Synthesis and characterisation of the novel metallocenes [Fe(η^5-C$_5$H$_5$EMe$_2$)$_2$] (E = Si, Sn) and [Fe(η^5-C$_5$H$_5$SnMe$_2$)(η^6-C$_6$H$_6$)]$_2$[Fe$_2$Cl$_6$]

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The novel bis-heterocyclohexadienyl metallocene complexes [Fe(η^5-C$_5$H$_5$EMe$_2$)$_2$] (E = Si, Sn) are prepared by reaction of anhydrous FeCl$_2$ with the appropriate lithium salt; [Fe(η^5-C$_5$H$_5$SnMe$_2$)$_2$] undergoes a further unusual reaction with CHCl$_3$ to displace one SnMe$_2$ fragment and afford the mixed sandwich complex [Fe(η^5-C$_5$H$_5$SnMe$_2$)(η^6-C$_6$H$_6$)]$_2$[Fe$_2$Cl$_6$].
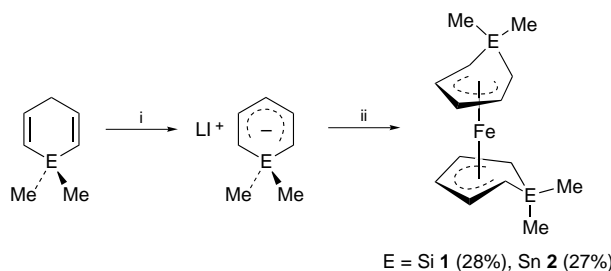
Despite the class of the open metallocenes having been long established by the pioneering work of Ernst,[1] there are few reported examples of systems employing ligands of the type C$_5$H$_5$ER$_2$ (E = C[2], P[3,4]), in which the open pentadienyl moiety is stabilised by linking the ends together in a non-conjugative mannar *via* a group 14 or 15 bridging unit ER$_2$.

Such ligands are of interest since they provide both the possibility of introducing sterically controlling groups R, and an electropositive heteroatom E that may increase electron density at the transition-metal centre. The activity of group 4 metallocene Ziegler–Natta catalysts may benefit from the increased electron density on the metal centre imposed by these electropositive ligands.[5]

Here we report the formation of the bis-heterocyclohexadienyl metallocene complexes [Fe(η^5-C$_5$H$_5$EMe$_2$)$_2$] (E = Si **1**, Sn **2**). The ligand precursors 1,1-dimethyl-1-stannacyclohexa-2,5-diene[6] and 1,1-dimethyl-1-silacyclohexa-2,5-diene[7,8] were prepared by literature methods. The heterocyclohexadienes were deprotonated with LDA and the resulting heterocyclohexadienyl anions were treated with anhydrous FeCl$_2$ to afford the metallocene complexes **1** and **2** (Scheme 1).

A formal displacement of Me$_2$SnCl$_2$ by CHCl$_3$ caused the precipitation of a few crystals of the mixed-sandwich complex [Fe(η^5-C$_5$H$_5$SnMe$_2$)(η^6-C$_6$H$_6$)]$_2$[Fe$_2$Cl$_6$] **3** from a solution of complex **2** in this halogenated solvent within several days, while complex **1** is not noticeably affected by CHCl$_3$.

