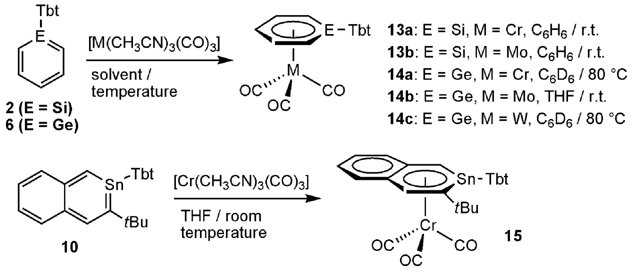
2.3 Heavy arenes as ligands for transition-metal complexes

As was anticipated, the above-described heavy aromatics have found an important application as π-arene ligands of the types η^6-C_5E (E = Si, Ge) and η^6-C_9E (E = Sn) for groups 6 (Cr, Mo, W) and 8 (Ru) transition-metal complexes.[39,47–49] Complexation reactions proceeded upon the ligand exchange between the transition-metal complexes $[M(CH_3CN)_3(CO)_3]$ (M = Cr, Mo, W) and silabenzene **2**,[29,30] germabenzene **6**[35] and 2-stannanaphthalene **10**[39] in either benzene or THF to form the corresponding [η^6-silabenzene]$M(CO)_3$ (M = Cr, Mo) **13a,b**,[47] [η^6-germabenzene]$M(CO)_3$ (M = Cr, Mo, W) **14a–c**[48,49] and [η^6-2-stannanaphthalene]$Cr(CO)_3$ **15**[39] complexes (Scheme 5).

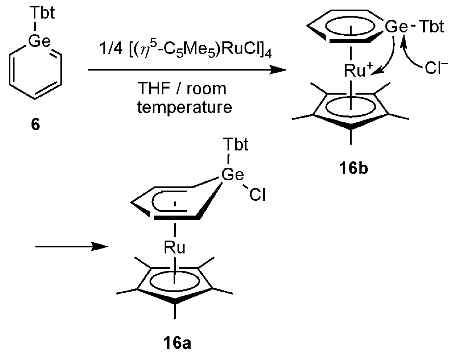
The most prominent structural features of all these complexes were the essential planarity of the heavy arene rings and their diagnostic hexahaptocoordination to transition metals. That is, the heavy arenes **2**, **6** and **10** can efficiently serve as novel π-arene ligands for transition-metal complexes, in the same way as the parent benzene.[49]

The reaction of germabenzene **6**[35] with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ in THF produced the novel Ru complex $[(\eta^5\text{-}C_5Me_5)Ru\text{-}\{(\eta^5\text{-}C_5H_5)GeTbt(Cl)\}]$ **16a** with a reduced hapticity of coordination, in which the germacyclohexadienyl ligand was pentahaptocoordinated to the Ru center (Scheme 6).[49] The formation of **16a** was realized in terms of the initial generation of cationic η^6-complex **16b**, followed by a nucleophilic chloride ion attack on the Ge atom accompanied by cleavage of the Ge–Ru bond (Scheme 6). In complex **16a**, both the η^5-C_5Me_5 ligand and the η^5-germacyclohexadienyl fragment are nearly coplanar, which is a characteristic feature of the sandwich complexes.[49]

Interesting sila- and 1,4-disilabenzene ruthenium complexes were recently synthesized by Tilley *et al.*[50] Thus, the first reported silabenzene transition-metal complex $[(\eta^5\text{-}C_5Me_5)\text{-}$



Scheme 5



Scheme 6

Ru(η^6-C_5H_5Si*t*Bu)]$^+$·[BH(C_6F_5)$_3$]$^-$, **17**$^+$·[BH(C_6F_5)$_3$]$^-$, was readily obtained by oxidation of the silacyclohexadienyl complex (η^5-C_5Me_5)Ru[(η^5-C_5H_5SiH*t*Bu)] with B(C_6F_5)$_3$ (Scheme 7). Based on spectroscopic methods, it was concluded that in **17**$^+$·[BH(C_6F_5)$_3$]$^-$, apart from the η^6-delocalized silabenzene to Ru atom bonding, there is some important mixed η^5,η^1-bonding contribution with limited delocalization in the silabenzene ligand.

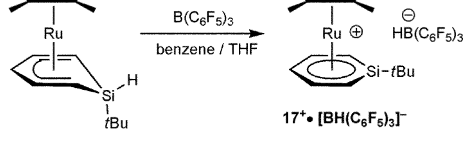
Heating of another Ru complex, (η^5-C_5Me_4Et)(PMe_3)$_2$-RuCH_2SiMe_3, with *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene in toluene unexpectedly produced the 1,4-disilabenzene complex (η^5-C_5Me_4Et)(PMe_3)RuH(η^2-hexamethyl-1,4-disilabenzene) **18** (Scheme 8).

Complex **18** exhibited a diagnostic hydride peak at −12.6 ppm with a typical $^2J_{P\text{–}H}$ coupling constant of 34 Hz.[50]

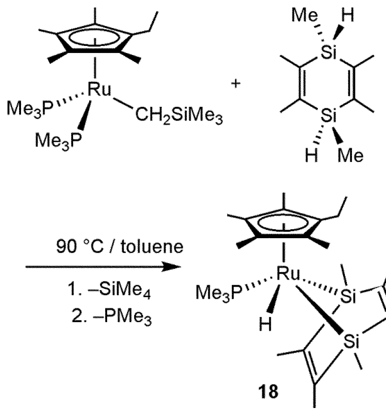
A computational study showed that the 1,4-disilabenzene ligand-Ru atom bonding in **18** is best described as intermediate between the two resonance extremes **18a** and **18b** (Scheme 9), in which the metallodisilanorbornadiene fragment features some degree of transannular Si–Si σ-bonding that can weakly interact with the Ru center.[50]

3. Heavy analogues of the cyclopentadienide ion

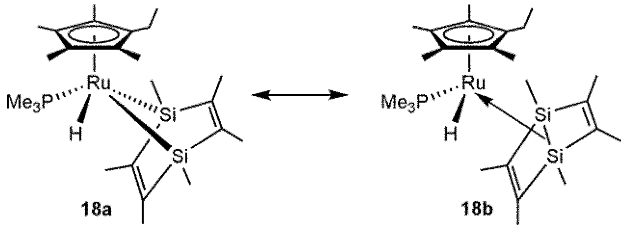
The cyclopentadienide ion, $C_5H_5^-$, obeying Hückel's ($4n + 2$) π-electron rule, is to be classified as an aromatic system, and is indeed aromatic with all of its six π-electrons occupying bonding orbitals.[51] It can be easily prepared by simple deprotonation with appropriate bases of cyclopentadiene, known as one of the most acidic hydrocarbons (pK_a = 16.0).[52] The spectral and structural characteristics of the cyclopentadienide ion definitely point to its planar delocalized D_{5h} structure, the aromaticity degree of which is smaller but still comparable with that of benzene: ∼80–90% estimated on the basis of magnetic criteria of aromaticity.[53] In fact, the cyclopentadienide ion is one of the oldest aromatic compounds, being known for more than 100 years. It was synthesized for the first time by the reduction of cyclopentadiene with potassium in benzene by Thiele in 1901.[54] Since then, the cyclopentadienide ion and its alkyl derivatives have been widely utilized as very useful organometallic reagents; in particular, as the ligands for a huge number of transition-metal complexes.



