

Bis(ferrocenyl)mercury as a source of ferrocenyl moiety in Pd-catalyzed reactions of carbon–carbon bond formation

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Dedicated to Professor J.F. Normant on the occasion of his 65th birthday

Abstract

The application of bis(ferrocenyl)mercury as a source of ferrocenyl group in Pd-catalyzed reactions with aryl halides, acid chlorides and electrophilic alkynes has been demonstrated. The formation of dimethyl-(*Z*)-2,3-di(ferrocenyl)-2-butenedioate in Pd-catalyzed addition of bis(ferrocenyl)mercury to dimethylacetylenedicarboxylate has been confirmed by X-ray analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bis(ferrocenyl)mercury; Ferrocenes; Cross-coupling reactions

1. Introduction

The last decade saw a surge of interest in the synthesis of aryl-, alkenyl-, and alkynylsubstituted ferrocenes owing to their potential applications as NLO chromophores [1], LC materials [2], in electrochemistry [3], polymer chemistry [4], material chemistry [5,6], etc. These classes of compounds have been proven to be most readily accessed by cross-coupling reactions, e.g. of iodoferrocene with arylboronic acids [7], and organotin compounds [8], or alternatively of aryl halides with tin [9], and zinc [6,10] derivatives of ferrocene, as well as ferrocenylboronic acids [11]. These reactions allow to attach one or several ferrocene residues to the aromatic ring, and to prepare oligo- and polymeric products, if bis(tin) or bis(zinc) derivatives of ferrocene are employed [6,10a,b].

We have investigated the application of ferrocenylmercuric derivatives in cross-coupling reactions leading to ferrocene-containing conjugated molecules. The derivatives of mercury have a number of notable advantages over other sorts of organometallic com-

pounds commonly used in cross-coupling chemistry, including higher selectivity of reactions, tolerance to a wide range of important functional groups, as well as easy availability by a direct mercuriation of ferrocene. In the preliminary communication we have shown that ferrocenylmercuric compounds are best suited for selective substitution of one of the halogen atoms in dihalo-substituted arenes [12]. Here we report the results of our further investigation on the application of bis(ferrocenyl)mercury in the cross-coupling reaction with aryl, hetaryl, acid halides and in the addition to alkynes.

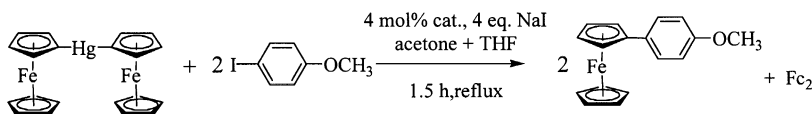
2. Results and discussion

2.1. Reaction of bis(ferrocenyl)mercury with aryl halides

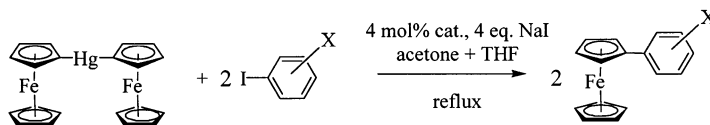
We have found that cross-coupling of bis(ferrocenyl)mercury with aryl iodides can be accomplished in the presence of 4 mol% of Pd catalyst and four equivalents of iodide salt, such as KI, Bu₄N⁺I[−] or NaI. As aryl iodides with electron-withdrawing substituents reacted more readily than those with electron-donating substituents, we have chosen the least reactive substrate

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Scheme 1.



Scheme 2.

4-iodoanisole (67% yield in the initial run in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ catalyst) in the search for an optimal catalyst (Scheme 1).

The complexes of PdCl_2 with dppf, DPEphos, and acetonitrile were less effective than $\text{PdCl}_2(\text{PPh}_3)_2$ and yielded bis(ferrocenyl) as the main product (yields of Fc_2 were about 70%) with moderate conversions of starting Fc_2Hg . The best result was obtained with $\text{Pd}(\text{PPh}_3)_4$ to give 80% of the cross-coupling product with quantitative conversion of Fc_2Hg . Iodide ions may perform multiple functions, from the regeneration of bis(ferrocenyl)mercury from less reactive FcHgI , to the nucleophilic catalysis well known in the reactions of organomercury compounds [13]. Halide ions have recently been reported to enhance the reactivity of zerovalent palladium through the formation of electron-rich anionic complexes $[\text{Pd}(0)\text{Hal}]^-$ [14]. The best results were obtained in the presence of NaI in THF–acetone (3:2, v/v) solvent at reflux. A higher temperature of the reaction allowed to markedly reduce the time of reaction. It should be noted that both ferrocene fragments of Fc_2Hg were involved in the reaction. The use of FcHgCl instead of Fc_2Hg under the same conditions gave lower yield of the cross-coupling product (52 vs. 80%).

