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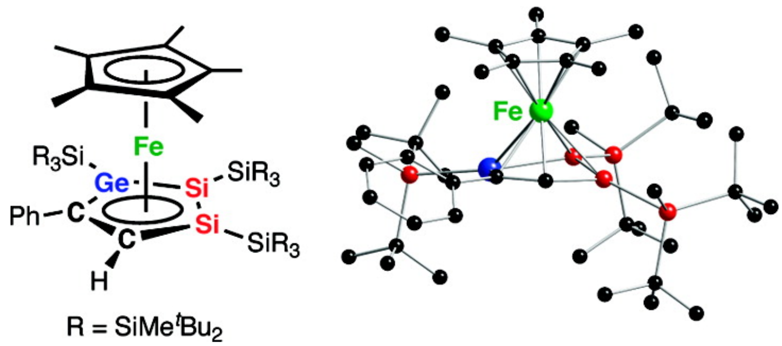

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Heavy Ferrocene: A Sandwich Complex Containing Si and Ge Atoms

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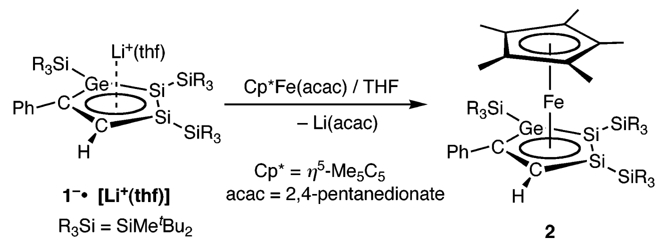
Ferrocene, the archetypal sandwich iron complex (η^5-H_5C_5)$_2$Fe synthesized by Kealy and Pauson in 1951,[1] is the first and most famous member of the huge family of metallocenes, which revolutionized the field of organometallic chemistry.[2] Apart from its fascinating structure and unusual bonding mode, ferrocene has found extensive applications in the field of material science: asymmetric catalysis, large scale olefin polymerization, and luminescent and fluorescent materials. The heteroferrocenes, incorporating skeletal atoms other than carbon in the cyclopentadienyl rings, are most widely represented by the derivatives of group 15 elements (E = P, As, Sb, Bi).[3] In sharp contrast, the examples of the ferrocene analogues containing heavy group 14 elements are rather scarce: two Ru complexes with one heteroatom (η^5-Me_5C_5)Ru[η^5-Me_4C_4-ESi($SiMe_3$)$_3$] (E = Si, Ge)[4a,b] and one Fe complex with two heteroatoms [η^5-Me_4C_4GeSi($SiMe_3$)$_3$]$_2$Fe.[4c] The most intriguing are derivatives consisting entirely of heavy group 14 elements, of which persilaferrocene (η^5-H_5Si_5)$_2$Fe was studied computationally at HF and MP2 levels to reveal the symmetrical D_{5d} structure, in which the Fe−ligand binding energy is smaller than that in the parent ferrocene: 113.6 versus 144.1 kcal/mol.[5] Experimentally, however, the synthesis of such an attractive compound has not yet been accomplished. In this paper, we report the synthesis of the first ferrocene derivative, incorporating *three* heavy group 14 elements (two Si and one Ge) in one of the cyclopentadienyl rings, thus representing a closest approach to the target ferrocenes (η^5-R_5E_5)$_2$-Fe (E = Si−Pb), and discuss its bonding situation.

