The Synthesis and Properties of Bimetallic $d-\pi$ Electron Systems Containing Metallocenyl Substituents of Fe or Ru, and $\pi$-Electron Spacers of Heavier Main Group Elements from Group 14 or 15

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Abstract: Relative to $\pi$-electron systems between elements from the second row of the periodic table, those between heavier main group elements should exhibit higher HOMO and lower LUMO levels. Moreover, such $\pi$-electron systems between heavier main group elements are expected to be good electron acceptors and donors, and they should also exhibit good electron transporting properties. With the ultimate goal to create unprecedented $\pi$-electron systems between heavier main group elements in mind, we designed $d-\pi$ electron systems containing heavier main group elements in the $\pi$-electron moiety and transition metals in the $d$-electron moiety. In this account article, we present our recent progress on the generation of bimetallic ferrocenyl- and ruthenocenyl–based $d-\pi$ electron systems containing $\pi$-bond spacers of heavier main group elements from group 14 or 15.

1. Introduction

Organic compounds containing $\pi$-electron systems, such as ethylene, benzene, or ketones comprise some of the most fundamental organic molecules and are undisputedly of great importance. Organometallic $\pi$-conjugated systems also have attracted considerable interest recently, as they exhibit a variety of unique electronic, optical, and magnetic properties. It is accordingly hardly surprising that $d-\pi$ electron systems of bimetallic complexes tethered with a $\pi$-electron spacer, i.e. $[M(Ligand)](\pi$-electron spacer)$-[M(Ligand)]$ ($M$=transition metal), have been investigated thoroughly. These compounds represent an unusual class of model compounds for mixed-valence states, allowing an insight into the potential of the $\pi$-electron system to act as a $\pi$-spacer, which is especially interesting with respect to fundamental applications in organic electronic materials, such as molecular switches and wires. In the context of $d-\pi$ conjugated systems, ferrocene is often used as an effective $d$-electron moiety, because it is conveniently stable, exhibits desirable redox properties, and can be easily modified with a wide variety of substituents via well-established synthetic techniques. Accordingly, bimetallic ferrocenyl-based $d-\pi$ electron systems should be ideal candidates for benchmark compounds in the examination of $\pi$-electron systems as $\pi$-spacers. Although several $d-\pi$ conjugated systems, where two ferrocenyl (Fc) moieties are bridged by a $\pi$-electron spacer, e.g. $\text{Ph}(\text{Fc})C\equiv C(\text{Fc})\text{Ph}$, $\text{Fc}C\equiv C\equiv \text{Fc}$, $\text{Fc}N\equiv N\equiv \text{Fc}$, and bis(Fc)thiophene derivatives have been investigated and reported, the $\pi$-electron systems in these compounds are confined to elements from the second row of the main group elements. In order to obtain the desired advantageous optoelectronic and magnetic properties for applications in organometallic electronic materials, the requirements for $d-\pi$ electron systems are: (i) relatively low redox potentials, (ii) the presence of a stable multi–step redox system, and (iii) a controllable redox behavior. With these requirements in mind, $\pi$-bonds between heavier main group elements are expected to be far superior to those of second row elements. In $d-\pi$ electron systems, $\pi$-spacers with a $\pi$-bond between heavier main group elements show a smaller $\pi-\pi^*$ energy gap relative to $\pi$-bonds of elements from the second row of the main group, due to the smaller overlap of $p$ orbitals. Points (ii) and (iii) could be investigated by the synthesis and electrochemical analysis of bimetallic systems containing a $\pi$-bond of heavier main group elements. It is feasible to assume that $\pi$-bonds between heavier main group elements are more effective $\pi$-electron spacers compared to those of second row elements (Scheme 1). However, progress in this area has been severely hampered by synthetic obstacles, as these compounds show extremely high reactivity towards auto–oligomerization and addition reactions with aerobic oxygen and moisture. Nevertheless, it has been elegantly demonstrated that $\pi$-bond compounds between heavier main group elements can be sufficiently stabilized to be treated under ambient conditions, when sterically demanding substituents are introduced as steric protection groups at the reactive $\pi$-bond. Following this discovery, a series of com-

Scheme 1. Bimetallic $d-\pi$ electron systems containing heavier main group elements.
ounds containing double bonds between heavier group 14 and 15 elements has been synthesized and isolated by taking advantage of bulky substituents. Spectroscopic and X-ray crystallographic analyses of these compounds, as well as electrochemical measurements in combination with detailed theoretical calculations allowed the elucidation of characteristic electrochemical properties, resulting from low-lying LUMO levels. Disilenes, for example, generally show, due to the smaller overlap between the 3p orbitals of the Si atoms, higher HOMO and lower LUMO levels relative to olefins. The extraordinary properties of disilenes have prompted many chemists to explore extended π-conjugated systems containing a Si=Si unit. Especially Scheschkewitz and Tamao should be mentioned in this context, as they independently reported the synthesis of various π-conjugated systems containing Si=Si units. Their disilenes consist of extended π-conjugated systems with bridged and terminal phenylene or phenyl groups, exhibiting particularly interesting photochemical properties. Wishing to combine the remarkable developments in the field of extended π-electron systems containing heavier main group elements and d-π electron systems, lead us to investigate the chemistry of a new type of d-π-electron systems with a π-electron spacer of heavier main group elements. In this article, we shall present our systematic studies on the synthesis of bis(ferroceny1)- and bis(ruthenocyl)-substituted compounds with double bonds between heavier group 14 and 15 elements (1-5), and we shall discuss their structural features, spectroscopic properties, and redox behavior (see Scheme 2).

Scheme 2.

2. The Synthesis of d-π Electron Systems with Two Ferrocenyl Groups Bridged by a π-Bond of Heavier Group 14 Elements: 1,2-Bis(ferroceny1)disilenes and 1,2-Bis(ferroceny1)digermenes

Compounds with π-bonds between heavier main group elements are highly reactive and accordingly difficult to isolate under ambient conditions (vide supra). In order to isolate stable π-bond compounds of heavier main group elements, at least one sterically demanding substituent is required to be introduced on the central heavier main group element in order to stabilize the reactive π-bond kinetically. Considering this restriction in the context of the molecular design for d-π electron systems containing heavier main group elements, we chose a Si=Si π-spacer between two ferroceny1 (Fc) moieties as a starting point for our investigations, because silicon atoms within a double bond (>Si=Si) possess two further valence bonds for the introduction of a sterically demanding group and the Fc substituent.

