[2+2+2] Cocyclotrimerization with Ferrocenylalkynes

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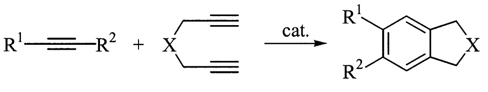
Keywords: Cyclotrimerization / Homogeneous catalysis / Metallocenes / Iron

Cocyclotrimerization of ferrocenylalkynes FcC≡CR (R = H and CH_2OH) with α,ω-diynes $X(CH_2C{\equiv}CH)_2$, where X = O, $C(CO_2Et)$, $C(CN)(CO_2Et)$, $C(COMe)_2$, and $C(COMe)(CO_2Et)$, to give functionalised ferrocenylarenes was attempted in the presence of various catalytic systems: $[RhCl(PPh_3)_3]$, $[CoBr(PPh_3)_3]$, $[NiBr_2(dppe)]/Zn$, $[\{Ir(cod)Cl\}_2]/dppe$ and $[CpCo(cod)]/PPh_3$ [Cp = η^5-cyclopentadienyl, cod = η^4-cycloocta-1,5-diene, and dppe = 1,2-bis(diphenylphosphanyl)ethane]. The results indicate that Wilkinson's catalyst effects the cocyclotrimerization to afford the respective ferrocenylarenes in good yields and under mild conditions regardless of the nature of the functional groups.

Introduction

Ferrocenylarenes have recently gained importance as a class of compounds that can be used for preparation of liquid crystals,[1] materials with non-linear optical properties,[2] and as redox switchable hemilabile ligands.[3] So far, ferrocenylarenes have usually been prepared by Friedel−Crafts arylation,[4a] cross-coupling reactions[1,4b] and by other methods.[1,4c] However, the scope of these reactions is often limited by the availability of a suitable starting material or hampered by side reactions and low yields. It is therefore of general synthetic interest to develop an alternative procedure for the preparation of ferrocenylarenes bearing functional groups that would allow for their further synthetic transformation.

One powerful synthetic tool that has been neglected in the chemistry of ferrocenes, is cyclotrimerization which enables the use of rather simple starting molecules for assembly into a material with a high degree of complexity. Of particular interest is cocyclotrimerization of alkynes with various diynes to afford the substituted benzocycloalkanes (Scheme 1). This process has found numerous applications in the synthesis of natural compounds or new materials.[5]



Scheme 1

Surprisingly, reports on the cyclotrimerization involving ferrocenylalkynes are still scarce. After the pioneering work by Schlögl[6] and Rosenblum,[7] who showed that ferrocenylalkynes undergo homocyclotrimerization into triferrocenylbenzenes in a reaction catalysed by $[Co_2(CO)_8]$, the only other report concerns the same reaction catalysed by $TaCl_5$.[8]

The synthetic potential of the reaction as well as the lack of any information about cyclotrimerizations involving ferrocenylalkynes provided strong a impetus to study this problem. Our interest in this area had two main goals; i) to check the possibility of selective cocyclotrimerization of ferrocenylalkynes with α,ω-diynes, and ii) to develop a general method that would enable preparation of ferrocenylarenes bearing various functional groups suitable for further transformations.

Results and Discussion

Cyclotrimerization is known to proceed in the presence of a catalytic amount of various transition metal complexes under very different reaction conditions. There are only three reports of catalytic homocyclotrimerization of ferrocenylethyne and so we undertook a systematic investigation of the catalytic activity of transition metal complexes that could be expected to induce a smooth cocyclotrimerization of ferrocenylalkynes with diynes. Thus, we decided to assess the activity of $[RhCl(PPh_3)_3]$,[9] $[NiL_2Br_2]/Zn$ (L_2 = $2PPh_3$,[10] dppe[11]), $[\{IrCl(cod)\}_2]/dppe$,[12] $[CpCo(cod)]/2PPh_3$,[5g] and $[CoBr(PPh_3)_3]$[13] as the catalyst precursors for the cocyclotrimerization of ferrocenylethyne (**1a**) with dipropargyl malonate (**2a**) to **3aa** (Scheme 2). The results are summarised in Table 1.