Scheme 7



Scheme 8



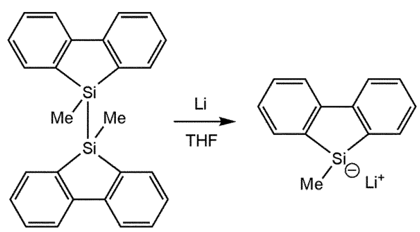
Scheme 9

3.1 Theoretical studies

The first wave of theoretical interest in the problem of the aromaticity of the heavy analogues of the cyclopentadienide ion dates back to the mid-1980s, when two papers addressing this problem were consecutively published. The first one by Gordon *et al.* claimed *ca.* 25% aromaticity of the planar C_{2v} form of the silacyclopentadienide ion $C_4SiH_5^-$, compared with that of the parent $C_5H_5^-$; however, these calculations used the relatively low HF/STO-2G level.[11] The higher HF/6-31G* level calculations by Damewood found that the pyramidal C_s form is the true minimum for the $C_4SiH_5^-$ anion, possesses only *ca.* 3% of the aromaticity of $C_5H_5^-$, whereas the planar C_{2v} structure was located only as a transition state for the pyramidal inversion at silicon.[55]

The groundbreaking achievements in the synthesis of the heavy analogues of the cyclopentadienide ion (so-called, silole and germole anions and dianions) in the 1990s (see section 3.2) revived a great deal of theoretical interest in the issue of aromaticity of such species.[56–60] Thus, in a series of papers published in the mid-1990s Schleyer *et al.* comprehensively studied this problem. They found that at the high computational levels the heavy analogues of the cyclopentadienide ion $H_4C_4EH^-$ (E = C, Si, Ge, Sn, Pb) and cyclopentadienediide ion $H_4C_4E^{2-}$ (as well as their lithium derivatives) showed appreciable aromaticity.[56–59] This largely disagreed with the results of earlier low-level calculations, predicting either small[11] or almost negligible[55] degrees of aromaticity of the silacyclopentadienide ion. Schleyer's calculation showed that the magnitude of the aromatic stabilization energy of the silacyclopentadienide ion $C_4H_4SiH^-$ was about half the value for the parent aromatic cyclopentadienide ion $C_5H_5^-$.[56] Moreover, the pentahaptocoordination of the Li^+ counterion to the silacyclopentadienide ring markedly increased its aromaticity, which was manifested in the planarization around the Si atom, equalization of the cyclic C–C bonds and increase in the aromatic stabilization energy of η^5-Li-silacyclopentadienide up to 80% (compared with that of η^5-Li-cyclopentadienide).[57] The silacyclopentadienediide ion $H_4C_4Si^{2-}$, as well as its alkali metal salts $H_4C_4SiLi_2$, $H_4C_4SiNa_2$ and $H_4C_4SiK_2$, were also found to be highly aromatic.[58] For example, the most stable configurations of the salts $H_4C_4SiLi_2$, $H_4C_4SiNa_2$ and $H_4C_4SiK_2$ were the η^5,η^5-"inverse sandwiches" with equalized C–C bonds, diagnostic of delocalized structures, and large aromatic ring currents responsible for the great shielding of the Li nucleus in $H_4C_4SiLi_2$ (calculated value −7.7 ppm).[58] The aromaticity of the C_s monoanions $H_4C_4EH^-$ (E = C, Si, Ge, Sn, Pb) markedly decreased descending group 14 in accordance with the increase in pyramidality at the heteroatom E and inversion barriers on going down from C to Pb.[59] The planar C_{2v} forms of the monoanions $H_4C_4EH^-$, being significantly more aromatic, represented only the transition states for the pyramidal inversion. In contrast, the aromaticity of the dianions $H_4C_4E^{2-}$ (as well as their dilithium salts $H_4C_4ELi_2$), lacking the problem of pyramidalization at the heteroatom, was remarkably constant regardless of the element E.[59] Consequently, the dilithium salt derivatives $H_4C_4ELi_2$ were found to be the most aromatic among all the calculated structures.

The most exciting example of an analogue of the cyclopentadienide ion consisting of all heavier group 14 elements, pentasilacyclopentadienide ion $H_5Si_5^-$, was also computationally studied by Schleyer *et al.*[61] Two nonplanar minima of C_s and C_2 symmetries with equal energies were located on the potential energy surface of $H_5Si_5^-$, whereas the planar delocalized D_{5h} form was found to be destabilized by 8.3 kcal mol^{-1}. The aromatic stabilization energy for the C_s form of $Si_5H_5^-$ of 52.8 kcal mol^{-1} was much smaller than 84.7 kcal mol^{-1} calculated for the carbon analogue $C_5H_5^-$, thus pointing to a markedly lower aromaticity degree for $Si_5H_5^-$.[61] However, such highly challenging persilacyclopentadienide derivatives $R_5Si_5^-$, as well as their heavier analogues $R_5E_5^-$ (E = Ge, Sn, Pb), have never been synthesized, remaining very attractive targets for organometallic chemists.



Scheme 10

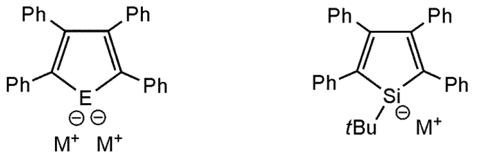
3.2 Experimental accomplishments

The first report on the generation of a silacyclopentadienide ion derivative was published in 1958 by Gilman and Gorsich, who reduced bis(dibenzosilole) with lithium (Scheme 10).[62] Interest in the silacyclopentadienide ion story was revived in the 1990s, initiated by a paper by Joo *et al.* on the generation of disodio-2,3,4,5-tetraphenyl-1-silacyclopentadienediide ion $\mathbf{19^{2-}}\cdot\mathbf{2Na^+}$ by the reduction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene with sodium in dioxane (Scheme 11: E = Si, M = Na).[63]

Hong and Boudjouk synthesized a monoanionic lithium salt of 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide $\mathbf{20^-}\cdot\mathbf{M^+}$ (**M** = **Li**, **Na**) by the reductive cleavage of the exocyclic Si–Si bond of bis(1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) with either lithium or sodium (Scheme 11: M = Li, Na).[64] Based on the deshielding of the skeletal Si atom observed upon the reduction, a significant delocalization of the negative charge over the five-membered ring and hence, its 6π-electron aromaticity was proposed.[64]

Hong and Boudjouk also prepared dilithio-2,3,4,5-tetraphenyl-1-silacyclopentadienediide $\mathbf{19^{2-}}\cdot\mathbf{2Li^+}$ and deduced its aromaticity from the deshielding of the Si atom and the shielding of the skeletal C atoms taking place upon reduction (Scheme 11: E = Si, M = Li).[65] The crystal structure of $\mathbf{19^{2-}}\cdot\mathbf{2Li^+}$ was reported later by West *et al.*[66] Appreciable aromaticity of the silacyclopentadienediide derivative was manifested by its essentially unfolded five-membered ring with a nearly planar geometry around the Si atom and almost equalized skeletal C–C bond lengths (1.426–1.448 Å). Particularly interesting was the arrangement of the two Li ions featuring different coordination modes: Li1 was pentahaptocoordinated to the five-membered ring, whereas Li2 was bound exclusively to the Si atom (Scheme 12: **a**).

