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An efficient iminophosphorane-mediated synthesis, NMR–IR spectroscopic and X-ray study of novel ferrocenylimidazole derivatives☆ Part 10. Study on ferrocenes

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Abstract

Starting from ethyl β-ferrocenyl-α-azidoacrylate (**2**), a series of novel 4-ferrocenylidene-1-aminoimidazolones (**6a–j**) was prepared in a pathway involving an *aza*-Wittig reaction followed by condensation of the resulting carbodiimidoester with hydrazines. Formation of [1,2,4]triazines of type **7** was not observed. Simultaneously with the formation of **2**, an interesting transformation was also observed to afford a novel imidazolone derivative (**3**) containing two ferrocenyl groups. The structures of the products were determined by IR, ^{1}H- and ^{13}C-NMR spectroscopy (including 2D-COSY, DEPT, 2D-HMQC, and 2D-HMBC measurements), and in the case of compound **3** also by single-crystal X-ray analysis. © 2001 Published by Elsevier Science B.V.

Keywords: Iminophosphorane; Ferrocenylimidazole derivatives; Ferrocenes; Structure elucidation by IR; NMR; X-ray

1. Synthesis

In the last few decades the chemistry of ferrocenes has led to a wide variety of interesting compounds with valuable catalytic properties and importance in materials science [2]. However, much less attention has been paid to heterocyclic derivatives of metallocenes with potential biological activity [3]. In the frame of our research programme to produce and investigate ferrocenyl-substituted heterocycles carrying pharmacophoric groups, applying a reaction sequence similar to that elaborated by Molina et al. [4–6], we tried to condense in situ prepared ethyl β-ferrocenyl-α-alkyl/arylcarbodiimidoacrylates (**5**) with hydrazines in order to obtain ferrocenylmethyl[1,2,4]triazines of type **7** or the isomeric **6**-type 1-amino-4-ferrocenylmethylideneimidazolones (Scheme 1). All these reactions resulted exclusively in imidazolones. The high stability of the products **6a–j** can probably be attributed to a pronounced push–pull character of the enone moiety bonded to the electron-releasing ferrocenyl group [7].

Attempted cyclisation of *N*-amino derivatives **6a–e** (R′ = H) with triethylorthoformate in the presence of catalytic amounts of *p*-toluenesulfonic acid gave iminoethers **8a–e** in yields of 29–70%, but ring closure to imidazotriazoles of type **9** did not take place even on prolonged reflux of the reaction mixtures.

In the reaction of formylferrocene (**1**) with ethyl-azidoacetate conducted in THF under Knoevenagel conditions, besides the expected ethyl-β-ferrocenyl-α-azidoacrylate (**2**) a considerable amount (20%) of 1-[ethoxyethoxycarbonylmethyl]-2-ferrocenyl-4-ferro-cenylmethylideneimidazole-5(1*H*)-one (**3**) was also formed. This

☆ Part 9: Ref. [1].

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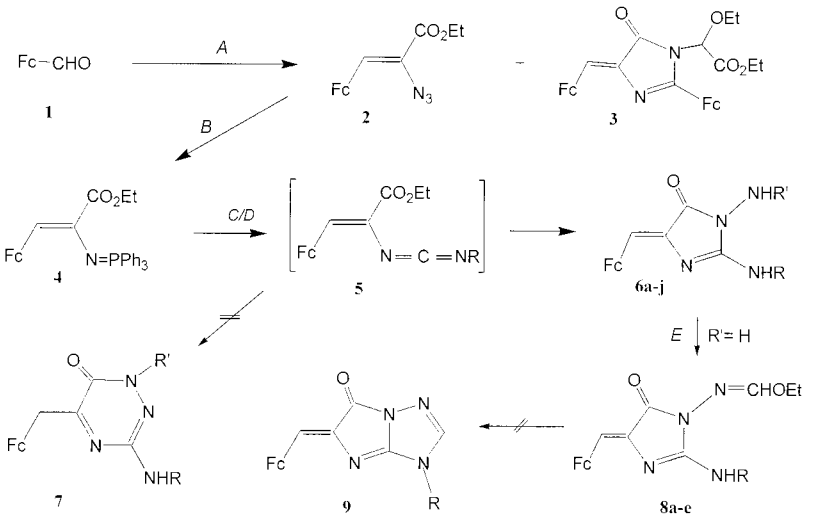


Fc = ferrocenyl-

	R	R'		R	R'
a	C_6H_5-CH_2-	H	**f**	C_6H_5-CH_2-	Me-
b	4-Cl-C_6H_4-	H	**g**	4-Cl-C_6H_4-	PhCH(OH)-CO-
c	4-F-C_6H_4-	H	**h**	C_6H_5-CH_2-	2-pyridyl-
d	2-CF_3-C_6H_4-	H	**i**	4-Cl-C_6H_4-	2-pyridyl-
e	3-CF_3-C_6H_4-	H	**j**	4-F-C_6H_4-	2-pyridyl-

A) $N_3CH_2CO_2Et$ / NaOEt, THF, -30°, 6 h; B) PPh_3 / CH_2Cl_2, RT, reflux, 10 h; C/D) R-NCO / CH_2Cl_2 (C) or THF (D), RT, 24 h + NH_2NHR' (C) or $NH_2NHCOCH(OH)Ph$ (D), RT, stirring 6 h; E) $(EtO)_3CH$ / TsOH reflux, 2 h

Scheme 1.