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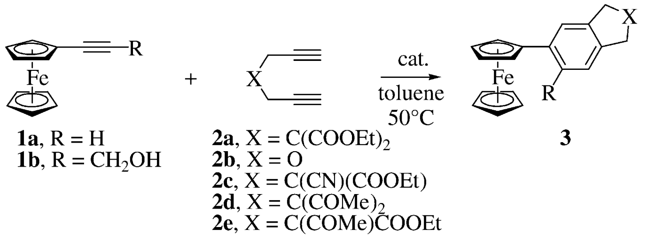
DOI: 10.1002/ejoc.200300119



Scheme 2

Table 1. Cocyclotrimerization of ferrocenylalkyne **1a** with **2a** to give **3aa**

Catalyst	Time (h)	T [C°]	Yield [%][a]
$[RhCl(PPh_3)_3]$	48	20	81 (57)
$[CoBr(PPh_3)_3]$	24	20	75 (70)
$[CpCo(cod)]/PPh_3$	24	140	80 (64)
$[NiBr_2(dppe)]/Zn$	168	50	(5)
$[\{Ir(cod)Cl\}_2]/dppe$	48	50	(32)

[a] ^1H NMR yields. Isolated yields are given in parentheses.

The best yields were obtained with Rh- and Co-based catalysts. The reaction catalysed by Wilkinsons's catalyst proceeded well at 20 °C in toluene to afford **3aa** in high yield (81%). In contrast to the procedures reported previously,[9a] formation of intractable mixtures was observed when the reactions were carried out in ethanol. A surprisingly good result was obtained with the rarely used but effective catalyst $[CoBr(PPh_3)_3]$.[10,13] The reaction with this complex proceeded at low temperature (20 °C) to provide **3aa** in 75% yield within a relatively short time. This complex was examined considering a report that a catalytic system composed of $CoI_2/2PPh_3/Zn$ cyclotrimerized triynes into benzocyclic compounds.[14] However, the use of stable $[CoBr(PPh_3)_3]$, which is easy to prepare,[15] was advantageous over the manipulation with hygroscopic anhydrous CoI_2. As expected, the use of the most often used catalytic system, $[CpCo(cod)]/2PPh_3$ required the reaction to be carried out at 140 °C in decane. But this disadvantage was countered by high yields of the arene **3aa** (80%). Rather surprisingly, the nickel-phosphane complexes, which are known to be effective cyclotrimerization catalysts,[10,16] gave only poor yields of **3aa** even after a long reaction time. Likewise, the iridium-dppe complex that has been recently reported as a highly active catalyst[12] gave **3aa** in a disappointingly low yield.

In subsequent work we focussed on the cocyclotrimerization of variously substituted ferrocenylalkynes with other diynes (Scheme 2). Due to their simple nature, high activity, and mild reaction conditions, both Wilkinson's catalyst $[RhCl(PPh_3)_3]$ and its cobalt analogue $[CoBr(PPh_3)_3]$ were chosen to promote the cocyclotrimerization. The reactions were performed in toluene at either 20 °C or 50 °C to increase the reaction rate. Representative examples are shown in Table 2.

Table 2. Cocyclotrimerization of ferrocenylalkynes **1** with **2** to give **3**

1	2	R.T. (h)	T[C°]	Product 3	Yield [%][a] Rh-cat[b]	 Co-cat[c]
1a	2a	48	20	3aa	81 (57)	75 (70)
1a	2b	48	50	3ab	75 (59)	61 (50)
1a	2c	48	50	3ac	48 (31)	62 (58)
1a	2d	12	20	3ad	73 (57)	34 (14)
1a	2e	12	20	3ae	35 (23)	77 (61)
1b	2a	72	50	3ba	56 (47)	0
1b	2b	120	50	3bb	(12)	0

[a] ^1H NMR yields. Isolated yield in parentheses. [b] $[RhCl(PPh_3)_3]$. [c] $[CoBr(PPh_3)_3]$.

Generally, the reaction of ferrocenylethyne (**1a**) with diynes **2a**, **b**, **d** catalysed with Wilkinson's catalyst proceeded smoothly to afford the corresponding ferrocenylarenes **3aa**, **ab**, **ad** in good yields. Lower catalyst activity was observed in the cases of the reactions of ferrocenylethyne **1a** with ethyl cyanoacetate (**2c**) that furnished a moderate yield of **3ac** and with ethyl acetoacetate (**2e**) that gave only a low yield of **3ae**. On the other hand, the reactions catalysed by $[CoBr(PPh_3)_3]$ gave good yields of the corresponding ferrocenylarenes in almost all cases, with the exception of the reaction with dipropargylpentadione (**2d**).

