Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 1165–1171
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

β-Ferrocenyl-α, β-unsaturated phosphonates and sulfones

Damian Plażuk [a], Agnieszka Rybarczyk-Pirek [b], Janusz Zakrzewski [a,*]

[a] Department of Organic Chemistry, University of Łódź, 90-136 Łódź, Narutowicza 68, Poland
[b] Department of Crystallography, University of Łódź, 90-236 Łódź, Pomorska 149/153, Poland

Received 13 October 2003; accepted 15 December 2003

Abstract

Ferrocene reacts with β-ketophosphonates and β-ketosulfones (or acetals of formylphosphonates and sulfones) in the presence of a strong acid (triflic or methanesulfonic) to afford β-ferrocenyl-α, β-unsaturated phosphonates and β-ferrocenyl-α, β-unsaturated sulfones in good yield. The (*E*)-stereochemistry of these compounds was confirmed by spectral and analytical data, as well as by X-ray diffraction.

Keywords: Ferrocene; Phosphonate; Sulfone; Unsaturated; Friedel–Crafts reaction; X-ray diffraction

1. Introduction

Ferrocene compounds play an important role in many fields of chemistry, biochemistry and materials science [1]. An intensive research have been carried out over last two decades on ferrocene-based ligands for asymmetric catalysis [1,2], nonlinear optical materials [3], red-ox active polymers and dendrimers [4], molecular electronic devices [5], biosensors [6], drugs [7], photochemical electron-transferring systems [8], etc.

Ferrocene displays remarkably high reactivity towards electrophiles [9] and Friedel–Crafts acylation, alkylation and hydroxyalkylation (alkenylation) reactions [1,10] constitute an attractive route for introduction to this metallocene carbon chains with desired functional groups. However, synthetic strategies based on sequential transformations of the products of these reactions [11] usually involve many steps and therefore are time- and reagent (solvent)-consuming.

A few years ago, we started a search for efficient electrophilic substitution reactions of ferrocene giving access in one-step to its more complex derivatives. We have developed a direct acetoacetylation [12] and β-carboalkoxyvinylation [13] of ferrocene (Scheme 1). The latter reaction has proven highly stereoselective giving exclusively the (*E*)-isomers.

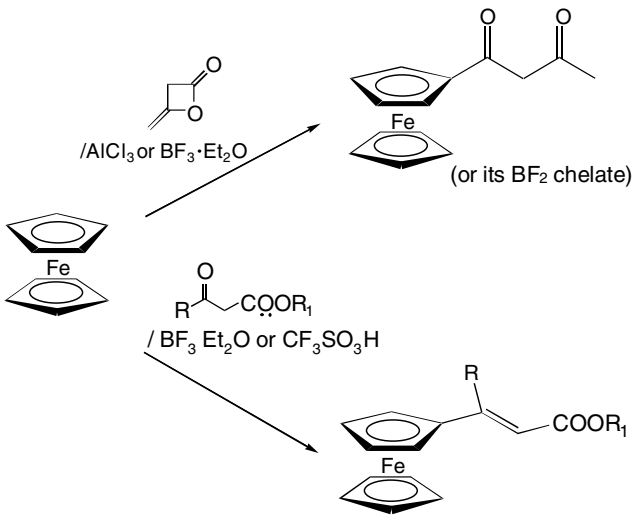
Here we report an extension of this methodology for stereoselective synthesis of hitherto unknown β-ferrocenyl-α, β-unsaturated phosphonates and β-ferrocenyl-α, β-unsaturated sulfones. α, β-Unsaturated phosphonates and sulfones are interesting compounds owing to their synthetic utility, biological activity and industrial applications [14,15]. Therefore, we thought that such compounds containing stable, redox-active ferrocenyl moieties would be of interest for various branches of materials science, as well as they could be useful starting materials for further syntheses of ferrocenyl compounds with anticipated biological activity, e.g., ferrocenyl hydroxy or aminophosphonates.

2. Results and discussion

Our synthetic approach to β-ferrocenyl-α, β-unsaturated phosphonates and β-ferrocenyl-α, β-unsaturated sulfones is shown in Scheme 2. We have chosen for this study commercially available β-ketophosphonates **1a**–**b** and β-ketosulfone **1c**. In place of formyl phosphonates $HCOCH_2P(O)(OR)_2$ and sulfones $HCOCH_2SO_2R$ we used the corresponding dimethyl acetals **2a**–**c** (**2a** and **2b** are commercially available and **2c** was prepared by oxidation of $(MeO)_2CHCH_2SMe$ with $KMnO_4$ [16]).

* Corresponding author. Tel.: +4842-678-4731; fax: +4842-678-6583.
E-mail address: janzak@uni.lodz.pl (J. Zakrzewski).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2003.12.044



Scheme 1. R = Me, Ph; R_1 = Me, Et.

