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Redox-mediated reactions of vinylferrocene: toward redox auxiliaries†

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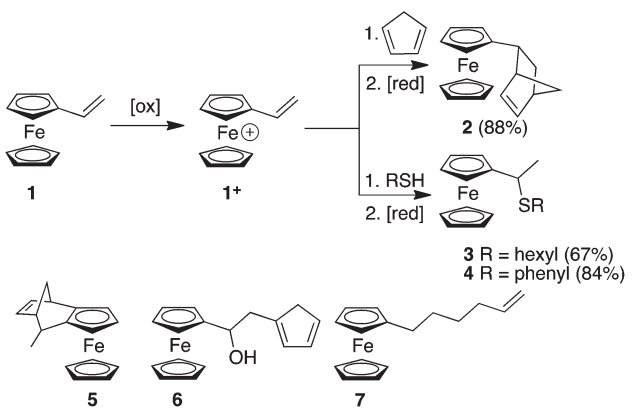
Chemical redox reactions have been exploited to transform unreactive vinylferrocene into a powerful dienophile for the Diels–Alder reaction and reactive substrate for thiol addition reactions upon conversion to its ferrocenium state. We have further investigated the ability of these reactions to facilitate redox-auxiliary-like reactivity by further hydrogenolyisis of the Diels–Alder adduct to the corresponding cyclopentane derivative.

Introduction

The fascinating structural and redox properties of ferrocene (Fc) have ensured that this metallocene has become a ubiquitous redox-active building block for a range of applications spanning materials science, catalysis and medicine.[1] Arguably the most important property of this unit is its ability to reversibly undergo a one-electron chemical or electrochemical oxidation to transform the electron rich Fc to the electron deficient ferrocenium (Fc^+) species. The propensity of this unit to undergo redox umpolung of this type has ensured that Fc and its derivatives have found a range of applications including a switchable motif for host–guest complexation,[2] sol–gel[3] and micelle[4] actuation, biological recognition,[5] recyclable catalysts[6] and switchable dyes.[7]

The Diels–Alder (DA) and conjugate addition (CA) reactions are two synthetically important reactions of alkenes, which generally require facilitation through a strongly electron withdrawing unit attached to the alkene. Therefore, reactions of this type are attractive vehicles for developing redox umpolung controlled transformations of appropriately functionalised redox active alkenes. Vinylferrocene (**1**) is a particularly attractive candidate for development of this type due to its commercial availability and its ability to undergo reversible oxidation, thereby transforming the electron donating Fc moiety to the more electron withdrawing Fc^+ state. The alkene moiety of **1** is electron rich due to the electron releasing nature of Fc unit. Indeed, the Alfrey–Price e parameter (a semi-empirical measure of electron richness of the double bond) is −2.1 for vinylferrocene which predicts a reactivity worse than 4-(*N*,*N*-dimethylamino)styrene (−1.37), a derivative which is likely to be a poor dienophile for DA reactions and electrophile for CA.[8] However, conversion to the Fc^+ species should reverse the reactivity of **1** providing a powerful dienophile and reactive alkene for CA.

Here, we report the synthesis of compounds **2**, **3** and **4** using redox umpolung-like reactions to transform **1** from an unreactive species for DA and thiol addition to a reactive ferrocenium-based reagent $\mathbf{1}^+$ upon the addition of a chemical oxidant (Scheme 1). DA reactions of ferrocene containing dienophiles have been reported,[9] however, they have been largely restricted to the reaction of β-acceptor-substituted vinylferrocenes[10] or acrolylferrocenes[11] with complementary dienes or by inverse electron demand reactions.[12] In addition,



Scheme 1 Redox umpolung-mediated reactions of vinylferrocene and the structures of derivatives **5**, **6** and **7**.

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compound **5** has previously been reported using a DA reaction of cyclopentadiene (CP) and the fulvalene[13] form of α-carbocation derived from $FcCH(OH)CH_3$. In other studies, cyclopentadienols have been isolated as the major products resulting from the oxygen-mediated decomposition of Fc^+ species in the presence a triazoline-based trapping agent.[14] In an interesting article, Gleixner *et al.* have shown that a single electron chemical oxidation of **1** leads to extensive decomposition of the starting material and produces a small amount of a Fc derivative that was tentatively assigned as cyclopentadiene-functionalized derivative **6**, possibly through a Friedel Crafts-like process between a cationic Fc derivative (resulting from the oxidation of **1**) and a vinylferrocene unit.[15] The CA of nucleophiles to appropriately functionalised Fc derivatives have been reported.[16] Nucleophilic thiol substitution reactions has been reported for ferrocenyl alcohols in the presence of the single electron oxidant cerium ammonium nitrate *via* a highly-delocalized ferrocenyl carbocation intermediate.[17] Furthermore, radical-mediated thiol–ene reactions have recently been reported for **1**, which afforded either the α- or β-hydrothiolated product depending upon the nature of the thiol and whether the radical reaction was thermally or photochemically initiated.[18]