Then we turned to cocyclotrimerizations using ferrocenylalkynes substituted at the other terminus of the triple bond. Interestingly, of several ferrocenylalkynes only ferrocenylpropargyl alcohol (**1b**) participated in these cocyclotrimerizations. The Rh complex catalysed reaction of **1b** with dipropargylmalonate **2a** yielded arylferrocene **3ba**, whilst the reaction in the presence of the Co complex did not proceed at all. A similar effect was observed in the case of the reaction with dipropargyl ether (**2b**) that resulted in only a poor yield of ferrocenylarene **3bb**. Attempts to cocyclotrimerize ferrocenylalkynes with diynes **2** bearing other substituents (R = Me, Ph, $SiMe_3$, COOR, etc.) were fruitless since the formation of the corresponding ferrocenylarenes was not observed. Although speculative, this could have been caused by steric hindrance of the triple bond that prevented cocyclotrimerization, favouring the homocyclotrimerization of the diyne. This assumption is supported by similar observations reported in the literature.[6,7]

X-ray crystallography

The solid-state structures of **1b**, **3aa**, **3ac**, and **3cc** were determined by X-ray crystallography. Compound **1b** crystallises in an orthorhombic unit cell with two independent molecules in the asymmetric unit. The structure of one of these molecules is shown in Figure 1 and the pertinent geometric parameters for both molecules are listed in Table 3. The molecules show very similar bond lengths and angles, differing only slightly by the orientation of the (hydroxymethyl)ethynyl side arm towards the ferrocene framework. Hence, the increased number of symmetrically independent molecules is probably due to solid-state interactions. In the crystal, the molecules associate via O−H···O hydrogen bonds into angular infinite chains running parallel to the crystallographic *a* axis. Each hydroxyl group acts as both a hydrogen bond donor and acceptor O1−H91···O2^{i}: O1−H91 0.77(4), O(1)−O(2)^{i} 2.672(2) Å; O1−H91···O2^{i} 162(3)°, and O2−H92···O1^{ii}: O2−H92 0.74(3), O(2)−O(1)^{ii} 2.705(2) Å; O2−H92···O1^{ii} 168(3)° (*i.* 1 − *x*,1/2 + *y*,1/2 − *z*; *ii.* 1/2 − *x*, −1/2 + *y*, *z*). This bonding situation is similar to the solid-state packing of 1′-(diphenylphosphanyl)ferrocenylmethanol[17a] and 1,1′-bis(hydroxymethyl)ferrocene.[17b]

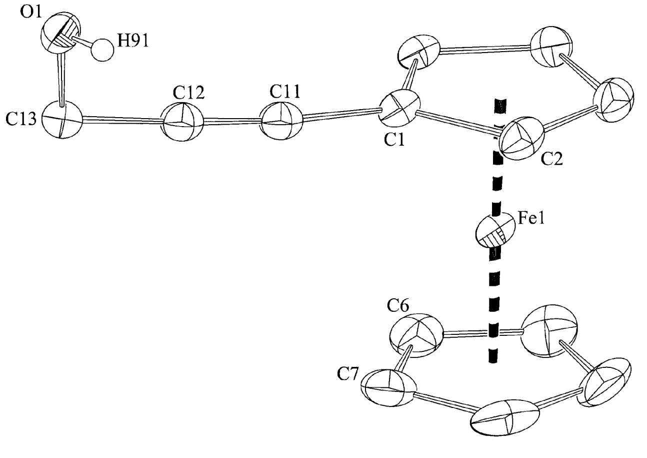


Figure 1. The molecular structure of **1b** (molecule 1) showing the atom labelling scheme; only the hydroxyl hydrogen atom is shown

Table 3. Selected geometric parameters for **1b** (in Å and °)[a]

Parameter	Molecule 1	Parameter	Molecule 2
O1−C13	1.417(3)	O2−C33	1.434(3)
C1−C11	1.419(3)	C21−C31	1.429(3)
C11−C12	1.201(3)	C31−C32	1.197(3)
C12−C13	1.473(3)	C32−C33	1.462(3)
Fe−Cg	1.654(1)	Fe−Cg	1.643(1)
Fe−Cg′	1.641(1)	Fe−Cg′	1.652(1)
C1−C11−C12	175.1(3)	C21−C31−C32	178.2(3)]
C11−C12−C13	177.8(2)	C31−C32−C33	177.7(2)
C12−C13−O1	114.2(2)	C32−C33−O2	111.7(2)
Cg−Fe−Cg′	178.76(7)	Cg−Fe−Cg′	178.87(6)

[a] Cg and Cg′ are centroids of the substituted and unsubstituted cyclopentadienyl rings, respectively.