Initially, we examined Tip (2,4,6-trisopropylphenyl) as a steric protection group, since the synthesis of TipSiCl₃ has already been accomplished. Moreover, TipSiCl₃ should be an appropriate synthetic precursor, as it is stable enough to be handled under ambient conditions. This assumption seems feasible, considering that the corresponding homoleptically substituted disilene TipSi=SiTip, with a distinct Si=Si double bond, exhibits sufficient stability. The synthetic route for the preparation of 1,2-bis(Fc)disilene 1 is outlined in Scheme 3. Dichlorosilane 6, containing a Tip group, was prepared in 49% isolated yield by the reaction between FeLi and TipSiCl₃ in THF at -78 °C. Dichlorosilane 6 is remarkably stable, probably due to the steric bulk of the Tip and Fc groups, and can even be manipulated in open air. The subsequent reduction of 6 with lithium naphthalenide (2.2 equiv.) in THF at -78 °C afforded 1 as orange-red crystals (49% isolated yield). Heating a toluene-d₄ solution of 1 in a sealed tube to 90 °C for 10 days demonstrated the outstanding thermal stability of 1, as no decomposition was observed according to the 'H NMR spectra. Also, 1 was found to be inert towards photo-irradiation (C₆D₆ solution, 24 h) from a medium pressure Hg lamp (through Pyrex® glass). In order to create π-bond compounds between heavier main group elements, the judicious choice of the steric projection group is of paramount importance, as they mustn’t be neither too small, nor too bulky. For example, the stable ferrocenylidibromosilane Tbt(Fc)SiBr₂ (Tbt=2,4,6-[CH₃(SiMe₃)₂]-C₆H₃) was reported to resist common reducing reagents, such as lithium naphthalenide or KC₆, most likely due to the extreme bulk of the Tbt group. However, the combination of Tip and Fc groups should allow the formation of the Si=Si π-bond, while at the same time it should provide sufficient stability for its intrinsic reactivity.

The 'Si NMR spectrum of 1 in C₆D₆ showed a characteristic signal at 70.6 ppm, which is in the typical range for silicon atoms within a double bond [δ₅ (tetraaryldisilenes): 53–66 ppm; δ₆ (tetraalkyldisilenes): 90–103 ppm]. The 'H NMR spectrum of 1 in C₆D₆ exhibited a pair of pseudo triplet peaks at 3.80 and 3.98 ppm, which should be assigned to the protons of the cyclopentadienyl (Cp) rings. Although the 'H NMR spectrum of 1 in C₆D₆ suggested that the Fc and Tip groups are able to rotate without any steric restriction around the Si=C bonds at room temperature (r.t.), two doublet signals were observed for the methyl groups of the ortho–isopropyl substituents. Considering these spectral features, it should be concluded that disilene 1 adopts a trans–bent structure in solution.

Recrystallization of 1 from THF provided single crystals suitable for X-Ray crystallographic analysis, which unambiguously revealed the structural parameters of 1 in the crystalline state. Similarly to previously reported disilene, a trans–bent conformation was observed for 1, with the crystallographic center of symmetry at the center of the Si=Si bond. In stark contrast to TipSi=SiTip, which was reported to be almost

planar, the trans–bent angle ($\theta$) in 1 was observed to be 27.9°. Based on a comparison with previously reported disilenes (2.14–2.26 Å), the observed Si–Si bond length in 1 [2.1733(15) Å] suggested a considerable double–bond character for the Si–Si bond in the solid state. The Si–C ($ipso$–Fc) bond length in 1 [1.848(3) Å] is slightly, but nevertheless distinctly shorter than the Si–C ($ipso$–Tip) bond [1.880(3) Å], suggesting conjugative interaction between the $\pi$-electrons of the disilene moiety with those of the Cp rings.

The UV/vis spectrum of 1 in hexane showed two characteristic absorption maxima at 332 ($\epsilon$ 5,900) and 427 nm (24,000). Previous reports on tetracycldisilenes described absorption maxima around 400–460 nm, which were assigned to $\pi$–$\pi^*$ electron transitions of the Si–Si chromophore. TD–DFT calculations for 1 suggested that the observed absorption at longer wavelength ($\lambda_{max}$=427 nm) should be assigned to the mixed electron–transition from both occupied $\pi$(Si–Si) orbitals, as well as filled $\pi$-orbitals of the Fe moiety into empty $\pi^*$ (Si–Si) orbitals, whereas the absorption at shorter wavelength ($\lambda_{max}$=332 nm) should be associated with $d$–$\pi^*$ electron transitions from the Fe moiety into the $\pi^*$ (Si–Si) orbital. These theoretical calculations furthermore suggested the characteristically observed strong absorptions to contain contributions from several types of $d$–$\pi^*$ electron transitions.

Changing the transition metal of the metalloocene from Fe to Ru was possible via an analogous synthetic route (Scheme 3), which allowed the successful synthesis and isolation of stable Tip(Re)Si=Si(Re)Tip (1; Re=ruthenocenyl). Structural and spectral features of 1 were found to be similar to those of 1, except for the color of the compounds. Whereas 1 is orange–red in the solid state and in solution of organic solvents, 1 is yellow. Although $\lambda_{max}$ values and molar extinction coefficients ($\epsilon$) are comparable for 1 and 1' ($\lambda_{max}$=340, $\epsilon$=5,000 and $\lambda_{max}$=430 nm, $\epsilon$=22,000), both showed different positions of the absorption shoulders, which is probably due to the $d$–$\pi^*$ electron transitions. While the broadened absorption of 1 ($\lambda_{max}$=427 nm) exhibited a absorption shoulder in direction of longer wavelengths, that of 1' ($\lambda_{max}$=430 nm) exhibited a shoulder in direction of shorter wavelengths. Consequently, the color of 1 and 1' should not arise from the $\pi$(Si–Si) to $\pi^*$ (Si–Si) electron transitions, but from the $d$–$\pi^*$ electron transitions between the metalloenyl $d$-orbitals and the $\pi^*$ (Si–Si) orbitals. It should be noted that the absorptions for the d(M) to $\pi^*$ (Si–Si) (M=Fe, Ru) electron transitions of 1 and 1' were clearly observed in the visible region of the electromagnetic spectrum.