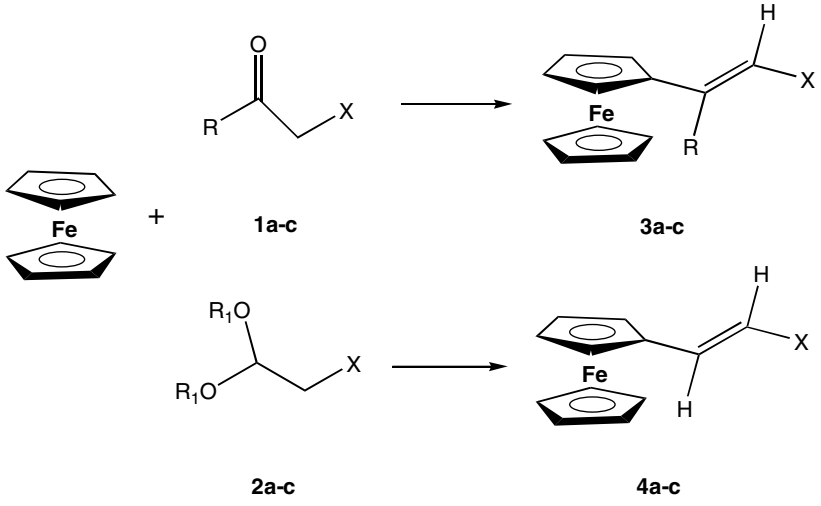
Firstly, we have examined the reaction of ferrocene with **1a**–**c** and **2a**–**c** under conditions described earlier for its reaction with β-ketoesters [13], i.e., in dichloromethane containing excess of trifluoromethanesulfonic acid (triflic acid, TfOH). We have found that this reaction affords the expected products in moderate to good yields (Table 1, method A). Only phosphonate **1b** proved almost unreactive under these reaction conditions. This may be explained by stabilization of its protonated form by delocalization of the positive charge onto the phenyl ring. We observed earlier similar low reactivity of ethyl benzoylacetate [13].

In recent years, much work has been published on the use of TfOH as acid catalyst for Friedel–Crafts and related reactions [17]. They emphasize some advantages of this acid such as extremely high acidity, non-oxidating and non-sulfonating properties, as well as a possibility of its recycling after the reaction. However, triflic acid does induce oxidation of so readily oxidizable substrate as ferrocene [18] and in all aforementioned reactions we observed appearance of the intense blue coloration of the reaction mixture, indicating formation of the ferrocenium cation (oxidation of ferrocene by TfOH is believed to proceed via the protonated metallocene [18]). Searching for acidic media that oxidize ferrocene to lesser extent we turned our attention to methanesulfonic acid, $MeSO_3H$ [19]. Cheaper (~10 times at Aldrich), and less acidic than TfOH, it seemed to be an ideal medium for fine Friedel–Crafts-type reactions of ferrocene.

We have found that neat $MeSO_3H$ is a good medium for the reactions of ferrocene with **1a**–**c** and **2a**–**c** (Table 1, method B).

The replacement of TfOH by $MeSO_3H$ restricted to some extent undesired oxidation of ferrocene (less intense blue coloration of the reaction mixture was observed) as well as formation of tars (presumably polymeric). The yields of phosphonates **3a**–**b** and **4a**–**b** are higher in reactions carried out in the latter acid. On the other hand, the isolated yields of sulfones **3c** and **4c** are the same, regardless of the acid used.

According to ^{1}H NMR spectra in reaction of ferrocene with **1a**–**c** and **2a**–**c** only one stereoisomer was formed in each case. The (*E*)-stereochemistry of **4a**–**c** was unambiguously confirmed by large values of vicinal coupling constants ^3J between the vinylic protons (15.1–17.2 Hz). Furthermore, the coupling constants $^3J_{P-H}$ of β-vinylic protons (~22 Hz) in **4a**–**b** are in the range typical for the *cis* arrangement of interacting nuclei (for a *trans* arrangement higher values, 45–55 Hz, are expected) [14a,14e,14f]. The ^{13}C NMR spectra of of phosphonates **3a**–**b** show $^3J_{P-C}$ coupling constants of ferrocenyl *ipso* carbon characteristic for its *trans* arrangement relative to phosphorus (26.6 and 24.2 Hz, for **3a** and **3b**, respectively). On the other hand, the $^3J_{P-C}$ coupling constants of the methyl carbon in **3a** (7.0 Hz) and phenyl *ipso* carbon in



Scheme 2. **1**(**3**): **a** R = Me, X = P(O)(OMe)$_2$; **b** R = Ph, X = P(O)(OEt)$_2$; **c** R = Me, X = SO_2Me. **2**(**4**): **a** R_1 = Me, X = P(O)(OMe)$_2$; **b** R_1 = Et, X = P(O)(OEt)$_2$; **c** R_1 = Me, X = SO_2Me.