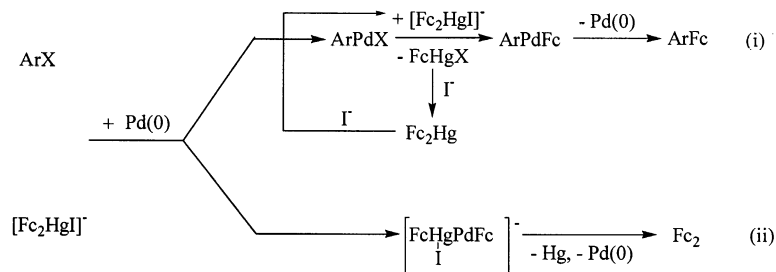
The procedure elaborated for 4-iodoanisole was used to perform the reactions of bis(ferrocenyl)mercury with other aryl (hetaryl) iodides (Scheme 2). The results are shown in Table 1.

We have found that in the presence of $\text{Pd}(\text{PPh}_3)_4$ bis(ferrocenyl)mercury gives from high to near quantitative yields of the cross-coupling products with a wide range of aryl iodides. High yields were obtained both with $\text{Pd}(\text{PPh}_3)_4$ and $\text{PdCl}_2(\text{PPh}_3)_2$ (entries 3, 4 and 17) with aryl iodides bearing electron-withdrawing substituents.

Ortho-substituted aryl iodides are considerably less reactive giving lower yields of target products in longer reaction times (with the exception of 2,4-dinitroiodobenzene, which readily reacts with bis(ferrocenyl)mercury even without Pd catalyst).

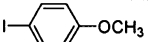
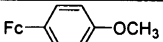
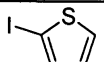
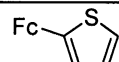
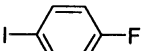
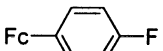
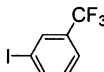
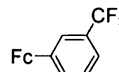
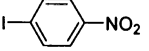
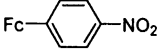
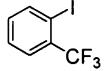
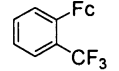
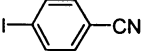
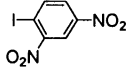
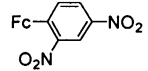
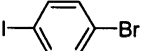
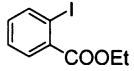
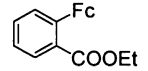
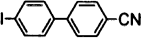
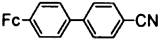
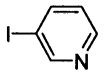
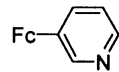
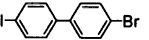
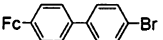
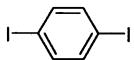
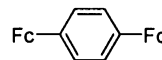
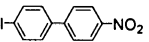
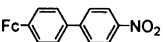
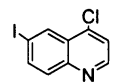
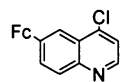
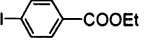
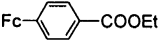
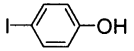
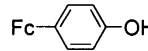
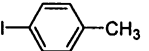
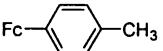
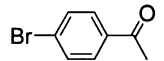
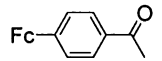
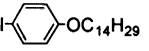
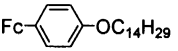
In most cases the reactions were complicated by a competitive formation of bis(ferrocenyl). The yields of Fc_2 were low for reactions with aryl iodides bearing electron-withdrawing substituents, while in the case of electron-rich substrates the yield of Fc_2 increases to reach 34% in the cross-coupling with 4-iodophenol, while the yield of the target arylferrocene (entry 20) decreases to 24%.

These results can be rationalized by considering two competing pathways: (i) the oxidative addition of aryl iodide to $\text{Pd}(0)$ and subsequent reaction of arylpalladium intermediate with Fc_2Hg giving arylferrocene; (ii) the possible insertion of $\text{Pd}(0)$ into the Hg-C bond with subsequent elimination of Hg and $\text{Pd}(0)$ giving Fc_2 [15]. Electron-withdrawing substituents in aryl iodide facilitate the oxidative addition giving preference to the first



Scheme 3.

