Cationic Metallocenophanes

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Synthesis and Reactivity of a Strained Silicon-Bridged [1]Ferrocenophanium Ion[**]

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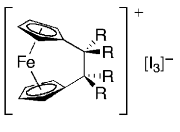
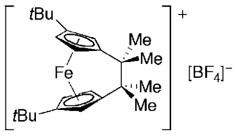
Ferrocene, $[Fe(\eta\text{-}C_5H_5)_2]$, first prepared in the 1950s as an orange solid,[1] is the prototypical metallocene. Its remarkable stability is attributed to the aromatic character of cyclopentadienyl (Cp) ligands and an 18-electron count.[2] This compound undergoes reversible one-electron oxidation to generate the dark blue 17-electron Fe^{III} ferrocenium ion, $[Fe(\eta\text{-}C_5H_5)_2]^+$, which can be isolated as stable salts.[2a,3]

An interesting class of ferrocene derivatives is represented by [*n*]ferrocenophanes.[4] Among these, the most explored are strained silicon-bridged [1]ferrocenophanes or sila[1]ferrocenophanes, because of their diverse reactivity and ability to be converted into polyferrocenylsilanes (PFSs) by a variety of ring-opening polymerization (ROP) methods.[5] Despite the large and rapidly increasing number of existing strained [*n*]ferrocenophanes,[6] only species with two or more atoms in the bridge, such as the 17-electron carbon-bridged [2]ferrocenophanium ions in **1** and **2**, have been successfully synthesized by oxidation and isolated as stable salts.[7]



1 (R = H, Me)



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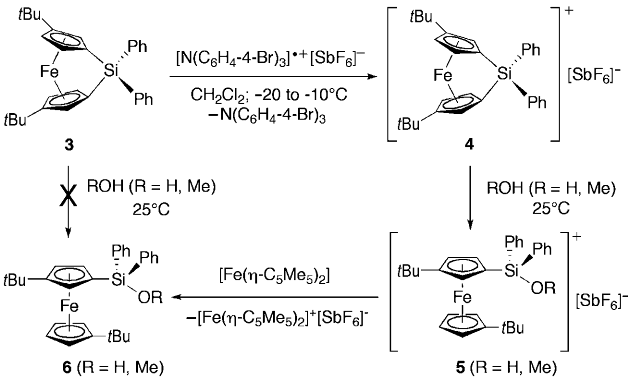
To date, only electrochemical studies of the one-electron oxidation of [1]ferrocenophanes have been reported.[8,9] Although the process is reversible on the timescale of cyclic voltammetry, salts of 17-electron [1]ferrocenophanium cations have not been isolated and their stability has been questioned.[9] On the other hand, recent studies by our research group have shown that improvements to the stability of oxidized PFS materials can be achieved by introducing electron-donating Me or *t*Bu groups on the Cp ligands.[10] This prompted us to study the oxidation of a sila[1]ferrocenophane precursor with such substituents.

Despite the reversible one-electron oxidation detected by cyclic voltammetry ($E_{1/2} = -0.24$ V in 0.1 M $[Bu_4N][PF_6]$ in CH_2Cl_2 vs ferrocene/ferrocenium), attempts to oxidize the electron-rich *t*Bu-substituted [1]ferrocenophane $[Fe(\eta\text{-}C_5H_3tBu)_2SiPh_2]$ (**3**)[10] to the corresponding 17-electron cation using I_2 or $AgPF_6$ failed to afford the desired [1]ferrocenophanium ion and only unidentified insoluble products or ring-opened species were obtained.[11] We therefore explored the use of a one-electron oxidant with a counteranion likely to be less reactive toward both Fe^{III}–Cp and Si–Cp bonds. Reaction of **3** with tris(4-bromophenyl)ammoniumyl hexafluoroantimonate $[N(C_6H_4\text{-}4\text{-}Br)_3]^{\bullet+}[SbF_6]^-$ in CH_2Cl_2 at −20 to −10 °C afforded the ferrocenophanium salt **4** in 74 % yield (Scheme 1, top).[12] Surprisingly, the desired product was isolated as red-brown crystals, very different in color from the dark blue or green typical of ferrocenium salts. The paramagnetic product was recrystallized and identified by single-crystal X-ray diffraction and elemental analysis.