Table 1
Reaction of ferrocene with **1a–c** and **2a–c**

Substrate	Method[a]	Product (yield, %)
1a	A	**3a** (52)
1a	B	**3a** (77)
1b	A	**3b** (traces)
1b	B	**3b** (34)
1c	A	**3c** (59)
1c	B	**3c** (59)
2a	A	**4a** (77)
2a	B	**4a** (82)
2b	A	**4b** (58)
2b	B	**4b** (77)
2c	A	**4c** (67)
2c	B	**4c** (67)

[a] Method A: CH_2Cl_2–TfOH, rt; method B: $MeSO_3H$ (neat) rt.

3b (7.8 Hz) are typical for their *cis* arrangement relative to phosphorus [14a,14e]. The ^1H NMR spectra of compounds **3a–c** show an Nuclear Overhauser (NOE) enhancement of the ferrocenyl α-protons caused by irradiation of the vinylic proton signal. On the other hand, no NOE was observed between the vinylic proton and methyl (**3a**, **3c**) or phenyl protons (**3b**). This strongly suggests the same, (*E*)-configuration, for all compounds. Finally, single crystal X-ray diffraction studies were carried out for **3a** and **3d** and provided ultimate evidence for the suggested stereochemistry (vide infra).

The relatively good yields of **3a–c** and **4a–c** are in keeping with the high stability of ferrocenylalkyl carbenium ions formed in the course of the reaction and the stereoselectivity can be explained assuming the *exo*-deprotonation of the sterically favored conformations of these ions as suggested earlier for the synthesis of β-ferrocenyl-unsaturated esters [13]. It is worth noting that the presence of phosphonate, sulfonyl or ester function in the β-position (relative to CO or acetal function) in the electrophilic reagent *is necessary for an efficient formation of unsaturated ferrocenyl product*. Under the same conditions (method A and B) reaction of ferrocene with acetone (**1**, R = Me, X = H) led to complex mixtures, that did not contain (according to ^1H NMR) the expected 2-ferrocenylpropene, $FcC(CH_3)=CH_2$.

2.1. Molecular structures of *3a* and *3c*

Complexes **3a** and **3c** were also characterized by X-ray diffraction (Figs. 1 and 2, Tables 2 and 3).

Compound **3a** adopts in the crystal a coplanar *s-cis* C=C/P=O conformation (Fig. 1), which according to theoretical studies is the most stable for alkenylphosphonic acid and their derivatives [20]. Interestingly, compound **3c** exists in the crystal in two different conformations **3cA** and **3cB** (Fig. 2). In the conformation **3cA** the S1–C14 bond is nearly coplanar with the to the C11–C13–S1 plane (dihedral angle C11–C13–S–C14∼175°), whereas in **3cB** this angle is close to 90°

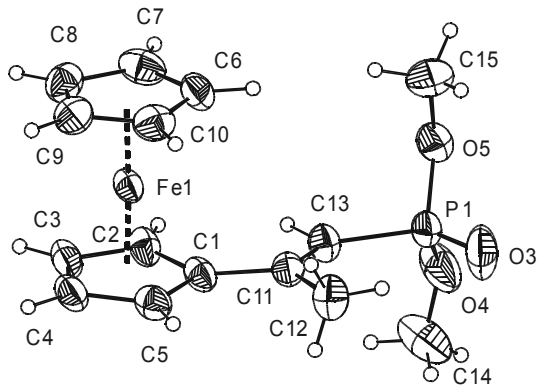


Fig. 1. X-ray molecular structure of **3a**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

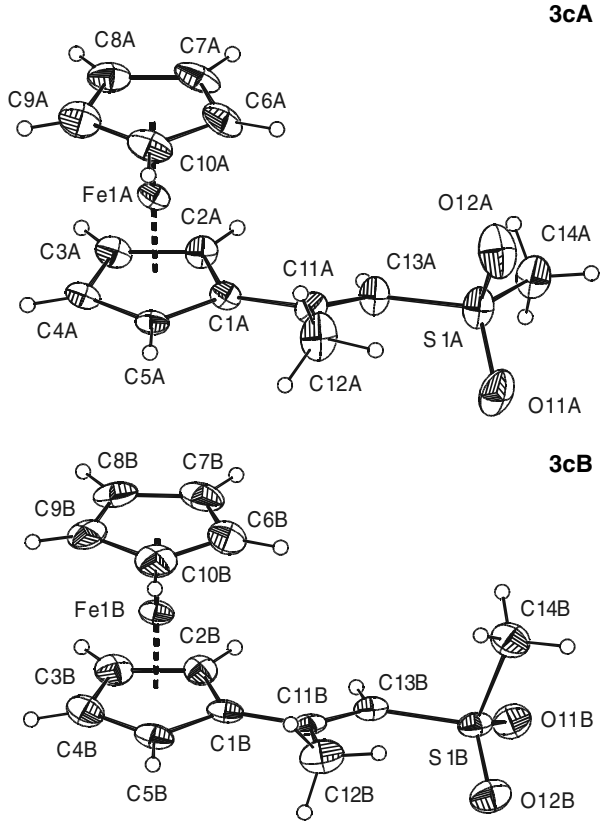


Fig. 2. X-ray molecular structure of **3c**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

(The S1–C14 bond is roughly perpendicular to the C11–C13–S1 plane). The conformer **3cB** forms centrosymmetric cyclic dimers with intermolecular C–H···O hydrogen bonds (Fig. 3).

