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Ferrocenyl-substituted Low-coordinated Heavier Group 14 Elements‡

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Several examples of stable low-coordinated species of heavier group 14 elements (Si, Ge, Sb, Pb) such as divalent species and multiple-bond compounds have been reported. With the goal in mind to create unprecedented low-coordinated species of heavier group 14 elements that exhibit considerably increased redox stability, ferrocenyl (Fc)-substituted low-coordinated species of heavier group 14 elements were designed. In this short account article, recent progress on the synthesis of Fc-based low-coordinated species of heavier group 14 elements is summarized.

1. Introduction

Low-coordinated species of heavier group 14 elements (E = Si, Ge, Sn, Pb) such as metallylenes (>E:), dimetallenes (>E=E<), and dimetallynes (–E≡E–) have attracted substantial attention due to their unique fundamental properties relative to their carbon-based analogues,[1] which play important roles in organic chemistry. Particularly, their extremely high reactivity toward stable small molecules such as a dihydrogen and ethylene has garnered interest as their activation of small molecules mimics that of transition-metal catalysts.[2] For example, isolable dimetallynes react with dihydrogen, alkenes, alkynes, and amines.[2-4] The reactivity of such low-coordinated species of heavier group 14 elements in these addition reactions can be interpreted in terms of an initial electrophilic attack on account of their high electrophilicity that arises from the low-lying LUMO, and a subsequent nucleophilic attack from the high-lying HOMO. However, only few studies on the redox behavior of such low-coordinated species have been reported, even though the reduction and oxidation behavior should reflect the frontier orbital situation.[1,4,5] Thus, low-coordinated species of heavier group 14 elements that show considerable electrochemical stability upon reduction/oxidation should be appropriate models for an investigation of the redox behavior. Although some reports have discussed the attempted chemical reduction and oxidation of low-coordinated species of heavier group 14 elements, it is particularly difficult to observe and/or synthesize anionic and cationic silylenes and germylenes due to their instability.[4,5]

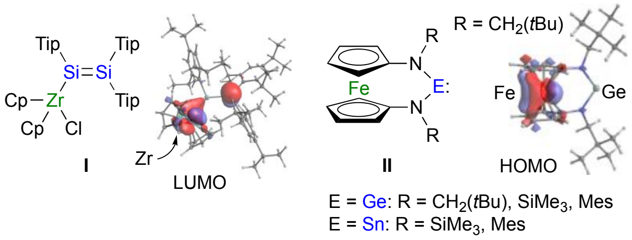

Figure 1. Examples of an isolable disilene (**I**),[8] as well as germylenes and stannylenes (**II**)[7] that contain a transition-metal moiety. The LUMO of **I** and the HOMO of **II** (E = Ge, R = CH$_2$(tBu)) shown were calculated at the B3PW91/3-21G//opt level of theory.[9]

One strategy to increase the redox stability of low-coordinated main group elements is based on the tethering of a transition metal moiety,[6,7] and this approach can also be expected to afford low-coordinated group 14 element species with increased redox stability.[7] However, in most cases, the frontier orbitals of redox-stable transition-metal-tethered low-coordinated main-group compounds are substantially perturbed and dominated by the contributions of the transition-metal moieties. For example, the LUMO of Zr-substituted disilene **I**, for which electrochemical properties have not been reported, is predominantly located on the Zr moiety (Figure 1).[8] Moreover, the HOMO of ferrocenophane-type germylene **II**, which contains *N*-substituents, is predominantly located on the ferrocenyl (Fc) moiety.[7] In other words, such electronically perturbed species can be expected to exhibit properties that differ from those characteristic of low-coordinated heavier group 14 element species. Accordingly, it seems more promising to focus on the synthesis of isolable low-coordinated species of heavier group 14 elements that exhibit (i) frontier orbitals predominantly composed of the central group 14 elements with high electrophilicity/nucleophilicity and (ii) stable redox behavior upon electrochemical reduction/oxidation.

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The molecular design for such low-coordinated heavier group 14 compounds used in our group meets requirements (i) and (ii) given that the low-valent heavier group 14 elements are directly tethered to a Fc group. The Fc group can be modified effectively via established methods, and carbon-substitution can be expected to result in lower levels of electronic perturbation toward the central heavier group 14 elements relative to π-electron donating hetero-atom substitution such as a nitrogen. In this article, our systematic studies on the synthesis of Fc-substituted low-coordinated compounds of Si and Ge (Chart 1, **1**-**4**) are presented,[10-13] and we discuss their structural features, spectroscopic properties, and redox behavior.

