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A rapid approach to ferrocenophanes via ring-closing metathesis

Andrew J. Locke, Claire Jones, Christopher J. Richards *

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK

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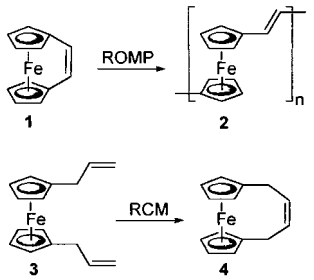
Abstract

The synthesis of [4]ferrocenophanes containing a (*Z*)-1,4-but-2-endiyl bridge is described. Starting from either achiral (R = H), *meso* (R = Me, Ph) or scalemic (R = Me, 4-MeOC$_6$H$_4$) 1,1′-di{CHR(OAc)}ferrocenes, vinylation with a mixture of vinyl magnesium chloride and zinc chloride proceeds readily and with significant retention of configuration to give allylferrocenes in an isomer ratio of > 3:1. Ring-closing metathesis with Ru(CHPh)Cl$_2$(PCy$_3$)$_2$ results in conversion of the achiral (R = H) and all the *meso*-diastereoisomers (R = Me, Ph, 4-MeOC$_6$H$_4$) to their corresponding *cis*-disubstituted [4]ferrocenophanes. Only a single *trans*-disubstituted [4]ferrocenophane was synthesised (R = Me), the larger substituents preventing cyclisiation by this method.

Keywords: Ferrocenes; Ferrocenophanes; Stereospecific substitution; Ring-closing metathesis

1. Introduction

Many new ferrocene-based structures, especially single enantiomer derivatives, are currently being studied as new catalysts and materials [1]. The very low energy barrier to rotation of the cyclopentadienyl rings in ferrocene (~ 4 kJ mol^{-1}) is often crucial to the application of these various derivatives. However, restricting this rotation by linking the rings leads to unique structural forms whose rigidity or constrained flexibility may itself be of benefit. Although many methods for the synthesis of ferrocenophanes are known [2], these are generally unsuitable for the synthesis of functionalised derivatives, and reports on the asymmetric synthesis of ferrocenophanes only appeared very recently [3]. In planning a more general approach, our attention focused on the use of ring-closing metathesis, which has been shown to be applicable for the generation of a variety of ring forms and sizes [4]. As highly strained *ansa*-(vinylene)[2]ferrocenophane **1** has been used as a monomer for ROMP to give poly(ferrocenylenevinylene) **2** (Scheme 1) [5], we reasoned that a ring-closure approach should be tested on 1,1′-diallylferrocene (**3**) for the synthesis of [4]ferrocenophane **4**. In this paper, we report on the applicability of this approach for the synthesis of **4** and derivatives of this ferrocenophane, and describe a new methodology for the generation of precursor 1,1′-diallylferrocenes.



Scheme 1.

2. Results and discussion

1,1′-Diallylferrocene **3** has previously been synthesised directly from allylcyclopentadiene and an iron(II) source [6]. In seeking a subtler approach for the generation of 1,1′-diallylferrocenes, we noted that α-ferrocenyl acetates have been shown to undergo substitution reactions with a variety of organozinc reagents, includ-

* Corresponding author. Present address: Department of Chemistry, Queen Mary, University of London, Mile End Road, London E1 4NS, UK. Fax: +44-29-2087-4030.

E-mail address: c.j.richards@qmul.ac.uk (C.J. Richards).

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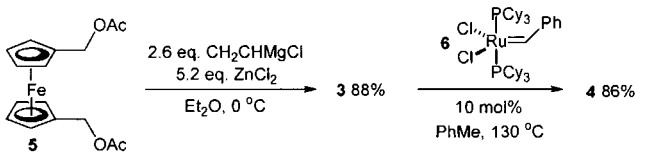
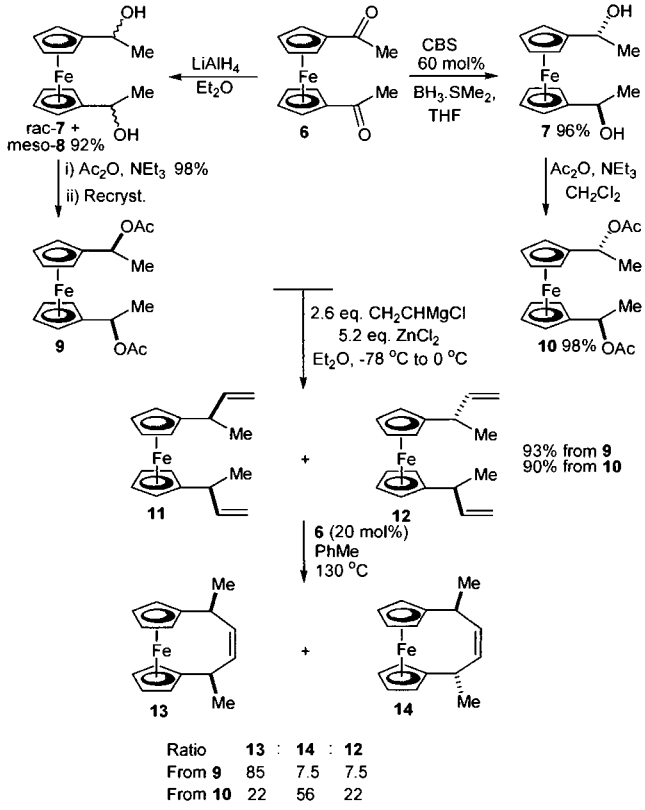


Scheme 2.