fact can be due to a subsequent transformation of the initial product (**2**) with unreacted formylferrocene (**1**) and ethyl-azidoacetate. The first step of the proposed mechanism, outlined in Scheme 2, is the base-catalyzed nitrogen elimination [8] leading to iminocarbonic acid ester **10**. Its acylation and subsequent addition of ethanol afford a β-ferrocenyl-α-azidoacrylamide (**10** → **11** → **12**), which then reacts with the unchanged formylferrocene in a redox process taking place with nucleophilic addition followed by 1,2-migration of a hydride anion and simultaneous loss of nitrogen (**12** → **13** → **14**). A closely related transformation is reported in Ref. [9]. In the last step, the resulting β-ferrocenylidene-α-ferrocenoylaminoacrylamide undergoes intramolecular condensation to give **3** as the isolable final product. This suggestion was supported by the result of a control experiment in the course of which equimolar amounts of **1** and **2** were treated with ethyl-azidoacetate under the same conditions applied also in the original reaction **1** → **2** which resulted in **3** with a significant yield (17%).

2. Structure determination

The structures of the new compounds **3**, **6a**–**j** and **8a**–**e** follow from the spectral data straightforwardly (Tables 1–3). Only the following remarks are necessary:

The five-membered ring—γ-lactame (type **6**)—structure of the products of the acylation–condensation reaction sequence follows from the high *ν*C=O IR frequency (1690–1725 cm^{-1}) and in case of compounds **6a**–**e** indirectly from the formation of the iminoethers **8a**–**e** with $CH(OEt)_3$. Type **7** δ-lactames should give lower IR frequencies [10] and derivatives with structures different from **8a**–**e**.

Ring-chain tautomerism in **6a**–**j** must also be considered. The NH signal of the NH–C=NR=N=C–NHR moiety is a triplet in the ^{1}H-NMR spectra of **6a**,**f**,**h** and **8a** proving the preference of the tautomeric form with *endo* C=N double bond and an NHR (R = CH_2Ph) group.

The significantly higher chemical shifts of the NH and ArH-2,6 hydrogens in compounds **6b**–**e** and **8b**–**e** (NH: 7.7–9.7 and 7.1–8.2, ArH-2,6: 7.75–9.0 and 7.69–9.0) as compared to **6a** and **8a** (NH: 5.67 and 5.47, ArH-2,6: 7.46 and 7.38) may be due to the −*I*-effect of the aryl group and its substituents, and can also suggest the shift of the tautomeric equilibrium to favour the form containing an exocyclic C=N double bond (more acidic ring-NH and anisotropic deshielding of the N=C bond [11] on the *ortho* aromatic hydrogens).

To decide between the two tautomers we used ^{1}H, ^{13}C and ^{1}H,^{15}N 2D-HMBC spectroscopy for com-

Table 1
^{1}H-NMR data [a] of compounds **6a**–**j** and **8a**–**e** [b]

Compound	NH_2/=CH s (2/1H) [c]	NH (1H) [d]	CH_2 d (2H)	=CH s (1H)	H-2′,5′ (2H)	H-3′,4′ (2H)	H-1″-5″ (5H)	H-2	H-6	H-3	H-5	H-4
					Substituted c-pentane ring			Aryl group [e]				
6a	4.02	5.67	4.69	6.66	4.97	4.40	4.12	7.46		7.39		7.33
6b	4.91 [f]	7.75	–	6.70	4.95	4.48	4.14	7.97		7.37		–
6c	4.15 [g]	~7.76 [g,h]	–	6.82	4.95	4.48	4.15 [g]	~7.76 [g,h]		7.11		–
6d	5.48	8.42	–	6.67	4.95	4.48	4.11	–	8.77	7.75	7.82	7.30
6e	5.29	9.69	–	6.59	4.98	4.45	4.10	8.96	8.11	–	7.57	7.37
6f [i]	~3.6 [h]	~7.2 [g]	5.15	6.70	4.88	4.35	4.09	7.12		7.23		7.18 [g]
6g [k]	10.6	9.25	–	6.51	4.88	4.41	4.05	7.88	7.45 [e]	7.39	7.29 [e]	7.25 [e]
6h [l]	~8.1 [g]	9.24	4.40	6.33	4.88, 5.08	5.56	4.10	7.45		7.35		7.26
6i [l]	9.63	9.34	–	6.62	~5.0 [h]	4.52	4.18	~8.1 [g]		7.46		–
6j [l]	9.52	9.31	–	6.57	~5.0 [h]	4.49	4.15	8.07		7.23		–
8a [m]	9.22	5.47	4.63	6.57	4.90	4.31	4.04	7.38		7.31		7.24
8b [m]	9.34	7.17	–	6.76	4.90	4.43	4.09	7.69		7.31		–
8c [m]	9.32	7.15	–	6.73	4.89	4.41	4.09	7.69		7.04		–
8d [m]	9.47	8.14	–	6.87	4.97	4.50	4.16	–	8.97	7.63	7.68	7.18
8e [m]	9.41	7.36 [g]	–	6.87	5.00	4.51	4.16	8.52	7.74	–	7.50	7.36 [g]

[a] In $CDCl_3$ solution at 500 MHz. Chemical shifts in ppm ($\delta_{TMS} = 0$ ppm), coupling constants in Hz.

[b] Assignments were supported by 2D-HSC (HMQC) measurements (except for **6a**,**f**,**h**,**i** and **8c**).

[c] NH_2, broad s (2H) for **6a**–**e**, N–NH, broad s (1H) for **6f**–**j**, =CH, s (1H) for **6a**–**e**.

[d] RNH or NH (ring, in the tautomeric form), broadened s, t for **6a**,**f** and **8a** (J: 6.0).