2.2. Dealkylation of *4b*

Phosphonates can be dealkylated under mild conditions to phosphonic acids, compounds of interest in

Table 2
Crystallographic data and structure refinement details

	3a	**3c**
Crystal data		
Formula	$C_{15}H_{19}FeO_3P$	$C_{14}H_{16}FeO_2S$
fw	334.12	304.18
Crystal description	Red plate	Red plate
Crystal size (mm)	$0.1 \times 0.3 \times 0.5$	$0.1 \times 0.5 \times 0.6$
Space group	$P\bar{1}$	$P2_1/a$
a (Å)	10.248(2)	10.430(2)
b (Å)	10.333(2)	22.966(1)
c (Å)	9.155(1)	11.856(2)
α (°)	114.073(1)	
β (°)	112.278(1)	110.383(1)
γ (°)	60.755(1)	
V (Å)^3	752.4(2)	2664.5(7)
Z	2	8
d_x (g/cm^3)	1.475	1.517
Data collection		
Diffractometer	Rigaku AFC5S	
Radiation type (λ) (Å)	Cu Kα (1.54178)	
μ (mm^{-1})	9.078	10.463
Temperature (K)	293(2)	
Data collected (h, k, l)	$-3 \leqslant h \leqslant 12$; $-10 \leqslant k \leqslant 12$; $-11 \leqslant l \leqslant 9$	$-11 \leqslant h \leqslant 11$; $-14 \leqslant k \leqslant 27$; $-14 \leqslant l \leqslant 13$
Number of reflections measured	2816	5034
Number of independent reflections	2656	4750
R_{int}	0.088	0.044
Number of reflections with $I > 2\sigma(I)$	1918	2728
Solution and refinement		
Solution	Direct methods	
Refinement method	Full-matrix least squares on F^2	
H atoms treatment	Constrained using riding body model	
Number of parameters	197	261
$R(F)$[a]	0.100	0.137
$wR(F^2)$[b]	0.202[c]	0.210[d]
$R(F)$[a]	0.076 for 1918 reflections	0.077 for 2728 reflections
$wR(F^2)$[b]	0.195 for 1918 reflections[c]	0.197 for 2728 reflections[d]
(Δ/σ)max	0.000	0.000
Differential peak/hole (e/Å^3)	1.058/−0.804	1.307/−1.623

[a] $R(F) = \sum(|F_o - F_c|)/\sum|F_o|$.
[b] $wR(F^2) = \left[\sum w(|F_o - F_c|)2/\sum|F_o|^2\right]^{1/2}$.
[c] $w = 1\Big/\left[\sigma^2(F_o^2) + (0.1511P)^2\right]$.
[d] $w = 1\Big/\left[\sigma^2(F_o^2) + (0.01317P)^2\right]$ where $P = \left[(F_o^2) + 2(F_c^2)\right]/3$.

many areas of modern science [21]. We have tested a standard dealkylation procedure [22], using **4b** as a model compound (see Scheme 3). We have found that **4b** readily reacts with trimethylbromosilane and then with water to afford ferrocenyl phosphonic acid **5** in good yield. The (*E*)-configuration of **5** was confirmed by coupling constants in its ^{1}H NMR spectrum (see Section 4).

3. Conclusions

We have developed a simple and highly *E*-stereoselective way to β-ferrocenyl-α, β-unsaturated phosphonates and β-ferrocenyl-α, β-unsaturated sulfones based on a Friedel–Crafts-type reaction of ferrocene with phosphonates and sulfones having β-carbonyl (or acetal) function. We expect that these compounds will undergo a variety of reactions either at the C=C bond or at the heteroatom functionalities and will open new entries in synthetic ferrocene chemistry.

4. Experimental

*4.1. Friedel–Crafts reaction of ferrocene with **1a–c** or **2a–c** in the presence of triflic acid*

Triflic acid (600 mg, 4 mmol) was added at room temperature to the magnetically strirred solution of ferrocene (186 mg, 1 mmol) in dichloromethane (5 mL).