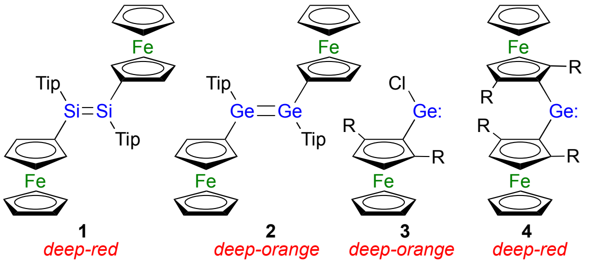


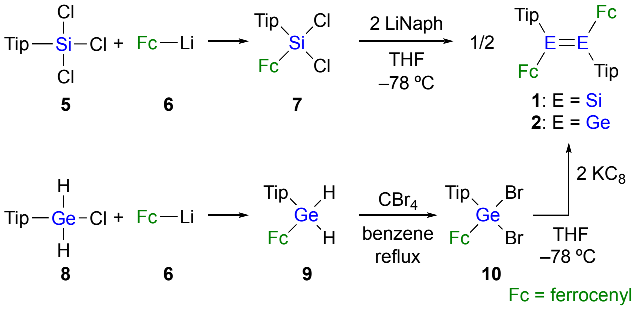
Chart 1. Fc-substituted disilene **1**, digermene **2**, and germylenes **3** and **4**, which have been reported by the author's group (Tip = 2,4,6-triisopropylphenyl, R = 3,5-di-*tert*-butylphenyl).[10-13]

2. 1,2-Bis(ferrocenyl)disilene 1 and 1,2-Bis(ferrocenyl)digermene 2

In order to isolate stable low-coordinated compounds of heavier group 14 elements, a sterically demanding substituent has to be introduced onto the central heavier group 14 element(s).[1] Considering this restriction in the context of the molecular design, we chose a disilene and a digermene that bear two Fc groups, *i.e.*, 1,2-bis(ferrocenyl)disilene **1** and 1,2-bis(ferrocenyl)digermene **2**, as a starting point for our investigations, because silicon or germanium atoms within a double bond (>E=) possess two valence bonds for the introduction of a sterically demanding group *and* the Fc substituent.

We examined 2,4,6-triisopropylphenyl (Tip) as a sterically demanding protecting group, as the ability of the steric demand of Tip to kinetically stabilize the disilene moiety has been well documented.[8,14,15] The synthetic route to 1,2-bis(ferrocenyl)disilene **1** and 1,2-bis(ferrocenyl)digermene **2** is outlined in Scheme 1.[10] Dichlorosilane **7**, which contains a Tip group, is obtained in 49% isolated yield from the reaction between TipSiCl$_3$ (**5**)[16] with FcLi (**6**) in THF at –78 °C. Dichlorosilane **7** is remarkably stable, and can even be manipulated in air. The subsequent reduction of **7** with lithium naphthalenide (LiNaph) in THF at –78 °C affords **1** as orange-red crystals. In the case of the Ge analogues,[11] the synthetic route is a bit different due to the difficulties associated with the purification of Tip(Fc)GeCl$_2$, which is obtained from the reaction of TipGeCl$_3$ with **6**. Therefore, Tip(Fc)GeH$_2$ (**9**) is synthesized and isolated by the reaction of TipGeH$_2$Cl (**8**) with **6**. The bromination of **9** with CBr$_4$ results in the quantitative formation of dibromogermane Tip(Fc)GeBr$_2$ (**10**), which can be isolated in pure form. It should be noted here that neither Br$_2$ nor NBS can be used for the bromination of **9**, because the ferrocenyl moiety of **9** is oxidized by Br$_2$ or NBS to afford insoluble green products. In contrast to the smooth reduction of dichlorosilane **7** to disilene **1**, the reduction of dibromogermane **10** with LiNaph furnishes only complex product mixtures. However, KC$_8$ acts as an effective reagent for the reductive coupling of **10** to give 1,2-bis(ferrocenyl)digermene **2** under the conditions shown in Scheme 1.[11]

Disilene **1** exhibits a remarkably high thermal stability, and no sign of decomposition was observed after 10 days in toluene-d_8 at 90 °C. In contrast, digermene **2** slowly decomposes in solution ($t_{1/2}$ = ca. 0.5 h at 60 °C in C_6D_6) to generate a complex mixture of products.