[e] Multiplicity (intensity): ~d (2/2 × 1H) for H-2,6 (**6a**,**f**,**h** and **8a**), H-3,6 (**6d**, **8d**) and H-4,6 (**6e** and **8e**), ~t for H-3,5 and H-4 (2H and 1H, **6a**,**f**,**h** and **8a**), H-4,5 (1H, **6d** and **8d**) and H-5 (1H, **6e** and **8e**), ~s (1H) for H-2 (**6e** and **8e**), AA′BB′-type spectrum, 2 × ~d (2 × 2H) for **6b**,**c**,**g**,**i**,**j** and **8b**,**c** (J: 8.8), the H-3,5 signal is a t for **6c**,**j** and **8c** due to F–H coupling, J(F,H): ~8.

[f] Doubled signal, split by 0.01 ppm.

[g] Overlapping signals.

[h] Broad.

[i] NCH_3, s (3H): 3.19.

[k] C(sp^3)H: 5.15 d (J: 4.5), OH: 6.28 d.

[l] Signals of the α-pyridyl group, H-3, d (J: 8.3): 6.68 (**6h**), 6.81 (**6i**), 6.78 (**6j**), H-4, dt (J: 7.8, 7.8, 1.8): 7.63 (**6h**,**i**), 7.66 (**6j**), H-5, dd (7.0, 5.0): 6.85 (**6h**–**j**), H-6, dd (J: 5.0 and 1.8): ~8.1[g] (**6h**,**i**): 8.06[g] (**6j**).

[m] CH_3 t (3H, J: 7.0): 1.27 (**6h**), 1.35 (**6i**,**j**), 1.43 (**8d**,**e**), CH_2 qa (2H, J: 7.0): 4.09 (**8a**), 4.20 (**8b**,**c**), 4.28 (**8d**,**e**).

Table 2
^{13}C-NMR chemical shifts [a] of compounds **6a–j** and **8a–e** [b,c]

Compound	CH_2	=CH	C-2	C-4	C=O	C-1′	C-2′,5′	C-3′,4′	C-1″-5″	C-1	C-2	C-6	C-3	C-5	C-4
			Imidazolinone ring			Substituted *c*-pentane ring				Aryl group					
6a	45.7	120.7	154.9	135.5	168.8	79.1	71.4	70.9	69.9	138.6	128.5		129.2		128.2
6b	–	120.6	151.3	134.3	166.6	~78 [d]	70.2	70.1	68.9	136.8	119.7		128.1		126.5
6c	–	123.8	150.7	?	167.5	?	71.5 [e]		70.2	134.3	120.3 [f]		116.3 [f]		159.2 [f]
6d	–	122.6	153.0	135.3	166.9	78.8	71.6 [g]	71.5 [g]	70.2	136.3	118.0 [f]	121.8	127.4 [f]	134.8	124.1 [f]
6e	–	121.0	154.0	135.8	167.5	79.2	71.3 [g]	71.2 [g]	70.2	140.7	116.3 [f]	123.7	130.3 [f]	130.6	119.5 [f]
6f	46.6	121.7	159.0	?	?	79.2	71.3	71.0	69.9	138.6	127.0		128.9		127.4
6g	–	121.5	152.0	134.8	165.6	78.9	71.5 [e]		70.2	138.4	121.9		129.6		127.5
6h	44.9	117.0	156.7	136.9	167.9	80.2	70.6 [h]	70.2	70.0	140.5	128.5		129.0		127.7
6i	–	121.3	153.3	135.3	166.7	79.2	71.4 [e]		70.2	138.8	121.9		129.4		127.2
6j	–	120.6	153.4	135.5	166.8	79.3	71.3 [e,i]		70.2	136.2	122.0 [f]		116.1 [f]		158.5 [f]
8a	45.8	120.8	153.9	135.7	166.1	79.2	71.3	70.9	69.9	138.8	129.2		128.4		128.2
8b	–	124.3	149.4	134.5	164.8	78.4	71.5 [e]		70.1	136.8	120.3		129.6		128.5
8c	–	123.8	149.7	134.6	164.9	78.5	71.5 [e]		70.1	134.4	120.5 [f]		116.2 [f]		159.1 [f]
8d	–	125.3	149.3	134.4	164.6	78.2	71.6 [e]		70.1	136.4	117.9 [f]	120.8	126.7 [f]	138.8	122.7
8e	–	125.3	149.3	134.2	164.7	78.1	71.6 [g]	71.7 [g]	70.1	138.8	116.0 [f]	121.8	132.0 [f]	130.0	120.0

[a] In $CDCl_3$ solution at 125 MHz. Chemical shifts in ppm ($\delta_{TMS} = 0$ ppm), coupling constants in Hz.

[b] Assignments were supported by DEPT, for **6b–d,g,j** and **8a,b,d,e** by HMQC (2D-HSC) and for **6a–e,g,j** and **8a,b,d,e** also by HMBC (2D-COLOC) measurements.

[c] Further signals: CF_3, qa: ~125 (**6d**), 125.2 (**6e**), 124.9 (**8d**), 124.5 (**8e**), NCH_3 (**6f**): 43.6, C=O (**6g**): 172.8; C(sp^3)H (**6g**): 74.3, C_{Ar}-1 (**6g**): 141.4, C_{Ar}-2,6 (**6g**): 128.3, C_{Ar}-3,5 (**6g**): 129.0, C_{Ar}-4 (**6g**): 128.7, α-pyridyl group, C-2: 158.1 (**6h–j**), C-3: 108.6 (**6h**), 10.9.2 (**6i,j**), C-4: 138.7 (**6h–j**), C-5: 117.0 (**6h**), 117.3 (**6i,j**), C-6: 148.5 (**6h–j**), CH_3: 14.5 (**8a**), 14.6 (**8b,c,e**), 14.4 (**8d**), CH_2: 63.6 (**8a**), 63.9 (**8c**), 64.0 (**8b,e**), 63.2 (**8d**), N=CH: 158.2 (**8a,b,c,e**), 156.8 (**8d**).