Complexes **1** and **2** have been fully characterised on the basis of their spectroscopic data.† Single-crystal X-ray structures of **1** and **3** are also presented. The molecular structures of complex **1** and of the mixed-sandwich cation in **3** are shown in Fig. 1 and 2, respectively.‡ The 1,1-dimethyl-1-stannacyclohexadienyl ring in the mixed-sandwich complex **3** is representative of the environment in **2**, and so may be usefully compared to the
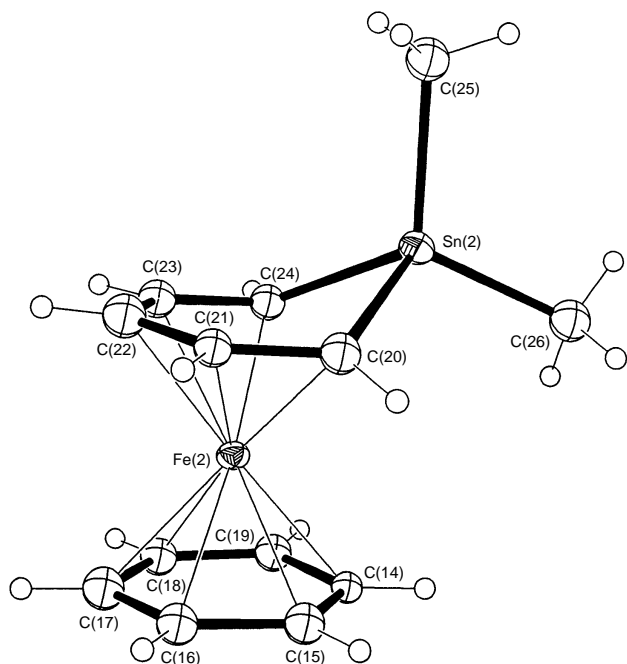
environment of the 1,1-dimethyl-1-silacyclohexadienyl rings in the symmetrical metallocene complex **1**. The heterocyclohexadienyl moiety in **1**, **2** and **3** bonds to Fe in an η^5 manner *via* the five essentially planar carbon atoms, the mean deviation from planarity being ±0.078 and ±0.0149 Å for complexes **1** and **3**, respectively. The heteroatom is pushed out of the plane away from the transition metal. The angle between the C(5)–Si(1)–C(1) plane and the C(1)···C(5) plane is 36.9° in **1**. The corresponding angle in complex **3** is of similar magnitude at 37.6°. The non-bonding FeSi(1) distance in **1** is 2.861 Å compared to a non-bonding Fe(2)···Sn(2) distance in **3** of 3.142 Å. These distances are remarkably short though the Fe···Si distance exceeds the shortest, to our knowledge, non-bonding Si···Fe contact at 2.636 Å in Ph$_2$Si(C$_5$H$_4$)$_2$Fe.[9]

The open and closed carbocyclic ligands in **1** and **3** adopt an essentially coplanar arrangement represented by interplanar angles of 3.7 and 3.8°, respectively. The conformational angle of 38.6° adopted by the ligands in **1** is significantly smaller than the value of 59.7° found in the open ferrocene bis(2,4-dimethylpentadienyl)iron **4**.[5] The distances from the heterocyclohexadienyl ring centroids to Fe remain comparable at 1.543 and 1.531 Å for complexes **1** and **3** respectively and are of the same order of magnitude as the distance of 1.50 Å in **4**, while the distance from the benzene ring centroid to Fe in **3** is slightly longer at 1.559 Å. This may be compared with the value
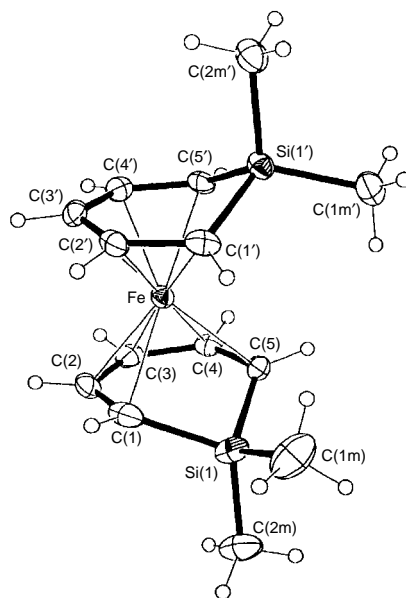
Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Si(1)–C(1m) 1.865(5), Si(1)–C(2m) 1.874(5), Si(1)–C(1) 1.842(5), Si(1)–C(5) 1.832(5), C(1)–C(2) 1.395(7), C(2)–C(3) 1.420(6), C(3)–C(4) 1.410(6), C(4)–C(5) 1.398(6), Fe–Si(1) 2.861(2); C(4)–C(5)–Si(1) 120.3(4), C(2)–C(1)–Si(1) 120.2(4), C(1m)–Si(1)–C(2m) 107.7(2), C(1)–Si(1)–C(5) 93.4(2), C(2)–C(3)–C(4) 122.0(4), C(1)–C(2)–C(3) 122.9(4), C(3)–C(4)–C(5) 123.0(4). C(1)–Si(1)–C(1m) 113.2(2), C(5)–Si(1)–C(2m) 114.1(2).