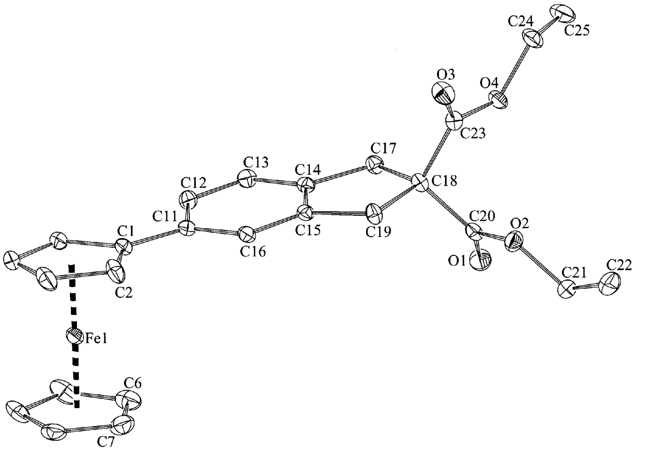


Figure 2. The molecular structure of **3aa** (molecule 1); hydrogen atoms are omitted for clarity

The unit cell of **3aa** contains four crystallographically independent molecules. The molecular structure of one of these molecules is shown in Figure 2, and selected geometric parameters for all the molecules are given in Table 4. The independent molecules differ only by the orientation of the ferrocene substituent towards the planar indane unit (cf. dihedral angle φ in Table 4). Other distances and angles are quite unexceptional and do not differ between the four molecules within the precision of the measurement. Although the different mutual rotations of the two molecular parts could tentatively be assigned to intermolecular forces in the solid state, there are no significant intermolecular contacts besides some weak offset π-π interactions between aromatic six-membered rings of the neighbouring molecules [molecules 1 and 2^{iii} Cg···Cg 4.664(1) Å, interplanar angle 3°; molecules 3 and 4 Cg···Cg^{iv} 5.293(1) Å, interplanar angle 1°; *iii.* (2 − *x*, 1 − *y*, 1 − *z*); *iv.* (1 − *x*, 1 − *y*, 1 − *z*)].

Similar to the above cases, the structure of **3ab** contains two crystallographically independent molecules. A view of one of the molecules is shown in Figure 3 with selected data for both molecules listed in Table 5. The molecules differ only slightly in bond lengths and angles but show different mutual rotations of the ferrocene and isobenzofuran units. The dihedral angle subtended by the planes of the fused bicyclic system amounts to 3.1(4) [1.8(4)]°. As revealed by the ring puckering amplitudes[18] Q_2 = 0.090(8) [0.084(8)] Å, the five-membered ring is very nearly planar but, as indicated by a larger thermal motion ellipsoid of the oxygen atom compared to the ring carbon atoms, this is rather a result of a time and/or a positional averaging.

The hydroxymethyl derivative **3bb** crystallises in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 4, Table 6). Similar to **3ab**, the ferrocene substituent and the dihydroisobenzofuran moiety are mutually rotated, the dihedral angle subtended by the least-squares planes of the aromatic six-membered ring and its adjacent cyclopentadienyl being 23.91(7)°. The fused six- and five-membered rings of the dihydroisobenzofuran unit are nearly perfectly coplanar, intersecting each other at an angle of only 2.17(7)°. In the solid state, the molecules associate via double hydrogen bonds O−H···O between molecules lying across the crystallographic inversion centre: O(2)−H(90)···O(1)^{v} (*v*: − *x*, 2 − *y*, −*z*); O(2)−H(90) 0.82(2), O(2)···O(1)^{v} 2.799(1) Å; O(2)−H(90)···O(1) 175(2)°. The formed dimeric motifs are packed at normal van der Waals distances.