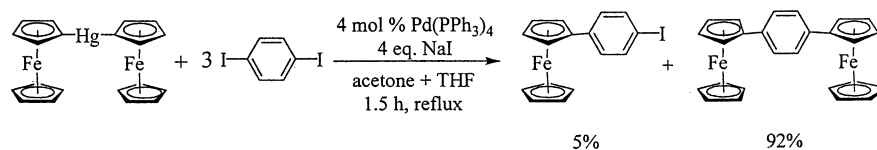
Table 1
The yields of cross-coupling products in the reaction of Fc_2Hg with aryl halides

№	ArI	time, h	product	Yield ¹ , %	№	ArI	time, h	product	Yield ¹ , %
1		1.5		80 (80)	12		1.5		94 (90)
2		1.5		94 (92)	13		1.5		97 (96)
3 ²		1		98 (96)	14		31		62 (60)
4 ²		1.5		97 (97)	15 ³		1.5		100 (96)
5		1.5		88 (88)	16		20		87 (85)
6		1.5		98 (97)	17 ²		1.5		84 (84)
7		1.5		89 (88)	18		1.5		92
8		1.5		98 (95)	19		1.5		(92)
9		1.5		98 (97)	20		1.5		24
10		1.5		93 (90)	21		4		36
11		1.5		85 (84)					

¹Estimated by NMR spectroscopy (isolated yields are given in the parentheses).

² $\text{PdCl}_2(\text{PPh}_3)_2$ used as catalyst.

³In the absence of catalyst.



Scheme 4.

pathway. Both pathways may involve nucleophilic catalysis by iodide ions (Scheme 3).

The reaction with 1,4-diiodobenzene leads to a di-substituted product in high yield (92%) (even in the presence of 50% excess of 1,4-diiodobenzene the di-substituted product predominates) (Scheme 4).

Selective substitution of iodine atom occurred in the cross-coupling reactions of 4-iodobromobenzene and 4,4'-diiodobromobiphenyl (Table 1, entries 5 and 7) with bis(ferrocenyl)mercury. The products of substitution of both halide atoms were formed in only 4–9% yields. Though chlorine atom in 4-chloro-6-iodoquinoline is

quite reactive in nucleophilic substitution, cross-coupling of this substrate gave exclusively 4-chloro-6-ferrocenylquinoline in high yield (entry 19) (Scheme 5).

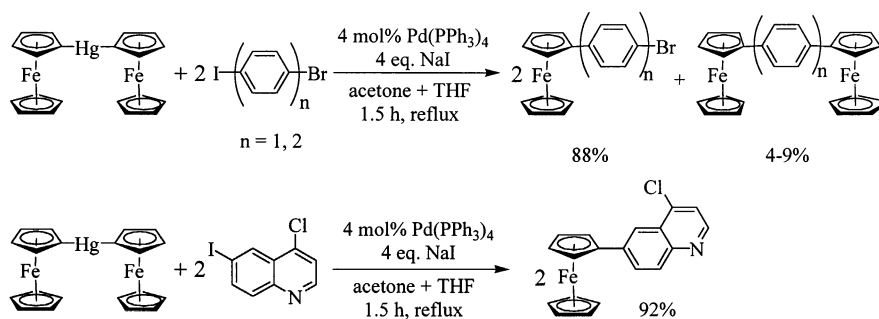
Under the conditions reported the substitution of bromine atom can be realized for substrates bearing electron-withdrawing substituents, such as 4-bromoacetophenone (entry 21).

4-Ferrocenylbromobenzene and 4,4'-ferrocenylbromobiphenyl could be used for further substitution of bromine atom by cross-coupling or Heck reactions to give extended systems potentially usable for the synthesis of new NLO or LC materials. Among the methods applicable for this purpose are (1) cross-coupling of organometallic derivative ($M = B, Sn, Zn$) obtained through lithiation of the above-mentioned ferrocenyl-halogenarenes with an appropriate aryl or alkenyl halide; (2) the cross-coupling of bromoarylferrocenes with an appropriate organometallic compound; (3) the Heck reaction (Scheme 6). The attempts to use the cross-coupling of the respective zinc derivative obtained through the lithiation of 4-ferrocenylbromobenzene failed, as phenylferrocene was obtained as the only product formed through reductive debromination. The expected cross-coupling product was not observed even in trace amounts. Notable with respect to this also are low yields of Grignard reagents from 4-bromophenylferrocene [16]. Nevertheless, 4-ferrocenylbromobenzene and 4,4'-ferrocenylbromobiphenyl smoothly reacted with 4-tolylboronic acid to give the expected cross-coupling products 4-ferrocenyl-4'-methylbiphenyl and 4-