Results and discussion

Initially we investigated the DA reactions of **1** and freshly-distilled CP. To bring about the conversion of Fc to Fc^+ we used $FeCl_3$ as the oxidant and ascorbic acid to reduce the Fc^+ species back to the neutral Fc derivative. The addition of the oxidant to a solution of **1** immediately gave rise to a blue/green solution indicating the formation of $\mathbf{1}^+$. Table S1 (ESI†) summarises some of the method development reactions undertaken. Of the reaction conditions investigated, the conditions described in entry 9 reliably gave the best yield of compound **2**. It is noteworthy that excess CP should be added to a solution of **1** at −40 °C before the oxidant is added. Unfortunately, this DA adduct was oil-like which prevented X-ray structure determination. However, solution-based NMR experiments were consistent with the *endo*-structure predominating (7 : 1, *endo* : *exo*) (ESI†).

We next investigated the reaction of $\mathbf{1}^+$ with hexanethiol and thiophenol. In both cases, the reactions progressed effectively, producing good yields of thiol-addition compounds **3** and **4**[19] following conversion of the Fc^+ state to the corresponding Fc derivative by treatment with ascorbic acid (ESI†). Interestingly, in all cases examined, NMR spectroscopy indicated that the sulfide unit is attached to the α-carbon, rather than the β-carbon of the alkene, which would be expected if the reactions proceeded *via* a CA-type reaction. The presence of the doublet for the hydrogen atoms of the methyl group is particularly diagnostic of α-addition. We have obtained the X-ray crystal structure of the thiol addition product **4** which corroborates our NMR data by clearly showing that it is the α-carbon that is functionalised (Fig. 1).[20] Furthermore, the

Fig. 1 X-Ray crystal structure of **4**. Colour scheme: Fe orange, S yellow, C black, H grey.

centrosymmetric $P2_1/c$ space group indicates that the compound is obtained as a mixture of enantiomers.

In control experiments, we have investigated the DA and thiol-addition reactions of **1** without the addition of the $FeCl_3$ as oxidant. In both cases, unreacted starting materials were recovered. Likewise, when reactions (including addition of the oxidant) were repeated with Fc derivative **7**, where the vinyl group is no longer in conjugation with the cyclopentadienyl moiety of Fc, only starting materials were obtained. Thus, our experiments indicate the importance of the alkene being conjugated to the metallocene skeleton and argues against the $FeCl_3$ merely activating the thiol component of the reaction for radical addition, or acting solely as a Lewis acid catalyst for the DA reaction.[21]

We have repeated the reaction described by Watts and co-workers[13] to synthesise compound **5** and found in DCM at room temperature and in THF at 55 °C (to mimic our conditions) that compound **5** was produced, and that there was no evidence for the formation of compound **2**. Thus these experiments argue against the possibility of a fulvalene-like structure being implicated in the DA reaction presented in this article (Fig. 2).[22] Interestingly, compound **5** was observed as a minor side product using our conditions, only when the reaction was performed at room temperature. We have also investigated the reaction of the carbocation derived from $FcCH(OH)CH_3$ with thiophenol which provided compound **4** in 65% yield.

In order to shed light on the enhanced reactivity of $\mathbf{1}^+$, we have employed density functional theory (DFT) calculations[23] to probe the molecular and electronic structure of this species, alongside that of **1**, the neutral vinylferrocene precursor (see Fig. 3). The optimised geometries indicate little difference in the structure of the vinylcyclopentadienyl moiety within **1** and $\mathbf{1}^+$. Moreover, no evidence for a fulvalene-like structure is observed with no significant bond alternation apparent in the substituted cyclopentadienyl moiety. Instead the major structural changes occur around the metal centre, with elongation

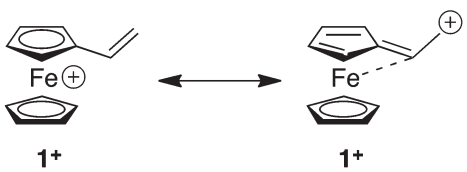


Fig. 2 Possible fulvalene-like structure of $\mathbf{1}^+$.