Conclusion

Cocyclotrimerization represents a convenient method for the preparation of substituted, redox-active ferrocenylarenes functionalised with various polar groups, which would otherwise be accessible only with difficulty. Both [RhCl(PPh$_3$)$_3$] and [CoBr(PPh$_3$)$_3$] complexes are compar-

Table 4. Selected distances and angles for **3aa**(in Å and °)[a]

Parameter	Molecule 1	Molecule 2	Molecule 3	Molecule 4
Fe−Cp	1.644(1)	1.654(9)	1.6456(9)	1.646(1)
Fe−Cp′	1.648(1)	178.53(5)	178.66(5)	179.16(5)
Cp−Fe−Cp′	178.67(5)	1.654(9)	1.6456(9)	1.646(1)
φ[b]	6.5(1)	8.1(1)	30.7(1)	27.4(1)
C(Cp)−C(Ar)	1.480(3)	1.480(3)	1.475(3)	1.475(3)
C(ring)-CO_2Et	1.522(2), 1.527(3)	1.526(2), 1.528(3)	1.522(2), 1.528(3)	1.522(2), 1.530(3)
C(ring)C−O	1.339(2), 1.337(2)	1.341(2), 1.342(2)	1.341(2), 1.342(2)	1.336(2), 1.338(2)
C=O	1.200(2), 1.203(2)	1.200(2), 1.200(2)	1.202(2), 1.200(2)	1.202(2), 1.197(2)
O−CH_2	1.453(2), 1.460(2)	1.455(2), 1.458(2)	1.447(2), 1.461(2)	1.449(2), 1.457(3)
O=C−O	123.9(2), 124.4(2)	124.8(2), 124.5(2)	124.6(2), 124.8(2)	124.4(2), 125.2(2)

[a] Plane definition: Cp (Cp′) = substituted (unsubstituted) cyclopentadienyl ring (Cg and Cg′ are the respective ring centroids); Ar = six-membered aromatic ring of the dihydroindene moiety. [b] Dihedral angle subtended by the Cp and Ar planes.

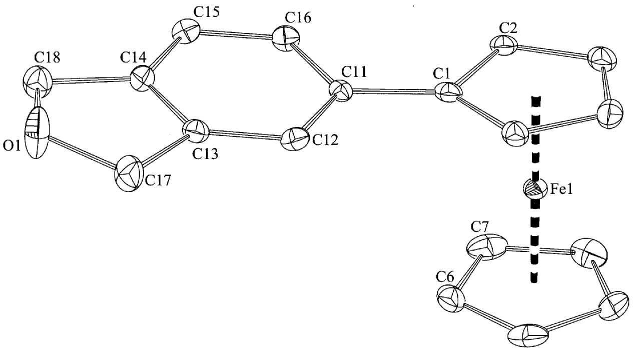


Figure 3. A view of one of the molecules in the structure of **3ab**; hydrogen atoms are omitted for clarity

Table 5. Selected distances and angles for **3ab** and **3bb** (in Å and °)[a,c]

Parameter	**3ab** Molecule 1	Molecule 2	**3bb**
Fe−Cg	1.647(3)	1.655(3)	1.655(3)
Fe−Cg′	1.655(3)	1.655(3)	1.6569(7
Cg−Fe−Cg′	179.0(2)	179.6(2)	178.95(3)
C(Cp)−C(Ar)	1.492(9)	1.466(9)	1.482(2)
φ[b]	6.3(3)	19.6(4)	23.91(7)

[a] Cg and Cg′ are centroids of the substituted and unsubstituted cyclopentadienyl rings, respectively. Cp = substituted cyclopentadienyl plane, Ar = aromatic ring of the isobenzofuran moiety. [b] Dihedral angle subtended by the Cp and Ar least-squares planes. [c] Further data: C12−C19 1.512(2), C19−O2 1.432(2) Å; C12−C19−O2 113.3(1)°.

ably efficient catalysts in the cocyclotrimerization of ferrocenylalkynes with functionalised diynes. The latter (cheaper) complex, however, gives somewhat higher yields in cocyclotrimerizations with ferrocenylethyne **1a**. In view of the above results for different catalytic systems, it is apparent that a careful choice of the catalyst for a specific alkyne-diyne pair may dramatically improve the yield of the respective cyclotrimers.