Scheme 1. Synthesis and ring-opening reactivity of ferrocenophanium salt **4**.

X-ray crystallography confirmed the bent-sandwich structure of the [1]ferrocenophanium ion in **4** (Figure 1). The two Cp ligands remain essentially planar, and the tilt angle ($\alpha = 28.9(13)°$) between their planes is considerably greater than for the 18-electron precursor **3** ($\alpha = 18.69(9)°$).[10] Other

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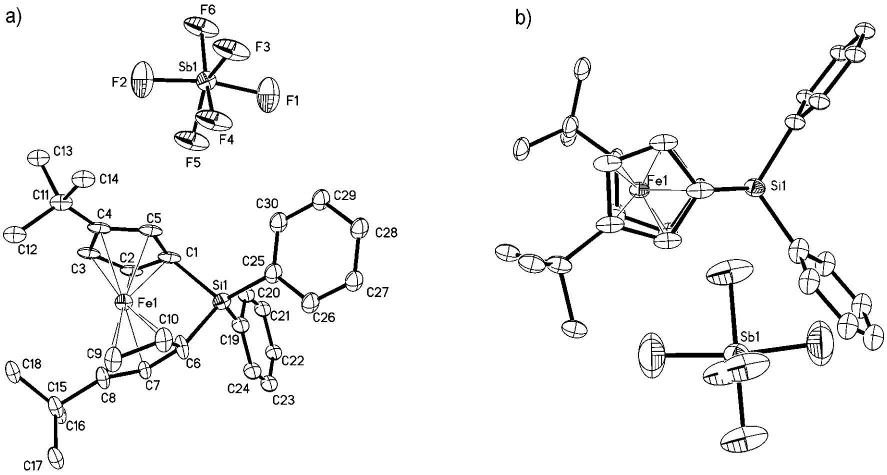


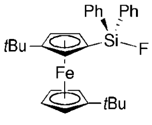
Figure 1. Side (a) and top (b) ORTEP views of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

significant differences in angles and iron displacement values are noted in the Supporting Information.[13]

Based on the substantially increased tilt-angle in the cation in **4** relative to that in **3**, ring-opening reactions would be expected to be even more favorable. Indeed, in contrast to **3** which, as previously reported,[10] does not react with either water or methanol at 25 °C, the [1]ferrocenophanium salt **4** was found to undergo both hydrolysis and methanolysis under similar conditions (Scheme 1). The product resulting from the hydrolysis of **4** was identified as **5** (R = H) by single-crystal X-ray diffraction. Following reduction with decamethylferrocene, the neutral compound, 1-(diphenylhydroxysilyl)-3,1′-di-*tert*-butylferrocene (**6**; R = H), was identified by NMR spectroscopy and mass spectrometry. The reaction of **4** with methanol followed by reduction with decamethylferrocene yielded an orange product identified by ^{1}H NMR spectroscopy and mass spectrometry as 1-(diphenylmethoxysilyl)-3,1′-di-*tert*-butylferrocene (**6**; R = Me). Further support was provided by ^{13}C and ^{29}Si NMR spectroscopy and the silicon connectivity was confirmed by 2D gHMBC ^{29}Si NMR spectroscopy.[12]

Ring-opening polymerization of **4** would be expected to lead to polymers constituted entirely of ferrocenium repeat units with silicon spacers. Notably, while ferrocenophane **3** undergoes ROP above 190 °C, the ring-opening reaction of [1]ferrocenophanium **4** occurs at a much lower temperature (65 °C). However, the product was not macromolecular, and following reduction, mass spectrometry indicated the presence of a molecular ion at *m*/*z* 498, corresponding to the molecular ferrocene derivative, 1-(diphenylfluorosilyl)-3,1′-di-*tert*-butylferrocene (**7**). The corresponding cation **8** was also obtained in the attempted synthesis of **4** by the reaction of **3** with $AgPF_6$[12] and **7** may form through an initial thermally induced fluoride transfer reaction between electrophilic **4** and $[SbF_6]^-$.[14]

To allow more in-depth comparative studies, the 1,1′-di-*tert*-butylferrocenium salt $[Fe(\eta\text{-}C_5H_4tBu)_2]^+[SbF_6]^-$ (**9**) was synthesized and characterized by X-ray diffraction. UV/Vis spectra of **3**–**5** (R = H) and **9** were acquired at room temperature in CH_2Cl_2 solution (5×10^{-3} M). The spectra are shown in Figure 2a (key data are summarized in the Supporting Information, Table 2). While the UV/Vis spectra of **5** (R = H) and **9** are typical of ferrocenium ions,[3] that of the sila[1]ferrocenophanium ion in **4** is very unusual, as implied by the red-brown color of the species.