Digermenes (R₂Ge=GeR₂), i.e. the germanium analogues of olefins and disilenes, are known to possess even smaller HOMO–LUMO gaps than disilenes, and they should therefore be even more promising candidates for the use as $\pi$–spacers in $d$–$\pi$ electron systems. The ability of digermene to readily undergo controlled retro–dimerizations in solution, as well as the ability of the Ge=Ge moiety to respond to external thermal, chemical and photo–induced stimuli, should result in highly interesting reactivity patterns. Ferrocenyldigermene 7 was prepared from the reaction of TipGeH₂Cl with FeLi. A bromination of 7 with CBr₄ in benzene resulted in the formation of dibromogermerane 8, which was subsequently reduced with KC₄ in THF to give 1,2–bis(Fc)digermene 2 as a stable, orange, crystalline solid (Scheme 4). Digermene 2 is stable in the solid state (mp. 159.4 °C/decomp.), but slowly decomposes in solution (t½=ca. 0.5 h at 60 °C in C₆D₆), resulting in a complicated mixture of products. Interestingly, disilene 1 exhibited much higher thermal stability, and no decomposition was apparent, even when a toluene–d₈ solution of 1 was heated to 90 °C for 10 days (vide supra).

The molecular structure of 2 was revealed by single crystal X–ray diffraction analysis, showing a center of symmetry in the middle of the Ge=Ge bond (Figure 2). The Ge=Ge bond length [2.3320(5) Å] is slightly longer than that in Tip₂Ge=GeTip₂ [2.2130(9) Å]. Digermene 2 exhibits a significantly larger trans–bent angle ($\theta$=43.7°) compared to previously reported tetraaryldigermenes (e.g. $\theta$=12.3° in Tip₂Ge=GeTip₂) and 1,2–bis(Fc)disilene 1 ($\theta$=27.9°). These structural parameters indicate a relatively weak Ge=Ge double–bond in 2, and suggest the possibility of thermally controlled dissociation of 2 in solution, yielding two equivalents of the corresponding germylene monomer Tip(Fc)Ge: (vide infra).

The UV/vis spectrum of 2 in hexane showed a strong and broadened absorption at $\lambda_{max}$=430 nm ($\epsilon$=17,000) with a shoulder around 500 nm. TD–DFT calculations for 2 suggested a combination of several MLCT modes to be responsi-

![Figure 1](image1.png)

![Figure 2](image2.png)
ble for this absorption, as well as effective interaction between the \(d\)-electrons of the Fe units and the \(\pi\)-electrons of the Ge=Ge moiety, representing the HOMO–LUMO transition (\(d-\pi^*\) transition). The HOMO orbital contains mainly contributions from the \(d\)-orbitals of Fe and minor contributions from the Csp \(\pi\)-orbitals, whereas the LUMO predominantly contains contributions from the Ge=Ge \(\pi^*\)-orbital and the Csp \(\pi\)-orbitals.

Exposing benzene solutions of 1,2-bis(Fc)disilene 1 and 1,2-bis(Fc)digermene 2 to atmospheric oxygen resulted in the formation of 1,3,2,4-dioxadimetallatanes 10 and 11, respectively. These were probably formed via the corresponding 1,2,3,4-dioxadimetallatanes 19 and 20, followed by subsequent isomerizations. The facile reactions of 1 and 2 with aerobic oxygen to give 10 and 11 suggested promising reactivity patterns, as they ultimately lead to the formation of heterocyclic compounds containing Si or Ge atoms and Fe substituents. Therefore, we turned our attention to chalcogenation reactions of 1 and 2 with elemental sulfur and selenium. In contrast to the reactions with oxygen, the sulfurization reactions of 1 and 2 with S resulted in the formation of thiadimetallatanes 12 and 13, as well as 1,2,3,4-dithiadimetallatanes 14 and 15, respectively. However, no evidence for the formation of the corresponding 1,2,3,4-dithiadimetallatanes was observed. The results of these sulfurization reactions are in sharp contrast to the previously reported sulfurizations of disilenes and digermenes with S\(_8\), which typically result in the formation of the corresponding thiadimetallatanes and/or 1,3,2,4-dithiadimetallatanes.12,23 Theoretical calculations suggested that both thiadimetallatanes 12 and 13, as well as 1,2,3,4-dithiadimetallatanes 14 and 15, should be the kinetic, rather than the thermodynamic products, i.e., the sulfurization reactions of 1 and 2 appear to be kinetically controlled reactions. Our calculations furthermore suggested that the sulfurization reactions of 1 or 2 to give the corresponding 1,3,2,4-dithiadimetallatanes should be highly exothermic relative to the formation of the thiadimetallatanes or 1,2,3,4-dithiadimetallatanes.21

All attempts to induce thermal interconversions between the obtained thiadimetallatanes and the 1,2,3,4-dithiadimetallatanes, i.e., a sulfurization of the thiadimetallatanes and/or a desulfurization of the corresponding 1,2,3,4-dithiadimetallatanes were unsuccessful, which advocates a direct reaction mechanism of dimetallenes 1 and 2 with S\(_8\) in favor of one via the corresponding metallylenes Tip(Fc):E (E=Si, Ge). It should also be considered that the activation energy barriers for the isomerizations of the 1,2,3,4-dithiadimetallatanes into thermally stable isomers are probably, due to the steric demand of the Fe substituents, very high. On the other hand, similar reactions of 1 and 2 with elemental selenium were found to proceed readily, affording selenadigermiranes 16 and 17, respectively, as the sole products in high yields. The formation of these heterocyclic compounds (12–17) strongly suggests that disilene 1 and digermene 2 should, in solution at r.t., be best interpreted as dimetallenes with distinct E=E double bonds, rather than as the corresponding metallylenes Tip(Fc):E (E=Si, Ge). In fact, the \(^1\)H NMR and UV/Vis spectra for 1 and 2 at slightly elevated temperatures (T \(\leq 70^\circ\)C) remained almost identical to those measured at r.t., suggesting that the thermally induced dissociation of the E=E double bonds in 1 and 2 is negligible.