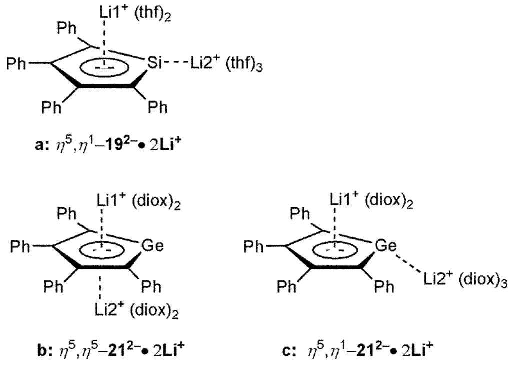
Calculations showed two dilithio derivatives as the minimum structures: the first one closely resembling the experimental η^5-Li,η^1-Li structure, and the second one of C_{2v} symmetry featuring the two Li ions above and below the ring plane (η^5-Li, η^5-Li structure) in the form of an "inverse



$\mathbf{19^{2-}\bullet\ 2M^+}$ (E = Si; M = Li, Na)
$\mathbf{21^{2-}\bullet\ 2Li^+}$ (E = Ge; M = Li)
$\mathbf{22^{2-}\bullet\ 2Li^+}$ (E = Sn; M = Li)

$\mathbf{20^{-}\bullet\ M^+}$ (M = Li, Na)

Scheme 11



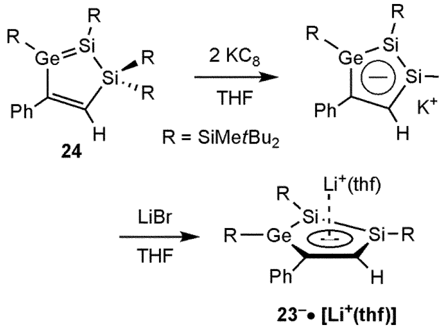
Scheme 12

sandwich". The latter configuration was more stable than the former by 21 kcal mol^{-1}.

The reduction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopentadiene with lithium in THF produced dilithio-2,3,4,5-tetraphenyl-1-germacyclopentadienediide $\mathbf{21^{2-}\cdot 2Li^+}$ (Scheme 11: E = Ge, M = Li) in two structurally distinct forms, namely, an η^5,η^5-"inverse sandwich" form crystallized at −20 °C (Scheme 12: **b**) and an η^5,η^1-structure crystallized at room temperature (Scheme 12: **c**).[67] Similar to the above case of the silacyclopentadienediide ion $\mathbf{19^{2-}\cdot 2Li^+}$, the symmetrical η^5,η^5-form of the calculated unsubstituted model of $\mathbf{21^{2-}\cdot 2Li^+}$ was found to be 25 kcal mol^{-1} more stable than the unsymmetrical η^5,η^1-structure. The germacyclopentadienediide ion $\mathbf{21^{2-}\cdot 2Li^+}$ was also recognized as an aromatic compound on the basis of structural (almost equal skeletal C–C bond lengths) and energetic (aromatic stabilization energy for the model $H_4C_4Ge^{2-}$ of 13.0 kcal mol^{-1}) considerations.[67]

The heaviest analogue of the cyclopentadienide ion, dilithio-2,3,4,5-tetraphenyl-1-stannacyclopentadienediide ion $\mathbf{22^{2-}\cdot 2Li^+}$, was recently prepared by the reduction of either bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl) or hexaphenyl-1-stannacyclopentadiene with lithium (Scheme 11: E = Sn, M = Li).[68–72] The stannacyclopentadienediide ion $\mathbf{22^{2-}\cdot 2Li^+}$ exists in a single structural η^5,η^5-modification, featuring a planar five-membered ring and nearly equal skeletal C–C bonds of 1.422(6)–1.446(6) Å, which pointed to its delocalized aromatic nature.[70] Interestingly, the calculations showed two minimum structures for the stannacyclopentadienediide ion: η^5,η^1 of C_1 symmetry and η^5,η^5 of C_2 symmetry. The latter, corresponding to the experimental structure, was 20 kcal mol^{-1} more stable. The Sn atom of $\mathbf{22^{2-}\cdot 2Li^+}$ was appreciably deshielded, whereas the Li atom was markedly shielded (−4.36 ppm), which was taken as the manifestation of aromatic delocalization of the negative charge into the five-membered ring.[70] This was also supported by the NICS calculations, which provided a negative value of −5.96.

Some other interesting examples of dianionic heterocyclic systems, incorporating sila-, germa- and stannacyclopentadiene fragments, were also synthesized and reported to possess some extent of 6π-electron aromaticity.[73–82] In contrast, the monoanionic heavy cyclopentadienide derivatives are exclusively represented by the localized (nonaromatic) structures with the characteristic pyramidalization at the heteroatoms, pronounced alternation of the cyclic C–C bonds and η^1-coordination of the countercations to the heteroatoms.[73,74,83–85]



Scheme 13

As mentioned above, the most challenging derivatives consisting of all heavy group 14 elements of the type $R_5E_5^-$ (R = Si, Ge, Sn, Pb) have not yet been experimentally realized. To date, the closest approach to this problem was achieved by the recent work of Sekiguchi and co-workers, who prepared the first analogue of the cyclopentadienide ion incorporating three heavy group 14 elements in the ring: two Si and one Ge atoms.[86,87] This compound, lithium 1,2-disila-3-germacyclopenta-2,4-dienide $\mathbf{23^-\cdot[Li^+(thf)]}$, was synthesized by the reduction of disilagermacyclopentadiene **24**[88] with potassium graphite, followed by the exchange of counter-cation from K^+ to Li^+ by treatment with LiBr (Scheme 13).[86,87]

A manifestation of the cyclic delocalization in $\mathbf{23^-\cdot[Li^+(thf)]}$ was clearly shown by its structural features; thus, all double bonds of the starting **24** (Si═Ge and C═C) were elongated, whereas all single bonds of **24** (Ge–C, Si–Si and Si–C) were shortened upon the reduction to form $\mathbf{23^-\cdot[Li^+(thf)]}$ (Fig. 2).

Noteworthy, the lengths of all cyclic bonds in the $\mathbf{23^-}$ anion are just in between those of typical single and double bonds. Moreover, the Li^+ ion in $\mathbf{23^-\cdot[Li^+(thf)]}$ is diagnostically pentahaptocoordinated to the anionic ring to form a "half-sandwich" structure characteristic of the aromatic cyclopentadienide derivatives C_5R_5Li. Overall, these structural peculiarities pointed to an appreciable aromaticity of $\mathbf{23^-\cdot[Li^+(thf)]}$; however, the extent of such aromaticity was certainly smaller than that of C_5H_5Li. The requirements of the

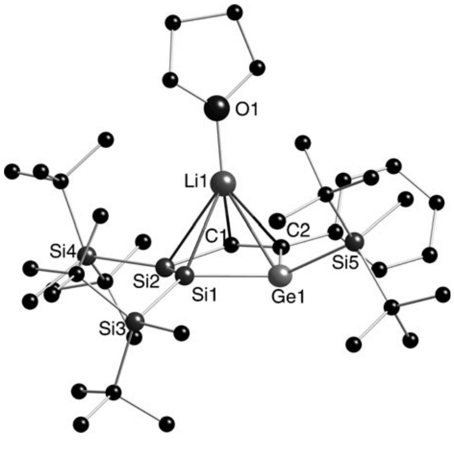
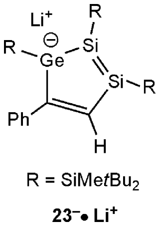


Fig. 2 Crystal Maker view of lithium 1,2-disila-3-germacyclopenta-2,4-dienide $\mathbf{23^-\cdot[Li^+(thf)]}$ (hydrogen atoms are not shown).