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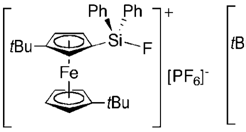

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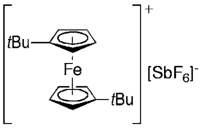

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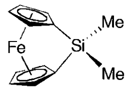

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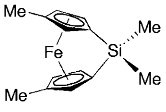

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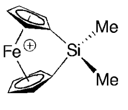

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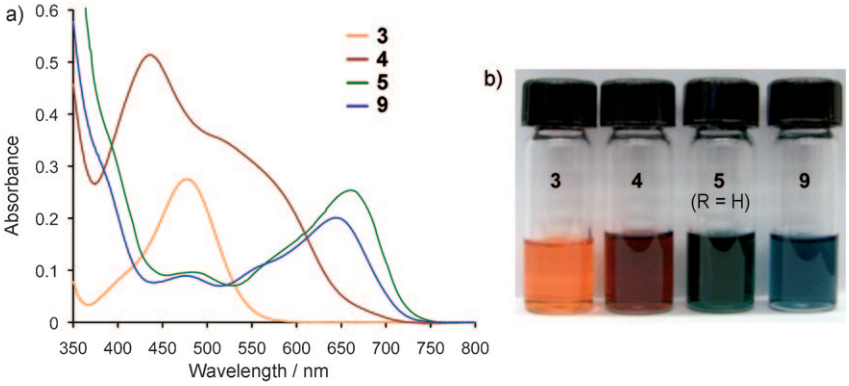

Figure 2. a) UV/Vis spectra of **3**, **4**, **5** (R = H), and **9**. b) Photographs of these species in CH_2Cl_2 solutions.

As shown previously, the ligand-to-metal charge-transfer (LMCT) band characteristic of ferrocenium ions undergoes a red shift from 620 to 650 nm upon substitution of Cp ligands with electron-donating groups such as *n*Bu.[3] In agreement with this, the LMCT band of the di-*tert*-butylferrocenium ion in **9** appeared at 645 nm and that of **5** (R = H) was located at 660 nm. Remarkably, the maximum absorption of ferrocenophanium salt **4** was observed at 435 nm as a more intense band than any observed for either the Fe^{II} precursor **3** or the ferrocenium derivatives **5** (R = H) and **9**. Also, the LMCT band for the ferrocenophanium ion in **4** appeared as a broad shoulder on a shorterwavelength d–d band,[3] blue-shifted relative to the characteristic position of LMCT bands in unstrained ferrocenium ions. The variation in color of CH_2Cl_2 solutions from orange for **3**, to unexpected red-brown for [1]ferrocenophanium ion in **4**, and to green or blue for the acyclic ferrocenium derivatives **5** (R = H) and **9**, respectively, can be seen in Figure 2b.

The LMCT band at 620 nm in the spectrum of the ferrocenium ion is assigned to a transition from the e_{1u} π orbitals of the Cp ligands to the hole in the metal-based e_{2g} level, and its intensity is attributed to the charge-transfer nature of the transition. Subsequent bands are vibronic d–d transitions; hence, they are of lower intensity. In the lower-symmetry metallocenophanium structure of **4**, d–d transitions become dipole-allowed, and as observed, are of greater intensity. The other effect on the electronic absorption spectrum on bending the Cp rings from a parallel configuration is the perturbation of the d levels.[15]