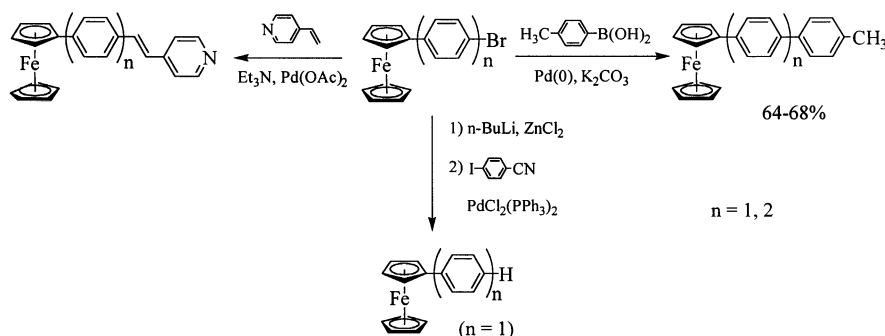
ferrocenyl-4'-methyl-[1,1';4',1'']terphenyl in 64 and 68% yields, respectively. We have also shown the principal possibility of Heck reaction of 4-ferrocenylbromobenzene with 4-vinylpyridine to give the respective stilbazole dye in moderate yield. Similar structures were recently proposed for NLO applications [1c], and our further investigation in this field is now under way.

2.2. Reaction of bis(ferrocenyl)mercury with acid chlorides

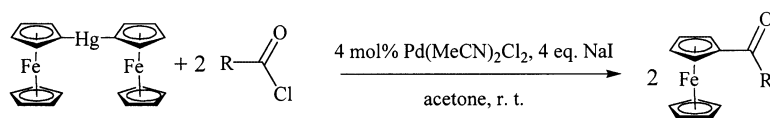
The procedure elaborated for arylation of bis(ferrocenyl)mercury has been applied for palladium-catalyzed acylation with acid chlorides. This reaction has also been established to require I^- as nucleophilic co-catalyst. Acetone has been used as solvent, as THF is cleaved by acid chlorides in the presence of iodide ion. The variation of catalysts has been performed for the reaction with 4-chlorobenzoyl chloride. In the presence of phosphine complexes of palladium ($Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$) the reaction at room temperature was found to be slow, and elevated temperatures were required to achieve moderate conversions. On the other hand, phosphine-free palladium complexes, such as $PdCl_2(MeCN)_2$ or $Pd(OAc)_2$ were very efficient to afford quantitative yields after 30 min stirring at room temperature (Scheme 7). This procedure has been used to carry out the reactions with other acid chlorides. The results are listed in Table 2.



Scheme 5.



Scheme 6.



Scheme 7.

While the yields obtained with acyl chlorides were consistently high, the reaction with cinnamoyl chloride gave a moderate yield (entry 5). In the latter case considerable quantity of bis(ferrocenyl) and ferrocene were found among products of the reaction.

The reaction of bis(ferrocenyl)mercury with 4-bromobenzoyl chloride is not selective, as both reactive centers are involved in apparently comparable rates. As was shown above, electron-withdrawing groups activate the bromine atom in the benzene ring towards substitution (Scheme 8).

2.3. Addition of bis(ferrocenyl)mercury to dimethylacetylenedicarboxylate

The carbopalladation of triple bond is known to be realized via two alternative ways depending on which precursor is taken for the generation of organopalladium intermediate—aryl halide (triflate, etc.) [17] or organometallic compound (possibly generated from a hydrocarbon in situ) [18]. The vinylpalladium intermediate formed by carbopalladation should be trapped to form stable products in a cascaded process. Among the numerous cascades initiated by carbopalladation of triple bond described in the literature [19], alkoxy-carbonylation (Scheme 1, route 'a') or hydride transfer (route 'b') are the best studied termination reactions for Pd(0) driven processes. In more rare Pd(II) driven processes vinylpalladium intermediate can be protolyzed by acid (route 'c') or trapped by nucleophilic organometallics (e.g. organotin compound). In the latter case the regeneration of Pd(II) requires the presence of an oxidant (route 'd') [18d] (Scheme 9).