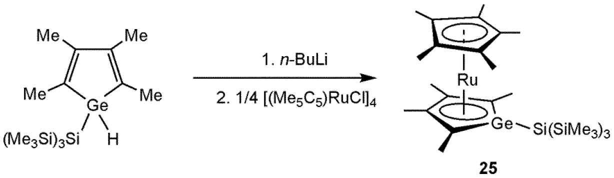
Scheme 14

magnetic criterion of aromaticity were also satisfied for **23^-·[Li$^+$(thf)]**, for which the NICS value (H_3Si-substituted model **23^-·Li$^+$**) was calculated to be markedly negative, −8.4, being smaller but still comparable with those of classical 6π-electron aromatics C_5H_5Li (NICS = −10.3) and C_6H_6 (NICS = −11.2).[87] The ^{7}Li NMR resonance of **23^-·[Li$^+$(thf)]** was observed in toluene at high field, −5.4 ppm, which definitely pointed to an aromatic nature for the heavy cyclopentadienide ion in toluene solution. Interestingly, the structure of **23^-·[Li$^+$(thf)]** was highly solvent-dependent: aromatic delocalized in nonpolar toluene (or benzene) and nonaromatic localized in polar THF. The predominant localization of the negative charge on the Ge atom was deduced from the characteristic deshielding of the Li resonance (−0.6 ppm, typical region of η^1-germyllithiums)[89] and a huge downfield shift of the resonances of the skeletal Si atoms (97.4 and 104.9 ppm, the typical region of doubly bonded Si atoms).[90] Apparently, in polar THF, the Li$^+$ coordination mode was changed from a delocalized η^5 to a localized η^1, which corresponds to the structure of the heavy cyclopentadienide ion, featuring Si═Si and C═C double bonds and the negative charge located on the Ge atom (Scheme 14).

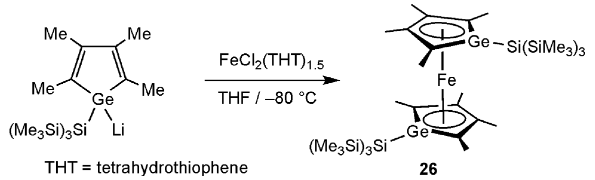
3.3 Heavy cyclopentadienes as ligands for transition-metal complexes

The first transition-metal complex featuring a heavy cyclopentadienyl ligand, namely, (η^5-Me_5C_5)Ru[η^5-($Me_4C_4GeSi(SiMe_3)_3$)] **25**, was synthesized by Tilley and co-workers by the reaction of lithium germacyclopentadienide Li[$Me_4C_4GeSi(SiMe_3)_3$] with [{(Me_5C_5)Ru(μ-Cl)}$_4$] in THF (Scheme 15).[91] Based on the spectral and structural characteristics of **25**, it was qualified as an aromatic compound. In due course, other transition-metal complexes (Zr, Hf, Ru, Rh, Ir) with either sila- or germacyclopentadienyl ligands were prepared by the same research group.[92–96]

An iron complex [η^5-$C_4Me_4GeSi(SiMe_3)_3$]$_2$Fe **26**, in which the two germacyclopentadienyl ligands sandwiched the central Fe atom, was synthesized by the coupling of germacyclopentadienide lithium [$C_4Me_4GeSi(SiMe_3)_3$]$^-$Li$^+$ with $FeCl_2$(tetrahydrothiophene)$_{1.5}$ in THF by Tilley and co-workers (Scheme 16).[97]



Scheme 15



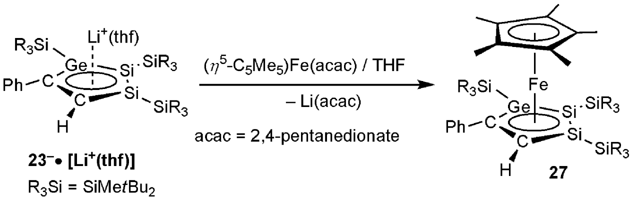
Scheme 16

The ferrocene derivatives with the cyclopentadienyl ligands consisting entirely of heavy group 14 elements are most intriguing, representing an inorganic version of classical metallocenes. Being unknown experimentally, persilaferrocene (η^5-H_5Si_5)$_2$Fe was studied computationally to disclose its D_{5d} symmetrical structure (like the parent ferrocene (η^5-H_5C_5)$_2$Fe), in which the Fe–(η^5-H_5Si_5) ligand binding energy was smaller than that in the parent ferrocene: 113.6 *vs.* 144.1 kcal mol^{-1} (HF level without electron correlation functions).[98] The HOMO–LUMO energy gap in persilaferrocene was smaller than that in the parent ferrocene, reflecting the smaller HOMO–LUMO separation in the pentasilacyclopentadienyl ligand compared with that of the cyclopentadienyl ligand.

As the closest approach to the problem of the synthesis of heavy ferrocenes (η^5-R_5E_5)$_2$Fe (E = Si, Ge, Sn, Pb), one should mention the recent work of Sekiguchi and co-workers, who prepared a ferrocene derivative incorporating three heavy group 14 elements (two Si and one Ge) in one of the cyclopentadienyl rings.[99] This complex (η^5-Me_5C_5)Fe[η^5-(CPh)(CH)Si_2Ge(SiMe*t*Bu$_2$)$_3$] **27** was synthesized by the reaction of the heavy lithium cyclopentadienide **23^-·[Li$^+$(thf)]** with the *in situ* generated (η^5-Me_5C_5)Fe(2,4-pentanedionate) complex in THF (Scheme 17).

The high degree of π-delocalization in the C_2Si_2Ge ligand of heavy ferrocene **27** was seen in a marked shielding of all skeletal C and Si atoms (in comparison with the starting **23^-·[Li$^+$(thf)]**), reinforced by the important Fe-heavy Cp ligand δ-back donation. Structurally, the cyclic π-delocalization was manifested in the tendency of the skeletal bond lengths of **27**, which were intermediate between those of typical single and double bonds. Moreover, the striking flattening of the C_2Si_2Ge ring and planarization around all skeletal atoms taking place upon complexation also point to its delocalized structure. As in the parent ferrocene, both cyclopentadienyl ligands in **27** (which are nearly coplanar and staggered relative to each other) are pentahaptocoordinated to the Fe atom, thus forming a sandwich metallocene complex (Fig. 3).