Table 3
Selected bond lengths (Å) and angles (°)

Parameter	3a	3cA	3cB
C1–C11	1.477(10)	1.483(6)	1.459(6)
C11–C12	1.511(10)	1.516(5)	1.536(2)
C11–C13	1.337(9)	1.336(5)	1.370(2)
C13–P1/S1	1.758(8)	1.757(4)	1.750(3)
P1–O3	1.437(6)		
P1–O4	1.595(8)		
P2–O5	1.557(5)		
O4–C14	1.286(12)		
O5–C15	1.419(12)		
C13–P1–O3	116.9(3)		
C13–P1–O4	105.3(4)		
C13–P1–O5	106.2(3)		
O3–P1–O4	116.6(4)		
O3–P1–O5	116.2(3)		
O4–P1–O5	92.5(4)		
C11–C13–P1–O3	−3.2(9)		
C11–C13–P1–O4	−134.5(7)		
C11–C13–P1–O5	128.3(7)		
S1–O11		1.423(2)	1.442(5)
S1–O12		1.418(2)	1.436(6)
S1–C14		1.748(5)	1.738(3)
C13–S1–O11		110.8(2)	105.2(3)
C13–S1–O12		110.4(2)	112.2(3)
C13–S1–C14		102.5(2)	106.3(4)
O11–S1–C14		108.6(2)	106.9(4)
O12–S1–C14		102.5(2)	108.2(4)
O11–S1–O12		115.7(1)	117.4(3)
C11–C13–S1–O11		69.1(3)	−164.1(3)
C11–C13–S1–O12		−60.4(3)	−35.4(4)
C11–C13–S1–C14		−175.2(3)	82.7(4)
C12···O12^{i}		3.382(6)	
C12–H23A···O12^{i}		167.7(2)	

Symmetry code: ^{i} $-x+1, -y, -z+1$.

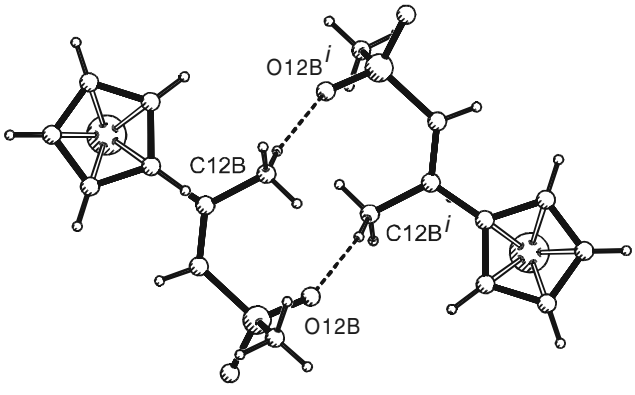
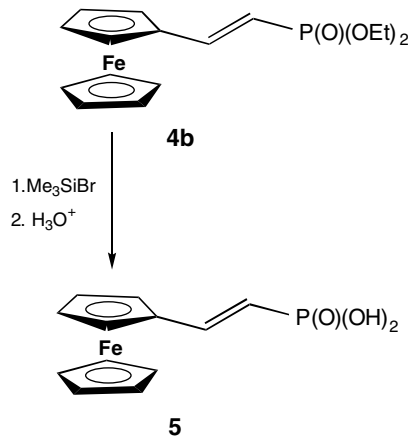


Fig. 3. Structure of the dimer of **3cB**.

The mixture was stirred for 2 min, then **1a**–**c** or **2a**–**c** (2 mmol) was added in one portion and the stirring was continued for 2 h.The reaction mixture was then poured onto ice-water (20 mL) and the product was extracted with dichloromethane. After evaporation to dryness the residue was treated with water (20 mL) and extracted with hexanes. Column chromatography afforded small amount of unreacted ferrocene and the products **3a**–**c** or **4a**–**c**. The yields are given in Table 1.



Scheme 3.

4.2. Friedel–Crafts reaction of ferrocene with *1a–c* or *2a–c* in the presence of methanesulfonic acid

To a magnetically stirred solution of ferrocene (186 mg, 1 mmol) in methanesulfonic acid (5 mL) **1a**–**c** or **2a**–**c** (2 mmol) was added in one portion at room temperature and the stirring was continued for 2 h. The reaction mixture was poured onto water (20 mL) and extracted with dichloromethane. The products were isolated by column chromatography. The yields are given in Table 1.