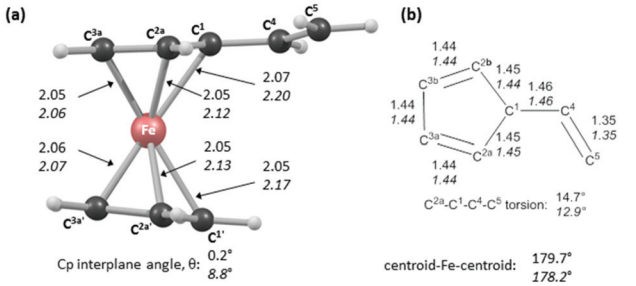


Fig. 3 BP86-optimised structural data (Å, °) for **1** and $\mathbf{1}^+$; (a) computed structure of $\mathbf{1}^+$ with selected data for $\mathbf{1}^+$ in italics and for **1** in plain text; average values for near-symmetry equivalent Fe–C distances are provided; (b) structure of the vinylcyclopentadienyl moiety; θ is the angle between the best fit planes through the two C_5 rings.

of the Fe–C^{2a}/C^{2b} bonds and, in particular, the Fe–C^1 bond (see Fig. 3 for details and the labelling scheme employed). Similar changes are computed in the unsubstituted cyclopentadienyl ring meaning that θ, the angle between the best fit planes through the two C_5 rings, increases from 0.2° in **1** (*i.e.* essentially co-planar) to 8.8° in $\mathbf{1}^+$.

These computed structures suggest the 1e oxidation of **1** is primarily localized on iron and involves a formal Fe^{2+}/Fe^{3+} couple. This is supported by a natural population analysis which indicates a large spin density of 1.08 on the Fe centre in $\mathbf{1}^+$ (the next largest spin density is 0.04 on the terminal vinyl carbon, C^5). The computed natural charge on the Fe centre also drops from −0.30 in **1** to +0.69 in $\mathbf{1}^+$. Inspection of the HOMO of **1** reveals it is dominated by the Fe $d_{x^2-y^2}$ orbital with some bonding character with the $C^1/C^{1\prime}$ positions (see Fig. 4). Depopulation of this orbital is therefore consistent with the computed structural changes that occur upon oxidation of **1**.

Of the low-lying unoccupied orbitals of **1** both the LUMO and LUMO+2 have significant π* character on the vinyl substituent and hence will be important in DA reactivity. Comparison with the equivalent orbitals of $\mathbf{1}^+$ revealed only minor differences in the make-up of these orbitals (see ESI†), consistent with the minimal geometric changes computed within the vinylcyclopentadienyl ligand upon oxidation. However, oxidation does result in a significant stabilisation of these orbitals of between 1.5 to 2.5 eV, and this would be consistent with the enhanced DA reactivity observed in $\mathbf{1}^+$. Accordingly, the computed barriers for the reaction with cyclopentadiene to give the *endo* DA product reduces from 20.3 kcal mol^{-1} with **1** to 10.3 kcal mol^{-1} for $\mathbf{1}^+$ while both reactions are exergonic, by 8.9 kcal mol^{-1} and 11.3 kcal mol^{-1}, respectively. Fig. 5 gives details of the computed transition state structures and indicates that $\mathbf{TS1}^+$ shows the greater asynchronicity, with $C^4\cdots C^6$ being almost 1 Å longer than $C^5\cdots C^7$ in $\mathbf{TS1}^+$, whereas in **TS1** this difference is only 0.5 Å. Similar transition states were located for the *exo* addition, but these were found to be less accessible by *ca.* 0.5–1 kcal mol^{-1} for $\mathbf{1}^+$ which is consistent with the observed *endo* : *exo* preference.

We next turned our attention to whether we could extend our methodology to develop Fc-based redox auxiliaries. In particular, whether we could couple the redox-mediated umpolung reactions with hydrogenolysis of the Fc moiety to remove the iron-containing "auxiliary" moiety to liberate the corresponding functionalised cyclopentane derivative (Scheme 2).[24] To investigate the viability of this chemistry, in line with previously reported protocols for the hydrogenolyis of Fc, the alkene unit of the norbornene moiety was first reduced using Pd/C and H_2 to afford compound **8** in quantitative yield. Further hydrogenolysis of **8** in the presence of trifluoroacetic acid (TFA) furnished the corresponding alkane **9** in near-quantitative yield (by GC-MS, ESI†).[25]