Because our initial attempts to synthesize a heavy ferrocene derivative by the classical coupling of either $FeCl_2$ or $FeCl_2$(thf)$_{1.44}$ complex with the heavy lithium cyclopentadienide $\mathbf{1}^-$•[Li^+(thf)][6] were unsuccessful, we have employed a novel strategy based on utilization of the Cp*Fe(acac) complex (Cp* = η^5-Me_5C_5, acac = 2,4-pentanedionate) as a convenient source of the Cp*Fe fragment.[7] Cp*Fe(acac), generated in situ by the reaction of Fe(acac)$_2$ with Cp*Li in THF,[8] was reacted with the stoichiometric amount of $\mathbf{1}^-$•[Li^+(thf)] in THF at −78 °C to produce the target (η^5-Me_5C_5)-Fe[η^5-(CPh)(CH)Si_2Ge(SiMe^{t}Bu$_2$)$_3$] derivative **2** (Scheme 1). The heavy ferrocene **2** was isolated by the silica gel chromatography in a glovebox followed by recrystallization from pentane as dark-red crystals in 31% yield.[9] The NMR spectral data of **2** are in line with the proposed pentahaptocoordination of the C_2Si_2Ge ligand to Fe atom. Thus, the ^{1}H NMR resonance of the skeletal C*H* proton was observed as a singlet at 4.49 ppm, in the region diagnostic of Cp ligands η^5-coordinated to transition metals.[10] Moreover, all skeletal C and Si atoms of the heavy cyclopentadienyl ligand in **2** were markedly shielded upon complexation, compared with those of the starting $\mathbf{1}^-$•[Li^+(thf)][6] (calculated GIAO values for **2** are given in parentheses): 80.5(88.6) versus 143.2 ppm (*C*H), 108.1(125.1) versus 181.4 ppm (*C*Ph), −49.3(−12.2) and 1.1(10.3) versus 54.4 and 69.1 ppm (*Si*Ge and *Si*CH). Such appreciable shielding can be attributed to two factors: a higher degree of π-delocalization in the C_2Si_2Ge ligand of ferrocene **2** compared with that of starting $\mathbf{1}^-$•[Li^+(thf)] and δ-backdonation from Fe to the ligand.

Scheme 1



The crystal structure of the heavy ferrocene **2** showed that both ligands are pentahaptocoordinated to the Fe atom, the two rings, C_5 and C_2Si_2Ge, are nearly coplanar, and the Fe atom is situated between them at 1.686 Å from the least-squares C_2Si_2Ge plane and 1.705 Å from the least-squares C_5 plane (Figure 1).[9] The heavy ferrocene **2** has a staggered conformation of the two five-membered rings because of significant steric interaction between their substituents.[11] The manifestation of the cyclic π-delocalization in the heavy Cp ligand of **2** was clearly seen by its geometrical features. Thus, the skeletal bond lengths in **2** are similar to those of aromatic $\mathbf{1}^-$•[Li^+(thf)][6], and markedly distinct from those of neutral 1,1,2,3-tetrakis(di-*tert*-butylmethylsilyl)-4-phenyl-1,2-disila-3-germacyclopenta-2,4-diene **3**,[12] precursor for $\mathbf{1}^-$•[Li^+(thf)]), in which Si=Ge and C=C double bonds are localized (below the endocyclic bond lengths of **2** versus those of $\mathbf{1}^-$•[Li^+(thf)] and **3** are shown): 2.3038(9) versus 2.3220(5) and 2.250(1) Å (Si1−Ge1), 2.2465(11) versus 2.2403(7) and 2.364(1) Å (Si1−Si2), 1.827(3) versus 1.8269(18) and 1.888(3) Å (Si2−C2), 1.419(4) versus 1.402(2) and 1.343(5) Å (C1−C2), 1.924(3) versus 1.9303(17) and 1.972(3) Å (Ge1−C1). Consequently, all skeletal bonds in the heavy Cp ligand in **2** are just intermediate between the typical single and double bonds, implying effective 6π-electron delocalization. Another manifestation of such important delocalization is the striking flattening of the heavy Cp ring upon complexation. This was clearly seen in the planarization around all skeletal atoms of heavy Cp ring of **2** compared with those of $\mathbf{1}^-$•[Li^+(thf)][6] (the sums of the bond angles are shown): Ge1 (360.00 versus 342.89°), Si1 (355.63 versus 350.75°), Si2 (358.96 versus 357.803°), C1 (359.70 versus 359.79°), C2 (360.00 versus 359.94°). Accordingly, the sum of the interior bond angles of the heavy Cp ring of **2** is greater than that of $\mathbf{1}^-$•[Li^+(thf)][6]: 538.0 versus 536.3°, and deviation of the skeletal atoms from the C_2Si_2Ge least-squares plane in **2** is smaller than that in $\mathbf{1}^-$•[Li^+(thf)]. The computational studies on the real compound with ^{t}Bu$_2$MeSi-substituents and on the Me_3Si-, H_3Si-, and H-substituted models showed, that upon successive decrease in the bulkiness and increase in the electronegativity of substituents, the heavy Cp ring becomes progressively distorted, and the conformation of ligands