We have shown that bis(ferrocenyl)mercury reacts in the presence of palladium catalyst and NaI with dimethyl acetylenedicarboxylate to give the product of *syn*-addition of two ferrocenyl residues to the triple bond. The formation of bis(ferrocenyl) as side product was also observed (Scheme 10).

The reaction can be catalyzed by either Pd(II) or Pd(0) complexes. The best yields were obtained for ligandless Pd catalysts (Table 3). For example, the reaction in the presence of PdCl₂ or Pd(OAc)₂ after 30 min refluxing in THF–acetone mixture gave 69–72% dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate along with 20% Fc₂. The formation of the *E*-adduct has not been observed.

Other diarylmercuric compounds can be used as well, e.g. in the reaction of dianisylmercury catalyzed by

PdCl₂(PPh₃)₂ under the same conditions as described above the respective adduct is formed in 40% yield. The results with other diarylmercuric compounds fall outside of the scope of this article and will be discussed elsewhere. On the other hand, the variation of alkyne was less successful, tolane and perfluorotolane gave Fc₂ as main product. Methyl propiolate reacted unselectively to give a complex mixture of products.

As soon as the reaction with Fc₂Hg does not require the presence of oxidant, the catalytic cycle is obviously driven by Pd(0), with the FcHgPdFc intermediate formed not by a usual route of transmetalation, but by oxidative addition of Fc₂Hg to Pd(0). Alkyne is likely to play an auxiliary role of supporting ligand preventing the formation of palladium black in the absence of phosphine ligands. A tentative mechanism is given in Scheme 11.

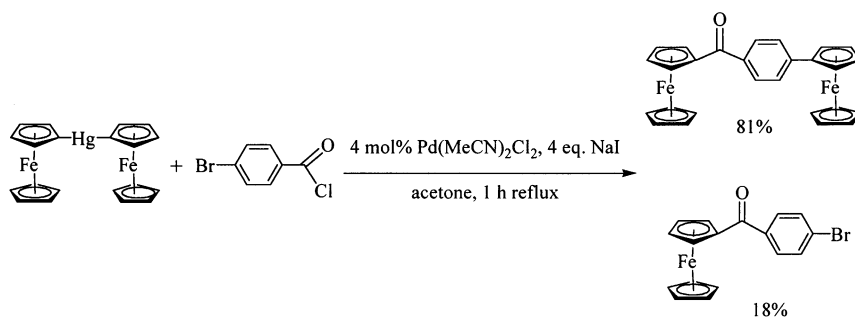
The insertion of Pd(0) into the C–Hg bond is a facile process not requiring phosphine ligands [15]. Moreover, the latter apparently have a deleterious effect, likely due to a retardation of a key step of reaction, the addition of intermediate A to the triple bond [the yield dropped from 72% for phosphine-free system down to a modest 31–32% obtained in the presence of Pd(PPh₃)₄ or PdCl₂(PPh₃)₂]. The elimination of Hg and Pd(0) leads to the target adduct. Alternatively, the intermediate A can eliminate Hg and Pd and give Fc₂. Apparently, this

Table 2

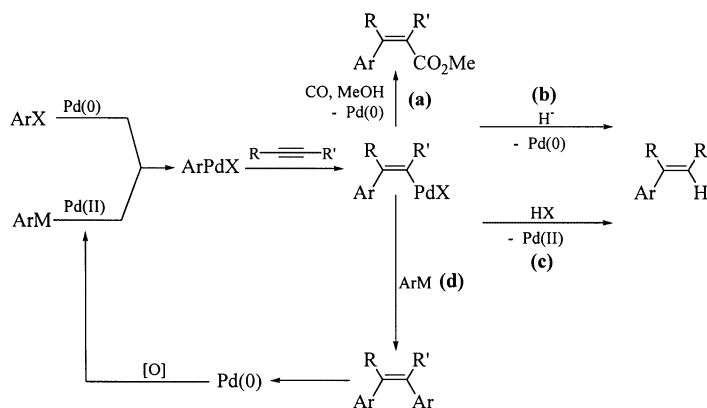
Yields of acylferrocenes in cross-coupling of Fc₂Hg with acid chlorides (4 mol% Pd(MeCN)₂Cl₂)

No	RCOCl	time, h	Product	Yield, % (isolated)
1		0.5		96
2		0.5		98
3		0.5		98
4 ¹		1		81 18
5		0.5		38

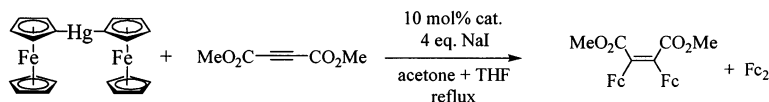
¹ ratio of bis(ferrocenyl)mercury to acid halide – 1.5 : 1



Scheme 8.