[d] Determined indirectly with limited accuracy from HMBC (2D-COLOC) measurement.

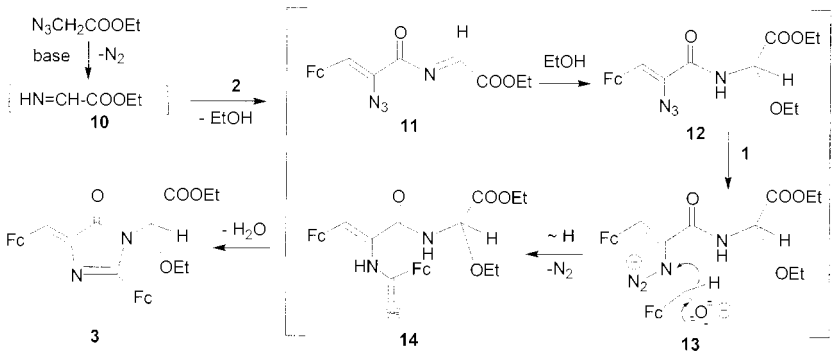
[e] Overlapping signals.

[f] Doublet (**6c,j** and **8c**)/quartet (**6d,e** and **8d,e**) split due to F,H-couplings, ^1J: 240.7 (**6c**), 272.0 (**6e** and **8e**), 239.4 (**6j**), 242.4 (**8c**), 275.8 (**8d**), ^2J: 22.7 (**6c**), 29.7 (**6d**), 22.2 (**6j**), 22.6 (**8c**), 30.5 (**6e**, **8d**), 32.5 (**8e**), ^3J: 8.4 (**6c**), ~8 (**6d,e**), 7.6 (**6j**, **8c**), 5.1 (**8d**), 3.8 (with H-2), <3 (with H-4) (**8e**), ^4J: ~3 (**6d**).

[g] Interchangeable assignments.

[h] Two lines (the second one appears at 71.2).

[i] Broadened signal.



Scheme 2.

Table 3
Characteristic IR frequencies (cm^{-1}) of compounds **6a**–**j**, and **8a**–**e** (KBr discs)

Compound	νNH band (broad or diffuse)	νC=O band [a]	νC=N band [b]	$\gamma C_{Ar}H$ band	ν_{as}Cp–Fe–Cp and tilt of Cp
6a	3325, 3250	1690	1657	750	480
6b	3320, 3190	1719	1653	835	492
6c	3380, 3315	1712	1661	840	514
6d	3395, 3330	1705	1655	767	501
6e	3600–3250	1701	1654	789	482, 492
6f	3326	1699	1654	721	481
6g	3500–3300 [c]	1712 [d]	1654	826 [e]	489
6h	3375	1720	1661	760	477
6I	3270	1711	1651	828	502
6j	3359, 3295	1725	1653	839	486
8a	3400	1696	1655, 1598	734	497
8b	3370	1701	1651, 1594	824	573, 489
8c	3370	1705	1653, 1588	837	~500
8d	3385	1703	1657, 1595	760	490
8e	3390	1699	1655, 1595	696	535, 496

[a] Amide-I-type band of the γ-lactame group.
[b] νC=N (ring) > νC=N (side chain) for compounds **8a**–**e**.
[c] Coalesced with the νOH band.
[d] νC=O (side chain),
[e] $\gamma C_{Ar}C_{Ar}$ band for **6a**,**e**,**f**,**g**,**h** and **8a**,**e**: 700 ± 3.

pound **6i**. $^{1}H,^{15}N$-correlations =CH(α),N-3 and N-1(pyridine) with H-5(pyridine), H-6(pyridine), and H(hydrazine-NH), respectively, prove the assignments for the signals of these nitrogens at 181 and 268 ppm. Similarly, N-1 must give the line at 157 ppm showing long-range correlations to both NHs. Thus, the two exocyclic nitrogens must have overlapping signals at 92 ppm. Indeed, in the ^{1}H-dimension two doubled cross-peaks are identifiable with $^{1}J(N,H)$: 91 (δNH: 9.30 ppm) and 93 Hz (δNH: 9.60 ppm). Since the ^{1}H signal at 9.30 ppm has cross-peaks also with N-1 and N-1(pyridine), while the other at 9.60 ppm with N-1 and N-3, the first one can be assigned as the hydrazine-NH and the second one to the exocyclic-NH in position 2. Thus, $^{1}H,^{13}C$-correlation via long-range couplings can be seen between the NH group having a signal at 9.60 ppm and the *ortho*-carbons of the *N*-aryl group (121.9 ppm) and, similarly between the NH-hydrogen having a shift at 9.30 ppm and the C-3 of the pyridine ring. Thus, the tautomeric form with the endocyclic C=N bond is predominant in these compounds independently from aromatic or aralkyl-type of the N-substituent. Nevertheless, significant differences were measured, e.g. for the shifts of the =CH, C-2 and C=O carbons (=CH: 120.8 and 123.8–125.3, C-2: 153.9 and 149.3–149.7, C=O: 166.1 and 164.6–164.9) in the benzyl (**a**) and aryl (**b**–**e**) derivatives of structure **8**. A similar but smaller difference in the carbonyl shift is also observable for **6a** as compared to **6b**–**e** (168.8 and 166.6–167.5), but the buffering effect of the NHR′ group can compensate here in case of **6**-type compounds the change in electron density about the ring atoms due to $-I$-effect of the N-substituents.