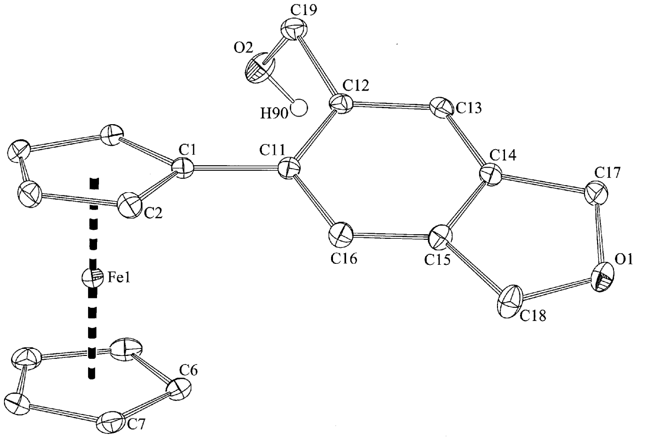


Figure 4. The molecular structure of alcohol **3bb**; only the hydroxyl hydrogen is shown

Experimental Section

General Remarks: Ferrocenylethyne,[19] 1-ferrocenylprop-1-yn-3-ol,[20] [$NiBr_2$(dppe)],[21] and [$CoBr(PPh_3)_3$][15] were synthesised by published procedures. Diynes **2a**, **2c**, **2d**, and **2e** were prepared by alkylation of the corresponding C-acids with propargyl bromide in the presence of K_2CO_3 in MeCN.[22] Propargyl ether and propargyl bromide were purchased from Aldrich. All other chemicals and solvents were of commercial purity and were used without further purification.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Unity Inova 400 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on a PE-640 Perkin−Elmer spectrometer. Mass spectra were obtained on a ZAB-SEQ VG Analytical spectrometer. Elemental analyses were obtained on a Perkin−Elmer 2400 elemental analyser. TLC was performed on Merck Silica Gel 60 F_{254} aluminium sheets and column chromatography was carried out on Fluka Silica Gel 60.

Typical Experimental Procedure: In an argon-purged glass vial, a mixture of a ferrocenylalkyne **1** (0.1 mmol), a diyne **2** (0.1 mmol) and a catalyst (0.01 mmol) in toluene (2 mL) was heated to 50 °C for a period given in Table 1 and 2. Subsequent evaporation of the solvent followed by column chromatography afforded ferrocenylalkynes **3**.

Table 6. Crystallographic data and refinement parameters for **2b**, **3aa**, **3ab**, and **3bb**

Parameter	**2b**	**3aa**	**3ab**	**3bb**
Formula	$C_{13}H_{12}FeO$	$C_{25}H_{26}FeO_4$	$C_{18}H_{16}FeO$	$C_{19}H_{18}FeO_2$
M (g mol^{-1})	240.08	446.31	304.16	334.18
Crystal system	orthorhombic	triclinic	triclinic	monoclinic
Space group	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	7.7249(2)	11.3285(1)	21.4438(6)	10.9862(2)
b (Å)	120.3015(4)	16.9440(2)	20.2460(6)	9.3962(2)
c (Å)	26.8195(7)	24.0092(2)	6.1262(2)	14.1206(2)
α (°)	90	110.156(1)	90	90
β (°)	90	90.778(1)	91.601(2)	96.505(1)
γ (°)	90	104.400(1)	90	90
V (Å^3)	4206.0(2)	4165.36(7)	2658.7(1)	1448.26(5)
Z	16	8	8	4
D_c (g·cm^{-3})	1.517	1.423	1.520	1.533
μ (cm^{-1})	1.400	0.754	1.125	1.045
Total no. of diffrns	32197	86859	30956	25827
Unique/observed diffrns	4688/4016	18910/14567	5226/4040	3306/3039
R_{int} (%)	3.6	2.9	8.4	3.7
R obsd (all) diffrns (%)	3.53 (4.47)	3.67 (5.40)	8.71 (11.0)	2.60 (2.89)
μ (cm^{-1})	1.400	0.754	1.125	1.045
wR obsd diffractions (%)	8.25	9.24	20.7	6.81

Diethyl 5-Ferrocenyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (3aa): ^{1}H NMR yield 81%. Column chromatography on silica gel (19:1 hexane/EtOAc) afforded 25 mg (57%) of an orange solid: m.p. 90−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.2 Hz, 6 H), 3.55 (s, 2 H), 3.60 (s, 2 H), 4.03 (s, 5 H), 4.21 (q, *J* = 7.2 Hz, 4 H), 4.27 (2H), 4.58 (2H), 7.10 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.28 (s, 1 H), 7.30 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 40.3, 40.4, 60.4, 61.7, 66.5, 68.6, 69.5, 85.8, 121.8, 124.0, 125.2, 137.7, 138.0, 140.1, 171.7 ppm. IR ($CHCl_3$): ṽ = 3023, 3016, 1729, 1299, 1278, 1250, 1215, 1211, 1190, 1070, 821 cm^{-1}. $C_{18}H_{16}FeO$: calcd. C 67.28, H 5.87; found C, 67.34, H 5.89. R_f (9:1 hexane/EtOAc) = 0.30.