Scheme 1. Synthesis of 1,2-bis(ferrocenyl)disilene **1**[10] and 1,2-bis(ferrocenyl)digermene **2**.[11]

The ^{29}Si NMR spectrum of **1** in C_6D_6 showed a characteristic signal at 70.6 ppm, which is in the typical range for silicon atoms within a double bond [δ_{Si} (tetraaryldisilenes): 53-66 ppm; δ_{Si} (tetraalkyldisilenes): 90-103 ppm].[17] Both the ^{1}H NMR spectra of **1** and **2** in C_6D_6 suggested that their Fc and Tip groups are able to rotate without any steric restriction around the E-C bonds (E = Si, Ge) at room temperature, and showed two doublets for the methyl groups of the *ortho*-isopropyl substituents. Considering these spectral features, it should be concluded that disilene **1** and digermene **2** adopt *trans*-bent structures in solution.

In the crystalline state, the *trans*-bent structures of **1** and **2** were confirmed by single-crystal X-ray diffraction (XRD) analyses.[10,11] Dimetallenes **1** and **2** exhibit higher *trans*-bent angles (**1**: θ = 27.9˚; **2**: 43.7˚) relative to those of tetraaryl-disilenes (Tip$_2$Si=SiTip$_2$: ~0˚)[14] and -digermenes (Tip$_2$Ge=GeTip$_2$: 12.3˚),[18] which should most likely be interpreted in terms of the larger singlet-triplet energy gap (ΔE_{st}) of Tip(Fc)E: relative to that of Ar$_2$E: (E = Si, Ge).[19,20] The selected structural parameters of 1,2-bis(ferrocenyl)dimetallenes **1** and **2**, which are summarized in Table 1, especially the Si=Si and Ge=Ge bond lengths, suggest their considerable double-bond character, given that these values are shorter than those of the corresponding single bonds (Si–Si: ~2.35 Å; Ge–Ge: ~2.48 Å).

Table 1. Selected structural parameters of (*E*)–Tip(Fc)E=E(Fc)Tip (**1**: E = Si; **2**: E = Ge).[10,11]

$Tip_2Fc_2E_2$	E=E/Å	E–C(Fc)/Å	E–C(Tip)/Å	C–E–C/°
1 (Si=Si)	2.173(2)	1.848(3)	1.880(3)	119.3(1)
2 (Ge=Ge)	2.3320(5)	1.935(3)	1.982(2)	106.8(1)

The UV/vis spectra of **1** and **2** in hexane are comparable, showing two characteristic absorption maxima for each compound [**1**: 332 (ε 5,900) and 427 nm (24,000), **2**: 430 (17,000) and 500 nm (sh)]. The results of TD-DFT calculations suggested that the observed strong absorptions should be assigned to the mixed electron-transition from both occupied π(Si=Si) orbitals, as well as from filled d-orbitals of the Fc moiety to the empty π*(Si=Si or Ge=Ge) orbitals.[10,11] These calculations furthermore suggested that the characteristic strong absorptions contain contributions from several types of d-π* electron transitions.

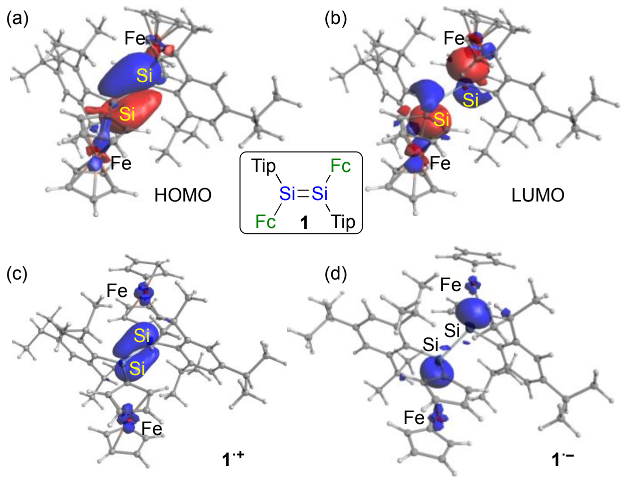
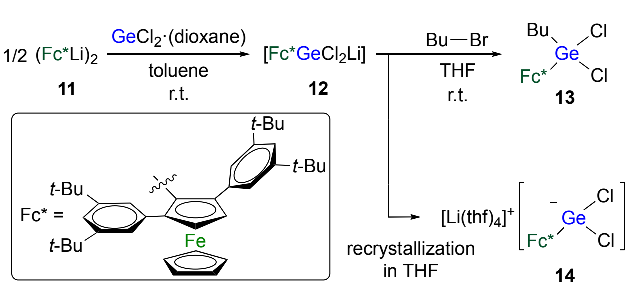