It is interesting to note that the H-2′,5′ signal (cyclopentadienyl ring) is doubled in the case of **6h** only, suggesting hindered rotation (coplanar arrangement of

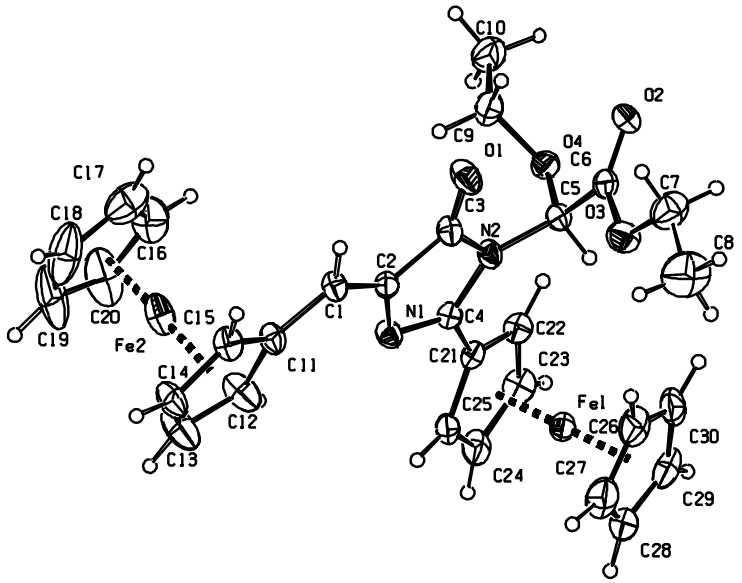


Fig. 1. Perspective view of the structure of compound **3** showing the X-ray labelling of non-hydrogen atoms and their 50% probability displacement ellipsoids. Hydrogen atoms are shown as small spheres with constant radius.

the C=C double bond and the cyclopentadiene ring) of the ferrrocenyl moiety. This fact may be interpreted by a steric hindrance between this group and the benzyl substituent.

Because of the individual single structure of **3**, the spectral data are given in Section 3 instead of in the tables.

In the IR spectrum two carbonyl band of relatively high frequencies (1765 and 1713 cm^{-1}) are present. Concerning the starting materials and the reaction conditions the presence of a saturated ester group (1713 cm^{-1}) and a carbonyl in the strained ring (1765 cm^{-1}, γ-lactone/lactame) are probable. ^{1}H- and ^{13}C-NMR signals of two different ethoxy and ferrocenyl groups appear in the corresponding spectra confirming the participation of two molecules of formylferrocene and azidoaceticester in the reaction. The ^{1}H- and ^{13}C-NMR signals of the atom pairs in positions 2′,5′ and 3′,4′ are separated pointing to hindered rotation of the ferrocenyl moieties due to steric hindrance or conjugation and, consequently coplanar arrangement of the substituted cyclopentadiene (Cp) rings with a double bond. Two separated CH groups, one of which containing an sp^2 or sp^3 carbon and two quaternary sp^2 carbon atoms, one vicinal to one or two heteroatoms (δC: 159.9 ppm) are also present in the molecule.

All the above data are consistent with structure **3** as determined by X-ray diffraction.

The X-ray crystal structure analysis of **3** revealed the structure depicted in Fig. 1. The structure shows a fairly perfect alignment of the Fe in their respective cyclopentadienyl ligands. Metal atoms have practically zero slippage with respect to their ring centres and are aligned near-perfectly collinear with angles at the Fe atom of 177 and 178°, respectively. The cyclopentadienyl rings of the ferrocenyl substituents adopt an almost perfect ecliptic conformation and they have the usual geometry and are also coplanar within one unit. With respect to the central imidazole ring they have similar and only slightly differing low dihedral angles with mean values of 13.3(3) and 22.2(3)°, respectively. The intramolecular geometry otherwise shows normal values.

Since no classic hydrogen bonds are possible we only found five (cf. Table 4) C–H···O-type interactions [12]. Two of these are intramolecular and both go to the same side of the chiral C atom. Here one H-atom of the $–CH_2$ moiety at C-9[1] is on one side, while atom O-4 connects H-22 of one of the CH hydrogen of the more twisted ferrocenyl group. A further disparity in these interactions is that two of the three intermolecular C–H···O attachments go also to this ether side arm: one connects to the other hydrogen of the 9-methylene group while one possible H-atom site of the methyl termini is also involved. The only interaction of the other ester side arm goes from O-2 to the ferrocenyl H-30. Note that virtually identically placed ferrocenyl H-atoms of the more twisted ferrocenyl group take part in the interactions. The relative importance of these forces fixing the respective ferrocenyl can be well assessed from the atomic displacement representations of Fig. 1. These are noticeably larger for the unbound ferrocenyl group.

[1] For X-ray numbering see Fig. 1.