*Dimethyl (E)-2-ferrocenyl-1-propenylphosphonate (**3a**)*. M.p. 84–86 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 5.68 (d, 1H, $J = 17.1$ Hz, =CH), 4.48 (t, 2H, $J = 1.8$ Hz, Cp), 4.36 (t, $J = 1.8$ Hz, 2H, Cp), 4.12 (s, 5H, Cp′), 3.73 (d, $J = 11.1$ Hz, 6H, OMe), 2.39 (d, $J = 3.3$ Hz, 3H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): 159.24 (d, $J = 8.9$ Hz, C_β), 105.38 (d, $J = 193.5$ Hz, C_α), 84.6 (d, $J = 26.6$ Hz, Cp- *ipso*), 70.29 (s, Cp), 69.60 (s, Cp′), 66.73 (s, Cp), 51.76 (d, $J = 5.4$ Hz, OMe), 18.55 (d, $J = 7.0$ Hz, Me). ^{31}P NMR (81 MHz, $CDCl_3$): 21.6. Anal. Calc. for: $C_{15}H_{19}FeO_3P$: C, 53.92; H, 5.73. Found: C, 54,21; H, 5.73%.

*Diethyl 2-ferrocenyl-2-phenylvinylphosphonate (**3b**)*. Red oil. ^{1}H NMR (200 MHz, $CDCl_3$): 7.39 (s, 5H, Ph), 6.08 (d, 1H, $J = 16.0$ Hz, =CH), 4.33 (t, 2H, $J = 1.8$ Hz, Cp), 4.28 (t, 2H, $J = 1.8$ Hz, Cp), 4.14 (s, 5H, Cp′), 3.8 (m, 4H, CH_2), 1.12 (t, 6H, $J = 7.0$ Hz, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 160.60 (d, $J = 6.8$ Hz, $=C_\beta$), 138.52 (d, $J = 7.8$ Hz, Ph *ipso*), 128.55 (d, $J = 1.7$ Hz, Ph), 127.91 (s, Ph), 127.43 (s, Ph), 109.61 (d, $J = 193.5$ Hz, $=C_\alpha$), 84.00 (d, $J = 24.2$ Hz, Cp *ipso*), 70.39 (s, Cp), 69.60 (s, Cp′), 66.84 (s, Cp), 61.12 (d, $J = 5.8$ Hz, CH_2), 16.12 (d, $J = 6.7$ Hz, CH_3). ^{31}P NMR (81 MHz,

$CDCl_3$): 17.8. Anal. Calc. for: $C_{21}H_{25}O_3FeP$: C, 62.28; H, 5.94. Found: C, 62.39; H, 5.98%.

*((E)-2-ferrocenyl-1-propenyl)methyl sulfone (**3c**)*. M.p. 136–137 °C. ^1H NMR (200 MHz, $CDCl_3$): 6.41 (s, 1H, =CH), 4.50 (bs, 2H, Cp), 4.45 (bs, 2H, Cp), 4.18 (s, 5H, Cp′), 3.00 (s, 3H, CH_3), 2.49 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$, all singlets): 155.05 (=C_β), 120.11 (=C_α), 82.64 (Cp *ipso*), 70.97 (Cp), 69.82 (Cp′), 66.96 (Cp), 44.20 (Me), 16.29 (Me). Anal. Calc. for: $C_{14}H_{16}FeO_2S$: C, 55.28; H, 5.30. Found: C, 55.20; H, 5.33%.

*Dimethyl (E)-ferrocenylvinylphosphonate (**4a**)*. M.p. 82–83 °C ^1H NMR (200 MHz, $CDCl_3$): 7.41 (dd, 1H, $J = 17.2$ Hz, $J = 22.0$ Hz, =C_βH), 5.75 (dd, $J = 17.2$ Hz. $J = 19.2$ Hz, =C_αH), 4.46 (t, 2H, $J = 1.8$ Hz, Cp), 4.39 (t, 2H, $J = 1.8$ Hz, Cp), 4.15 (s, 5H, Cp′), 3.75 (d, $J = 11.1$ Hz, 6H, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 150.64 (d, $J = 7.0$ Hz, =C_β), 107.94 (d, $J = 192.8$ Hz, =C_α), 79.24 (d, $J = 26.2$ Hz, Cp *ipso*), 70.70 (s, Cp), 69.63 (s, Cp′), 68.23 (s, Cp), 52.18 (d, $J = 5.4$ Hz, CH_3). ^{31}P NMR (81 MHz, $CDCl_3$): 23.6. Anal. Calc. for: $C_{14}H_{17}FeO_3P$: C, 52.53; H, 5.36. Found: C, 52,35; H, 5.47%.

*Diethyl (E)-ferrocenylvinylphosphonate (**4b**)*. M.p. 63–64 °C ^1H NMR (200 MHz, $CDCl_3$): 7.37 (dd, 1H, $J = 17.8$ Hz, $J = 21.8$ Hz, =C_αH), 5.79 (pseudo t, $J = 17.8$ Hz, C_αH), 4.46 (t, 2H, $J = 1.8$ Hz, Cp), 4.38 (t, 2H, $J = 1.8$ Hz, Cp), 4.15 (s, 5H, Cp′), 4.07 (m, 4H, CH_2), 1.36 (t, 6H, $J = 6.7$ Hz, CH_3). Anal. Calc. for: $C_{16}H_{21}FeO_3P$: C, 52.53; H, 5.36. Found: C, 52.35; H, 5.47%.