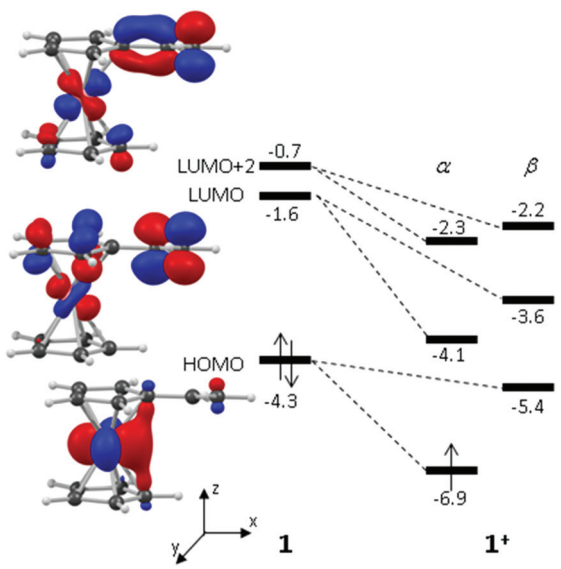


Fig. 4 Key frontier molecular orbitals of **1** with computed energies (eV) for **1** and for the equivalent orbitals of $\mathbf{1}^+$; energies computed with the BP86 functional in THF solvent (PCM approach); orbitals plotted with a maximum contour value of 0.06 au.

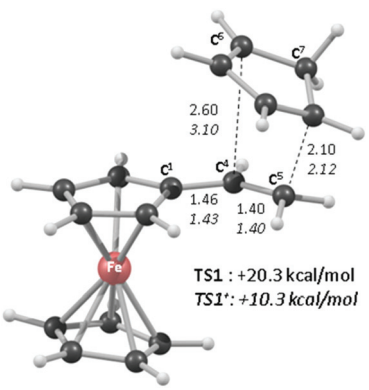
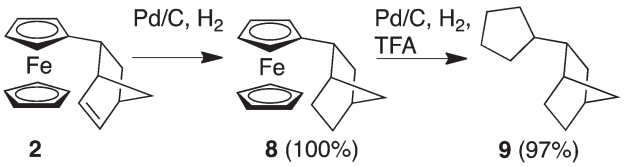


Fig. 5 BP86-optimised transition states for the DA reactions of **1** and $\mathbf{1}^+$ with C_5H_6 (*endo* selectivity); selected distances are in Å and free energies (kcal mol^{-1}) are at the BP86-D3(THF) level and are quoted relative to the separated reactants set to 0.0 kcal mol^{-1} in each case.



Scheme 2 Conversion of **2** to its corresponding cyclopentane derivative **9**.

In conclusion, we have developed redox-umpolung chemistry to undertake DA and thiol-addition reactions of oxidised vinylferrocene. Methodologies have been developed to furnish functionalised Fc derivatives in good yield, which should open up new methods for the chemical and electrochemical functionalisation of surfaces and synthetic and biological macromolecules. Moreover, the redox-umpolung chemistry combined with the reductive cleavage of the Fc moiety described here, provides synthetic protocols to furnish functionalised cyclopentanes, which may find application in the synthesis of complex natural products such as prostaglandins.[26]

Experimental section

General

Dry solvents were obtained using an Innovative Technology Inc. Pure Solv 400-5-MD solvent purification system (activated alumina columns). Reactions were monitored using thin layer chromatography using SiO_2-coated aluminium plates. Flash column chromatography was performed using Silica gel 40–63 μm 60 Å. Melting points were recorded on a SMP-10 Stuart Scientific melting point apparatus and are uncorrected. NMR experiments were performed on either Bruker Avance 500, Bruker Avance 400 spectrometer. All, spectra and were processed using the Mestrelab research iNMR© package (for MacOS X®).

GC-MS was performed on a Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu GCMS-QP2010S gas chromatograph-mass spectrometer, fitted with a 30 m Zebron ZB-5MS column. Column oven temperature: 50.0 °C; injection temperature: 250 °C; injection mode: split; split ratio: 20; pressure: 65.2 kPa; column flow: 1.16 mL min^{-1}. GC program: 50 °C hold 3.00 min, ramp rate 10, max temperature 250 °C hold 2 min, total time 25 min. MS program: start time: 3 min; end time: 25 min, scan speed: 666; start *m*/*z*: 40.00 end *m*/*z*: 350.00.