Table 4
Possible C–H···O type contacts in the crystal of **3**

Type	Donor–H···acceptor	D–H	H···A	D···A	D–H···A
Intra	C(9)–H(9A)···O(2)	1.083	2.517	3.102(5)	112.8
	C(9)–H(9B)···O(1)[a]	1.083	2.498	3.405(5)	140.6
	C(10)–H(10A)···O(2)[a]	1.083	2.462	3.425(5)	147.5
Intra	C(22)–H(22)···O(4)	1.083	2.354	3.189(4)	132.7
	C(30)–H(30)···O(2)[b]	1.083	2.458	3.395(6)	144.2

Note that the C–H bond lengths are idealised, thus the geometry proposed here is the best possible one. Estimated S.D.s are only given where meaningful values exist. Translation of symmetry codes to equivalent positions: (a) = x, $5/2-y$, $-1/2+z$; (b) = $1-x$, $2-y$, $1-z$.

3. Experimental

The ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution in 5 mm tubes at room temperature (r.t.), in a Bruker DRX 500 spectrometer at 500.13 (^{1}H) and 125.76 (^{13}C) MHz, with the deuterium signal of the solvent as the lock and TMS as internal standard. Distortionless enhancement by polarisation transfer (DEPT) spectra were run in a standard manner, using only the $\Theta = 135°$ pulse to separate CH/CH_3 and CH_2 lines phased 'up' and 'down', respectively. The 2D-HMQC and 2D-HMBC spectra were obtained by using the standard Bruker pulse programs INV4GSSW and INV4GSLRNDSW, respectively. The IR spectra were recorded as KBr pellets in a Bruker IFS 55 spectrometer.

Melting points (uncorrected) were determined with a Boetius apparatus.

A summary of crystallographic data for **3** is compiled in Table 5. A crystal of **3** was mounted on a glass fibre. Cell parameters were determined by least-squares of the setting angles of 25 ($10.06 \leq \Theta \leq 11.49°$) reflections. Intensity data were collected in an Enraf–Nonius CAD4 diffractometer (graphite monochromator; Mo–K_α radiation, $\lambda = 0.71070$ Å) at 295(2) K in the range $2.34 \leq \Theta \leq 26.14°$ using $\omega/2\Theta$ scans. The scan width was $0.50 + 0.68\text{tg}(\Theta)°$ in ω. Backgrounds were measured in half the total time of the peak scans. The intensities of three standard reflections were monitored regularly (every 60 min). The intensities of the standard reflections indicated a crystal decay of 4%, and the data were corrected for decay [13].

A total of 5512 reflections was collected of which 5218 were unique [$R_{int} = 0.0209$, $R(\sigma) = 0.1486$]; intensities of 2418 reflections were greater than $2\sigma(I)$. Completeness to $\Theta = 0.982$. An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.8053 and 0.8486) [14]. The initial structure model was obtained from direct methods [15] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement [16] on F^2 for all non-hydrogen atoms yielded $R_1 = 0.0465$ and $wR_2 = 0.0891$ for 2418 [$I > 2\sigma(I)$] and $R_1 = 0.0503$ and $wR_2 = 0.1028$ for all (5218) intensity data. (Goodness-of-fit = 0.827, extinction coefficient = 0.00023(19),

Table 5
Crystal data and structure refinement parameters for **3**

Empirical formula	$C_{30}H_{30}Fe_2N_2O_4$
Formula weight	594.26
Temperature (K)	295(2)
Radiation and wavelength	Mo–K_α, $\lambda = 0.71070$ Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	17.441(2)
b (Å)	15.091(2)
c (Å)	10.108(1)
α (°)	90.00
β (°)	93.47(1)
γ (°)	90.00
V (Å^3)	2655.6(5)
Z	4
D_{calc} (Mg m^{-3})	1.486
Absorption coefficient, μ (mm^{-1})	1.132
$F(000)$	1232
Crystal colour	Pale yellow
Crystal description	Block
Crystal size (mm)	$0.20 \times 0.20 \times 0.15$
Absorption correction	Empirical
Max/min transmission	0.8486, 0.8053
Theta range for data collection (°)	$2.34 \leq \theta \leq 26.14$
Index ranges	$0 \leq h \leq 21$, $7 \leq k \leq 18$, $12 \leq l \leq 12$
Reflections collected	5512
Completeness to 2θ	0.982
Number of standard reflections	3
Decay (%)	4
Independent reflections	5218 [R(int) = 0.0209]
Reflections [$I > 2\sigma(I)$]	2418
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5218/0/346
Goodness-of-fit on F^2	0.827
Extinction coefficient	0.00023(19)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.0891$
R indices (all data)	$R_1 = 0.1503$, $wR_2 = 0.1028$
Max and mean shift/estimated S.D.	0.000; 0.000
Largest difference peak and hole (e Å^{-3})	0.324 and −0.386