When a benzene solution of disilene 1 was treated with an excess of 2,3-dimethyl-1,3-butadiene at 80 \(^\circ\)C for 1 h, most of 1 remained unchanged according to the \(^1\)H NMR spectrum, demonstrating a pronounced insensitivity of 1 towards butadienes, even at elevated temperatures. On the other hand, treating a benzene solution of 2 under the same conditions (80 \(^\circ\)C, 1 h, excess of 2,3-dimethyl-1,3-butadiene), resulted in the formation of two products: germolene 18 (55% yield), and germylgermolene 19 (36% yield) (Scheme 6).25 The generation of 18 and 19 can be tentatively explained by an initial nucleophilic attack of one of the C=C double bonds of the butadiene towards the low-lying LUMO of the Ge=Ge moiety in 2. The resulting weakening of the Ge=Ge double bond should subsequently lead to an expulsion of one equivalent of germylene 9, resulting in the formation of 18. An alternative explanation could envision an initial, thermally induced 1,2-migration of one of the Tip groups, leading to one equivalent of 20, which would be trapped by 2,3-dimethyl-1,3-butadiene to give 19. Heating C\(_2\)D\(_2\) solutions of germolene 18 or germylgermolene 19 to 80 \(^\circ\)C in the presence of an excess amount of isoprene did, however, not initiate any further reactions. Thus, the regeneration of germylene 9 or 20 from 18 or 19, respectively,
via a potential retro-[1+4]-cycloaddition could not be observed. Examining a C×D₂ solution of 2 in the presence of an excess of 2,3-dimethyl-1,3-butadiene to photol-irradiation (medium pressure Hg lamp, through Pyrex® glass) did not induce any reaction, underlining the extraordinary stability of 2 toward UV light. In conclusion, 2,3-dimethyl-1,3-butadiene can be used as an effective trigger to thermally scissor the Ge=Ge bond in 2, but not for the Si=Si bond in 1,2-bis(Fc)disilene 1. The cleavage of dimerene 2, induced by the addition of 2,3-dimethyl-1,3-butadiene can possibly be used to interrupt the electronic interaction between the two Fe moieties via the Ge=Ge π bond.

3. The Redox Behavior of 1,2-Bis(Fc)disilene 1, 1,2-Bis(Rc)disilene 1', and 1,2-Bis(Fc)digermerene 2

With stable 1,2-bis(Fc)disilene 1, 1,2-bis(Rc)disilene 1', and 1,2-bis(Fc)digermerene 2 in hand, we wanted to examine their electrochemical properties. We were particularly interested, if these d-π electron systems were able to demonstrate (i) an ability of the E=Ε bonds to function as π-spacers. Therefore we conducted a comparison between the E=Ε bonds of consecutively heavier group 14 elements (C=ε, Si=ε, and Ge=Ge); (ii) a compatibility of the d-electron moiety with the Si=επ bond. Therefore we conducted a comparison between d-π electron systems containing metalloconyl moieties of Fe or Ru.

The redox potentials of 1, 1', and 2 were obtained from cyclic and differential pulse voltammetry measurements. They are summarized in Table 1 together with those of the related compounds Ph(Fc)C=C(Fc)Ph (21) and Me(Rc)C=C(Rc)Me (22). In these electrochemical experiments, 1,2-bis(Fc)disilene 1 exhibited two reversible redox couples in the reduction region at 6.24 V (2 e- and -3.09 V (1 e-) vs. Fe/H/H⁺ in THF with 0.1 M Bu₄NPF₆), while germanium analogue 2 showed only one reversible redox couple at 6.24 V vs. Fe/H/H⁺. The significantly lower reduction potential of 2 relative to 1 suggests a lower LUMO level of the Ge=Ge π bond with respect to the Si=Si π bond. Interestingly, 1,2-bis(Fc)dimetalene 1 and 2 underwent, in contrast to the carbon analogue (E)-Ph(Fc)C=C(Fc)Ph (21) and other previously reported tetraaryldisilenes, a reversible reduction, indicating that the C=ε systems stabilize the anionic state of the d-π electron systems in 1 and 2. In the oxidation region, 1 and 2 exhibited two-step reversible redox couples at 6.24 V (1 e-) and +0.24 V (1 e-) for 1, and -0.41 V (1 e-) and +0.33 V (1 e-) for 2 [E₁/₂ vs. Fe/H/H⁺] in o-dichlorobenzene with 0.1 M Bu₄NB(C₆F₅)₄, suggesting a desirable coupling of the two Fe moieties via the Si=Si or Ge=Ge π bond. Interestingly, the first oxidation potential of dimerene 2 was much lower than that of ferrocene or disilene 1. The separation of the half wave oxidation potentials (ΔE₁/₂) is indicative of the magnitude of electronic interaction between two redox centers. The separation is significantly larger in 2 (ΔE₁/₂=0.44 V) than in disilene 1 (ΔE₁/₂=0.19 V), and (E)-Ph(Fc)C=C(Fc)Ph (21). The value of 0.18 V) reflecting the increased degree of d-π electron interaction in 2 relative to its silicon (1) and carbon (21) analogues. With respect to objective (i), the electrochemical analysis indicated that dimerene 2 is a very effective d-π electron system, exhibiting in comparison to disilene 1 and olefin 21 a stable, multi-step redox behavior. A consolidated analysis of the photophysical and electrochemical properties moreover suggested an effective overlapping of d and π° orbitals in 2.

