Silicon-bridged bis(cyclohexadienyl) iron complexes: the first structurally characterised [1⁴]ferrocenophane†

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Reaction of the Me_2Si bridged bis(6,6-dimethylcyclohexadienyl) dianion with $FeCl_2 \cdot 1.5THF$ gives mono-, di- and tetrametallic complexes; $\{[Me_2Si(DMCh)_2]Fe\}_4$ is the first crystallographically characterised [1⁴]metallocenophane.

[1ⁿ]Metallocenophanes, molecules consisting of *n* metallocene units joined by single atom bridges,[1] are of interest for several reasons. For example, it is now well established that strained, ring-tilted, [1¹]ferrocenophanes (*ansa*-bridged ferrocenes) undergo thermal, anionic and metal-catalysed ring-opening polymerisation (ROP),[2,3] yielding well-defined, high molecular weight, soluble metal-containing polymers. Oligomeric [1ⁿ]ferrocenophanes are also of considerable interest due to, for example, their novel structural properties and the possibility of metal–metal interactions.[1,4] To date, polymerisation reactions have been limited to metallocenophanes containing cyclopentadienyl rings. We are interested in developing new ligand systems that could offer more flexibility and diverse substitution patterns in order to extend this chemistry.

As part of this research, we have studied metal complexes of the 6,6-dimethylcyclohexadienyl anion (DMCh),[5] which are related to 'open metallocenes'[6] as the ligand can bind to the metal centre though an η^5-pentadienyl moiety. The dimethylcyclohexadienyl ferrocene analogue, $(DMCh)_2Fe$, has been reported;[5] however, metallocenophanes with bridged cyclohexadienyl ligands are unknown, although recently titanium complexes of the 'constrained geometry' ligand Me_2Si-$(Bu^tN)DMCh$ have been reported.[7]

A silicon-bridged bis-dimethylcyclohexadienyl ligand was synthesized according to Scheme 1. Thus, addition of 2 equiv. of the potassium salt $K^+(DMCh)^{-5,8}$ to Me_2SiCl_2 gave dimethylbis(dimethylcyclohexadienyl)silane, the NMR spectrum of which (ESI†) is consistent with a C_{2v} symmetric 1,4-diene, indicating reaction has taken place exclusively at the

3-position of the cyclohexadienyl rings. The ligand could be deprotonated with 2 equiv. Bu^tLi to yield $Me_2Si(DMChLi)_2$. Reaction of this dianion with $FeCl_2 \cdot 1.5THF$ in THF gives a complex mixture, presumably containing products due to reduction by the DMCh anion[5] as well as insoluble polymeric material. Three products, however, could be isolated: the [1]ferrocenophane analogue, $[Me_2Si(DMCh)_2]Fe$ **1** as well as dimeric and tetrameric species.