Table 6
Physical and analytical data of compounds **6a–j** and **8a–e**

Compound	Appearance	M.p. (°C)	Formula	Calc. (%)			Found (%)		
				C	H	N	C	H	N
6a	Purple powder	181–183	$C_{21}H_{20}FeN_4O$	63.00	5.00	14.00	63.15	4.93	14.07
6b	Orange plates	225–227	$C_{20}H_{17}ClFeN_4O$	57.14	4.04	13.33	57.23	4.10	13.42
6c	Purple plates	206–209	$C_{20}H_{17}FFeN_4O$	59.40	4.20	13.86	59.56	4.18	13.91
6d	Orange powder	203–204	$C_{21}H_{17}F_3FeN_4O$	55.50	3.74	12.33	55.41	3.79	12.40
6e	Orange powder	109–112	$C_{21}H_{17}F_3FeN_4O$	55.50	3.74	12.33	55.42	3.75	12.39
6f	Red powder	163–166	$C_{22}H_{22}FeN_4O$	63.76	5.31	13.52	63.64	5.26	13.58
6g	Red needles	212–214	$C_{28}H_{23}ClFeN_4O_3$	60.64	4.15	10.10	60.51	4.21	10.14
6h	Red plates	201–204	$C_{26}H_{23}FeN_5O$	65.40	4.82	14.67	65.37	4.91	14.65
6i	Red plates	205–207	$C_{25}H_{20}ClFeN_5O$	60.36	4.02	14.08	60.43	4.11	14.12
6j	Red plates	196–199	$C_{25}H_{20}FFeN_5O$	62.37	4.15	14.55	62.52	4.23	14.63
8a	Purple powder	170–172	$C_{24}H_{24}FeN_4O_2$	63.15	5.26	12.28	63.19	5.33	12.35
8b	Purple powder	187–188	$C_{23}H_{21}ClFeN_4O_2$	57.98	4.41	11.76	58.01	4.45	11.84
8c	Purple powder	162–165	$C_{23}H_{21}FFeN_4O_2$	60.00	4.56	12.17	60.13	4.63	12.19
8d	Purple powder	185–187	$C_{24}H_{21}F_3FeN_4O_2$	56.47	4.11	10.98	56.49	4.18	11.07
8e	Purple powder	156–158	$C_{24}H_{21}F_3FeN_4O_2$	56.47	4.11	10.98	56.50	4.20	11.02

the maximum and mean shift/estimated S.D. is 0.000 and 0.000.) The maximum and minimum residual electron density in the final difference map was 0.324 and -0.386 e Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atomic positions were calculated from assumed geometry. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U_{eq} value of the atom they were bonded to, all calculation were performed also using normalised geometries [17].

Compounds **2** and **4** are described in the literature [4–6].

In the course of the preparation of **2**, 1-(1-ethoxy-1-ethoxycarbonylmethyl)-2-ferrocenyl-(*E*)-4-ferrocenylmethylideneimidazolin-5(1*H*)-one (**3**) was also formed and isolated as a slowly eluting component by chromatography over silica (eluent: $CHCl_3$), yield 20%.

IR (KBr disc, cm^{-1}): *v*C=O (γ-lactame): 1765; *v*C=O (ester): 1713; *v*C–O: 1220, 1155, 1124, 1027; ferrocenyl (v_{as}Cp–Fe–Cp and tilt vibr. of Cp rings): 505, 479, 457.

^{1}H-NMR (δ, ppm, $CDCl_3$, 500 MHz): CH_3: 1.01,[2 a] 1.35,[b] 2 × t (2 × 3H), $J = 7.3$, 6.9 Hz; CH_2: 4.03, qa (2H),[a] 3.73 and 3.89, 2 × qa (2H),[b] H-2″-5″, 2 × s (2 × 5H):[c] 4.13,[e] 4.17;[f] H-3′,4′, ∼s (4 × 1H):[d] 4.38,[e] 4.46,[e] 4.53,[f] 4.55,[f] H-2′,5′, ∼s:[d] 5.01 (1H),[f] 5.06 (1H),[e] 5.13 (2H); C(sp^3)*H*, s (1H): 5.97; =C*H*, s (1H): 7.07.

^{13}C-NMR (δ, ppm, $CDCl_3$, 126 MHz): CH_3: 14.3,[a] 15.5;[b] CH_2: 62.8,[a] 64.8;[b] C-2″-5″:[c] 70.4, 70.6; C-1′:[d] 73.0,[e] 78.0;[f,g] C-2′,5′:[d] 69.4,[e] 71.2,[e] 72.4,[f,h] 72.7;[f] C-3′,4′:[d] 71.6,[f,i] 72.4,[f,h] 72.6;[f] *C*(sp^3)H: 78.0;[g] =*C*H: 130.7; C-4: 136.2; C-2: 159.9; C=O:[a] 167.2; C=O (C-5): 170.1.

The appropriate 1-amino- (**6a–e**), 1-(methyl)amino- (**6f**), 1-(mandeloyl)amino (**6g**) and 1-(2-pyridyl)amino-2-arylamino-4-ferrocenylmethylideneimidazolin-5-ones (**6h–j**) were prepared by condensation of compound **4** with the corresponding isocyanates followed by reaction with hydrazine or hydrazine derivatives (yields: 15–92%).

The 1-amino-2-arylamino-4-ferrocenylmethylideneimidazolin-5-ones (**6a–e**) with triethyl orthoformate gave 1-(ethoxymethylidene)amino derivatives (**8a–e**) in yields of 29–70%.

3.1. General procedure for preparation of 1-amino-, 1-(methyl)amino-, 1-(mandeloyl)amino- and 1-(2-pyridyl)amino-2-arylamino-4-ferrocenylmethylideneimidazolin-5-ones

To a solution of **4** (0.4 g, 0.0007155 mol) in anhydrous CH_2Cl_2 (30 ml) the corresponding isocyanate was added and the mixture was stirred at r.t. for 24 h to form carbodiimides **5**. Then, hydrazine or hydrazine derivatives (0.0007155 mol) were added to the reaction mixture to give imidazolinones **6a–j** by stirring at r.t. for another 6 h. The solvent was removed under reduced pressure and the crude solid was chromatographed on silica (Kieselgel type 9385; eluent: *n*-hexane–ethyl acetate 3:1). Recrystallisation from petroleum ether 40–70 °C gave the pure products. Product **6g** was prepared in the same way but the solvent was anhydrous tetrahydrofuran in which mandeloyl hydrazide is fairly soluble (see Table 6).