With respect to the objective (ii), the electrochemical examination of 1,2-bis(Fc)disilene 1 and its Ru analogue 1' showed two reversible one-electron redox couples corresponding to the stepwise oxidation of the two intramolecular redox centers at 6.24 V (1 e-) and +0.24 V (1 e-) (1), and 6.24 V +0.36 V (1 e-) and +0.56 V (1 e-) (1') [E₁/₂ vs. Fe/H/H⁺] in o-dichlorobenzene with 0.1 M Bu₄NB(C₆F₅)₄. The oxidation potentials of 1 are higher than those of 1', most likely reflecting the intrinsic properties of the different metallocones, i.e. a higher oxidation potential of ruthenocene relative to ferrocene. The electrochemical properties of the respective metallocones should then also be reflected in the characteristic redox potentials of 1,2-bis(metalloconyl)disilenes 1 and 1' when considering them as d-π electron systems. The separation of the half wave oxidation potentials were measured as ΔE₁/₂ =0.19 V (1) and ΔE₁/₂=0.20 V (1'), which is comparable to the carbon analogue (E)-Ph(Fc)C=C(Fc)Ph (21) (ΔE₁/₂=0.18 V), indicating a significant coupling between the two metalloconyl moieties in 1 and 1' via the Si=Si π bond. Interestingly, the two ruthenocenyl moieties in disilene 1' were found to be able to communicate electrochemically through the Si=Si π electrons, which is in stark contrast to the corresponding carbon analogue (E)-Me(Rc)C=C(Rc)Me (22). Compound 22 was reported to exhibit only one-step oxidation couple (2 e-), indicating negligible electronic communication of the two Ru moieties through the C=C unit under ambient conditions. The C=C π-electron system should accordingly not be able to facilitate conjugation of d and π electrons between the two Ru moieties, which is probably due to the large size difference between the orbitals of the Ru and ethylene moieties. The expanded π-orbital of the disilene unit (Si=Si) is, however, able to allow effective communication with the d-π orbitals of the Ru groups, which was observed for 1', but not for 22.

4. Design and Synthesis of Bulky Fe Groups: Steric Protection from the d-Electron Moeity

In the previous sections, we described the successful synthesis of new d-π electron systems containing π-electron moieties of heavier group 14 elements, and the systematic investigation of their structural, spectroscopic, and electrochemical properties. However, systematic investigations into the synthesis and properties of d-π electron systems containing heavier main group element π-spacers outside of group 14 still remain scarce. Recent reports on phosphorus-based π-electron systems have hinted at the immense potential of these compounds, ranging from the provision of fundamental insights to applica-
tions in functional materials. Most of their desirable properties can be directly attributed to the nature of phosphorus, for example the ability to use the lone pair for coordination, an electronegativity close to that of carbon, and the availability of multiple stable oxidation states (+III/+V). The development of extended π-electron systems containing phosphorus atoms prompted us to investigate the chemistry of the corresponding phosphorus-containing d-π electron systems. Compounds with double bonds between heavier group 15 elements can be similar to heavier group 14 elements, stabilized enough to be treated under ambient conditions, when sterically demanding substituents are introduced as steric protection groups at the reactive π-bond (vide supra). Accordingly, several heavier dipnictenes, i.e. compounds containing a double bond between heavier group 15 elements, were synthesized and isolated by taking advantage of very bulky substituents, and these compounds were found to exhibit interesting electrochemical properties due to their low-lying LUMOs. We have also reported that these heavier dipnictenes can be reduced by Li metal to give the corresponding anion radical species. Hence, these π-bonds between heavier group 15 elements should be able to work as effective π-spacers between transition metal moieties. The simplest conceivable model compound for 1,2-bis(Fc)diphosphenes is Fc−P=P−Fc, i.e. the phosphorus analogue of Fc−N=N−Fc. Unfortunately, all our attempts, as well as those of other research groups, to isolate Fc−P=P−Fc have so far been unsuccessful. The alleged preparation of Fc− P=P−Fc from the reductive dehalogenation of FcPCl₂ has been mentioned in a “private communication”, but unfortunately, we were unable to obtain any synthetic and/or characterization details from this reference. Although the absence of evidence for the formation of this compound is not evidence of its absence, the postulated instability of Fc−P=P−Fc under ambient conditions seems plausible, considering the limited steric demand of the ferrocenyl groups, resulting in insufficient protection for the highly reactive P=P bond. In order to provide a solution for this synthetic challenge, we decided to start investigations into a custom-tailored Fc substituent with an increased ability to provide steric protection, which we intended to implement in the synthesis of stable 1,2-bis(ferrocenyl)diphosphenes.

Therefore, we targeted bulky 2,5-diaryl-1-iodoferrocenes with bulky aryl groups in 2- and 5-positions of one Cp unit. As bulky aryl groups, we chose 3,5-dimethylphenyl (Dmp) and 3,5-di-t-butylphenyl (Dtp). A Negishi cross-coupling reaction between ferrocenyphosphynosulfide (23) and ArX (DmpI or DtpBr) by successive addition of LDA, ZnCl₂, and a catalytic amount of Pd(PPh₃)₄ resulted in the formation of sulfoxide 24. The reduction of 24 with NaI and (CF₃CO)₂O afforded sultide 25, and was followed by an oxidation with nCPBA to give sulfoxide 26, which is a structural isomer of 24. The inversion of sulfoxide 24 to 26 is the key step for the following procedures: a second Negishi cross-coupling reaction under similar conditions between 26 and ArX (DmpI or DtpBr) produced sulfoxide 27, which was treated consecutively with t-BuLi and I₂ to give FcI (28a) and Fc⁺ (28b), respectively. Treatment of these bulky ferrocenyliodides with n-BuLi should correspondingly afford FcLi or Fc⁺Li, to which a wide variety of substituents should be easily introduced. Even though the synthesis of the appropriate bulky precursors (28a,b) was thus accomplished, the synthetic strategy is rather laborious (6 steps from FcH; Scheme 7). Therefore, we developed an alternative synthetic route for these haloferrocenes: Lithiation of bromoferrocene with LiTMP (TMP=2,2,6,6-tetramethylpiperidide) resulted in the formation of 1,2-bromolithioferrocene, which was subjected to a Negishi cross-coupling reaction with ArX (DmpI or DtpBr), affording the 1-bromo-2-Ar-ferrocenes (29). The introduction of another Ar group was achieved by subjecting 29 to a second Negishi cross-coupling reaction to give the corresponding 1-bromo-2,5-Ar₂-ferrocenes (30). The generation of FcLi and Fc⁺Li by treatment of 30a and 30b with n-BuLi was proven by the subsequent addition of water.