5-Ferrocenyl-1,3-dihydroisobenzofuran (3ab): ^{1}H NMR yield 75%. Column chromatography on silica gel (19:1 hexane/EtOAc) afforded 16 mg (59%) of an orange solid: m.p. 129−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.04 (s, 5 H), 4.30 (2H), 4.62 (2H), 5.08 (s, 2 H), 5.12 (s, 2 H), 7.15 (dd, *J* = 7.8, 0.8 Hz, 1 H), 7.34 (s, 1 H), 7.40 (dd, *J* = 7.8, 0.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.5, 68.9, 69.6, 73.5, 85.4, 118.4, 120.8, 125.5, 136.8, 138.6, 139.4 ppm. IR ($CHCl_3$): ṽ = 3020, 2857, 1363, 1215, 1106, 1045, 900, 821 cm^{-1}. $C_{18}H_{16}FeO$: calcd. C 70.23, H 5.57; found C, 69.49, H 5.15. R_f (9:1 hexane/EtOAc) = 0.55.

Ethyl 5-Ferrocenyl-2-cyano-2,3-dihydro-1*H*-indene-2-carboxylate (3ac): ^{1}H NMR yield 62%. Column chromatography on silica gel (19:1 hexane/EtOAc) afforded 23 mg (58%) of an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.2 Hz, 3 H), 3.58 (m, *J* = 16.0 Hz, 2 H), 3.68 (m, *J* = 16.0 Hz, 2 H), 4.04 (s, 5 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 4.31 (2H), 4.60 (2H), 7.14 (m, 1 H), 7.31 (s, 1 H), 7.36 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 43.0, 43.0, 47.5, 63.2, 66.4, 66.5, 68.9, 69.6, 85.1, 120.7, 121.9, 124.3, 125.9, 135.7, 138.4, 139.2, 168.5, IR (CCl_4): ṽ = 3094, 2987, 1749, 1515, 1235, 1216, 820 cm^{-1}: *m*/*z* (EI) 399 (100) [M$^+$], 325 (25), 178 (35), 121 (60), 56 (45). HRMS calcd. for $C_{23}H_{21}FeNO_2$ 399.0922, found 399.0944. R_f(9:1 hexane/EtOAc) = 0.45.

1,1′-[5-Ferrocenyl-(1,3-dihydro-2*H*-inden-2-ylidene)]bisethanone (3ad): ^{1}H NMR yield 73%. Column chromatography on silica gel (10:1 hexane/EtOAc) afforded 22 mg (57%) of an orange solid: m.p. 100−103 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 6 H), 3.48 (s, 2 H), 3.52 (s, 2 H), 4.04 (s, 5 H), 4.30 (2H), 4.58 (2H), 7.10 (m, 1 H), 7.28 (m, 1 H), 7.30 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 37.4, 37.5, 66.6, 68.9, 69.8, 74.8, 86.0, 122.0, 124.2, 125.4, 137.4, 138.3, 139.9, 204.9 ppm. IR (CCl_4): ṽ = 3023, 3018, 1700, 1515, 1428, 1359, 1225 cm^{-1}. $C_{26}H_{28}FeO$: calcd. C 70.52, H 5.74; found C, 70.16, H 5.84. R_f (9:1 hexane/EtOAc) = 0.32.

Ethyl 5-Ferrocenyl-2-acetyl-2,3-dihydro-1*H*-indene-2-carboxylate (3ae): ^{1}H NMR yield 77%. Column chromatography on silica gel (10:1 hexane/EtOAc) afforded 25 mg (61%) of an orange solid: m.p. 98−101 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.2 Hz, 3 H), 2.20 (s, 3 H), 3.48−3.52 (m, 4 H), 4.04 (s, 5 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 4.30 (2H), 4.58 (2H), 7.10 (m, 1 H), 7.28 (m, 1 H), 7.30 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 26.1, 38.8, 38.9, 61.8, 66.6, 66.6, 66.9, 68.9, 69.8, 86.3, 122.0, 124.1, 125.3, 137.6, 138.1, 140.0, 172.4, 202.8 ppm. IR (CCl_4): ṽ = 3022, 1713, 1516, 1477, 1424, 1357, 1237, 1225, 1206 cm^{-1}**.** $C_{27}H_{30}FeO_3$: calcd. C 68.24, H 5.81; found C, 68.13, H 5.61. R_f (9:1 hexane/EtOAc) = 0.26.