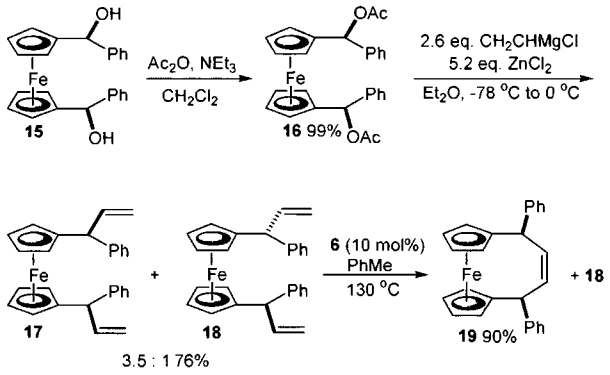
Scheme 3.

ing (*E*)-styrylzinc bromide [7]. These reactions require the addition of $BF_3 \cdot OEt_2$ to promote formation of intermediate α-ferrocenylcarbenium ions. Thus, diacetate **5** was treated at room temperature with a premixed combination of vinylmagnesium chloride (2.6 equivalents) and zinc chloride (2.6 equivalents), this mixture having previously been reported to generate vinylzinc chloride in situ (Scheme 2) [8]. Satisfyingly this led to the isolation of **3** in 57%, but only when $BF_3 \cdot OEt_2$ was omitted from the reaction mixture. In its presence the starting material was consumed but the product(s) obtained could not be isolated and characterised. In the absence of $ZnCl_2$ only 1,1′-di(hydroxymethyl)ferrocene was obtained. The yield for this step was found to increase to 88% by increasing the quantity of $ZnCl_2$ to 5.2 equivalents. Thus $ZnCl_2$ is the likely Lewis acid in the this reaction promoting removal of the acetate leaving group, and it is noteworthy that application of this reagent is known to result in a similar reaction between α-ferrocenylacetates and silyl enol ethers [9].

Subsequent treatment of **3** with 10 mol% of the commercially available metathesis catalyst **6**, at room temperature under a nitrogen atmosphere in CH_2Cl_2, gave ferrocenophane **4** [10] in 59% yield contaminated with a small amount of starting material (ratio 6:1). When repeated in toluene at 130 °C the yield of **4** increased to 86%, accounting for unreacted starting material (**4**:**3** = 7.5:1). The purification of this parent ferrocenophane proved troublesome due to its lack of polarity.

To use this method for the synthesis of ferrocenophanes containing substituents α to ferrocene introduces a stereochemical dimension to the chemistry. To examine the effect of methyl substituents, diketone **6** was reduced with $LiAlH_4$ to give a 1:1 diastereomeric mixture of the *racemic* and *meso* diols **7** and **8** (Scheme 3). Following acetylation, the *meso* isomer **9** of the resulting diesters was isolated by repeated recrystallisation from EtOAc–petroleum ether. The corresponding scalemic diastereoisomer **10** was isolated via application of the CBS oxazaborolidine catalyst [11] to **6** as previously reported [12], followed by acetylation to the diester. The minor *meso* isomer formed during the CBS reduction constituted $< 5\%$ of the material used to investigate the diastereoselectivity of acetate/vinyl substitution.

The vinylation of **9** and **10** was carried out by adding these α-ferrocenylacetates separately to suspensions of pre-mixed zinc chloride/vinyl magnesium chloride in Et_2O cooled to -78 °C. The reaction mixtures were allowed to slowly warm to room temperature followed by isolation of the resulting diallylferrocenes in good yield. However, the products of both reactions gave identical ^{1}H-NMR spectra such that the ratio of diastereosomers **11** and **12** could not be determined by this means, nor could they be separated by HPLC. Subsequent ring-closing metathesis with 20 mol% of Grubbs' catalyst in toluene at 130 °C for 24 h converted the diallylferrocenes into two ferrocenophanes, the presence of which was indicated by new peaks in the ^{1}H-NMR spectra at 3.24 and 3.31 ppm. Under these conditions, the vinylation product arising originally from *meso*-**9** gave essentially a single ferrocenophane in 87%, accounting for a small amount of unreacted starting material. Thus vinylation of **9** proceeds with retention of relative stereochemistry to give predominantly **11** which in turn undergoes facile ring-closing metathesis to **13**. In contrast, the vinylation products arising originally from **10** required an increase in the reaction time to 48 h to achieve a reasonable conversion to the C_2-symmetric ferrocenophane **14**. Given the forcing conditions required, the unreacted starting material is assigned as **12** indicating that vinylation of **10** to this compound also preceded with retention of stereochemistry ($> 3:1$). That conversion