Electrochemical oxidation of **27** (Ag/Ag$^+$, CH_2Cl_2, 0.1 M nBu$_4$NClO$_4$) revealed an irreversible oxidation wave at E_p^{ox} = −0.53 V, most probably corresponding to a heavy ferrocene



Scheme 17

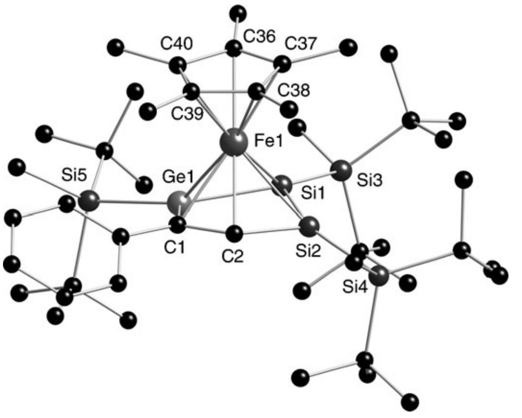


Fig. 3 Crystal Maker view of the heavy ferrocene ($(\eta^5\text{-}Me_5C_5)Fe[\eta^5\text{-}(CPh)(CH)Si_2Ge(SiMe\textit{t}Bu_2)_3]$) **27** (hydrogen atoms are not shown).

cation-radical. Notably, this one-electron oxidation process proceeded at markedly more negative potentials than the corresponding processes for the parent decamethylferrocene[99] (−0.32 V, reversible) and even bis(germacyclopentadienyl)ferrocene $[\eta^5\text{-}C_4Me_4GeSi(SiMe_3)_3]_2Fe$ **26**[97] (−0.45 V, irreversible). This suggests that the heavy cyclopentadienyl ligand $[\eta^5\text{-}(CPh)(CH)Si_2Ge(SiMe\textit{t}Bu_2)_3]$ in **27** is a more powerful electron donor to the Fe center than cyclopentadienyl $\eta^5\text{-}Me_5C_5$ and even germacyclopentadienyl $\eta^5\text{-}C_4Me_4GeSi(SiMe_3)_3$ ligands.

Computational analysis of the model complex $(\eta^5\text{-}H_5C_5)Fe[\eta^5\text{-}(CPh)(CH)Si_2Ge(SiH_3)_3]$ showed that the most important contribution to the overall bonding in **27** results from the strong π-donation from the doubly occupied heavy cyclopentadienyl ligand 1a and 2a orbitals to the vacant doubly degenerate e_1 orbitals of the $(H_5C_5)Fe^+$ unit (Fig. 4). In contrast, mixing of σ- and δ-type orbitals between the $(H_5C_5)Fe^+$ and heavy cyclopentadienyl fragments is much less important. Such a bonding situation in **27** is highly reminiscent of that of the parent $(H_5C_5)_2Fe$ ferrocene, for which 63.8% π-, 14.6% σ- and 21.6% δ-contributions were determined for the covalent bonding between the $(H_5C_5)Fe^+$ and cyclopentadienyl ligands.[100] The theoretical studies also demonstrated that the electrostatic bonding (52.4%) in **27** dominates over the covalent contribution (47.6%).

4. Heavy analogues of the cyclobutadiene dianion

Although both the cyclobutadiene dianion and the cyclopentadienide ion belong to the class of 6π-electron compounds, which should be formally classified as aromatic derivatives, the extent of their aromaticity is dramatically different. This marked distinction can be understood by realizing that the specific behavior of small doubly charged systems, such as the 6π-electron cyclobutadiene dianion, is primarily dictated by the important Coulomb repulsion between the two negative charges, which can outbalance the advantage gained through cyclic π-delocalization and aromatic stabilization.[101–103] If the monoanionic cyclopentadienide ion greatly benefits from the cyclic π-delocalization and overall aromatic stabilization, the same delocalization in the doubly charged cyclobutadiene dianion has a destabilizing effect because of unavoidable interaction of the two extra electrons producing a strong Coulomb repulsion. This results in a highly pronounced trend for electron localization and separation, and finally in a significant departure of the cyclobutadiene dianion ring from planarity.

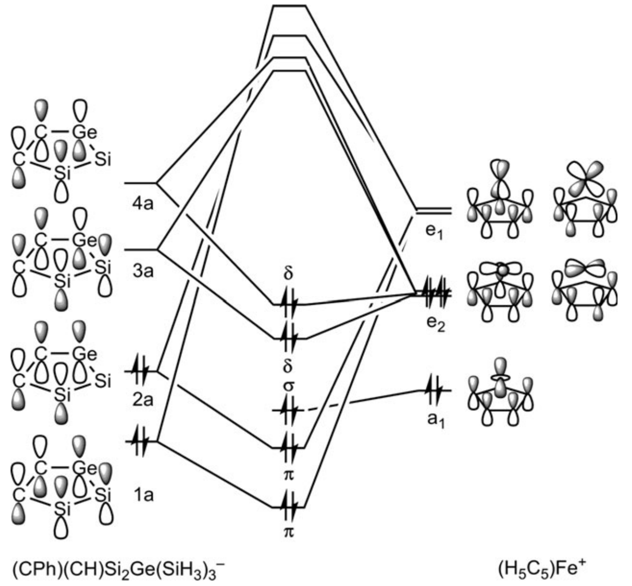


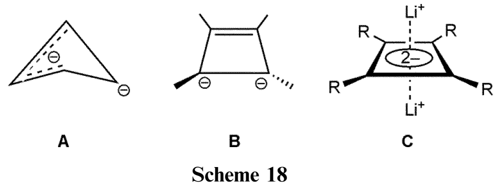
Fig. 4 Simplified MO correlation diagram for the interaction between the model $[(CPh)(CH)Si_2Ge(SiH_3)_3]^-$ ligand and the $(H_5C_5)Fe^+$ fragment (only most important bonding interactions are shown, symmetrical bonding π-MO of the $[(CPh)(CH)Si_2Ge(SiH_3)_3]^-$ ligand, which could be identified as a σ-donor orbital, was not located).

Moreover, in the planar delocalized D_{4h} structure of the cyclobutadiene dianion, four (out of six) π-electrons are forced to occupy nonbonding orbitals to form a pair of doubly degenerate HOMOs, giving rise to the strongly repulsive 1,3-antibonding interactions responsible for the overall destabilization and high reactivity of these species.

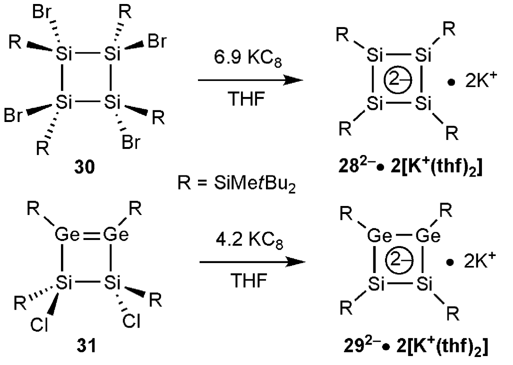
4.1 Theoretical studies

The development of the theoretical representation of the $[H_4C_4]^{2-}$ cyclobutadiene dianion structure passed through several evolutionary steps. At the early beginning, it was described as a folded four-membered ring featuring two distinct differently distributed negative charges: one of them being localized on a cyclic carbon atom, whereas the other one was of an allylic-type, delocalized over the remaining three skeletal carbon atoms, implying a small extent of cyclic delocalization of the six π-electrons (Scheme 18: **A**).[102]

More precise calculations showed that the above-discussed puckered structure, possessing an imaginary frequency, is not a minimum on the potential energy surface, whereas the real optimized geometry was represented by a trapezoid four-