Scheme 1 Synthesis of the novel metallocenes **1** and **2**. *Reagents and conditions*: i, LDA, thf, 0.5 h, 258 K; ii, FeCl$_2$, thf, 1 h 200 K, 12 h, 298 K, subsequent work-up by filtration through silica and crystallisation of **1** from hexane.

E = Si **1** (28%), Sn **2** (27%)

Fig. 2 Molecular structure of the complex cation **3** with the $Fe_2Cl_6^{2-}$ counter ion omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(2)–C(25) 2.11(2), Sn(2)–C(26) 2.09(2), Sn(2)–C(24) 2.14(2). Sn(2)–C(20) 2.11(2), C(24)–C(23) 1.40(2), C(23)–C(22) 1.41(2), C(22)–C(21) 1.39(2), C(21)–C(20) 1.38(2), Fe(2)–Sn(2) 3.142(1), C(14)–C(15) 1.37(2), C(15)–C(16) 1.41(2), C(16)–C(17) 1.42(2), C(17)–C(18) 1.40(2), C(18)–C(19) 1.38(2), C(19)–C(14) 1.39(2), C(25)–Sn(2)–C(26) 113.6(7), C(20)–Sn(2)–C(24) 82.2(7), C(20)–Sn(2)–C(25) 114.1(7), C(24)–Sn(2)–C(26) 116.4(7), C(21)–C(22)–C(23) 122(2), C(22)–C(23)–C(24) 126(2). C(22)–C(21)–C(20) 127(2), C(21)–C(20)–Sn(2) 122.0(13), C(23)–C(24)–Sn(2) 119.9(14).

of 1.55 Å found in the analogous complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Et_6)]PF_6$.[10]

Spectroscopic data show that the heteroatom methyl substituents are non-equivalent and may be classified as *mexo* and *mendo*. The difference in chemical shift between the *mendo* and *mexo* methyl groups is a function of the ring carbon–heteroatom distance, since the ring current generated by the heterocyclohexadienyl system decreases in strength away from the ring centroid. The C(24)–Sn(2) distance in **3** is indeed longer, at 2.14(2) Å, than the C(5)–Si(1) distance in **1**, 1.832(5) Å, and the *mendo–mexo* methyl NMR signals have a greater difference in **2** than **1** as a result.

The electrochemical behaviour of **1** and **2** resemble that of the open ferrocene **4**[11] with the reversible one-electron oxidation occurring at a far lower potential for **1** than **2** reflecting the greater electron density at the Fe centre for the system with the more electropositive heteroatom.§ Likewise, an orthorhombic *g* tensor is observed in the EPR spectra of both **1** and **2** in frozen solution.

This new class of metallocene complexes employing heterocyclic ligands is being extended to include the early transition-metal elements, and further direct replacement of the $SnMe_2$ moiety by a variety of other heteroatoms is under examination.

Footnotes

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† *Selected spectroscopic data* for **1**: ^{1}H NMR (CDCl$_3$, 250 MHz, 295 K) δ −0.65 [s, 3 H, C(2m)–H *mexo*-CH$_3$], 0.66 [s, 3 H, C(1m)–H, *mendo*-CH$_3$], 2.20 [d, 2 H, $^3J(o,m)$ 10.2 Hz, C(1,5)–H, *o*-CH], 4.85 [dd, 2 H, $^3J(m,o)$ 10.2 Hz, $^3J(m,p)$ 5.8 Hz, C(2,4)H, *m*-CH], 4.97 [t, 1 H, $^3J(p,m)$ 5.8 Hz, C(3)–H, *p*-CH]; ^{13}C NMR (CDCl$_3$, 250 MHz, 295 K) δ −1.14 [C(2m), CH$_3$], 7.78 [C(1m), CH$_3$], 38.87 [C(1,5), *o*-CH], 78.54 [C(2,4), *m*-CH], 94.47 [C(3), *p*-CH]; EPR (**1**$^+$, CHCl$_3$, 77 K), g_1 = 2.033, g_2 = 2.090, g_3 = 2.165; EIMS (70 eV) 302 (61%, [M]$^+$), 287 (69%, [M − CH$_3$]$^+$), 244 (11%, [M − SiMe$_2$]$^+$), 229 (100%, [M − SiMe$_2$ − CH$_3$]$^+$), 179 (40%, [M − C$_7$H$_{11}$Si]$^+$, 164 (51%, [M − C$_7$H$_{11}$Si − CH$_3$]$^+$). HRMS: *m/z* 302.06014, mass deviation 7.62 ppm.