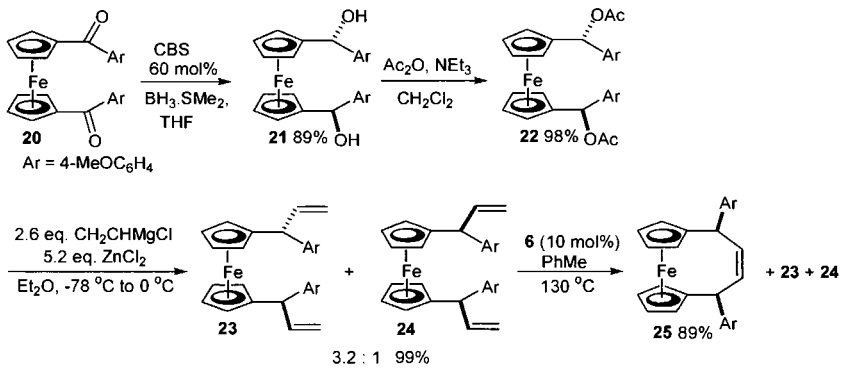
Scheme 4.

to the *cis*-ferrocenophane is preferred is presumably due to the product, and the metallacycle leading to it, being able to adopt a conformation with two pseudo-equatorial methyl substituents.

In light of this preference, we next sought to test the methodology with the synthesis of the corresponding *cis*-ferrocenophane containing two phenyl substituents. Fortunately, the required diol **15** (Scheme 4) is known, being readily obtained by recrystallisation of a 1:1 mixture of *meso* and *racemic* diastereoisomers [13]. Following acetylation, the diester **16** was subject to vinylation as before to give a 3.5:1 ratio of diallyl diastereoisomers. In this instance there was no ambiguity about the ratio of products formed due to differences in their ^{1}H-NMR spectra. Ring-closing metathesis led to conversion of the major isomer to a new ferrocenophane, confirming the precursor as **17** and the product as **19**. This was isolated free of the unreacted diallyl derivative **18** by recrystallisation. Although the divinylation steps in this and the previous sequences proceed with fair retention of stereochemical integrity, related reactions of α-ferrocenyl acetates [7] and α-ferrocenyl amines [14] with organozinc reagents, and α-ferrocenyl ethers with silyl ketene acetals [13,15], proceed with essentially complete retention of configuration. In an attempt to improve the selectivity, Et_2O was replaced by THF, this change in solvent having previously been demonstrated to increase the selectivity of a related reaction [7]. However, although the reaction proceeded cleanly, the ratio of **17** to **18** decreased to only 1.55:1.

As a final test of the method, we aimed to synthesise a functionalised ferrocenophane displaying C_2 symmetry. It was reasoned that use of 4-methoxyphenyl substituents would aid stabilisation of intermediate α-ferrocenyl carbenium ions, and following deprotection the resulting phenol group is synthetically versatile. Thus diketone **20** was reduced using the existing CBS methodology and the resulting diol **21** acetylated as before to give a 9:1 ratio of (*R*,*R*) to *meso* diastereoisomers (Scheme 5). Attempts to use 4-bromo or 4-iodophenyl substituents in the reduction step resulted in extremely insoluble diols that prevented further manipulation. Thus, divinylation was restricted to **22**, and this proceeded to give an essentially quantitative yield of a 3.2:1 mixture of **23**–**24**, the assumption of **24** being the minor isomer being confirmed by its conversion to the new ferrocenophane **25**. This was isolated following recrystallisation but all attempts to ring-close **23** proved unsuccessful despite increased catalyst loadings, prolonged reaction times, and replacement of **6** with the more reactive catalyst $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$, Ar = 2,6-di-^{i}PrC$_6H_3$) [16].

In conclusion, we have demonstrated that ferrocenophanes may be synthesised in two steps from α-ferrocenyl acetates. Starting with α-substituted derivatives (R = Me, Ph, 4-MeOC$_6$H$_4$) stereospecific vinylation proceeds largely with retention of configuration to give allylferrocenes with an isomer ratio of greater than 3 to 1. Ring-closing metathesis proceeds readily on all the *meso*-diastereoisomers to give *cis*-disubstituted ferrocenophanes. Only a single *trans*-disubstituted ferrocenophane was synthesised (R = Me), larger substituents preventing cyclisiation. The use of this methodology for the construction of conformationally restricted bidentate ligands is currently under investigation.



Scheme 5.