Scheme 9.



Scheme 10.

side process prevails for alkynes with less electrophilic triple bond in comparison with dimethyl acetylenedicarboxylate.

The structure of dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate was established by X-ray spectroscopy.

The unit cell contains two independent molecules of dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate (Table 4). The ORTEP drawing of these molecules is presented in Fig. 1 together with the atomic labeling scheme.

Let us denote the molecules M(2,3) and M(4,5) in accordance with the numbering of iron atoms. Bond distances Fe–C in Cp rings for molecules M(2,3) and M(4,5) are equal within experimental error to 2.037(5) Å. Average lengths of bonds Fe(3)–(C35–C39) in molecule M(2,3) and Fe(5)–(C55–C59) in molecule M(4,5) are slightly smaller to be equal to 2.029(5) Å for Fe(3)–(C35–C39) and 2.022(5) Å for Fe(5)–(C55–C59). For the same cycles an average bond length of the carbon–carbon bond also have a minimal value of 1.392(6) Å in comparison with the carbon–carbon bond lengths in other Cp cycles. This deviation is likely

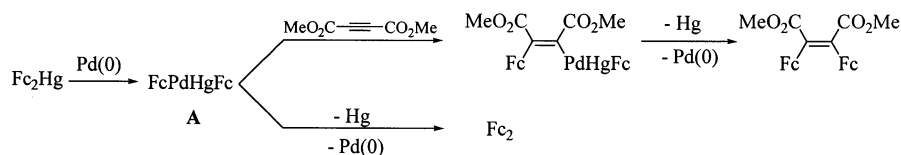
to be accounted for by a considerable conformational mobility of the cycles in crystal. This conclusion is supported by the ORTEP plot in Fig. 1 which shows markedly larger thermal ellipsoids of free Cp rings, as compared to Cp rings bonded to the olefinic fragment. It is worth noting that the tilt angle of the cycle (C35–C39) plane relative to the cycle (C30–C34) plane is equal to 8.3(5)°, while the angle between cycle (C55–C59) and cycle (C50–C54) is equal to 10.5°, which

Table 3

The dependence of yield of dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate on catalyst

Catalyst	Time (h)	Yield ^a (%)
Pd(PPh ₃) ₄	1.5	31
PdCl ₂ (PPh ₃) ₂	1.5	32
PdCl ₂ (MeCN) ₂	1.5	38
PdCl ₂	0.5	72
Pd(OAc) ₂	0.5	69

^a Isolated yield.



Scheme 11.

is also larger than the tilt angle of cycle (C20–C24) relative to cycle (C25–C29) being equal to $7.1(5)^\circ$, and the angle between cycle (C40–C44) and cycle (C45–C47) being equal to $3.7(5)^\circ$.

The molecules are sterically crowded, which leads to considerable deformations of bond angles in the olefinic fragment for both molecules. Thus, in M(2,3) the angles are: C(8)–C(3)–C(2)— $120.6(4)^\circ$, C(3)–C(2)–C(6)— $120.4(4)^\circ$, C(8)–C(3)–C(34)— $114.5(4)^\circ$, C(6)–C(2)–C(28)— $114.3(4)^\circ$, C(2)–C(3)–C(34)— $124.9(5)^\circ$, C(3)–C(2)–C(28)— $125.2(5)^\circ$, while the respective angles in M(4,5) are equal to $121.2(4)^\circ$, $120.6(4)^\circ$, $113.6(4)^\circ$, $115.3(4)^\circ$, $125.2(4)^\circ$, $125.0(4)^\circ$.