Compound 2. Cyclopentadiene (1.8 mL, 23.5 mmol) was added to a solution of **1** (0.10 g, 0.47 mmol) in anhydrous THF (5 mL). The mixture was stirred under nitrogen and cooled to −40 °C. $FeCl_3$ (80.4 mg, 0.50 mmol) was then added to the reaction mixture which was stirred at −40 °C for a further 30 minutes. The reaction mixture was then allowed to warm to room temperature before being left to stir at reflux for 24 hours under nitrogen. After this time the reaction mixture was allowed to cool down to room temperature before adding a solution of L-ascorbic acid (0.25 g, 1.40 mmol) in water (10 mL). The solvent was removed under reduced pressure and the product extracted into DCM (5 × 20 mL). The combined organics were then dried over $MgSO_4$, filtered and the solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (100% petroleum ether) to yield the title compound as a yellow oil (116 mg, 88%) as an inseparable mixture of diastereomers (7 : 1, *endo* : *exo*); *endo*-6-ferrocene-bicyclo[2.2.1]hept-2-ene. δ_H (500 MHz, $CDCl_3$) 1.13 (1H, ddd, *J* 11.6, 4.5, 2.6, CH), 1.39 (1H, br. d, *J* 8.1, CH), 1.45 (1H, m, *J* 8.1, CH), 2.14 (1H, ddd, *J* 11.6, 9.1, 3.7, CH), 2.77 (1H, br. m, CH), 2.86 (1H, br. m, CH), 3.07 (1H, ddd, *J* 9.1, 4.5, 4.0, CH), 3.81 (1H, m, Cp), 3.98 (1H, m, Cp), 4.01 (1H, m, Cp), 4.08 (1H, m, Cp), 4.1 (5H, s, Cp′), 5.74 (1H, dd, *J* 5.7, 3.0, =CH), 6.19 (1H, dd, *J* 5.7, 2.9, =CH); δ_C (125 MHz, $CDCl_3$) 34.0 (CH_2), 38.7 (CH), 43.1 (CH), 49.3 (CH), 50.5 (CH_2), 67.0 (Cp), 67.1 (Cp), 67.2 (Cp), 68.4 (Cp), 92.5 (Cp), 68.7 (Cp), 133.5 (=CH), 137.0 (=CH); *m*/*z* (CI^+) 278.0757 $[M]^+$ ($C_{17}H_{18}{}^{56}Fe$ requires 278.0758).

General procedure for thiol additions

Compound **1** (0.47 mmol) was dissolved in dry THF (5 mL) and cooled to −40 °C. $FeCl_3$ (0.52 mmol) was then added to the reaction mixture, and after 5 minutes the thiol (0.52 mmol) was also added. The reaction mixture was allowed to warm to room temperature and was left to stir at room temperature overnight. After this time a mixture of L-ascorbic acid (127 mg, 0.72 mmol) in water (10 mL) was added to the reaction mixture. The crude product was then extracted with DCM (3 × 20 mL) and washed with brine (30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure.

Compound 3. The product was then purified by flash column chromatography (DCM : petroleum ether; 5 : 95) to yield the title compound as a brown oil (53 mg, 67%); δ_H (500 MHz, $CDCl_3$) 1.88 (3H, t, *J* 7.0, CH_3), 1.25–1.37 (6H, m, CH_2), 1.68–1.54 (2H, m, CH_2), 1.65 (3H, d, *J* 6.9, CH_3), 2.44 (2H, td, *J* 7.4, 2.1, CH_2), 3.72 (1H, q, *J* 6.9, CH), 4.11 (2H, t, *J* 1.9, Cp), 4.14 (6H, s, Cp and Cp′), 4.17 (1H, q, *J* 1.7, Cp); δ_C (125 MHz, $CDCl_3$) 14.1 (CH_3), 21.7 (CH_3), 22.7 (CH_2), 28.9 (CH_2), 29.9 (CH_2), 31.2 (CH_2), 31.6 (CH_2), 39.2 (CH), 66.0 (Cp), 67.6 (Cp), 67.7 (Cp), 68.0 (Cp), 68.8 (Cp), 92.2 (Cp); *m*/*z* (EI^+) 330.1108 $[M]^+$ ($C_{18}H_{26}{}^{56}FeS$ requires 330.1105).

Compound 4.[19] The product was then purified by flash column chromatography (DCM : petroleum ether; 1 : 10) to yield the title compound as an orange solid (128 mg, 84%): m.p. 89–90 °C; δ_H (500 MHz, $CDCl_3$) 1.56 (3H, d, *J* = 6.9, CH_3), 3.95–3.96 (1H, m, CH), 4.01–4.03 (1H, m, Cp), 4.04–4.06 (1H, m, Cp), 4.08 (7H, s, Cp′ and Cp), 7.16–7.21 (3H, m, Ph), 7.27–7.29 (2H, m, Ph); δ_C (125 MHz, $CDCl_3$) 21.3 (CH_3), 43.7 (CH), 66.1 (Cp), 67.6 (Cp), 67.7 (Cp), 67.9 (Cp), 68.6 (Cp), 90.8 (Cp), 127.2 (Ph), 128.7 (2 × Ph), 133.1 (2 × Ph), 135.3 (Ph); *m*/*z* (ESI^+) 345.0358 $[M + Na]^+$ ($C_{18}H_{18}{}^{56}FeNaS$ requires 345.0371).