3. Experimental

All melting points were carried out using a Reichert hot stage microscope and are uncorrected. All NMR spectra were recorded using a Bruker Fourier Transform DPX400MHz spectrometer. Samples were recorded in deuteriochloroform unless otherwise stated. All coupling constants are measured in Hertz. Elemental analyses were recorded using a Perkin–Elmer 240 °C elemental analyser. High-resolution mass spectra were recorded at the EPSRC National Mass Spectrometry Service at University of Wales, Swansea. THF and Et_2O were distilled from sodium benzophenone ketal. Dichloromethane and toluene, were distilled from calcium hydride. Petroleum ether refers to the fraction boiling in the 40–60 °C range. Kieselgel 60 F_{254} aluminium sheets were used for TLC and Matrix silica 60, 35–70 μm used for all column chromatography. All reactions were carried out under an atmosphere of nitrogen. Starting materials **5** [17] **15** [13] and **20** [18] have been previously reported, and **6** is commercially available.

3.1. Synthesis of (R,R)-1,1′-bis(α-hydroxy-4-methoxybenzyl)ferrocene (21)

Following the previously reported procedure [3c], **20** (2.00 g, 4.40 mmol), (*S*)-α,α-diphenyl-β-methyloxazaborolidine (0.73 g, 2.63 mmol), $BH_3 \cdot THF$ (1.76 ml, 1.76 mmol) $BH_3 \cdot Me_2S$ (1.76 ml, 3.52 mmol) and THF (120 ml) gave a yellow solid (1.79 g, 3.91 mmol, 89%). Melting point: 117–119 °C. IR (Nujol, cm^{-1}):ν_{max} 3451.8, 1610.0, 1581.9. ^{1}H-NMR (acetone-d_6, 400 MHz): δ 3.65 (s, 6H, OCH_3), 4.01 (m, 2H, Fc), 4.10 (m, 2H, Fc), 4.13 (s, 2H, Fc), 4.31 (s, 2H, Fc), 5.18 (d, 2H, $J = 2.4$ Hz, FcCHOH), 5.50 (d, 2H, $J = 2.4$ Hz, FcCHOH), 6.73 (d, 4H, $J = 8.8$ Hz, Ar), 7.20 (d, 4H, $J = 8.4$ Hz, Ar). ^{13}C-NMR (acetone-d_6, 100 MHz): δ 55.83 (OCH$_3$), 67.70 (Fc), 67.83 (Fc), 68.82 (Fc), 69.00 (Fc), 73.08 (FcCH), 93.06 (Fc-*ipso*), 114.50 (Ar), 128.62 (Ar), 139.28 (Ar-*ipso*), 160.07 (Ar-*ipso*). LSIMS; m/z: 458.1 ([M$^+$], 100%), 441.0 ([M − OH], 25). HRES; m/z Found: [M$^+$], 458.1185. Calc. for $C_{26}H_{26}FeO_4$: 458.1180.

3.2. General procedure A. The acetylation of 1,1′-bis(α-hydroxy)ferrocenes

The appropriate 1,1′-bis(α-hydroxy)ferrocene (1.0 mmol) was dissolved in dry CH_2Cl_2 (7.5 ml) at room temperature (r.t.). Acetic anhydride (2.1 mmol), Et_3N (2.1 mmol) and DMAP (0.01 mmol) were added to the solution. After being stirred for 120 min, the reaction mixture was quenched by the addition of saturated $NaHCO_3$(aq.) (7.5 ml) and the two phases separated. The aqueous phase was extracted with CH_2Cl_2 (2 ml), the organic phases combined and washed with saturated NaCl(aq.) (7.5 ml). The two phases were separated and the aqueous phase extracted with additional CH_2Cl_2 (2 ml). The organic phases were combined, dried ($MgSO_4$), filtered and evaporated in vacuo. Yields refer to material isolated after aqueous workup.

3.2.1. Synthesis of (R,S)-1,1′-bis(α-acetoxyethyl)ferrocene (9)

Following general procedure A, a mixture of *rac*-**7** and *meso*-**8** (from $LiAlH_4$ reduction of **6** [19]) (2.357 g, 8.60 mmol) gave a yellow crystalline solid (3.018 g, 8.42 mmol, 98%). Repeated recrystallisation from petroleum ether–EtOAc, yielded a pure sample of the (*R*,*S*)-diastereoisomer. Melting point: 80–82 °C. IR (Nujol, cm^{-1}): ν_{max} 1737.6. ^{1}H-NMR (400 MHz): δ 1.57 (d, 6H, $J = 6.8$ Hz, FcCHCH_3), 2.07 (s, 6H, COCH_3), 4.17 (brds, 4H, Fc), 4.21 (brds, 2H, Fc), 4.27 (brds, 2H, Fc), 5.84 (q, 2H, $J = 6.7$ Hz, FcCH). ^{13}C-NMR (100 MHz): δ 20.42 (FcCHCH$_3$), 21.81 (COCH$_3$), 67.08 (FcCH), 68.97 (Fc), 69.30 (Fc), 69.43 (Fc), 69.67 (Fc), 88.99 (Fc-*ipso*), 170.92 (C=O). LSIMS; m/z: 358.1 ([M$^+$], 100%), 359.1 ([MH$^+$], 23), 299.1 ([M − CH_3CO_2], 45) and 207.7 ([M − $C_5H_4CH(CH_3)OAc$], 54). HRES; m/z Found: [M$^+$], 358.0871. Calc. for $C_{18}H_{22}FeO_4$: [M$^+$], 358.0867.