Scheme 7.

![Scheme 7](image-url)
which resulted in the formation of the corresponding protonated compounds (FcH and Fc`H) in quantitative yield. The molecular structures of 28a and 28b are shown in Figure 3.

5. Synthesis of d-π Electron Systems Bearing Two Bulky Fc Groups Connected by a π-Bond Spacer Containing Heavier Group 15 Elements: 1,2-Benzoferrocenyl(dipnictenes

Successive treatment of iodoferrocene 28a with n-BuLi and PCl₃ afforded FcPCl₂ (31), which was reduced with LiAlH₄ to give FcPH₂ (32), which was then treated with Fc`PHLi, which was obtained from the treatment of 32 with n-BuLi, followed by dehydration with DBU afforded the first example of a stable 1,2-bis(ferrocenyl)dihalopnictanes Fc`PCl₂ (33) and Fc`SbCl₂ (34) with which were comparable to previously reported ferrocenyldiphosphenes and diaryldiphosphines, supporting a considerable π-bond character in solution.

The structural parameters of 1,2-bis(ferrocenyl)diphosphenes 3a, 3b, 4, and 5 were determined by X-ray diffraction analysis. While diphosphenes 3a, b were found to adopt C₁ symmetry, both distibene 4 and dibismuthene 5 possess a crystallographic center of symmetry in the middle of their E=E bonds, resulting in Cₛ symmetry. The structural parameters and crystal data are summarized in Table 2.

Table 2. Selected structural parameters for 1,2-bis(ferrocenyl)diphosphenes 3a, 3b, 4, and 5.

<table>
<thead>
<tr>
<th></th>
<th>E-E [Å]</th>
<th>E-C [Å]</th>
<th>E-E-C [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe<code>P=PF</code>c(3a)</td>
<td>2.031(8)</td>
<td>1.826(2)</td>
<td>99.8(7)</td>
</tr>
<tr>
<td>Fe<code>P=PF</code>c(3b)</td>
<td>2.037(8)</td>
<td>1.824(2)</td>
<td>100.7(7)</td>
</tr>
<tr>
<td>Fe<code>Sb=PF</code>c(3b)`</td>
<td>2.028(6)</td>
<td>1.808(17)</td>
<td>111.2(3)</td>
</tr>
<tr>
<td>Fe<code>Sb=PF</code>c(4)`</td>
<td>2.670(7)</td>
<td>2.158(5)</td>
<td>98.2(8)</td>
</tr>
<tr>
<td>Fe<code>Bi=BiF</code>c(5)`</td>
<td>2.830(3)</td>
<td>2.260(3)</td>
<td>96.1(19)</td>
</tr>
</tbody>
</table>

*ref. 31; † Two independent molecules (A, B) were found per asymmetric unit; ‡ ref. 32; † ref. 33.
The E=E bond lengths in dipnictenes 3–5 are shorter, relative to those in the corresponding compounds with single bonds, e.g. 2.215 Å in Ph₂P–PPh₂, 2.837 Å in Ph₂Sb–SbPh₂, and 2.990 Å in Ph₂Bi–BiPh₂, and similar to those in previously reported dipnictenes, e.g. 2.043(1) Å in Bb₁P=PbB₁t (36), 2.7037(6) Å in Bb₁Sb=SbB₁t (37), and 2.8699(6) Å in Bb₁Bi=BìB₁t (38). Hence, the bond length of the E=E bonds in 3–5 suggests a considerable double–bond character, which is corroborated by the observed vibrational frequencies of the E=E bonds in 3–5. A closer look at the E–C(Fc⁺) bond lengths in 4 and 5 revealed that these are slightly shorter than the E–C(Ar) bond lengths in previously reported diaryldipnictenes, e.g. 2.158(5) Å for Sb–C(Fc⁺) in 4 vs. 2.197(4) Å for Sb–C(Bbt) in 37, and 2.268(3) Å for Bi–C(Fc⁺) in 5 vs. 2.291(5) Å for Bi–C(Bbt) in 38, indicating a small, but distinct conjugative electronic communication between the Fc moieties and the E=E π-bond. The dihedral angles between the Cp ring and the P–C–C(Fc⁻) plane in 3a are ca. 40°, again indicating small, but significant contributions of the π-conjugation between the P=P π-bond and the Cp rings. Due to the steric repulsion between the two 3.5–di-tert-butylphenyl groups in 3b, one of the dihedral angles between the Cp ring and the P–P–C(Fc⁻) plane is almost perpendicular (ca. 88°), whereas the other is nearly parallel (ca. 23°). On the side where the P–P–C plane is almost parallel to the Cp ring, the P–C(Fc⁻) bond length [1.0808(17) Å], on the side where the P–P–C plane are almost parallel to the Cp ring, is shorter than the other [1.1435(17) Å], supporting the existence of conjugative electronic communication between the Fe moieties and the P=P π-bond, especially when the P=P π-plane is aligned in parallel to the Cp plane. The E–E–C(Cp) angles in 4 and 5 are 98.28(13)° and 96.17(9)°, respectively, i.e. the E=E–C(Cp) angles consecutively decrease and approximate 90° as the central element E descends the main group elements. The dihedral angles between the E–E–C(Cp) and the Cp planes in 4 and 5 are 38° (E=Sb) and 37° (E=Bi), showing effective conjugation between the E=E π-electrons and those of the Fc⁺ moieties, relative to Ar=E=E–Ar, where the aryl rings are aligned almost perpendicular to the E=E–C(Cp) plane and hence prevent conjugation.