Compound 7. Potassium *tert*-butoxide (250 mg, 2.2 mmol) was added to a solution of (6-bromohexyl)ferrocene (700 mg, 2.0 mmol) in dry DMF (2 mL). The reaction was stirred at

room temperature for 1 h then extracted in Et_2O and washed with water (3 × 50 mL). The organic layer was then dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (petroleum ether) to yield the title compound as an orange oil (320 mg, 60%); δ_H (500 MHz, $CDCl_3$) 1.40–1.46 (2H, m, CH_2), 1.49–1.55 (2H, m, CH_2), 2.05–2.10 (2H, m, CH_2), 2.33 (2H, t, *J* 7.7, CH_2), 4.05 (2H, br-s, 2 × Cp), 4.07 (2H, br-s, 2 × Cp), 4.11 (5H, s, Cp′), 4.95 (1H, dd, *J* 10.2, 2.0, C=CH_2), 5.02 (1H, dd, *J* 17.1, 2.0, C=CH_2), 5.82 (1H, ddt, *J* 17.1, 10.2, 6.7, C=*CH*); δ_C (125 MHz, $CDCl_3$) 29.0 (CH_2), 29.6 (CH_2), 30.7 (CH_2), 33.8 (CH_2), 33.8 (CH_2), 67.2 (Cp), 68.2 (Cp), 68.6 (Cp), 89.5 (Cp), 114.5 (C=*C*H_2), 139.1 (C=*C*H); *m*/*z* (ESI^+) 268.0907 $[M]^+$ ($C_{16}H_{20}{}^{56}Fe$ requires 268.0909).

Compound 8. Pd/C (200 mg) was added to a solution of compound **2** (188 mg, 0.68 mmol) in ethanol (10 mL). The reaction was stirred at room temperature under an atmosphere of H_2 for 4 hours. The palladium residue was then filtered off and the organics were washed with an aqueous solution of L-ascorbic acid (0.1 g in 10 mL). The product was then extracted into DCM (50 mL) and dried over $MgSO_4$, filtered and the solvent was then evaporated under reduced pressure to yield the title compound as a yellow oil (190 mg, 100%) as an inseparable mixture of diastereomers; 1R-ferrocene-bicyclo-[2.2.1]heptane (7 : 1, R : S). δ_H (500 MHz, $CDCl_3$) 1.11–1.26 (3H, m, 3 × CH), 1.28–1.32 (1H, m, CH), 1.36 (1H, m, CH), 1.5 (2H, m, 2 × CH), 1.96 (1H, dddd, *J* 15.0, 11.5, 4.0, 2.0, CH), 2.04 (1H, br. t, CH), 2.24 (1H, br. t, CH), 2.93 (1H, dddd, *J* 11.5, 5.6, 4.0, 1.8, CH), 4.02–4.04 (1H, m, Cp), 4.07–4.09 (3H, m, Cp), 4.10 (5H, s, Cp′); δ_C (125 MHz, $CDCl_3$) 23.4 (CH_2), 30.2 (CH_2), 36.0 (CH_2), 37.5 (CH), 40.7 (CH_2), 41.4 (CH), 43.7 (CH), 66.8 (Cp), 67.2 (Cp), 67.7 (Cp), 68.4 (Cp), 69.2 (Cp), 90.9 (Cp); *m*/*z* (EI^+) 280.0916 $[M]^+$ ($C_{17}H_{20}{}^{56}Fe$ requires 280.0915).

Compound 9. Compound **8** (238 mg, 0.85 mmol) and 10% Pd/C (200 mg) were dissolved/suspended in anhydrous THF (5 mL). TFA (5 mL) was then added to the reaction mixture at 0 °C. The reaction was then stirred for 48 hours at room temperature under an atmosphere of H_2. After this time the black palladium residue was filtered off on a pad of celite and the solvent was removed under reduced pressure. The product was then dried over NaOH and extracted into DCM (3 × 20 mL). Subsequently the combined organics were washed with water (30 mL) and brine (30 mL) and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oil was then dissolved in petroleum ether and filtered through a pad of SiO_2. The solvent was then carefully removed under reduced pressure to yield a mixture of isomers of the title compound as a colourless oil (137 mg, 97%). GC-MS, *m*/*z* (EI), retention time = 13.1 min: 164.1 $[M]^+$.

Acknowledgements

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Notes and references

1 (*a*) *Ferrocenes: Compounds, Properties and Applications*, ed. E. S. Phillips, Nova Science Publishers Inc., 2011; (*b*) *Ferrocenes: Ligands, Materials and Biomolecules*, ed. P. Stepnicka, John Wiley and Sons, 2008; (*c*) *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, ed. A. Togni and T. Hayashi, VCH, Weinheim, 1995.