The three products could be separated by virtue of their differing solubilities, and have been characterised by X-ray crystallography‡ in addition to NMR, and microanalysis (ESI†). The monomer **1** is highly soluble in pentane. Its structure (Fig. 1) reveals it to be analogous to a ring-tilted *ansa*-bridged ferrocene. As an indication of the strain in **1**, the value of α, the angle between the average planes defined by the pentadienyl carbons, is 14.5°. For comparison, an angle of 20.8° was observed between the Cp rings in the analogous $[Me_2Si(C_5H_4)_2]Fe$.[9] Thus, on this basis, the replacement of Cp rings with DMCh would appear to have reduced the strain somewhat. Conversely however, the average value of β, the angle between each plane and the bridging atom–bridgehead bond, is slightly greater for $[Me_2Si(DMCh)_2]Fe$ (40.0°) than $[Me_2Si(C_5H_4)_2]Fe$ (37.0°). This deviation from planarity of the sp^2 bridgehead atom of **1** is also reflected in its ^{13}C NMR resonance, which is found at δ 47.4, an upfield shift relative to unbridged compounds. For comparison, the corresponding value for $(DMCh)_2Fe$ is δ 77.9.[5] It should also be noted that, in general, bis-pentadienyl iron complexes prefer to adopt a *gauche* eclipsed conformation, in which the pentadienyl units are rotated relative to each other by a conformation angle χ of *ca.* 60°.[6] While the structure of $(DMCh)_2Fe$ has not been reported, the related 6-*tert*-butylcyclohexadienylferrocene analogue exhibits such a conformation.[10] In contrast, the silicon bridge of $[Me_2Si(DMCh)_2]Fe$ constrains the DMCh rings to be *syn*-eclipsed ($\chi \approx 0$), thus representing a potential additional source of strain in this molecule.
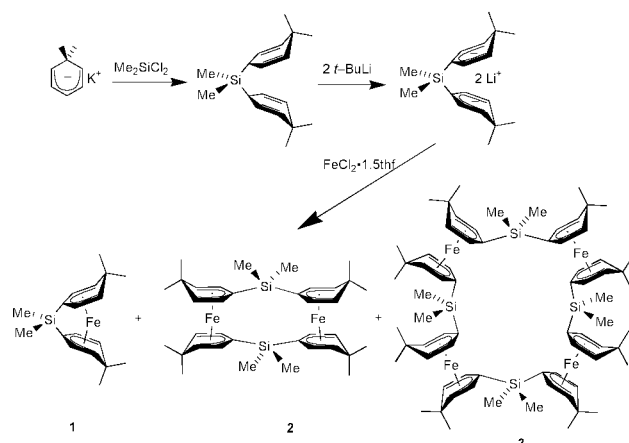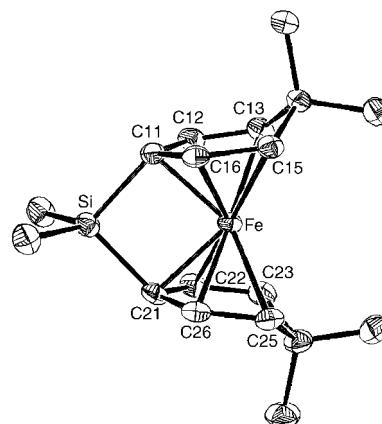
Scheme 1

Fig. 1 Molecular structure of $[Me_2Si(DMCh)_2]Fe$ **1**. Selected bond lengths (Å): Fe–C11 2.038(2), Fe–C12 2.052(2), Fe–C13 2.166(2), Fe–C15 2.131(2), Fe–C16 2.038(2), Fe–C21 2.037(2), Fe–C22 2.042(2), Fe–C23 2.149(2), Fe–C25 2.152(2), Fe–C26 2.045(2), Si–C11 1.902(2), Si–C21 1.897(2).

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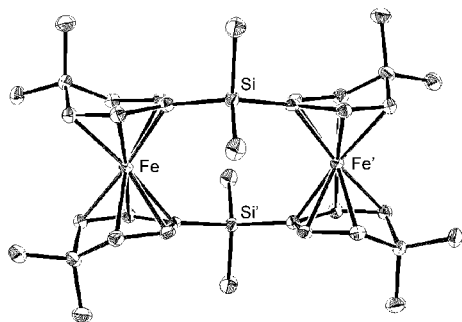
Fig. 2 Molecular structure of {[Me₂Si(DMCh)₂]Fe}₂ **2**. Labelling scheme for pentadienyl carbons is analogous to that in Fig. 1. Primed atoms are generated by symmetry. Selected bond lengths (Å): Fe–C11 2.094(2), Fe–C12 2.051(2), Fe–C13 2.117(2), Fe–C15 2.133(2), Fe–C16 2.056(2), Fe–C21 2.108(2), Fe–C22 2.056(2), Fe–C23 2.115(2), Fe–C25 2.125(2), Fe–C26 2.057(2), Si–C11 1.876(2), Si–C21′ 1.876(2).