2: ^{1}H NMR (CDCl$_3$, 250 MHz, 295 K) δ −0.29 (s, 3 H, *mexo*-CH$_3$), 0.63 (s, 3 H, *mendo* CH$_3$), 2.32 [d, 2 H, $^3J(o,m)$ 9.17 Hz, *o*-CH], 4.83 (m, 1 H, *p*-CH], 4.85 (m, 2 H, *m*-CH); ^{13}C NMR (CDCl$_3$, 250 MHz, 295 K) δ −8.79 (*mexo*-CH$_3$), 0.67 (*mendo*-CH$_3$), 39.62 (*o*-CH), 79.74 (*p*-CH), 97.55 (*m*-CH); EPR (**2**$^+$, CHCl$_3$, 77 K), g_1 = 2.011, g_2 = 2.052, g_3 = 2.127; EIMS (70 eV) 484 (6%, [M]$^+$), 336 (2%, [M − SnMe$_2$]$^+$), 321 (4%, [M − SnMe$_2$ − CH$_3$]$^+$), 186 (100%, [M − 2SnMe$_2$]$^+$). HRMS: *m/z* 485.9155, mass deviation 8.4 ppm.

‡ *Crystal data*: for **1**: C$_{14}$H$_{22}$FeSi$_2$, 0.27 × 0.19 × 0.16 mm, *T* = 150(2) K, *M* = 302.35, monoclinic, space group *P*2$_1$/*c*, *a* = 13.209(7), *b* = 9.516(7), *c* = 11.997(7) Å, β = 100.06(5)°, *U* = 1485(2) Å^3, *Z* = 4, *D*$_c$ = 1.353 Mg m^{-3}, λ = 0.71073 Å, *F*(000) = 640, *R*$_1$ = 0.0407 [1914 reflections with *F*$_o$ > 4σ(*F*$_o$)], *wR*$_2$ = 0.0902 for 1922 independent reflections corrected for adsorption [µ(Mo-Kα) = 1.154 mm^{-1}] and 189 parameters (all non-H atoms anisotropic).

For **3**: C$_{13}$H$_{17}$Cl$_3$Fe$_2$Sn, 0.12 × 0.10 × 0.10 mm, *T* = 154(2) K, *M* = 510.01, monoclinic, space group *P*2$_1$/*n*, *a* = 14.843(5), *b* = 14.209(5), *c* = 17.098(6) Å, β = 106.97(2)°, *U* = 3449(2) Å^3, *Z* = 8, *D*$_c$ = 1.964 Mg m^{-3}, λ = 0.71073 Å, *F*(000) = 1984, *R*$_1$ = 0.0701 [2723 reflections with *F*$_0$ > 4σ(*F*$_o$)], *wR*$_2$ = 0.1844 for 4492 independent reflections and 295 parameters (Fe, Sn and Cl atoms anisotropic). Compound **3** crystallises with two half-dianions and two cations per asymmetric unit; each anion possessing a crystallographic centre of symmetry. The benzene ring of one cation is disordered over two sites with partial occupancies of 0.62 and 0.38.

The structures were solved by direct methods,[12] and a series of difference Fourier maps were used to locate all light atoms except the H atoms, these being added in calculated positions (C–H 0.96 Å) riding on the respective C atoms. All other calculations were performed using SHELXL-93.[13]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/436.

§ The cyclic voltammograms (CVs) of **1** and **2** were recorded using a glassy-carbon/platinum electrode system referenced to calomel in dme–0.1 **m** NBu$_4$PF$_6$, *v* = 100 mv s^{-1} at 298 K. A one-electron reversible oxidation with $E_{\frac{1}{2}}$ (0/+1) {Δ*E*$_p$} = 169 {67} and −200 {58} mV was observed for **1** and **2** respectively. Irreversible reduction waves were registered at E_{pc} = −2.315 and −2.191 V for **1** and **2**, respectively.

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