Similarly, (*R*, *R*)-1,1′-bis(α-hydroxyethyl)ferrocene **7** (0.183 g, 0.67 mmol — obtained by CBS reduction of **6** [12b]), gave **10** [12b] as a yellow crystalline solid (0.234g, 0.65 mmol, 98%).

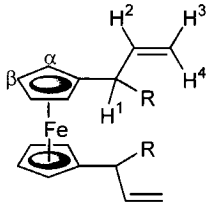
3.2.2. Synthesis of (R,S)-1,1′-bis(α-acetoxybenzyl)ferrocene (16)

Following the general procedure A, **15** [13] (0.365 g, 0.92 mmol) gave a yellow crystalline solid (0.439 g, 0.91 mmol, 99%). Melting point: 125–127 °C. IR (Nujol, cm^{-1}): ν_{max} 1725.1. ^{1}H-NMR (400 MHz): δ 2.02 (s, 6H, COCH_3), 3.91 (brds, 2H, Fc), 3.97 (brds, 2H, Fc), 4.02 (brds, 2H, Fc), 4.15 (brds, 2H, Fc), 5.65 (s, 2H, FcCH), 7.21–7.29 (m, 10H, Ph). ^{13}C-NMR (100 MHz): δ 20.29 (COCH$_3$), 67.34 (Fc), 67.58 (Fc), 68.24 (Fc), 68.38 (Fc), 73.04 (FcCH), 87.37 (Fc-*ipso*), 126.18 (Ph), 127.08 (Ph-*para*), 127.79 (Ph), 138.88 (Ph-*ipso*), 168.97 (C=O).

3.2.3. Synthesis of (R,R)-1,1′-bis(α-acetoxy-4-methoxybenzyl)ferrocene (22)

Following the general procedure A, **21** (0.257 g, 0.56 mmol) gave an amorphous orange solid (0.299 g, 0.55 mmol, 98%). IR (Nujol, cm^{-1}) ν_{max} 1731.8 and 1609.4. ^{1}H-NMR (400 MHz): δ 2.02 (s, 6H, COCH_3), 3.74 (s, 6H, OCH_3), 3.82 (m, 2H, Fc), 3.97 (m, 2H, Fc), 4.02 (m, 2H, Fc), 4.23 (m, 2H, Fc), 6.53 (s, 2H, FcCH), 6.80 (dt, 4H, $J = 9.3$, 2.4 Hz, Ar), 7.23 (dt, 4H, $J = 9.3$, 2.3 Hz, Ar). ^{13}C-NMR (100 MHz): δ 20.35 (COCH$_3$), 54.25 (OCH$_3$), 67.34 (Fc), 67.52 (Fc), 68.24 (Fc), 68.29

Table 1
^{1}H-NMR data for allylferrocenes[a]



Compound	H^1	H^2	H^3	H^4	α,β	R
3	3.01, 4H, *J* 6.6	5.91, 2H, m	4.92–5.00, 4H, m	4.92–5.00, 4H, m	3.95–4.10, 8H, m	$=H^1$
11	3.10, 2H, pent, *J* 7.0	5.90, 2H, ddd, *J* 17.2, 10.0, 7.2	4.89, 2H, brd, *J* 10.8	4.93, 2H, dt, *J* 17.2, 1.4	3.87–4.02, 8H, m	1.22, 6H, d, *J* 6.8
12	3.10, 2H, pent, *J* 7.0	5.90, 2H, ddd, *J* 17.2, 10.0, 7.2	4.89, 2H, brd, *J* 10.1	4.93, 2H, dt, *J* 17.2, 1.4	3.87–4.02, 8H, m	1.22, 6H, d, *J* 6.7
17	4.31, 2H, d, *J* 7.6	6.17, 2H, ddd, *J* 17.2, 10.0, 7.4	5.04, 2H, dt, *J* 10.0, 1.6	4.90, 2H, dt, *J* 17.1, 1.6	3.88, 2H, m. 3.99–4.04, 6H, m.	7.04–7.23, 10H, m.
18	4.23, 2H, d, *J* 7.2	6.17, 2H, ddd, *J* 17.2, 10.0, 7.4	5.01, 2H, dt, *J* 10.0, 1.6	4.86, 2H, dt, *J* 17.2, 1.6	3.84, 2H, m. 3.99–4.04, 6H, m.	7.04–7.23, 10H, m.
23	4.19, 2H, d, *J* 7.6	6.15, 2H, ddd, *J* 17.0, 10.0, 7.2	5.00, 2H, dt, *J* 10.0, 1.6	4.84, 2H, dt, *J* 16.8, 1.4	3.83, 2H, m. 4.00–4.03, 6H, m.	3.71, 3H, s, OCH_3. 6.74, 4H, d, *J* 8.8, Ar. 6.97, 4H, d, *J* 8.4, Ar.
24	4.27, 2H, d, *J* 7.6	6.16, 2H, ddd, *J* 17.4, 9.8, 7.2	5.02, 2H, dt, *J* 10.0, 1.2	4.88, 2H, dt, *J* 17.0, 1.4	3.86, 2H, m. 4.00–4.03, 6H, m.	3.70, 3H, s, OCH_3. 6.74, 4H, d, *J* 8.8, Ar. 6.97, 4H, d, *J* 8.4, Ar.