Figure 2. (a) HOMO and (b) LUMO of **1**, as well as spin densities of the (c) radical cation and (d) radical anion of **1**; calculated at the B3PW91-D3(BJ)/6-311G(2d,p)//opt level of theory.[9,10]

The HOMOs and LUMOs of **1** and **2** are predominantly composed of their E=E (E = Si, Ge) π-bond moieties (Figure 2). Thus, the electrochemical properties of **1** and **2** should be of great interest, because they can be expected to reflect the redox behavior of the E=E π-bond. Cyclic voltammetry (CV) and differential potential voltammetry (DPV) measurements revealed that disilene **1** exhibits two reversible redox couples in the reduction region at $E_{1/2}$ = –2.64 V (2 e^-) and –3.09 V (1 e^-) (all $E_{1/2}$ vs. FcH/FcH^+ in THF using 0.1 M $[Bu_4N]^+[PF_6]^-$ as the supporting electrolyte),[10] while germanium analogue **2** showed only one reversible redox couple at $E_{1/2}$ = –2.27 V (1 e^-).[11] The significantly lower reduction potential of **2** relative to **1** suggests a lower energy level of the Ge=Ge π*-orbital in **2** compared to that of the Si=Si π*-orbital in **1**. Interestingly, 1,2-bis(Fc)dimetallenes **1** and **2** undergo reversible reductions, which stands in sharp contrast to the carbon analogue (*E*)-Ph(Fc)C=C(Fc)Ph (**III**)[21] and other previously reported tetraaryldisilenes,[17] indicating that the Fc groups stabilize the anionic state of **1** and **2**. In the oxidation region, **1** and **2** exhibit two-step reversible redox couples [**1**: $E_{1/2}$ = +0.05 V (1 e^-) and +0.24 V (1 e^-); **2**: –0.41 V (1 e^-) and +0.03 V (1 e^-); all $E_{1/2}$ vs. FcH/FcH^+ in *o*-dichlorobenzene using 0.1 M $[Bu_4N]^+[B(C_6F_5)_4]^-$ as the supporting electrolyte], suggesting a desirable coupling of the two Fc moieties via the Si=Si or Ge=Ge π-bond. Interestingly, the first oxidation potential of digermene **2** is lower than that of ferrocene or disilene **1**. The separations of the half wave oxidation potentials (**1**: $\Delta E_{1/2}$ = 0.19 V; **2**: 0.44 V; at 25 °C) can be converted into the corresponding comproportionation constants K_{com}[22] for the equilibrium $\mathbf{A}^{2+}$ + **A** ⇋ 2 $\mathbf{A}^{+}$ (**A** = **1** or **2**; **1**: K_{com} = 1.63 × 10^3; **2**: 2.74 × 10^7), which suggest strong electronic communication between the two ferrocenyl moieties through Ge=Ge bond in **2** relative to those in the carbon system such as (*E*)-Ph(Fc)C=C(Fc)Ph (**III**; $\Delta E_{1/2}$ = 0.18 V; K_{com} = 1.10 × 10^3) and those in **1**.[21,22] On the basis of this electrochemical analysis, we concluded that digermene **2** is a very effective d-π electron system relative to the corresponding carbon and silicon systems exhibiting multi-step, reversible redox behavior.[23] Notably, the theoretically optimized structures of the neutral, cationic, anionic, and dicationic species of **1** are comparable (Figure 2), suggesting negligible structural relaxation during the redox processes. Furthermore, as shown in Figure 2, the spin density of the anionic/cationic radical species of **1** is located not only on the Si orbitals, but also on the Fe orbitals, showing effective delocalization of the electron spin through the Si=Si π-orbital and Fe d-orbitals. In their entirety, these results unambiguously demonstrate that the introduction of Fc groups at the E=E double bond affords considerable stability through redox processes.[23]