2 For representative examples see: (*a*) V. Balzani, J. Becher, A. Credi, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, A. M. Talarico and M. Venturi, *J. Org. Chem.*, 2000, **65**, 1947–1956; (*b*) D. Sobransingh and A. E. Kaifer, *Org. Lett.*, 2006, **8**, 3247–3250; (*c*) L. Yang, A. Gomez-Casado, J. F. Young, H. D. Nguyen, J. Cabanas-Danés, J. Huskens, L. Brunsveld and P. Jonkheijm, *J. Am. Chem. Soc.*, 2012, **134**, 19199–19206; (*d*) J. Guo, C. Yuan, M. Guo, L. Wang and F. Yan, *Chem. Sci.*, 2014, **5**, 3261–3266; (*e*) Y. Ahn, Y. Jang, N. Selvapalam, G. Yun and K. Kim, *Angew. Chem., Int. Ed.*, 2013, **52**, 3140–3144; (*f*) Q. Yan, A. Feng, H. Zhang, Y. Yin and J. Yuan, *Polym. Chem.*, 2013, **4**, 1216–1220; (*g*) T. Matsue, D. H. Evans, T. Osa and N. Kobayashi, *J. Am. Chem. Soc.*, 1985, **107**, 3411–3417.

3 For representative examples see: (*a*) J. Liu, P. He, J. Yan, X. Fang, J. Peng, K. Liu and Y. Fang, *Adv. Mater.*, 2008, **20**, 2508–2511; (*b*) M. A. Hempenius, C. Cirmi, F. L. Savio, J. Song and G. J. Vancso, *Macromol. Rapid Commun.*, 2010, **32**, 772–783; (*c*) M. Nakahata, Y. Takashima, Y. Harada and A. Harada, *Nat. Commun.*, 2011, **2**, 511, DOI: 10.1038/ncomms1521; (*d*) C. Yuan, J. Guo, M. Tan, M. Guo, L. Qiu and F. Yan, *ACS Macro Lett.*, 2014, **3**, 271–275.

4 T. Saji, K. Hoshino and S. Aoyagui, *J. Am. Chem. Soc.*, 1985, **107**, 6865–6868.

5 For representative examples see: (*a*) M. E. Hays, C. M. Jewell, D. M. Lynn and N. L. Abbott, *Langmuir*, 2007, **23**, 5609–5614; (*b*) N. L. Abbott, C. M. Jewell, M. E. Hays, Y. Kondo and D. M. Lynn, *J. Am. Chem. Soc.*, 2005, **127**, 11567–11577; (*c*) B. S. Aytar, J. P. E. Muller, S. Golan, Y. Kondo, Y. Talmon, N. L. Abbott and D. M. Lynn, *J. Colloid Interface Sci.*, 2012, **287**, 56–64; (*d*) B. S. Aytar, J. P. E. Muller, Y. Kondo, Y. Talmon, N. L. Abbott and D. M. Lynn, *J. Am. Chem. Soc.*, 2013, **135**, 9111–9120.

6 For representative examples see: (*a*) C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford and J. P. White, *J. Am. Chem. Soc.*, 2006, **128**, 7410–7411; (*b*) V. C. Gibson, N. J. Long, P. J. Oxford, A. J. P. White and D. J. Williams, *Organometallics*, 2006, **25**, 1932–1939; (*c*) M. Sűßner and H. Plenio, *Angew. Chem., Int. Ed.*, 2005, **44**, 6885–6888; (*d*) C. A. Fleckenstein and H. Plenio, *Adv. Synth. Catal.*, 2006, **348**, 1058–1062; (*e*) X. Wang, A. Thevenon, J. L. Brosmer, I. Yu, S. I. Khan, P. Mehrkhodavandi and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2014, **136**, 11264–11267; (*f*) P. Neumann, H. Dib, A.-M. Caminade and E. Hey-Hawkins, *Angew. Chem., Int. Ed.*, 2015, **54**, 311–314; (*g*) Q. Zhang, X. Cui, L. Zhang, S. Luo, H. Wang and Y. Wu, *Angew. Chem., Int. Ed.*, 2015, **54**, 5210–5213.

7 For representative examples see: (*a*) L. Asselberghs, K. Clays, A. Persoons, A. M. McDonagh, M. D. Ward and J. A. McCleverty, *Chem. Phys. Lett.*, 2003, **368**, 408–411; (*b*) M. Malaun, Z. R. Reeves, R. L. Paul, J. C. Jefferey, J. A. McCleverty, M. D. Ward, I. Asselberghs, K. Clays and A. Persoons, *Chem. Commun.*, 2001, 49–50; (*c*) S. Nagashima, M. Murata and H. Nishishara, *Angew. Chem., Int. Ed.*, 2006, **45**, 4298–4301; (*d*) W.-Y. Wang, N.-N. Ma, S.-L. Sun and Y.-Q. Qiu, *Organometallics*, 2014, **33**, 3341–3352.