The shift in the first band is reflected in the differences between the photoelectron (PE) spectra of ferrocene and **10**.[16] A PE spectrum maps selected ion states of the molecular cation: the onset of the first band corresponds to the ground state of the cation and subsequent bands correspond to excited states where the hole has been filled by promotion of an electron from one of the occupied molecular orbitals. Thus, the separation of the first adiabatic ionization energy and the e_{1u} band of the PE spectrum of ferrocene should correspond in energy to the e_{1u} to e_{2g} transition discussed above. For ferrocene, the band separation is 2.07 eV, which is roughly equivalent to 600 nm.[17] For **10**, the separation of the bands increases to 2.39 eV (corresponding to 520 nm) in the region of the broad shoulder exhibited by **4**.[16] The PE spectrum of **3** has not been measured, but that of the methyl-substituted analogue (**11**) has a band separation of 2.1 eV (corresponding to 590 nm), showing a similar blue shift from the band position in the ferrocenium ion. The PE spectra indicate that the differences between the electronic absorption spectra of **4** and unbridged ferrocenium ions (e.g., **9**) are primarily due to the increase in energy of the metal d orbitals on bending, rather than a perturbation of the Cp π levels.

Time-dependent density functional theory (TD-DFT) calculations were used to investigate the nature of the unexpected electronic absorption spectrum obtained for **4**. The less computationally demanding dimethylsila[1]ferrocenophane (**10**) and the corresponding dimethylsila[1]ferrocenophanium (**12**), which do not contain ring substituents besides the *ansa* bridge, were chosen for the calculations. The DFT-optimized structure for **10** (C_{2v}) is in excellent agreement with the X-ray crystal structure with a weighted root-mean-square deviation (RMSD) calculated for all heavy atoms of only 0.0517 Å.[15] The structure of **12** was optimized without symmetry constraints as the C_1 structure was found to be 10 kJ mol^{-1} more stable than the C_{2v} structure. The calculated structures show the same trends upon oxidation as the X-ray structures of **3** and **4** (see the Supporting Information, Table 1).

Figure 3a shows an overlay of the experimental and simulated absorption spectra of **10** (Gaussian03 B3LYP/6-31+G(d)), while Figure 3b compares the calculated electronic absorption spectra for the ferrocenophanium ion **12** with the experimental electronic absorption spectrum of **4**. Both calculations give excellent qualitative and quantitative fits with experiment. Minor transitions to four excited states in the calculated structure of **12** were combined to reproduce the UV/Vis spectrum of **4**. If we compare the energy of the β LUMO in $[FeCp_2]^+$ with that of **12**, it increases by 0.87 eV whereas the energy of the highest occupied Cp π level only changes by 0.1 eV (see the Supporting Information). This confirms that the main origin of the blue shift is the perturbation on bending of the Fe d orbitals.[19]

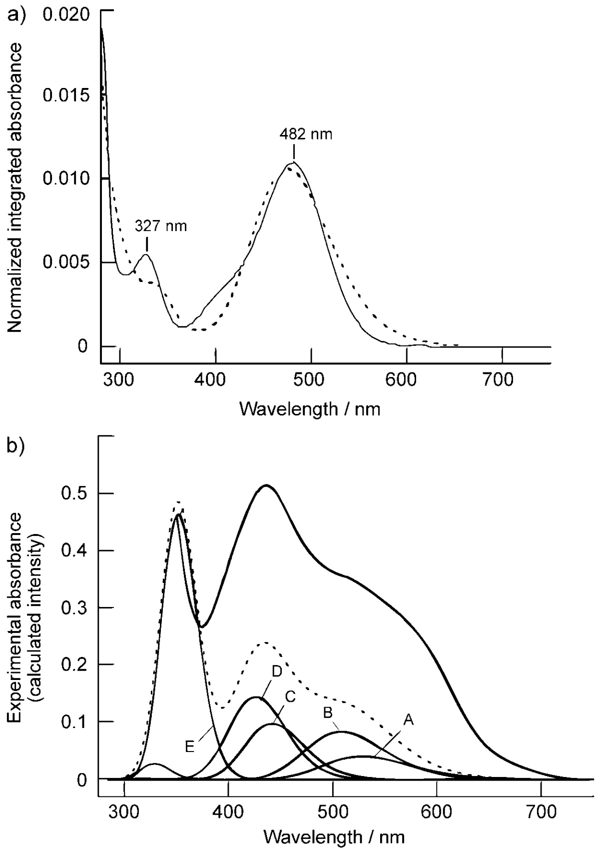

Figure 3. a) Overlay of the best fit of the simulated spectrum (– – –) with the experimental electronic absorption spectrum (——; [**10**] = 7.8 mM in hexanes). The fit was optimized using a scaling factor of 0.996 for the calculated transition energies. b) Plot of the calculated electronic absorption intensity vs. wavelength for the C_1 structure of **12** (– – –: simulated, ——: experimental **4**). Several minor transitions have been combined. The calculated wavelengths have been corrected by +32 nm to provide the best fit with experiment (in $CHCl_3$). MO contributions to bands A–E are presented in the Supporting Information.