Diethyl 5-Ferrocenyl-6-hydroxymethyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (3ba): ^{1}H NMR yield 56%. Column chromatography on silica gel (10:1 hexane/EtOAc) afforded 22.5 mg (47%) of an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.2 Hz, 6 H), 3.58 (s, 2 H), 3.64 (s, 2 H), 4.13 (s, 5 H), 4.22 (q, *J* = 7.2 Hz, 4 H), 4.29 (2H), 4.52 (2H), 4.68 (d, *J* = 5.6 Hz, 2 H), 7.25 (s, 1 H), 7.60 (s, 1 H);) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 40.2, 40.3, 60.4, 61.7, 63.5, 68.2, 69.5, 69.7, 86.7, 124.5, 126.5, 136.3, 137.3, 138.6, 139.5, 171.6. *m*/*z* (EI) 476 (55) [M$^+$], 191 (30), 138 (25), 94 (100), 57 (43). IR (CCl_4): ṽ = 3617, 2984, 1736, 1367, 1278, 1245, 1187, 1157, 1068, 1053 cm^{-1}. HRMS calcd. for $C_{26}H_{28}FeO_5$ 476.1286, found 476.1259. R_f(2:3 hexane/EtOAc) = 0.48.

5-Ferrocenyl-6-hydroxymethyl-1,3-dihydroisobenzofuran (3bb): Column chromatography on silica gel (10:1 hexane/EtOAc) afforded 4 mg (12%) of an orange solid: m.p. 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.15 (s, 5 H), 4.33 (2H), 4.55 (2H), 4.74 (d, *J* = 5.2 Hz, 2 H), 5.10 (s, 2 H), 5.70 (s, 2 H), 7.28 (s, 1 H), 7.65

(s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 63.5, 68.4, 69.6, 69.8, 73.4, 121.1, 123.2, 136.8, 137.7, 138.6 ppm. IR (CCl$_4$): $\tilde{\nu}$ = 3261, 3097, 2852, 1363, 1107, 1059, 1003, 907 cm^{-1}: *m*/*z* (EI) 34 (100) [M$^+$], 325 (25), 267 (12), 195 (15), 165 (48), 152 (43), 121 (48), 83 (24). HRMS calcd. for $C_{19}H_{18}FeO_2$ 334.0656, found 334.0660. R_f(2:3 hexane/EtOAc) = 0.42.

X-ray Crystallographic Study: Single crystals suitable for X-ray diffraction analysis were obtained by recrystallisation from hexane (**1b**: orange prism, 0.25 × 0.25 × 0.30 mm^3; **3aa**: orange plate, 0.20 × 0.35 × 0.38 mm^3; **3ab**: orange bar, 0.01 × 0.15 × 0.50 mm^3) or heptane (**3bb**: very thin orange plates, 0.01 × 0.50 × 0.60 mm^3; due to the crystal shape, the diffraction data for **3ab** were of a relatively lower precision, resulting in large residual extremes on the otherwise featureless final difference electron density maps, close to iron atoms). The diffraction data were collected on a Nonius KappaCCD diffractometer equipped with Oxford cryostream cooler at 150 K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and analysed with the HKL program package[23] (Table 6). All structures were solved by direct methods (SIR97)[24] and refined by weighted full-matrix least-squares on F^2 (SHELXL-97).[25] The non-hydrogen atoms were refined with anisotropic thermal motion parameters. With the exception of the hydroxyl hydrogen in the structure of **3cc**, which was identified from the difference electron density map and refined isotropically, all hydrogen atoms were included in calculated positions and assigned U_{iso}(H) = 1.2 (aromatic and methylene) or 1.5 times U_{eq}(C).

CCDC-194875 (**1b**), -186920 (**3aa**), -194876 (**3ab**), and -194877 (**3bb**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work is a part of a research project Z4 055 905 and was financially supported by the Grant Agency of the Czech Republic (grant No. 203/01/0863 to M. K). The authors thank Iva Tišlerová for the measurement of the NMR spectra.

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Received February 26, 2003