Scheme 18



Scheme 19

membered ring manifesting a cyclic C═C bond and the two negative charges situated on the two adjacent tetrahedral skeletal carbons (Scheme 18: **B**).[104] However, in all of the above-discussed computations, the important factor of the interaction of the cyclobutadiene dianion with countercations was not taken into account. In fact, positively charged lithium ions may very efficiently counteract the destabilizing Coulomb repulsion and significantly decrease the unfavorable mixing of the two extra electrons, which results in a much greater extent of cyclic π-delocalization and, overall, in the aromatic stabilization of the dianionic system.[105–107] Consequently, dilithium cyclobutadiene dianion $[H_4C_4]^{2-}\cdot 2Li^+$was predicted to exist in a planar delocalized D_{4h} "inverse sandwich" form (Scheme 18: **C**, R = H).[105–107] Indeed, the experimentally realized trimethylsilyl-substituted analogue $[(Me_3Si)_4C_4]^{2-}\cdot 2Li^+$ was shown to possess a planar four-membered ring with a delocalized aromatic system of the six π-electrons (Scheme 18: **C**, R = SiMe$_3$).[108,109] A computational study on the three-dimensional aromaticity of $[(Me_3Si)_4C_4]^{2-}\cdot 2Li^+$ was also recently reported.[110] The analogues of the cyclobutadiene dianion, in which all skeletal C atoms are replaced with heavy group 14 elements, were unknown (both synthetically and computationally) prior to our investigation. A sole theoretical paper on the topic of a heavy cyclobutadiene dianion described the C_s tetrasilabicyclo[1.1.0]butane-2,4-diide as the most favorable form of the parent tetrasilacyclobutadiene dianion $[H_4Si_4]^{2-}$, stabilized by 29.9 kcal mol^{-1} compared with the planar delocalized D_{4h} structure.[111]

4.2 Experimental accomplishments

The first heavy analogues of the cyclobutadiene dianion, 1,2,3,4-tetrasila- and 1,2-disila-3,4-digermacyclobutadiene dianion derivatives **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]**, were readily synthesized by the dehalogenative reduction of *trans*,*trans*,*trans*-1,2,3,4-tetrabromo-1,2,3,4-tetrasiletane **30**[87] and *trans*-1,2-dichloro-$^3\Delta$-1,2,3,4-disiladigermetene **31**,[112] respectively, with potassium graphite in THF (Scheme 19).[113]

The crystal structures of both **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]**[87,113] are very similar, being distinctly different from that of the above-mentioned D_{4h} aromatic carbon analogue $[(Me_3Si)_4C_4]^{2-}\cdot 2Li^+$.[108] Thus, the Si$_4$ ring in **28^{2-}·2[K$^+$(thf)$_2$]** is markedly puckered (folding angle 34°) with both K$^+$ ions, above and below, dihaptocoordinated to the ring (instead of the tetrahaptocoordination indicative of the delocalized planar D_{4h} structure) (Fig. 5). The four-membered ring in **28^{2-}·2[K$^+$(thf)$_2$]** has the shape of a folded trapeze with Si1–Si4 and Si2–Si3 equal (2.3301(8) and 2.3300(8) Å)), Si1–Si2 shorter (2.2989(8) Å) and Si3–Si4 longer (2.3576(8) Å) bonds. Such a geometry resembles that predicted by the early calculations for $C_4H_4^{2-}$ (Scheme 18: **A**);[102] however, the electron distribution is different. The puckering of the Si$_4$ ring in **28^{2-}·2[K$^+$(thf)$_2$]** originates apparently from the Coulomb repulsion between the two negative charges, which cannot be efficiently overcome by the spatially remote potassium cations: this conclusion is well supported by the recent computations.[114,115] Such structural features of both **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]** definitely do not satisfy the geometrical requirements for aromaticity (ring planarity, cyclic bonds equalization, tetrahaptocoordination). The magnetic criterion of aromaticity is also not fulfilled: NICS for the model **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]** (Me$_3$Si instead of tBu$_2$MeSi) are positive, +4.3 and +6.1, respectively, pointing to the absence of an aromatic ring current. Thus, the heavy cyclobutadiene dianion species **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]** should be classified as nonaromatic compounds despite their 6π-electron systems formally obeying Hückel's rule.

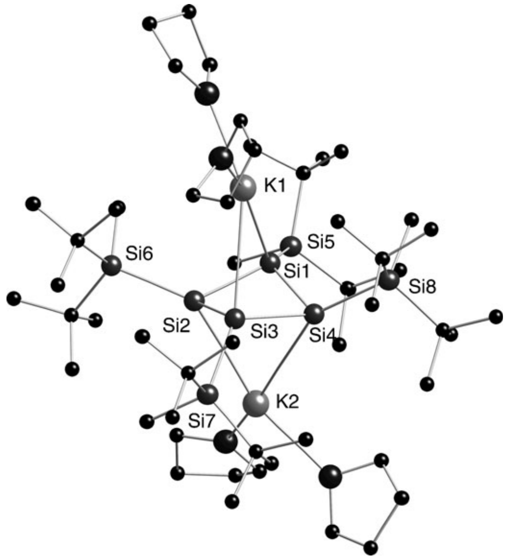
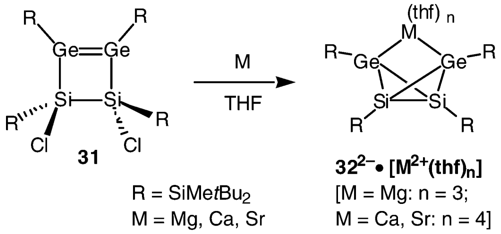


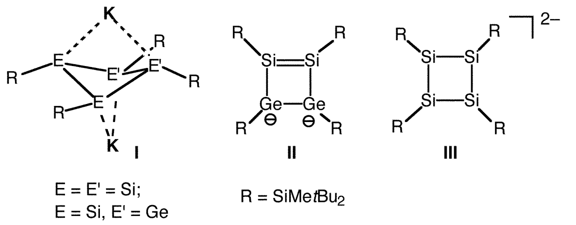
Fig. 5 Crystal Maker view of the dipotassium 1,2,3,4-tetrasilacyclobutadiene dianion **28^{2-}·2[K$^+$(thf)$_2$]** (hydrogen atoms are not shown).

Surprisingly, when **31** was reduced with alkaline earth metals (instead of alkali metals), different products, namely, alkaline earth metal derivatives of 1,3-disila-2,4-digermabicyclo[1.1.0]butane-2,4-diide **32^{2-}·[M^{2+}(thf)$_n$]** (M = Mg, n = 3; M = Ca, n = 4; M = Sr, n = 4), were formed,[116] whose structures were very similar to that of the tetrasilabicyclo[1.1.0]butane-2,4-diide found as a minimum for $[Si_4H_4]^{2-}$ (Scheme 20).[111]

In contrast to the crystalline state (Scheme 21, **I**), the solution structures of both **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]** are dramatically different. Thus, the most important contribution to the structure of heteronuclear Si$_2$Ge$_2$ **29^{2-}·2[K$^+$(thf)$_2$]** is represented by the resonance form **II** (Scheme 21), in which both negative charges are located on