In the UV/vis spectra of the 1,2-bis(ferrocenyl)dipnictenes 3–5, characteristic absorptions were observed, including those corresponding to the d–π* electron transitions from filled d–orbitals of Fe center to the π*–orbital of the E=E π-spacer (Table 3). For dipnictenes 3a and 3b, three characteristic absorption bands around 350, 440, and 550 nm were observed in THF or hexane. The first and second absorption band were, based on a comparison with previously reported diaryldiphosphenes, assigned to symmetry–allowed π–π* and symmetry–forbidden n–π* electron transitions. On the basis of theoretical calculations (TD–B3PW91), the third absorption was assigned to d–π* electron transitions. The observed d–π* electron transition of 1,2-bis(ferrocenyl)diphosphenes 3a exhibited small degrees of solvochromism (λmax=546 nm in hexane, λmax=556 nm in THF; λΔmax=9 nm), while that of dipnictene 3b showed no apparent solvent dependency in those solvents. The UV/vis spectra of distibene 4 and dibismuthene 5 in THF or hexane showed two characteristic absorption bands around 500 and 600 nm. Similar to dipnictenes 3a, 5 and based on a comparison with previously reported diaryldistibenes and dibismuthenes, the absorptions at shorter wavelengths were assigned to symmetry–allowed π–π* transitions of the Sb=Sb and Bi=Bi chromophores, whereas the absorptions at longer wavelengths most likely be interpreted in terms of an overlap of several d–π* electron transitions from filled d–orbitals of Fe to the π*–orbitals of the E=E π-spacers. The absorption associated with the d–π* electron transitions in dibismuthene 5 showed no apparent solvent dependency. Distibene 4, on the other hand, exhibited marginal solvochromism (λΔmax=606 nm in hexane, λΔmax=612 nm in THF; λΔmax=6 nm).

These negligible solvent effects regarding the d–π* electron transitions in the UV/vis spectra of 1,2-bis(ferrocenyl)dipnictenes 3–5 can be tentatively explained by the symmetric structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>λmax [nm] (e)</th>
<th>λmax [nm] (e)</th>
<th>λmax [nm] (e)</th>
<th>λmax [nm] (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe⁺⁺P=Fe⁺⁺Fe⁺⁺ (3a)</td>
<td>hexane</td>
<td>349(6100)</td>
<td>436(4400)</td>
<td>440(47700)</td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺P=Fe⁺⁺Fe⁺⁺ (3b)</td>
<td>hexane</td>
<td>354(9000)</td>
<td>436(14000)</td>
<td>440(17000)</td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺Sb⁻⁻Sb⁻⁻Fe⁺⁺ (4)</td>
<td>hexane</td>
<td>462(6700)</td>
<td>Overlapped</td>
<td>606(3800)</td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺Bi⁺⁺Bi⁺⁺Fe⁺⁺ (5)</td>
<td>hexane</td>
<td>522(3300)</td>
<td>Overlapped</td>
<td>603(4000)</td>
<td></td>
</tr>
<tr>
<td>Bb₁P=PbB₁t (36)</td>
<td>hexane</td>
<td>618(12000)</td>
<td>532(10000)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Bb₁Sb=SbB₁t (37)</td>
<td>hexane</td>
<td>490(6000)</td>
<td>594(2000)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Bb₁Bi=BìB₁t (38)</td>
<td>hexane</td>
<td>537(6000)</td>
<td>670(2000)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
tures of their excited states, which should, due to the extended d–π conjugation, possess little polarity. Even though it still remains difficult to draw clear conclusions on the details of the electron transitions at this stage, we found that the π–π* absorptions arising from the E=E chromophores are bathochromically shifted as the central elements descend group 15 from P to Bi. Conversely, the absorptions resulting from the d–π transitions in 3 are hypsochromically shifted relative to those of distibene 4 and dibismuthene 5, which are comparable to each other. These results indicate (i) lower levels of the occupied d– and π–orbitals, and a higher π*–orbital (LUMO) in 3 compared to those in 4 and 5; (ii) a marginally higher π*–orbital (LUMO) in 4 compared to 5. However, the minimal higher level of the occupied d– and π–orbitals in 4, which would be affected by the orbital level of the Sb=Sb moiety relative to that in 5, result in similar λmax values for the d–π* electron transitions in 4 and 5.

6. The Redox Behavior of 1,2-Bis(ferrocenyl)diphosphene 3b, 1,2-Bis(ferrocenyl)distibene 4, and 1,2-Bis(ferrocenyl)-

dibismuthene 5

The electrochemical properties of 1,2-bis(ferrocenyl)-dipnictenes FeX=E=Fe(Fe=X=E(Fe)3b, 4b, 5) 37 with the same substituents, were systematically investigated by cyclic and differential potential voltammetry (Table 4), as described for disilene 1 and digermene 2 (vide supra). At –78 °C, 3b, 4b, and 5 showed two-step, pseudo–reversible, one-electron redox couples in the reduction region (E1/2 = –2.05/–3.02 V for 3b; E1/2 = –1.13/–2.14 V for 4; E1/2 = –1.56/–2.37 V for 5; E1/2 vs. Fc/F+. Table 4) and the corresponding diaryl derivatives [E1/2 = –1.84 V for Bbt–P–P–Bbt (36), –1.65 V for Bbt–Sb=Sb–Bbt (37), –1.79 V for Bbt–Bi=Bt–Bbt (38)] 37,38 these compounds exhibited significantly lower reduction potentials. The lower reduction potentials of 3b, 4b, and 5 relative to those of the corresponding diaryl–substituted analogues 36–38 should be explained by the d–π conjugation between the FeX moieties and the π*–orbitals of the E=E moiety. It is therefore plausible to assume that the bulky FeX ligands stabilize the corresponding anionic species, and it should even be possible to generate the dianionic species of these 1,2-bis(ferrocenyl)dipnictenes under the applied conditions. In a systematic comparison, 1,2-bis(ferrocenyl)distibene 4 showed the lowest reduction potential among the 1,2-

bis(ferrocenyl)dipnictenes and diaryldipnictenes. Thus, 4 can be considered as a very effective electron acceptor, reflecting the intrinsic nature of the Sb=Sb bond in this d–π electron system.