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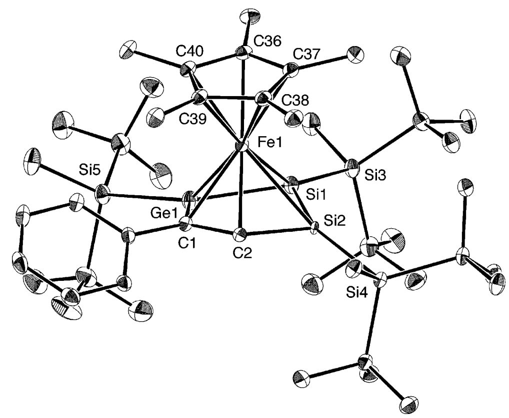

Figure 1. ORTEP drawing of **2** (hydrogen atoms are not shown). Selected bond lengths (Å): Ge1−Si1 = 2.3038(9), Si1−Si2 = 2.2465(11), Ge1−C1 = 1.924(3), Si2−C2 = 1.827(3), C1−C2 = 1.419(4), Ge1−Fe1 = 2.5313(5), Si1−Fe1 = 2.4691(9), Si2−Fe1 = 2.4682(8), C1−Fe1 = 2.170-(3), C2−Fe1 = 2.114(3), C36−Fe1 = 2.085(3), C37−Fe1 = 2.093(3), C38−Fe1 = 2.094(3), C39−Fe1 = 2.116(3), C40−Fe1 = 2.102(3). Selected bond angles (deg): C1−Ge1−Si1 = 98.71(9), Ge1−Si1−Si2 = 96.34(4), Si1−Si2−C2 = 99.49(10), C2−C1−Ge1 = 117.8(2), Si2−C2−C1 = 125.7(2).

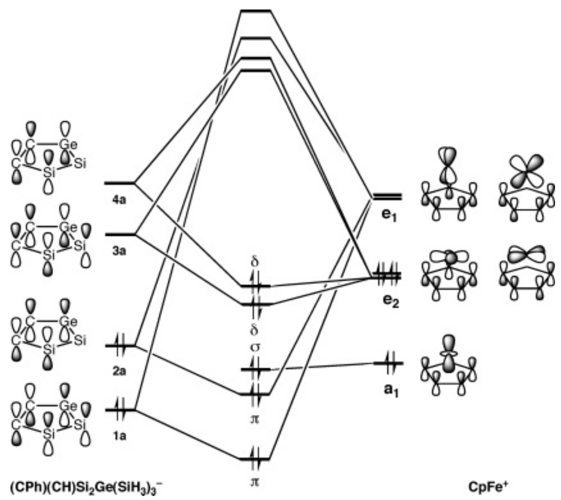

Figure 2. MO correlation diagram for the interaction between the model heavy Cp ligand $[(CPh)(CH)Si_2Ge(SiH_3)_3]^-$ and the $CpFe^+$ fragment.

changes from staggered to eclipsed.[13] Certainly, such a phenomenon has both steric (flattening of the ring upon the introduction of very bulky substituents) and electronic (hyperconjugative stabilizing interaction: π(heavy Cp ligand)−σ^*(Si−C(^{t}Bu) bonds of substituents) origins.

The CV measurement of **2** displayed two irreversible oxidation waves at $E_p(1) = -0.53$ V and $E_p(2) = -0.24$ V (vs Ag/Ag^+, CH_2Cl_2, 0.1 M $^n Bu_4NClO_4$). The first oxidation process, apparently corresponding to the formation of a heavy ferrocene cation-radical, proceeded at significantly more negative potential (−0.53 V) than the corresponding one-electron oxidation of decamethylferrocene Cp^*_2Fe (−0.32 V, reversible) measured under the same conditions, and even more negative than the oxidation of $[\eta^5\text{-}Me_4C_4GeSi(SiMe_3)_3]_2Fe$[4c] (−0.45 V, irreversible, vs SCE, CH_2Cl_2, 0.1 M $^n Bu_4NClO_4$). This suggests that the heavy Cp ligand in **2** is the more powerful electron donor to the Fe atom compared with Cp* and even germacyclopentadienyl ligand $[\eta^5\text{-}Me_4C_4GeSi(SiMe_3)_3]$.