3. Chloro(ferrocenyl)germylene 3 and Bis(ferrocenyl)germylene 4

The reduction of dichlorosilane **7** and dibromogermane **10** results in the formation of the corresponding double-bond compounds, *i.e.*, the dimer of the respective silylene and germylene (Scheme 1).[24] In order to isolate the corresponding monomeric ferrocenyl-substituted silylene or germylene, a ligand that is much bulkier than Tip or Fc should be required. As previously reported reduction reactions of a dibromo(ferrocenyl)silane with the much bulkier aryl group Tbt(Fc)$SiBr_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)[25] were unsuccessful under various reaction conditions, we decided to use a sterically demanding ferrocenyl group, *i.e.*, 2,5-bis(3,5-di-*tert*-butylphenyl)ferreocenyl, Fc*),[26] to isolate the monomeric ferrocenyl-substituted silylene or germylene. Initially, chloroferrocenyl metallylenes Fc*(Cl)E: (E = Si, Ge) were identified as attractive synthetic targets, because they could potentially be appropriate precursors for several types of monomeric Fc*-substitued metallylenes, Fc*(R)E:, *via* nucleophilic substitution reactions. Although Fc*-substituted trichlorosilane Fc*$SiCl_3$ was synthesized successfully, it resisted further modifications/reductions under a variety of conditions. Thus, we focused on the synthesis of the monomeric chloroferrocenylgermylene **3** using $GeCl_2$·(dioxane) as the germanium source.[12]

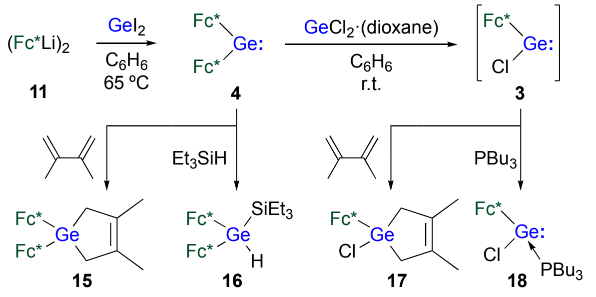


Scheme 2. Reaction of (Fc*Li) with $GeCl_2$·(dioxane).[12]

According to established synthetic methods for arylchlorogermylenes,[27] $GeCl_2$·(dioxane) was treated with the isolated dimer $(Fc^*Li)_2$ (**11**)[26c] in toluene. The crude mixture was then treated with bromobutane as a trapping reagent for the germylene. However, the thus obtained trapped product is not butylbromochlorogermane Fc*(Bu)GeClBr, but butyldichlorogermane Fc*(Bu)$GeCl_2$ (**13**). Thus, it seems feasible to assume that the product of the reaction between **11** and $GeCl_2$·(dioxane) is not chlorogermylene Fc*(Cl)Ge: (**3**), but chlorogermylenoid $Fc^*GeCl_2^-$ (**12**), which could undergo a nucleophilic substitution with bromobutane to give **13**.[12] Recrystallization of **12** from THF furnishes single crystals of the separated ion pair of the germylenoid, $[Li(thf)_4]^+[Fc^*GeCl_2]^-$ (**14**),[12] which were characterized by single-crystal XRD analysis.

When GeI_2 is used instead of $GeCl_2$·(dioxane) for the reaction with $(Fc^*Li)_2$, bis(ferrocenyl)germylene Fc^*_2Ge: (**4**) is obtained in the form of deep red crystals (Scheme 3).[13] A single-crystal XRD analysis of these crystals revealed a monomeric structure for **4** in the crystalline state,[13] with a closest intermolecular Ge···Ge distance of 11.7 Å. The structural parameters of **4** suggest a germylene character with slight π-conjugative contribution from the Cp moieties toward the vacant 4p(Ge) orbital at the germylene center. Compound **4** engages in [1+4]cycloaddition and Si–H insertion reactions with 2,3-dimethyl-1,3-butadiene and triethylsilane to give adducts **15** and **16**, respectively (Scheme 3), suggesting chemical reactivity that is characteristic for a germylene with a singlet ground state, an s-type lone pair of electrons, and a vacant 4p(Ge) orbital.[13]

As in the cases of Fc-substituted dimetallenes **1** and **2**, the results of theoretical calculations suggested that the frontier orbitals (HOMO and LUMO) of germylene **4** are predominantly composed of Ge orbitals, *i.e.*, n(Ge) (HOMO) and 4p(Ge) (LUMO), together with smaller contributions from d(Fe) orbitals (Figure 3). The UV/vis spectra of **4** in toluene exhibit two characteristic absorptions at λ_{max} = 405 (ε = 2,600) and 476 (ε = 2,600) nm.[13] In sharp contrast to stable bis(organo)germylenes, which show only very weak absorption corresponding to the symmetry-forbidden n-p transitions, the absorption coefficients of **4** are significantly higher, suggesting a considerable contribution of the LMCT from the Fc* to the germylene moieties.