[a] 400 MHz, $CDCl_3$.

(Fc), 72.76 (Fc*C*H), 87.57 (Fc-*ipso*), 112.58 (Ar), 127.57 (Ar), 131.25 (Ar-*ipso*), 158.25 (Ar-*ipso*), 169.02 (*C*=O).

3.3. General procedure B. The vinylation of 1,1′-bis(α-acetoxy)ferrocenes

Under vacuum $ZnCl_2$ (5.2 mmol) was melted and allowed to cool to r.t. under an atmosphere of nitrogen prior to dissolution in dry Et_2O (45 ml). After cooling to 0 °C, magnesium vinyl chloride (1.6 M in THF, 2.6 mmol) was added dropwise over 15 min after which the resultant white suspension was stirred at 0 °C for a further 60 min, followed by cooling to −78 °C. In a separate vessel the appropriate 1,1′-bis(α-acetoxy)ferrocene (1.0 mmol) was dissolved in dry Et_2O (55 ml), cooled to −78 °C, and then added to the $ZnCl_2$/vinyl Grignard mixture via canula (washed through with further dry Et_2O (5 ml)). The reaction mixture was maintained at −78 °C for at least an hour and allowed to warm to r.t. overnight. The resultant opaque yellow solution was quenched with water (100 ml), the two phases separated and the aqueous phase extracted with Et_2O (10 ml). The organic phases were combined and washed with saturated $NaHCO_3$(aq.) (100 ml). Following separation, the aqueous phase was extracted with additional Et_2O (10 ml). The organic phases were combined and washed with saturated NaCl(aq.) (100 ml), dried ($MgSO_4$), filtered and evaporated in vacuo, to yield a crude product (Tables 1 and 2).

3.3.1. Synthesis of 1,1′-diallylferrocene (3)

Following the general procedure B, **5** (0.156 g, 0.47 mmol) gave **3** [6] an orange oil (0.111g, 0.42 mmol, 88%).

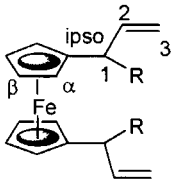
3.3.2. Synthesis of (R,S)-1,1′-di(1-methyl-2-propenyl)-ferrocene (11)

Following the general procedure B, **9** (0.200 g, 0.56 mmol) gave an orange oil containing predominantly **11** and a smaller amount of **12** — the exact ratio could not be determined (0.152 g, 0.52 mmol, 93%). IR (Nujol, cm^{-1}): ν_{max} 1634.3. LSIMS; *m*/*z*: 295.1 ([MH^+], 100%), 294.1 ([M^+], 100%). HRES; *m*/*z* Found: [MH^+], 295.1145. Calc. for $C_{18}H_{23}Fe$: 295.1149.

3.3.3. Synthesis of (S,S)-1,1′-di(1-methyl-2-propenyl)-ferrocene (12)

Following the general procedure B, **10** (0.186 g, 0.52 mmol) gave an orange oil containing predominantly **12** and a smaller amount of **11** — the exact ratio could not be determined (0.138 g, 0.47 mmol, 90%). IR (Nujol, cm^{-1}): ν_{max} 1634.5. LSIMS; *m*/*z*: 295.1 ([MH^+], 100%), 294.1 ([M^+], 100%). HRES; *m*/*z* Found: [MH^+], 295.1145. Calc. for $C_{18}H_{23}Fe$: 295.1149.

Table 2
^{13}C-NMR data for allylferrocenes[a]



Compound	C(1)	C(2)	C(3)	*Ipso*	α,β	R
3	34.03	137.94	115.48	87.51	68.41, 68.94	
11	36.12	142.56	111.57	92.44	65.81, 66.08, 66.73, 66.90	19.78
12	36.13	142.58	111.56	92.44	65.75, 66.15, 66.73, 66.90	19.76
17	48.66	143.01	113.83	90.25	67.09, 67.14, 67.46, 67.70	125.20, Ph (*para*). 127.04, Ph (*ortho*/*meta*). 127.17, Ph (*ortho*/*meta*). 140.08, Ph (*ipso*)
18	48.62	142.94	113.75	90.19	66.78, 67.14, 67.53, 67.98	125.20, Ph (*para*). 127.10, Ph (*ortho*/*meta*). 127.17, Ph (*ortho*/*meta*). 140.16, Ph (*ipso*)
23	47.73	140.47	113.45	90.52	66.72, 67.09, 67.50, 67.92	54.12, –OCH_3. 112.50, Ar. 128.03, Ar. 135.21, Ar (*ipso*-FcCH). 156.92, Ar (*ipso*-OCH_3)
24	47.77	140.39	113.53	90.58	67.01, 67.12, 67.43, 67.66	54.24, –OCH_3. 112.50, Ar. 127.98, Ar. 135.27, Ar (*ipso*-FcCH). 156.92, Ar (*ipso*-OCH_3)

[a] 100 MHz, $CDCl_3$.