In summary the first strained [1]ferrocenophanium ion was successfully isolated as a $[SbF_6]^-$ salt (**4**) by one-electron oxidation of sila[1]ferrocenophane **3**. Both the considerable structural changes and the unexpected electronic absorption spectrum of **4** were reproduced by TD-DFT calculations. Consistent with the presence of additional ring strain, and in contrast to the 18-electron precursor **3**, ferrocenophanium **4** undergoes both hydrolysis and methanolysis at 25 °C. Under thermal ROP conditions, a ring-opening reaction of **4** occurs, but this does not generate a polymer, presumably because of competitive fluoride transfer involving the counteranion $[SbF_6]^-$.[14] As a result, in our future attempts to induce the ROP of sila[1]ferrocenophanium cations we will replace $[SbF_6]^-$ with an even more stable counterion such as $[BPh_4]^-$.

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Keywords: iron · metallocenophanes · oxidation · ring-opening polymerization · ring strain

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[11] The reaction of **3** with $AgPF_6$ in CH_2Cl_2 led to the formation of a green solid product which was identified as $[Fe(\eta\text{-}C_5H_4t\mathrm{Bu})\{\eta\text{-}C_5H_3(t\mathrm{Bu})SiFPh_2\}][PF_6]$ (**8**). X-ray diffraction and mass spectrometry characterized the product as a ring-opened ferrocenium derivative with a fluorine atom at silicon (see the Supporting Information). This unexpected result confirmed that $[PF_6]^-$ was a non-innocent anion acting as a source of HF, presumably formed by hydrolysis (see R. Fernandez-Galan, B. R. Manzano, A. Otero, M. Lanfranchi, M. A. Pellinghelli, *Inorg. Chem.* **1994**, *33*, 2309), which cleaves the Si–Cp bond and opens the ring with formation of the fluorosilane ferrocenium derivative.

[12] Synthetic procedures and characterization data can be found in the Supporting Information.

[13] Crystal structure data for **4**: $C_{30}H_{34}F_6FeSbSi$, 714.26 g mol^{-1}, orthorhombic, space group $Pmn21$; $a = 11.172(2)$, $b = 10.877(2)$, $c = 12.196(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1482.0(5)$ Å^3; $Z = 2$, $\rho_{\text{calcd}} = 1.601$ g cm^{-3}; crystal dimensions: $0.30 \times 0.22 \times 0.06$ mm^3; diffractometer: Nonius Kappa-CCD; Mo$_{K\alpha}$ radiation, 150(2) K, $2\theta_{\max} = 54.96°$; 6163 reflections, 2837 independent ($R_{\text{int}} = 0.0776$), direct methods; absorption coefficient ($\mu = 1.497$ mm^{-1}), absorption correction: semi-empirical from equivalents; refinement (against F^2_0) with SHELXTL V6.1, 253 parameters, 113 restraints, $R_1 = 0.0601$ ($I > 2\sigma$) and $wR_2 = 0.1648$ (all data), Goof = 1.020, residual electron density: 1.210/−0.795 e Å^{-3}. CCDC 690321 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[19] For 1,1'-trimethylene-bridged carba[3]ferrocenophanium salts, no such perturbations are observed and LMCT bands shift to lower energy. The effect of the three-carbon bridge in the electron absorption spectra is consistent with simple alkylation of the Cp ring and reflected in the moderate tilt angles ($\alpha \approx 9$–$14°$) of such species. See: M. D. Duggan, D. N. Hendrickson, *Inorg. Chem.* **1975**, *14*, 955; T.-Y. Dong, S.-H. Lee, *J. Organomet. Chem.* **1995**, *487*, 77. The absorption spectra of triiodide-containing [2]ferrocenophanium (**1**; $X = I_3^-$) is complicated by partial interaction of the anion and the Fe(III) center (see reference [7a]). Accordingly, the electronic structure of [2]ferrocenophanium ions with non-interacting counterions (e.g. **1**; $X = BF_4^-$) are the subject of on-going investigations.