Selected dihedral angles characteristic for defining the molecular structure are given in Table 5. For both molecules iron atoms Fe(2), Fe(3) and Fe(4), Fe(5) deviate to opposite directions from the least-squares plane of the olefinic fragment C(6)–C(2)–C(3)–C(8). In M(2,3) the deviation of iron atoms from the least-squares plane C(6)–C(2)–C(3)–C(8) are (+1.704 Å) for Fe(2), and (–1.425 Å) for Fe(3), while the respective deviations in M(4,5) are (+1.430 Å) for Fe(4), and (–1.440 Å) for Fe(5). The oxygen atoms of carbonyl groups are also located at different sides of the olefinic fragment plane both with respect to each other and with respect to the closest iron atom. The iron–oxygen bond distances (of carbonyl and methoxy groups) are within a narrow range: Fe(2)–O(1)— $4.054(5)$ Å, Fe(2)–O(2)— $4.040(5)$ Å, Fe(3)–O(3)— $4.145(5)$ Å, Fe(3)–O(4)— $3.793(5)$ Å; Fe(4)–O(5)— $3.823(5)$ Å, Fe(4)–O(6)— $4.184(5)$ Å, Fe(5)–O(7)— $4.060(4)$ Å, Fe(5)–O(8)— $3.954(5)$ Å.

3. Experimental

3.1. The reactions of bis(ferrocenyl)mercury with aryl and heteroaryl halides

3.1.1. General procedure

In a flask equipped with reflux condenser and gas inlet 70 mg Fc_2Hg (0.12 mmol), ArI (0.28 mmol), 74 mg NaI (0.48 mmol), 3 ml absolute THF, and 2 ml absolute Me_2CO were placed under Ar atmosphere. To the reaction mixture heated to boiling a catalyst (4.8 μmol , 4 mol%) was added. After the mixture was stirred at reflux for the time given in Table 1 (TLC control), it was filtered through a pad of silica and evaporated in

vacuum. The product was purified by column chromatography using a benzene–hexane mixture for elution.

3.1.2. 4-Methoxyphenylferrocene

Orange solid (80%, m.p. $106\text{--}107^\circ\text{C}$, lit. 113°C [7a]). $^1\text{H-NMR}$ (CDCl_3): 7.38 (m, 2H), 6.83 (m, 2H), 4.56 (m, 2H), 4.25 (m, 2H), 4.02 (s, 5H), 3.80 (s, 3H).

3.1.3. 4-Fluorophenylferrocene

Orange solid (92%, m.p. 106°C , lit. 104°C [7a]). $^1\text{H-NMR}$ (CDCl_3): 7.42 (m, 2H), 6.97 (m, 2H), 4.57 (m, 2H), 4.28 (m, 2H), 4.02 (s, 5H).

3.1.4. 4-Nitrophenylferrocene

Dark-red solid (96%, m.p. 171°C , lit. $169\text{--}170^\circ\text{C}$ [20]). $^1\text{H-NMR}$ (CDCl_3): 8.12 (m, 2H), 7.54 (m, 2H), 4.73 (m, 2H), 4.46 (m, 2H), 4.04 (s, 5H).

Table 4

Crystal data and structure refinement for dimethyl (Z)-2,3-di(ferrocenyl)-2-butenedioate

Empirical formula	$\text{C}_{26}\text{H}_{24}\text{Fe}_2\text{O}_4$
Formula weight	511.7
Color	Red
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	9.114(2)
<i>b</i> (Å)	11.370(3)
<i>c</i> (Å)	23.386(3)
α ($^\circ$)	89.58(2)
β ($^\circ$)	91.19(2)
γ ($^\circ$)	111.87(3)
<i>Z</i>	4
Crystal size (mm)	$0.05 \times 0.07 \times 0.08$
Theta range for data collection ($^\circ$)	$0.87\text{--}25.98$
Index ranges	$-11 \leq h \leq 11, -14 \leq k \leq 14, 0 \leq l \leq 28$
Reflections collected/unique	9037/8808 [$R_{\text{int}} = 0.0222$]
Reflections observed [$I > 2\sigma(I)$]	6111
Number of parameters refined	583
Completeness to $\theta = 25.98$ (%)	100.0
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.976
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R = 0.0515$, $^a R_w = 0.1187$ ^b
<i>R</i> indices (all data)	$R = 0.0858$, $^a R_w = 0.1370$ ^b

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w = \{\Sigma [W(F_o^2 - F_c^2)^2] / \Sigma [W(F_o^2)^2]\}^{1/2}$.