*3.3.4. Synthesis of (R,S)-1,1′-di(1-phenyl-2-propenyl)-ferrocene (**17**) and (R*,R*)-1,1′-di(1-phenyl-2-propenyl)ferrocene (**18**)*

Following the general procedure B, **16** (0.370 g, 0.77 mmol) gave an orange oil as a 3.5:1 mixture of diastereoisomers **17** and **18** (0.245 g, 0.59 mmol, 76%). IR (Nujol, cm^{-1}): ν_{max} 3085.2, 1634.3, 1601.3. LSIMS; *m*/*z*: 418.0 ([M^+], 100%), 419.1 ([MH^+], 34). HRES; *m*/*z* Found: [M^+], 418.1381. Calc. for $C_{28}H_{26}Fe$: [M^+], 418.1384.

*3.3.5. Synthesis of (R,R)-1,1′-di(1-{4-methoxyphenyl}-2-propenyl)ferrocene (**23**) and (R,S)-1,1′-di(1-{4-methoxyphenyl}-2-propenyl)ferrocene (**24**)*

Following the general procedure B, **22** (0.299 g, 0.55 mmol) gave an orange solid as 3.2:1 mixture of diastereoisomers **23** and **24** (0.260 g, 0.54 mmol, 99%). IR (Nujol, cm^{-1}): ν_{max} 3076.5, 1633.3, 1608.9, 1582.6. LSIMS; *m*/*z*: 479.0 ([MH^+], 35%), 478.0 ([M^+], 100). HRES; *m*/*z* Found: M^+, 478.1600. Calc. for $C_{30}H_{30}FeO_2$: [M^+], 478.1595.

3.4. General procedure C. The ring-closing metathesis of 1,1′-bis(2-propenyl)ferrocenes

To a solution of $Ru(CHPh)Cl_2(PCy_3)_2$ (**6**) (0.028 g, 0.034 mmol)[1] in dry toluene (14 ml) was added via canula a solution of the appropriate diallyl ferrocene (0.34 mmol) dissolved in dry toluene (18 ml). The reaction mixture was refluxed at 130 °C for 24 h before cooling to r.t. The solution was filtered through SiO_2, washing through with petroleum ether to remove catalyst residues, and the solvent evaporated in vacuo to yield the metathesis product(s) (Tables 3 and 4).

*3.4.1. Synthesis of 1,1′-((Z)-1,4-but-2-endiyl)ferrocene (**4**)*

Following the general procedure C, **3** (0.111 g, 0.42 mmol) and **6** (0.034 g, 0.042 mmol) gave **4** [10] as oily orange crystals consisting of a 7.5:1 ratio of **4**:**3** (0.088 g). The yield of **4** is 86% accounting for recovered starting material. Kugelrohr sublimation gave yellow crystals of **4** essentially free of the starting material. IR (Nujol, cm^{-1}): ν_{max} 3086.1, 1461.2. *m*/*z* Found: [M^+], 238.0447. Calc. for $C_{14}H_{14}Fe$: [M^+], 238.0445.

*3.4.2. Synthesis of (R,S)-1,1′-((Z)-1,4-dimethyl-1,4-but-2-endiyl)ferrocene (**13**)*

Following the general procedure C, the 1,1′-di(1-methyl-2-propenyl)ferrocene derived from **9** (0.038 g, 0.13 mmol) and **6** (0.021 g, 0.026 mmol) gave a yellow oil (0.030 g) consisting of a 85:7.5:7.5 mixture of **13**:**14**:**12**. The yield of **13** is 87%, based on recovered starting material. IR (Nujol, cm^{-1}); ν_{max} 3086.1, 1636.8. LSIMS; *m*/*z*: 294.1 (unreacted starting material **12**, 100%), 266.1 ([M^+] 20%). Acc Mass ES; *m*/*z* Found: [MH^+], 267.0835. Calc. for $C_{16}H_{19}Fe$: [MH^+], 267.0836.

[1] In some examples the catalyst loading was increased to 0.056 g, 0.068 mmol.

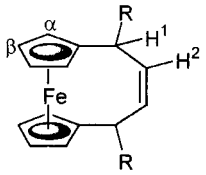
3.4.3. Synthesis of (S,S)-1,1′-((Z)-1,4-dimethyl-1,4-but-2-endiyl)ferrocene (**14**)

Following the general procedure C, the 1,1′-di(1-methyl-2-propenyl)ferrocene derived from **10** (0.029 g, 0.10 mmol) and **6** (0.016 g, 0.019 mmol) gave a yellow oil (0.022 g) consisting of a 56:22:22 mixture of **14**:**13**:**12**. The yield of **14** from **12** is 78%, based on recovered starting material. IR (Nujol, cm^{-1}): ν_{max} 3096.2, 1637.7. LSIMS; *m*/*z*: 294.1 (unreacted starting material **12**, 100%), 266.1 ([M^+] 20%). HRES; *m*/*z* Found: [MH^+], 267.0835. Calc. for $C_{16}H_{19}Fe$: 267.0836.