Scheme 3. Synthesis of Fc*-substituted germylenes **3** and **4**.[13]

The electrochemical properties of bis(Fc*)germylene **4** were investigated by CV and DPV measurements (1.0 mM, r.t., in THF with 0.1 M $[nBu_4N]^+[B(C_6F_5)_4]^-$ as the supporting electrolyte).[13] A reversible one-step one-electron redox couple can be observed in the reduction region ($E_{1/2}$ = –2.34 V; 1 e^-) and a reversible two-step redox couple in the oxidation region ($E_{1/2}$ = +0.11 V; 2 e^-; +0.36 V; 1 e^-). The lower oxidation/reduction potentials of **4** relative to Ge(IV) compounds should consequently be ascribed to its germylene character. Based on the results of theoretical calculations, the optimized structures of **4** and its dication $\mathbf{4}^{2+}$ are very similar (Figure 3), whereby $\mathbf{4}^{2+}$ represents the triplet ground state. Although the HOMO of $\mathbf{4}^{2+}$ seems to be predominantly composed of the 4s orbital of the Ge atom as well as the neutral species of **4**, the spin density of $\mathbf{4}^{2+}$ (triplet) is localized on the two Fe atoms (Figure 3). Accordingly, it can be concluded that during the first two-electron oxidation process of **4**, two electrons should be abstracted from the HOMO of **4** with n(Ge) character, followed by a relaxation process via a facile intramolecular electron transfer from the Fe atoms to the Ge moiety, which results in a "ferrocenium-substituted germylene". The sterically demanding Fc* groups maintain the geometry of germylene **4** throughout the redox processes, which should enhance the stability of the anionic and cationic species of **4**. Subsequently, the generated dication $\mathbf{4}^{2+}$ most likely undergoes a further 1-electron oxidation at the lone pair of the germylene moiety (s-character). In total, **4** should thus exhibit a one-step one-electron reduction and a two-step three-electron oxidation.

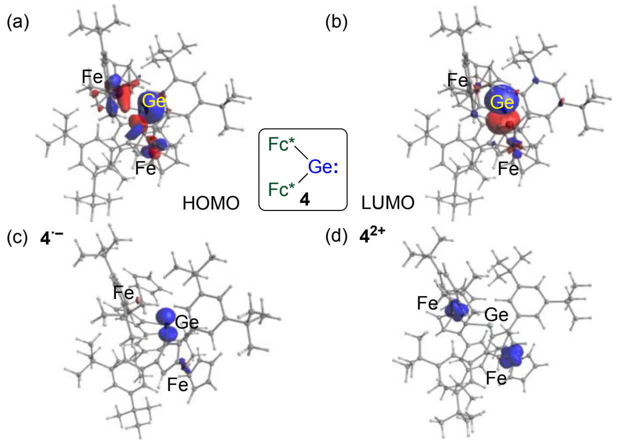


Figure 3. (a) HOMO and (b) LUMO of **4**, as well as spin densities of the (c) radical anion and the (d) dicationic species of **4**, calculated at the B3PW91-D3(BJ)/6-311G(2d,p)//opt level of theory.[9,13]

During the investigation on the reactivity of germylene **4**, we also discovered an effective synthetic route to the corresponding chloro(ferrocenyl)germylene **3**: Treatment of germylene **4** with an equimolar amount of $GeCl_2$·(dioxane) at r.t. affords **3** via a facile ligand redistribution (Scheme 3).[13,28] Unfortunately, **3** could not be isolated in pure form, but the quantitative formation of **3** was demonstrated by a trapping reaction with 2,3-dimethyl-1,3-butadiene, which furnished the corresponding [1+4]cycloadduct (**17**) (Scheme 3). Furthermore, **3** was isolated and characterized as the corresponding tributylphosphine-adduct (**18**). The synthesis of a variety of ferrocenylgermylenes using **18** as a precursor is currently under investigation.