*((E)-2-ferrocenylvinyl)methyl sulfone (**4c**)*. M.p. 129–130 °C .^1H NMR (200 MHz, $CDCl_3$): 7.54 (d, 1H, $J = 15.1$ Hz, =CH), 6.50 (d, 1H, $J = 15.1$ Hz, =CH), 4.49 (bs, 4H, Cp), 4.19 (s, 5H, Cp′), 2.96 (s, 3H, CH_3), ^{13}C NMR (50 MHz, $CDCl_3$, all singlets): 145.37 (=C_β), 121.62 (=C_α), 75.86 (Cp *ipso*), 71.50, 69.78, 68.88 (Cp), 43.44 (Me). Anal. Calc. for: $C_{13}H_{14}FeO_2S$: C, 53.81; H, 4.86. Found: C, 53.78; H, 4.98%.

4.3. Dealkylation of *4b*

Me_3SiBr (129 mg, 0.85 mmol) was added to the solution of 4b (98 mg, 0.28 mmol) in dichloromethane (5 mL). After 2 h stirring a mixture of concentrated aq. HCl (5 mL) and water (5 mL) was added and the (*E*)-2-ferrocenylvinylphosphonic acid **5** was repeatedly extracted with dichloromethane-methanol and purified by column chromatography (eluent–methanol). Yield 55 mg (67%). ^1H NMR (200 MHz, methanol-d_4): 6.92 (pseudo t, 1H, $J = 17.3$ Hz, =C_βH), 5.80 (pseudo t, 1H, $J = 17.3$ Hz, =C_βH), 4.33 (t, 2H, $J = 1.9$Hz, Cp), 4.17 (t, 2H, $J = 1,9$ Hz, Cp), 4.00 (s, 5H, Cp′). ^{31}P NMR (81 MHz, methanol-d_4): 8.41. Anal. Calc. for: $C_{13}H_{17}O_4FeP$ (monohydrate): C, 46.48; H, 4.88. Found: C, 46.42; H, 4.58%.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 221603 and 221604 for compounds **3a** and **3c**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

[1] (a) A. Togni, T. Hayashi, Ferrocenes: Homogenous Catalysis, Organic Synthesis, Material Science, Weinheim, NY, 1995;
(b) N.J. Long, Metallocenes, Blackwell, London, 1995.
[2] (a) C.J. Richards, A.J. Locke, Tetrahedron-Asymmety 9 (1998) 2377;
(b) A. Togni, Angew. Chem. Int. Ed. Engl. 35 (1996) 1475;
(c) A. Togni, R. Dorta, C. Koelner, G. Pioda, Pure. Appl. Chem. 70 (1998) 1477.
[3] (a) S. Di Bella, Chem. Soc. Rev. 30 (2001) 355;
(b) I.R. Whittall, M.G. McDonagh, M. Samoc, M.G. Humphrey, Advanced Organometallic Chemistry, Academic Press, San Diego, 1995;
(c) N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.
[4] (a) R.D.A. Hudson, J. Organomet. Chem. 637–639 (2001) 47;
(b) H. Plenio, J. Hermann, A. Sehring, Chem. Eur. J. 6 (2000) 1820;
(c) G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. (1999) 1689;
(d) J. Alvarez, T. Ren, A.E. Kaifer, Organometallics 20 (2001) 3543.
[5] (a) C. Engratkul, L.R. Sita, NanoLetters 1 (2001) 541;
(b) D.T. Gryko, F. Zhao, A.A. Yasseri, K.M. Roth, D.F. Bocian, W.G. Kuhr, J.S. Lindsey, J. Organomet. Chem. 65 (2000) 7356.
[6] (a) P.D. Beer, Acc. Chem. Res. 31 (1998) 71;
(b) P.D. Beer, Chem. Commun. (1966) 689;
(c) P.D. Beer, Chem. Soc. Rev. 18 (1989) 409;
(d) H. Tsukube, H. Fukui, S. Shinoda, Tetrahedron Lett. 42 (2001) 7583.
[7] S. Top, A. Vessieres, C. Cabestaing, L. Laios, G. Leclerq, C. Provot, G. Jaouen, J. Organomet. Chem. 637–639 (2001) 500.
[8] (a) S. Fery-Forgues, B. Delavaux-Nicot, J. Photochem. Photobiol. A: Chem. 132 (2000) 137;
(b) Y. Yamaguchi, C. Kutal, Macromolecules 33 (2000) 1152;
(c) K. Uosaki, T. Kondo, X.Q. Zhang, M. Yanagida, J. Am. Chem. Soc. 11 (1997) 8367.
[9] (a) M. Rosenblum, Chemistry of the Iron Group Metallocenes, Wiley, New York, 1965;
(b) A. Pearson, Metallo-Organic Chemistry, Wiley, Chichester, 1985.
[10] (a) B. Misterkiewicz, J. Organomet. Chem. 224 (1982) 43;
(b) B. Misterkiewicz, R. Dabard, H. Patin, Tetrahedron 41 (1985) 1685.
[11] See for a recent reference W.G. Jary, A.K. Mahler, T. Purkathofer, J. Baumgartner, J. Organomet. Chem. 629 (2001) 208.
[12] D. Plazuk, A. Klys, J. Zakrzewski, A. Rybarczyk-Pirek, T.A. Olszak, Organometallics 20 (2000) 4448.
[13] D. Plazuk, J. Zakrzewski, J. Org. Chem. 67 (2002) 8672.
[14] (a) For recent examples related to vinyl phosphonates, see: A.A.A. Quantar, M. Srebnik, J. Organomet. Chem. 66 (2001) 6650;
(b) A.A. Thomas, K.B. Sharpless, J. Organomet. Chem. 64 (1999) 8379;