3.4.4. Synthesis of (R,S)-1,1′-((Z)-1,4-diphenyl-1,4-but-2-endiyl)ferrocene (**19**)

Following the general procedure C, a 3.5:1 ratio of **17**:**18** (0.141 g, 0.34 mmol) and **6** (0.028 g, 0.034 mmol) gave a yellow solid (0.123 g) consisting of a 76:24 mixture of **19**:**18**. The yield of **19** is 90% based on recovered starting material. Recrystallisation of the mixture from toluene–petroleum ether resulted in the isolation of a pure sample of **19**. Melting point: 223.5–225 °C. IR (Nujol, cm^{-1}): ν_{max} 1598.0. LSIMS; *m*/*z*: 390.1 ([M^+], 100%). HRES; *m*/*z* Found: [M^+], 391.1151. Calc. for $C_{26}H_{22}Fe$: [M^+], 391.1149.

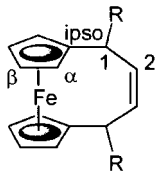
Table 3
^{1}H-NMR data for ferrocenophanes[a]



Compound	H^1	H^2	α,β	R
4	2.89, 4H, d, *J* 6.4	5.96 2H, tt, *J* 5.0, 2.0	3.87–4.00, 8H, m	$=H^1$
13	3.24, 2H, qd, *J* 7.0, 4.4	5.61 2H, d, *J* 4.4	3.90, 2H, m, Fc. 3.97, 2H, m, Fc. 4.00, 2H, m, Fc. 4.09, 2H, m, Fc.	1.22, 6H, d, *J* 6.8
14	3.31, 2H, pt, *J* 6.8, 2.0	5.81 2H, dd, *J* 4.6, 1.8	3.85–4.28, 8H, m, Fc	1.30, 6H, d, *J* 6.8
19	4.61, 2H, d, *J* 4.6	5.92, 2H, d, *J* 4.7	4.04, 2H, s. 4.12, 4H, s. 4.18, 2H, s.	7.11, 2H, tt, *J* 6.6, 2.0, Ph (*para*). 7.17–7.23, 8H, m
25	4.53, 2H, d, *J* 4.4	5.87, 2H, d, *J* 4.4	4.03, 2H, s. 4.09, 2H, s. 4.11, 2H, s. 4.17, 2H, s.	3.70, 6H, s, OCH_3. 6.75, 4H, d, *J* 8.7, Ar. 7.09, 4 H, d, *J* 8.6, Ar

[a] 400 MHz, $CDCl_3$.

Table 4
^{13}C-NMR data for ferrocenophanes[a]



Compound	C(1)	C(2)	*Ipso*	α,β	R
4	23.07	129.62	86.51	66.39, 66.94	
13	29.79	135.63	94.34	64.97, 65.32, 67.17, 67.27	23.43
14	29.37	135.08	Not recorded	64.99, 66.00, 66.29, 67.03	20.16
19	42.70	136.22	92.59	67.58, 67.94, 69.55, 69.84	126.57, Ph (*para*). 127.89, Ph (*ortho*/*meta*). 128.78, Ph (*ortho*/*meta*). 145.77, Ph (*ipso*)
25	39.94	134.44	91.15	65.64, 65.93, 67.61, 67.86	53.80, –OCH_3. 112.23, Ar. 126.89, Ar. 136.19, Ar (*ipso*-FcCH). 156.44, Ar (*ipso*-OCH_3)

[a] 100 MHz, $CDCl_3$.

*3.4.5. Synthesis of (R,S)-1,1′-((Z)-1,4-di{4-methoxyphenyl}-1,4-but-2-endiyl)ferrocene (**25**)*

Following the general procedure C, a 3.2:1 mixture of **23** and **24** (0.100 g, 0.21 mmol) and **6** (0.017 g, 0.021 mmol) gave an orange oily solid (0.090 g) consisting of a 76:18:24 mixture of **25**:**23**:**24**. The yield of **25** from **24** is 88%, based on recovered starting material. Trituration of the mixture with toluene–pertoleum ether resulted in the isolation of a pure sample of **25**. Melting point: 159.5–161 °C. (Found: C, 74.55; H, 6.14. $C_{28}H_{26}FeO_2$ requires C, 74.66; H, 5.83%). IR (Nujol, cm^{-1}): ν_{max} 2076.1, 1632.9, 1608.7, 1582.2. HRES; *m*/*z* Found: M^+, 450.1285. Calc. for $C_{28}H_{26}FeO_2$: [M^+], 450.1282.

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