In addition to the monomer **1**, air stable dimeric and tetrameric species are also obtained in low but reproducible yields. The oligomers are much less soluble in hydrocarbon solvents, and can be separated by fractional crystallisation from CH_2Cl_2. The structure of the dimer {[Me₂Si(DMCh)₂]Fe}₂ **2** (Fig. 2),‡ reveals a molecule on an inversion centre, in which the two halves of the dimer are crystallographically equivalent. The formation of **2** allows significant relief of the strain observed in the *ansa*-bridged species **1**, as demonstrated by an angle α of 5.4°, and an average value of β of 6.5°. The silicon bridged cyclopentadienyl [1²]ferrocenophane, {[Me₂-Si(C₅H₄)₂]Fe}₂, which was reported simultaneously by three groups,[11–13] has a similar ring tilt [α = 4.9(3)°].[12] In both cases, the ring tilt is opposite to that of the monomeric species; the greatest inter-ring separation is observed at the silicon-bridged end of the ring. Furthermore, {[Me₂Si(DMCh)₂]Fe}₂ is able to adopt the preferred *gauche* eclipsed conformation with an angle χ of 50.7°. Such a conformation is presumably also favoured to reduce steric interactions between the Me₂Si groups; indeed a similar conformation is observed in the structure of {[Me₂-Si(C₅H₄)₂]Fe}₂. The Fe⋯Fe separation in {[Me₂-Si(DMCh)₂]Fe}₂ is 5.496(1) Å, which is greater than in the cyclopentadienyl analogue (*ca.* 5.17 Å).[11,12]

The third product that can be isolated is the silicon-bridged cyclic tetramer {[Me₂Si(DMCh)₂]Fe}₄ **3** which is unprecedented in cyclopentadienyl chemistry. The CH₂-bridged parent [1⁴]ferrocenophane has been reported,[14,15] and we have reported the synthesis of a partially methylated analogue,[16] but, to our knowledge, there are no examples of structurally characterized [1⁴]metallocenophanes.§ The structure of {[Me₂-Si(DMCh)₂]Fe}₄ is shown in Fig. 3.‡ It crystallises in the tetragonal space group *P4/n* and lies on a crystallographic 4-fold axis. Thus, as with the dimer, the asymmetric unit of {[Me₂Si(DMCh)₂]Fe}₄ is a single (DMCh)₂Fe unit. The four iron atoms are by necessity coplanar, and the overall shape of the molecule resembles a square. The angle between the planes (α) for each unit is 8.75°, perhaps indicating slightly more strain than in the dimer, while the average β is 5.1°. The Fe⋯Fe distance between neighbouring iron centres is 6.320(1) Å, a greater separation than in the dimer, while the The Fe⋯Fe separation across the ring is 8.938(1) Å. Interestingly, while the ¹H NMR spectrum of the [1⁴]ferrocenophane {[CH₂(C₅H₄)₂]Fe}₄ shows only one peak due to the Cp protons,[14,15] the pentadienyl protons of {[Me₂Si(DMCh)₂]Fe}₄ **3** are observed as eight separate resonances, varying considerably in chemical shift from δ 1.24 to δ 5.35 (C₆D₆). Presumably the upfield-shifted resonances correspond to the protons which are located toward the interior of the cavity, in analogy to the NMR spectra of cyclophanes. The fact that all of the ring protons in {[Me₂Si(DMCh)₂]Fe}₄ are chemically inequivalent at room temperature suggests the molecule is conformationally rigid, which could perhaps explain why replacement of Cp with DMCh groups has facilitated crystallisation of a [1⁴]metallocenophane analogue.
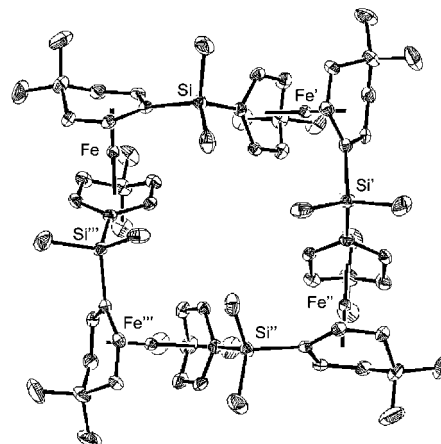

Fig. 3 Molecular structure of {[Me₂Si(DMCh)₂]Fe}₄ **3**. Labelling scheme for pentadienyl carbons is analogous to that in Fig. 1. Primed atoms are generated by symmetry. Selected bond lengths (Å): Fe–C11 2.090(2), Fe–C12 2.057(2), Fe–C13 2.132(2), Fe–C15 2.131(2), Fe–C16 2.051(2), Fe–C21 2.092(2), Fe–C22 2.057(2), Fe–C23 2.139(2), Fe–C25 2.121(2), Fe–C26 2.056(2), Si–C11 1.870(2), Si–C21′ 1.873(2).

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