(c) J.M. Gil, D.Y. Oh, J. Organomet. Chem. 64 (1999) 2950;
(d) K. Afarinkia, H.M. Binch, C. Modi, Tetrahedron Lett. 39 (1998) 7419;
(e) H.-J. Cristau, X.Y. Mbianda, Y. Beziat, M.-B. Gasc, J. Organomet. Chem. 529 (1997) 301;
(f) C. Grison, C. Comoy, D. Chatenet, P. Coutrot, J. Organomet. Chem. 662 (2002) 83.

[15] (a) For recent examples related to vinyl sulfones, see: Y.-S. Lin, B.E. Ali, H. Halper, J. Am. Chem. Soc. 123 (2001) 7719;
(b) W.-C. Cheng, M.M. Olmstead, M.J. Kurth, J. Organomet. Chem. 66 (2001) 5528;
(c) B. Ravindran, K. Sakthivel, K.C.G. Suresh, T. Pathak, J. Organomet. Chem. 65 (2000) 2637;
(d) H.S. Overkleeft, P.R. Bos, B.G. Hekking, E.J. Gordon, H.L. Ploegh, B.M. Kessler, Tetrahedron Lett. 41 (2000) 6005;
(e) R.B. Clark, W.H. Pearson, Org. Lett. 1 (1999) 349;
(f) T.G. Back, R.J. Bethell, M. Parvez, D. Wehrli, J. Organomet. Chem. 63 (1998) 7908.

[16] M. Bobek, J. Heterocyclic Chem. 19 (1982) 131.

[17] (a) K.W. Anderson, J.J. Tepe, Tetrahedron 58 (2002) 8475;
(b) K.W. Anderson, J.J. Tepe, Org. Lett. 4 (2002) 459;
(c) S. Fukuzawa, T. Tsuchimoto, T. Hiyama, J. Organomet. Chem. 62 (1997) 151;
(d) J.P. Hwang, G.K. Surya Prakash, G.A. Olah, Tetrahedron 56 (2000) 7199;
(e) T. Yamazaki, S. Saito, T. Ohwada, K. Shudo, Tetrahedron Lett. 36 (1995) 5747;
(f) D.A. Klumpp, K.Y. Yeung, G.K. Surya Prakash, G.A. Olah, Syn. Lett. (1998) 918;
(g) D.A. Klumpp, G.V. Sanchez Jr., S.L. Aquire, Y. Zhang, S. De Leon, J. Organomet. Chem. 67 (2002) 5028.

[18] R.M.G. Roberts, A.S. Wells, Inorg. Chim. Acta 112 (1986) 112,167.

[19] As a recent example of the use of $MeSO_3H$ in a Friedel–Crafts-type reaction see: S. Aki, T. Fujioka, M. Ishigami, J. Minawikama, Bioorg. Med. Chem. Lett. 12 (2002) 231.

[20] (a) C.I. Sainz-Diaz, A. Hernandez-Laguna, N.J. Smeyers, Y.G. Smeyers, J. Mol. Struct. (Theochem.) 330 (1995) 231;
(b) A. Hernandez-Laguna, C.I. Sainz-Diaz, Y.G. Smeyers, J.L.G. de Paz, E. Galvez-Ruano, J. Phys. Chem. 98 (1994) 1109;
(c) R. Robiette, J. Marchand-Brynaert, D. Peeters, J. Mol. Struct. (Theochem.) 587 (2002) 159.

[21] (a) M.C. Mitchell, T.P. Kee, Coord. Chem. Rev. 158 (1997) 359;
(b) S.R. Alley, W. Henderson, J. Organomet. Chem. 637–639 (2001) 83, references therein.

[22] C.E. McKenna, M.T. Higa, N.H. Cheung, M.-C. McKenna, Tetrahedron Lett. (1977) 155.