1-Amino-2-benzyl-4-ferrocenylmethylideneimidazolin-5-one (**6a**) (74%); 1-amino-2-*p*-chlorophenyl-4-ferrocenylmethylideneimidazolin-5-one (**6b**) (91%); 1-

[2] a—Ester group; b—ether group; c,d—cyclopentadiene ring unsubstituted/substituted; e,f—ferrocenyl group bonded to the imidazolone ring in position 2/in side chain; g,h,i—two coalesced lines.

amino-2-*p*-fluoro-phenyl-4-ferrocenylmethylideneimidazolin-5-one (**6c**) (92%); 1-amino-2-α,α,α-trifluoro-*o*-tolyl-4-ferrocenylmethylideneimidazolin-5-one (**6d**) (60%); 1-amino-2-α,α,α-trifluoro-*m*-tolyl-4-ferrocenylmethylideneimidazolin-5-one (**6e**) (52%); 1-(methyl)-amino-2-benzyl-4-ferrocenylmethylideneimidazolin-5-one (**6f**) (15%); 1-(mandeloyl)amino-2-*p*-chlorophenyl-4-ferrocenylmethylideneimidazolin-5-one (**6g**) (42%); 1-(2-pyridyl)amino-2-benzyl-4-ferrocenylmethylideneimidazolin-5-one (**6h**) (63%); 1-(2-pyridyl)amino-2-*p*-chlorophenyl-4-ferrocenylmethylideneimidazolin-5-one (**6i**) (66%); 1-(2-pyridyl)amino-2-*p*-fluorophenyl-4-ferrocenylmethylideneimidazolin-5-one (**6j**) (54%).

3.2. General procedure for preparation of 1-(ethoxymethylidene)amino-2-arylamino-4-ferrocenylmethylideneimidazolin-5-ones

To a solution of **6** (0.0005 mol) in triethyl orthoformate (5 ml) *p*-tolylsulfonic acid was added in catalytic amount and the mixture was heated to reflux temperature under stirring for 2 h. Then, the solvent was removed under reduced pressure and the crude solid was chromatographed on silica (Kieselgel type 9385; eluent: *n*-hexane–ethyl acetate 1:1). Recrystallisation from anhydrous ethanol gave the pure products (see Table 6).

1-(Ethoxymethylidene)amino-2-benzyl-4-ferrocenylmethylideneimidazolin-5-one (**8a**) (70%); 1-(ethoxymethylidene)amino-2-*p*-chlorophenyl-4-ferrocenylmethylideneimidazolin-5-one (**8b**) (64%); 1-(ethoxymethylidene)amino-2-*p*-fluorophenyl-4-ferrocenylmethylideneimidazolin-5-one (**8c**) (65%); 1-(ethoxymethylidene)amino-2-α,α,α-trifluoro-*o*-tolyl-4-ferrocenylmethylideneimidazolin-5-one (**8d**) (29%); 1-(ethoxymethylidene)amino-2-α,α,α-trifluoro-*m*-tolyl-4-ferrocenylmethylideneimidazolin-5-one (**8e**) (34%).

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References

[1] Á. Abrán, A. Csámpai, A. Kotschy, O. Barabás, P. Sohár, J. Mol. Struct. 569 (2001) 185.
[2] A. Togni, T. Hayashi (Eds.), Ferrocenes (Homogeneous Catalysis, Organic Synthesis, Materials Science), VCH Verlagsgesellschaft, Weinheim, 1995.
[3] (a) K.E. Dombrowski, W. Baldwin, J.E. Sheats, J. Organomet. Chem. 302 (1986) 281;
(b) E.W. Neuse, M.G. Meirim, N.F. Blam, Organometallics 7 (1988) 2562;
(c) A. Houlton, R.M.G. Roberts, J. Silver, J. Organomet. Chem. 418 (1991) 107.
[4] P. Molina, A. Pastor, M.J. Vilaplana, M.V. Desamparados, Organometallics 16 (1997) 5836.
[5] P. Molina, A. Tarraga, D. Curiel, C.R. de Arellano, Tetrahedron 55 (1999) 1417.
[6] A. Tarraga, P. Molina, D. Curiel, J.L. Lopez, M.V. Desamparados, Tetrahedron 55 (1999) 14701.
[7] W.E. Watts, J. Organomet. Chem. Library 7 (1979) 399 (and references therein).
[8] D. Knittel, Synthesis (1985) 186.
[9] D.H.R. Barton, A.N. Starratt, J. Chem. Soc. (1965) 2444.
[10] S. Holly, P. Sohár, in: L. Láng (Ed.), S. Holly, P. Sohár (Collaborators), Theoretical and Technical Introduction to the Series: Absorption Spectra in the Infrared Region, Akadémiai Kiadó, Budapest, 1975, p. 113.
[11] P. Sohár, Nuclear Magnetic Resonance Spectroscopy, vol. 2, CRC Press, Boca Raton, FL, 1983, p. 89.
[12] For C–H···Acceptor interactions: Th. Steiner, Crystallogr. Rev. 6 (1996) 1.
[13] K. Harms, XCAD4 Data Reduction Program for CAD4 Diffractometers, Philipps-Universität Marburg, Germany, 1996.
[14] A.C. North, D.C. Philips, F. Mathews, Acta Crystallogr. Sect. A 24 (1968) 350.
[15] SHELXS: G.M. Sheldrick, SHELXS-97, Program for Crystal Structure, University of Göttingen, Göttingen, Germany, 1997.
[16] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
[17] PLATON: A.L. Spek, Acta Crystallogr. Sect. A 46 (1990) C-34. ORTEP: M.N. Burnett, C.K. Johnson, ORTEP-III, ORNL Report 6895, 1996.