Scheme 20



Scheme 21

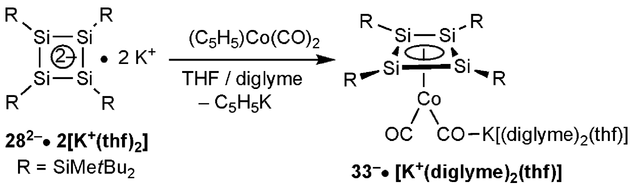
the more electronegative Ge atoms. This is in accord with a general tendency: electronegativity difference favors electron localization, resulting in the overall nonaromaticity of the compound.[104] However, the contribution **III** with a higher degree of π-delocalization becomes more important for homonuclear Si_4 **28^{2-}·2[K$^+$(thf)$_2$]**. This was clearly seen in the distinctly different resonances of the skeletal Si atoms: 113.7 ppm in **29^{2-}·2[K$^+$(thf)$_2$]** (region of the doubly bonded silicons)[90] and 17.0 ppm in **28^{2-}·2[K$^+$(thf)$_2$]** (outside the range of doubly bonded silicons). It is worth mentioning that the resonance form **II** for **29^{2-}·2[K$^+$(thf)$_2$]** (Scheme 21) resembles the structure **B** (Scheme 18) of the localized cyclobutene-1,2-diide,[104] whereas the contribution **III** for **28^{2-}·2[K$^+$(thf)$_2$]** (Scheme 21) more closely approaches the planar delocalized D_{4h} structure **C** (Scheme 18).[105–107]

4.3 Heavy cyclobutadienes as ligands for transition-metal complexes

In contrast to a number of known cyclobutadiene η^4-R_4C_4 transition-metal complexes,[117–119] those with the heavy cyclobutadiene ligands η^4-R_4E_4 (E = Si, Ge) are represented only by a few examples of Co and Fe complexes. Except for the (η^5-cyclopentadienyl)(η^4-silacyclobutadiene)cobalt complex recently reported by Kira and co-workers, which was prepared by the thermal reaction of 4-silatriafulvene with [η^5-H_5C_5]Co(CO)$_2$,[120] other representatives were synthesized, employing the heavy cyclobutadiene dianion derivatives **28^{2-}·2[K$^+$(thf)$_2$]** and **29^{2-}·2[K$^+$(thf)$_2$]** as starting materials.

Thus, the 18-electron anionic Co complex, [η^4-tetrasilacyclobutadiene]dicarbonylcobalt [η^4-(^{t}Bu$_2$MeSi)$_4$Si$_4$]Co(CO)$_2^-$·[K$^+$(diglyme)$_2$(thf)], **33^-·[K$^+$(diglyme)$_2$(thf)]**, was readily prepared by the reaction of **28^{2-}·2[K$^+$(thf)$_2$]**[87,113] with an excess of [η^5-H_5C_5]Co(CO)$_2$ in THF and isolated in the form of its diglyme complex (Scheme 22).[121]

This reaction overall is rather unusual, because it involves elimination of the typically "innocent" C_5H_5 ligand instead of the weaker bound and readily removable CO groups. The reason for such a preference could be rationalized by taking into account the overloading of the starting **28^{2-}·2[K$^+$(thf)$_2$]** with the two negative charges, one of which strongly tends to be removed in the form of an aromatic $C_5H_5^-$ anion. The spectral data of **33^-·[K$^+$(diglyme)$_2$(thf)]** definitely point to appreciable 3d (Co) → π* (Si$_4$) π-back donation. The cyclic π-delocalization in the Si_4 fragment was deduced based on a consideration of its structural features: η^4-coordination to Co, rectangular-planar geometry sharply distinctive from the highly folded structure of the starting **28^{2-}** and cyclic Si–Si bond lengths (2.2570(9)–2.3154(8) Å) intermediate between those of typical single and double bonds (Fig. 6).[121]



Scheme 22

The iron complex of tetrasilacyclobutadiene [η^4-(^{t}Bu$_2$MeSi)$_4$Si$_4$]Fe(CO)$_3$ **34**, as a silicon version of Pettit's famous [(η^4-(H$_4$C$_4$)]Fe(CO)$_3$, was readily available by the treatment of dibromocyclotetrasilene **35** with an excess of Na$_2$[Fe(CO)$_4$] in THF (Scheme 23).[122] Again, an important 3d (Fe) → π* (Si$_4$) π-back donation was clearly evident from the high-field resonances of the cyclic Si atoms (−15.8 ppm). Structurally, the tetrasilacyclobutadiene ring in **34** exhibited features similar to those of **33^-·[K$^+$(diglyme)$_2$(thf)]** (hapticity of coordination, planarity, lengths of the cyclic Si–Si bonds) (Fig. 7). The most striking difference between the two complexes was the shape of the Si_4 ligand: exceptionally rectangular in **33^-·[K$^+$(diglyme)$_2$(thf)]**[121] in contrast to the usual nearly square structure in **33**.[122] This was attributed to the combined influence of the two factors on the overall structure of the anionic **33^-·[K$^+$(diglyme)$_2$(thf)]**: electronic (partial distribution of the negative charge over the Si_4 ring) and geometrical (spatial orientation of the CO groups superimposing the two opposite cyclic Si–Si bonds, which results in their stretching).

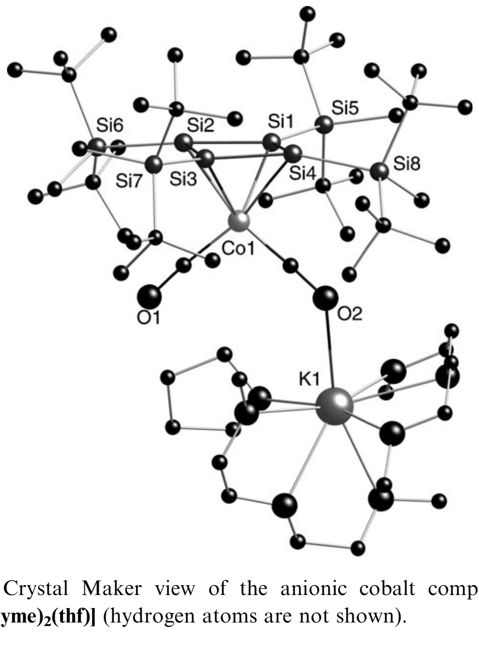
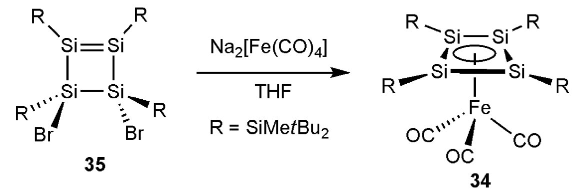


Fig. 6 Crystal Maker view of the anionic cobalt complex **33^-·[K$^+$(diglyme)$_2$(thf)]** (hydrogen atoms are not shown).



Scheme 23

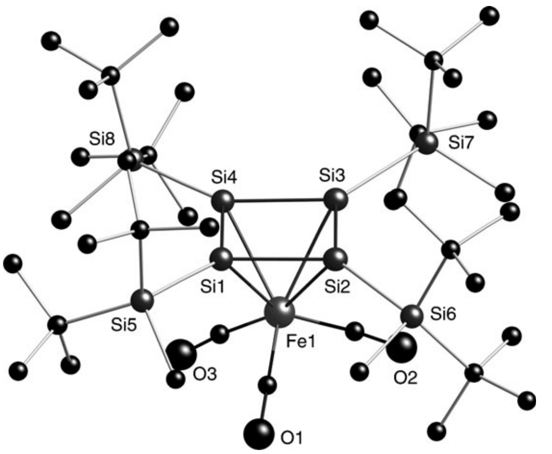


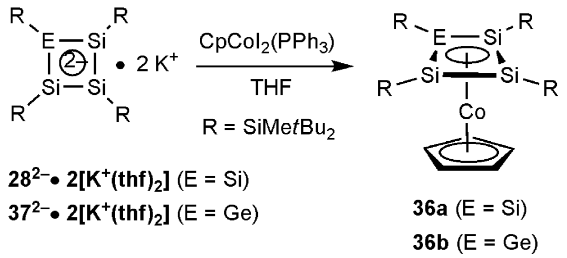
Fig. 7 Crystal Maker view of the iron complex **34** (hydrogen atoms are not shown).