Conclusions

Ferrocenyl-substituted low-coordinated species of silicon(II) and germanium(II) can be synthesized and isolated as stable compounds. Their redox behavior can be examined by electrochemical measurements such as cyclic voltammetry (CV) and differential potential voltammetry (DPV). The HOMOs and LUMOs of Fc-substituted disilene **1** and digermene **2** are predominantly composed of the π- and π^*-orbitals, respectively, similar to conventional disilenes and digermenes. However, in contrast to previously reported carbon-substituted dimetallenes, **1** and **2** exhibit reversible redox behavior, which suggests considerably higher stability for the corresponding anionic/cationic species, and the increased stability should be attributed to the introduction of the Fc groups. In addition, bis(ferrocenyl)germylene **4**, which contains significantly more bulky Fc* ligands (Fc* = 2,5-bis(3,5-di-*tert*-butylphenyl)Fc), was synthesized, and reversible redox behavior was observed. Interestingly, theoretical calculations suggest that dicationic $\mathbf{4}^{2+}$ should be considered a ferrocenium-substituted germylene (Fc^{*+}_{2}Ge:), although the HOMO of **4** is predominantly located on the Ge atom and not on the ferrocenyl moieties. These results suggest the possibility that the stability of low-coordinated species of heavier group 14 elements via electrochemical redox processes could be affected by the introduction of a Fc group.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ dedicated to Emeritus Professor Mitsuo Kira on the occasion of his 77th birthday.

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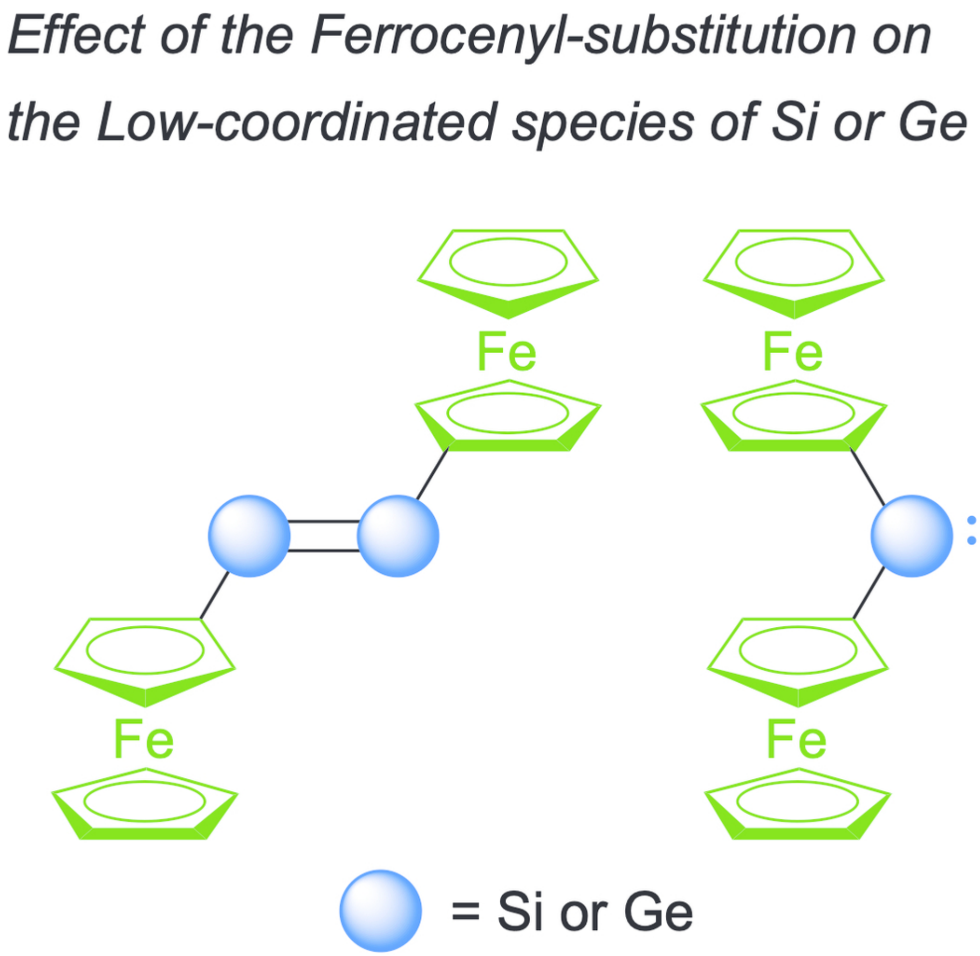

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