In the oxidation region, dipnictenes 3b, 4b, and 5 showed three one-electron oxidation steps at –78 °C (Table 4). The first two oxidation potentials should be assigned to the oxidation processes of the two Fe moieties, whereas the third should be assigned to those of the E=E π spacer. Even though pseudo–reversible redox couples were observed for the first and second oxidation steps in dipnictene 3b (E1/2 = +0.23/ +0.78 V), the third oxidation wave was irreversible (E1/2 = +1.74 V), which is comparable to the third oxidation step of previously reported ferrocenyldipnictene Tbt–P–P–Fe (E1/2 = +1.75 V). 37 Both distibene 4 and dibismuthene 5 showed reversible redox couples for all steps (E1/2 = +0.28/+0.70 V for 4, E1/2 = +0.09/+0.57 V for 5). While all the 1,2-bis(ferrocenyl)dipnictenes 3b, 4b, and 5 exhibit higher oxidation potentials compared to Fe=N=N=Fe (E1/2 = +0.08/+0.29 V; r.t. in PhCN), 39 the first oxidation potential of dibismuthene 5 is the lowest oxidation potential among the 1,2-bis(ferrocenyl)dipnictenes and closest to that of Fe=N=N=Fc, which suggests that the Bi=Bi moiety should be considered as a effective electron donor, reflecting the intrinsic nature of the Bi=Bi bond in this d–π electron system. Although both Fe=N=N=Fc and Fe=N=Bi=Bi=Fc 5 exhibited very low and comparable oxidation potentials, their origins should be different. The N=N moiety in Fe=N=N=Fc should raise the energy level of the d-electrons in the HOMO via mesomeric effects from a donation of π-electrons, thereby lowering the oxidation potentials of the Fe moieties. On the other hand, the Bi=Bi moiety itself as an electron donor, because the Bi=Bi π-orbital is the HOMO in 5, and exhibits a higher energy level compared to the energy levels of the d-orbitals of the Fe moieties. After the oxidation of 5, the electron distribution in the cationic species [FeX=Fe=Bi=Bi=Fc+] 37 should be relaxed through the d–π electron conjugation, as time for the relaxation during the adiabatic excitation in the electrochemical measurements should be sufficient. Thus, the π-orbital levels of the E=E moiety should play an especially important role in the d–π electron systems of the heavier pnictogen elements. Again, the difference between the oxidation potentials can be used as an indicator for the extent of electronic communication between the two electron transfer sites (vide supra). It should be noted that the oxidation processes for both Fe moieties were observed as two separated steps (ΔE=E=E−E=−) with ΔE=0.55 (3b), 0.42 (4), and 0.48 V (5), respectively. These ΔE values are considerably larger than those observed for Fe=C=N=Fe (ΔE=0.21 V), 11c (E–Fe=C–C=Fc=C=Fc) 24 (E–FctipFc)=S=Fc=Fctip (ΔE=0.19 V), 11d (E–Fc=Fctip) 24 and (E–Fctip) (ΔE=0.38 V), 39 suggesting a significantly increased and effective ability for conjugation of the heavier group 15 element π-spacers relative to those of second row elements, and even heavier group 14 elements. Notably, the ΔE of dipnaphosphene 3b was found to be

Table 4. Redox potentials of 1,2–bis(FeC)3dipnictenes 3b, 4, and 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe+P−P+/Fe−P−P−</th>
<th>Fe+Sb−Sb+/Fe−Sb−Sb−</th>
<th>Fe+Bi−Bi+/Fe−Bi−Bi−</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3b)</td>
<td>(4)</td>
<td>(5)</td>
<td></td>
</tr>
<tr>
<td>E1/2</td>
<td>1.00</td>
<td>1.35</td>
<td>1.77</td>
</tr>
<tr>
<td>E1/2</td>
<td>1.22</td>
<td>1.55</td>
<td>2.05</td>
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<tr>
<td>E1/2</td>
<td>3.33</td>
<td>3.63</td>
<td>3.95</td>
</tr>
<tr>
<td>E1/2</td>
<td>2.71</td>
<td>3.02</td>
<td>3.33</td>
</tr>
<tr>
<td>ΔE=E=E−E=−</td>
<td>0.97</td>
<td>1.01</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Vide supra

1 Conditions: 4.0 mM in acetonitrile with 0.1 M in n-Bu4NBF4 (–78 °C); in THF; in CH2Cl2.

25,35b, 36, 38
the largest of the 1,2-bis(ferrocenyl)dipinnetenes. The characteristic electrochemical properties of the 1,2-bis(ferrocenyl) dipinnetenes reflect the intrinsic nature of the individual E=E π-bond (π-spacer) in these d-π-electron systems. In summary, the P=O moiety works as an effective π-spacer, stabilizing the corresponding mixed-valence state, the Sb=Sb moiety enhances the electron-accepting ability of the system, and the Bi=Bi moiety exhibits the lowest oxidation potential, reflecting the high energy level of the Bi=Bi π-orbital.

7. Conclusions

In pursuit of "novel functionality" in the area of heavier main group elements, we started systematic investigations into the synthesis of unprecedented d-π-electron systems containing double bonds of heavier main group elements. We succeeded in the isolation of bimetallic ferrocenyI- and ruthenocyl-based d-π-electron systems containing π-bonds of heavier group 14 or 15 elements, which serve as benchmark compounds in the investigations on the ability of these π-electron systems to act as π-spacers. We found that these d-π-electron systems exhibit extraordinary electrochemical properties, which decidedly depend on the nature of the element in the central π-electron system, and thus reflect the intrinsic nature of the heavier main group element. Further studies into the chemistry of such d-π systems containing π-bonds of heavier main group elements, in order to characterize their functionality and explore potential applications are currently in progress in our lab and will be reported shortly.

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References


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