The most essential bonding interaction in **34** between the singly occupied tetrasilacyclobutadiene ligand π-orbitals and the d_{xz}, d_{yz} orbitals of the Fe atom ends up with the formation of two pairs of doubly degenerate bonding (HOMO−1 and HOMO) and antibonding (LUMO and LUMO + 1) hybrids. The HOMO–LUMO gap for the model iron complex $[(\mathrm{Me_3Si})_4\mathrm{Si_4}]\mathrm{Fe(CO)_3}$ was markedly smaller (4.61 eV) than that of the hypothetical carbon analogue $[(\mathrm{Me_3Si})_4\mathrm{C_4}]\mathrm{Fe(CO)_3}$ (5.64 eV). Particularly notable was the appreciable increase in the tetrasilacyclobutadiene ligand HOMO level, responsible for its stronger π-donating ability compared with that of the C_4 ligand in cyclobutadiene complexes. Like the parent Pettit's $(\mathrm{H_4C_4})\mathrm{Fe(CO)_3}$ complex, **34** was also classified as a three-dimensional aromatic: NICS = −12.5 (for the $\mathrm{Me_3Si}$-substituted model).

Heavy cyclobutadiene dianions have also been successfully utilized for the design of novel sandwich complexes. Thus, (η^5-cyclopentadienyl)(η^4-tetrasilacyclobutadiene)cobalt {η^4-[($^t\mathrm{Bu_2MeSi})_4\mathrm{Si_4}$]}CpCo **36a** and ($\eta^5$-cyclopentadienyl)($\eta^4$-trisilagermacyclobutadiene)cobalt {η^4-[($^t\mathrm{Bu_2MeSi})_4\mathrm{Si_3Ge}$]}CpCo **36b** were synthesized by the reaction of tetrasilacyclobutadiene dianion **$28^{2-}\cdot 2[\mathrm{K^+(thf)_2}]$**[87,113] and trisilagermacyclobutadiene dianion **$37^{2-}\cdot 2[\mathrm{K^+(thf)_2}]$**[123] salts with $\mathrm{CpCoI_2(PPh_3)}$ in THF (Scheme 24).[123]

Following the general tendency of transition metal (d) → tetrasilacyclobutadiene (π*) π-back donation, **36a** showed an up-field (compared with the typical values of sp^2-Si atoms)[124] resonance of the endocyclic silicons at 0.4 ppm.

The geometry of the $\mathrm{Si_4}$ unit in **36a** closely resembled that of the iron complex **34**: an almost regular square-planar four-membered ring tetrahaptocoordinated to the Co atom. The endocyclic silicon–silicon bond lengths in **36a** spread over the narrow range of 2.2718(10)–2.2725(9) Å, being again intermediate between the typical silicon–silicon single and double bond lengths (Fig. 8).



Scheme 24

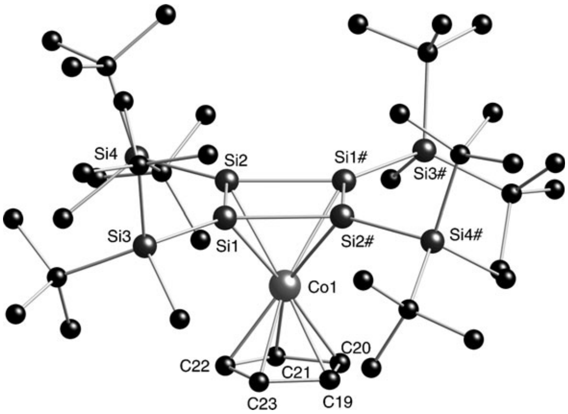


Fig. 8 Crystal Maker view of the cobalt sandwich complex **36a** (hydrogen atoms are not shown).

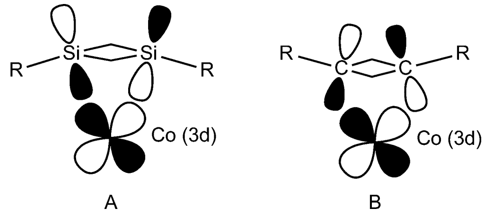


Fig. 9 Schematic illustration of the pπ(($\mathrm{Me_3Si})_4\mathrm{E_4}$, E = Si, C)–3d(Co) orbital interactions in the calculated complexes **A** and **B**.

Calculations on the $\mathrm{Me_3Si}$-substituted model complex (η^4-($\mathrm{Me_3Si})_4\mathrm{Si_4}$)CoCp **A** and its carbon analogue [η^4-($\mathrm{Me_3Si})_4\mathrm{C_4}$]-CoCp **B** disclosed an interesting structural distinction between them. Thus, whereas the substituent Si atoms in **A** are tilted towards the Co atom from the $\mathrm{Si_4}$-mean plane by 0.236–0.261 Å, those in **B** are bent away from the Co atom, being situated at 0.294–0.330 Å above the C_4 ring. This was explained in terms of the difference in the ring size of the cyclobutadienes $(\mathrm{Me_3Si})_4\mathrm{E_4}$ (E = Si, C), implying different extents of the effective pπ($\mathrm{R_4E_4}$)–3d(Co) orbital interactions based on the size of the carbon 2pπ- and silicon 3pπ-orbitals, as depicted in Fig. 9.

5. Conclusion

In contrast to the well-advanced (both experimentally and theoretically) field of the 6π-electron aromatics, such as benzene, cyclopentadienide ion and cyclobutadiene dianion, the chemistry of their heavy congeners containing Si, Ge, Sn and Pb atoms is still in its infancy. Sila- and germabenzene, sila- and germacyclopentadienide ion, as well as tetrasila- and disiladigermacyclobutadiene dianion derivatives became readily available as stable species only during the past fifteen years. Several examples of each class of the 6π-electron aromatic compounds of heavy group 14 elements have been synthesized and thoroughly investigated; these accomplishments have been covered in the present review. However, work in this field is still far from completion, and much remains to be done in the future. This concerns, first of all, the synthesis of the most desired all-heavy group 14 elements containing representatives, such as hexasilabenzene or pentasilacyclopentadienide ion derivatives. Apart from these experimental breakthroughs, detailed theoretical considerations of the structures, particular bonding situations and specific reactivity of the heavy aromatics are highly and impatiently awaited. As a culmination, one would expect an increasing interest in the application of 6π-electron heavy aromatics as novel cyclic polyene ligands for a new generation of transition-metal complexes. As the first examples of such complexes, one can mention those featuring sila- and germabenzene; sila-, germa- and disilagermacyclopentadienyl; tetrasila- and disiladigermacyclobutadiene ligands, described in our review. Hopefully, such a very promising start would stimulate further investigations in the field to discover transition-metal complexes with novel unexpected properties crucial in applied science for the design of new advanced materials.

Acknowledgements

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