8 C. U. Pittman, T. V. Jayaraman, R. D. Priester, S. Spencer, M. D. Rausch and D. Macomber, *Macromolecules*, 1981, **14**, 237–241.

9 G.-N. Li, G.-Y. Chen, Z. G. Niu, B.-X. Lei and H. J. Feng, *J. Heterocycl. Chem.*, 2014, **51**, E367–E371.

10 M. Prokešová, S. Toma, A. Kennedy and G. R. Knox, *Tetrahedron*, 1998, **54**, 9175–9186.

11 M. Prokešová, E. Solčániová, S. Toma, K. W. Muir, A. A. Torabi and G. R. Knox, *J. Org. Chem.*, 1996, **61**, 3392–3397.

12 F. A. Khan and S. K. Upadhyay, *Synthesis*, 2009, 2773–2777.

13 T. D. Turbitt and W. E. Watts, *J. Chem. Soc. D*, 1971, 631.

14 J. Lorans, F. Pierre, L. Toupet and C. Moinet, *Chem. Commun.*, 1997, 1279–1280.

15 R. M. Gleixner, K. M. Joly, M. Tremayne, B. M. Kariuki, L. Male, D. M. Coe and L. R. Cox, *Chem. – Eur. J.*, 2010, **16**, 5769–5777.

16 H. J. Al-Najjar, A. Barakat, A. M. Al-Majid, Y. N. Mabkhot, M. Weber, H. A. Ghabbour and H.-K. Fun, *Molecules*, 2014, **19**, 1150–1162.

17 R. Jiang, Y. Zhang, Y.-C. Shen, X. Zhu, X.-P. Xu and S. J. Ji, *Tetrahedron*, 2010, **66**, 4073–4078.

18 (*a*) I. Martínez-Montero, S. Bruña, A. M. González-Vadillo and I. Cuadrado, *Macromolecules*, 2014, **47**, 1301–1315; (*b*) A. Enríquez, A. M. González-Vadillo, I. Martínez-Montero, S. Bruña, L. Leemans and I. Cuadrado, *Organometallics*, 2014, **33**, 7307–7317.

19 B. Misterkiewicz, C. Kajdas, M. Dominiak, J. Dabrowski and J. Wasilewski, *Chem. Ind.*, 1981, 433–434.

20 Crystal data for **4**: $C_{18}H_{18}FeS$, M_r = 322.23, monoclinic system, space group $P2_1/c$, a = 19.1342(5), b = 7.59440(10), c = 10.3523(2) Å, β = 92.834(2), V = 1502.48(5) Å^3. Z = 4, ρ_{calcd} = 1.425 g cm^{-3}; Mo Kα radiation, λ = 0.71073 Å, μ = 1.129 mm^{-1}, T = 150 K. 23151 data (2958 unique, R_{int} = 0.0233, θ < 26°) were collected on an Oxford Diffraction Gemini A Ultra CCD diffractometer and were corrected for absorption (transmission 0.729–0.953). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to give wR_2 = 0.058, R_1 = 0.025, S = 1.047 for 182 parameters. Residual electron density extrema were 0.28 and −0.35 e Å^{-3}. CCDC number is 1439981.

21 C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.*, 2004, **104**, 6217–6254.

22 (*a*) G. Gokel, P. Hoffman, H. Klusacek, D. Marquarding, E. Ruch and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 64; (*b*) T. Ireland, J. J. A. Perea and P. Knochel, *Angew. Chem., Int. Ed.*, 1999, **38**, 1457–1460; (*c*) R. Gleiter, C. Bleiholder and F. Rominger, *Organometallics*, 2007, **26**, 4850–4859; (*d*) K. Kowalski, M. Linseis, R. F. Winter, M. Zabel, S. Záliš, H. Kelm, H.-J. Krüger, B. Sarkar and W. Kaim, *Organometallics*, 2009, **28**, 4196–4209.

23 DFT calculations were run with the Gaussian 03 and 09 suite of programs. Optimisations employed the BP86 functional in combination with an SDD pseudopotential and basis set on Fe and 6-31g** basis sets on C and H. See ESI† for full details and references.

24 A. M. Allgeier and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 1998, **37**, 894–908.

25 (*a*) V. I. Sokolov, L. L. Troitskaya, N. S. Khrushcheva and O. A. Reutov, *J. Organomet. Chem.*, 1989, **378**, 227–233; (*b*) F. V. Meurs, F. W. Metselaar, A. J. A. Post, J. A. A. M. V. Rossum, A. M. V. Wijk and H. V. Bekkum, *J. Organomet. Chem.*, 1975, **84**, C22–C24.

26 S. Das, S. Chandrasekhar, J. S. Yadav and R. Grée, *Chem. Rev.*, 2007, **107**, 3286–3337.