To get an insight into the bonding nature of **2**, we calculated the model compound $CpFe[(CPh)(CH)Si_2Ge(SiH_3)_3]$ **2′**, for which the interactions between the two fragments, heavy Cp ligand $[(CPh)(CH)Si_2Ge(SiH_3)_3]^-$ and $CpFe^+$ unit, were analyzed.[13] The complex **2′** has only C_1 symmetry, however we were able to identify those orbitals, which are comparable to the σ-, π-, and δ-orbitals of ferrocene. The fragment molecular orbital (FMO) analysis of ADF[13] revealed that the most important contribution to the overall bonding of **2′** comes from the strong π-donation from the occupied 1a and 2a orbitals of heavy Cp^- ligand to the vacant e_1 orbitals of the $CpFe^+$ unit (Figure 2). Mixing of the σ- and δ-type orbitals between $CpFe^+$ and heavy Cp^- ligand is much less important. A previous energy decomposition analysis (EDA) of ferrocene[14] disclosed that the covalent bonding between the $CpFe^+$ and Cp^- units comes from 63.8% π-, 14.6% σ-, and 21.6% δ-bonding,[14b] thus suggesting that ferrocene and **2′** have very similar bonding situations. Since the breakdown of the orbital interaction term in the EDA analysis of **2′** was impossible owing to the lack of symmetry, the EDA calculations considering interaction of $CpFe^+$ and heavy Cp^- ligand were carried out by deleting the vacant orbitals of one fragment. The results indicate that electrostatic bonding (52.4%) dominates over covalent bonding (47.6%), and the heavy $Cp^- \rightarrow CpFe^+$ donation contributes 54.5% to the overall orbital interaction, whereas $CpFe^+ \rightarrow Cp^-$ backdonation contributes 45.5%. Since the former contribution can be identified as π-donation, it can be concluded that the covalent bonding between $CpFe^+$ and heavy Cp^- in **2′** (and probably in **2**) is best described in terms of π-donation from the heavy Cp ligand to the metal. The reactivity of heavy ferrocene **2**, including formation of charge-transfer complexes, is under current investigation.

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Supporting Information Available: Experimental procedure, spectral and crystallographic data for **2** including atomic positional and thermal parameters, detailed description of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.
(2) (a) *Ferrocenes. Homogenous Catalysis, Organic Synthesis, Material Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995. (b) *Metallocenes. Synthesis, Reactivity, Applications*; Togni, A., Halterman, R., Eds.; VCH: Weinheim, Germany, 1998; Vols. 1 and 2. (c) *J. Organomet. Chem.* **2001**, *637*−*639* (issue dedicated to 50th anniversary of ferrocene synthesis).
(3) See, for example: (a) Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 1491. (b) Ashe, A. J., III; Kampf, J. W.; Pilotek, S.; Rousseau, R. *Organometallics* **1994**, *13*, 4067. (c) Ashe, A. J., III; Al-Ahmad, S.; Pilotek, S.; Puranik, D. B.; Elschenbroich, C.; Behrendt, A. *Organometallics* **1995**, *14*, 2689. (d) Black, S. J.; Francis, M. D.; Jones, C. *J. Chem. Soc., Dalton Trans.* **1997**, 2183. (e) Sava, X.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2000**, *19*, 4899.
(4) (a) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (b) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1744. (c) Freeman, W. P.; Dysard, J. M.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **2002**, *21*, 1734.
(5) Kudo, T.; Nagase, S. *J. Mol. Struct. (Theochem)* **1994**, *311*, 111.
(6) Lee, V. Ya.; Kato, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 13142.
(7) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.
(8) Manriquez, J. M.; Bunel, E. E.; Oelckers, B. *Inorg. Synth.* **1997**, *31*, 214.
(9) For the experimental procedure, spectral and crystal data of **2**, see Supporting Information.
(10) Elschenbroich, C. *Organometallics*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2006.
(11) Cp^*_2Fe itself also has a staggered conformation; see ref 10.
(12) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604.
(13) All calculations were performed using TURBOMOLE 5.8 program package at the RI-BP86/def2-TZVPP level and the ADF2005.1 program at the BP86/TZ2P level.
(14) (a) Rayón, V. M.; Frenking, G. *Organometallics* **2003**, *22*, 3304. (b) Lein, M.; Frunzke, J.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 2504.

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