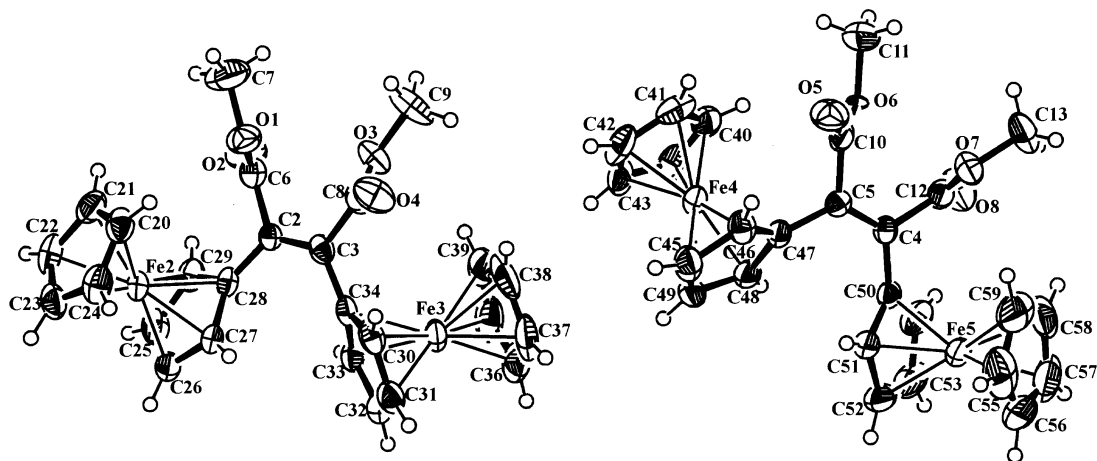


Fig. 1. The ORTEP drawing of two independent molecules of the unit cell of dimethyl (Z)-2,3-di(ferrocenyl)-2-butenedioate.

3.1.5. 4-Cyanophenylferrocene

Orange–red solid (97%, m.p. 141–142 °C, lit. 145–146 °C [20]). ¹H-NMR (CDCl₃): 7.52 (m, 4H), 4.68 (m, 2H), 4.41 (m, 2H), 4.03 (s, 5H).

3.1.6. 4-Bromophenylferrocene

Orange–red solid (88%, m.p. 124 °C, lit. 122–123 °C [20]). ¹H-NMR (CDCl₃): 7.58 (m, 2H), 7.32 (m, 2H), 4.59 (m, 2H), 4.31 (m, 2H), 4.02 (s, 5H).

3.1.7. 4-Cyano-4'-ferrocenylbiphenyl

Orange–red solid (97%, m.p. 190 °C). ¹H-NMR (CDCl₃): 7.69 (m, 4H), 7.53 (m, 4H), 4.68 (m, 2H), 4.35 (m, 2H), 4.05 (s, 5H). Anal. Found: C, 76.06; H, 4.40; N, 3.54. Calc. for C₂₃H₁₇FeN: C, 76.05; H, 4.72; N, 3.86%.

3.1.8. 4-Bromo-4'-ferrocenylbiphenyl

Orange–red solid (88%, m.p. 199 °C). ¹H-NMR (CDCl₃): 7.53 (m, 4H), 7.46 (m, 4H), 4.66 (m, 2H), 4.33 (m, 2H), 4.05 (s, 5H). Anal. Found: C, 64.93; H, 4.36; Fe, 13.15. Calc. for C₂₂H₁₇BrFe: C, 65.35; H, 4.11; Fe, 13.39%.

3.1.9. 4-Ferrocenyl-4'-nitrobiphenyl

Red solid (95%, m.p. 224–225 °C). ¹H-NMR (CDCl₃): 7.74 (m, 2H), 7.55 (m, 4H), 7.28 (m, 2H), 4.70 (m, 2H), 4.37 (m, 2H), 4.06 (s, 5H). Anal. Found: C, 68.50; H, 4.78; N, 3.14. Calc. for C₂₂H₁₇FeNO₂: C, 68.95; H, 4.47; N, 3.66%.

3.1.10. 4-Ethoxycarbonylphenylferrocene

Orange–red solid (97%, m.p. 92–93 °C, lit. 88–90 °C [20]). ¹H-NMR (CDCl₃): 7.94 (m, 2H), 7.48 (m, 2H), 4.71 (m, 2H), 4.38 (m, 2H), 4.36 (q, 2H), 4.03 (s, 5H), 1.39 (t, 3H).

3.1.11. 4-Methylphenylferrocene

Orange solid (90%, m.p. 136–138 °C, lit. 140–142 °C [20]). ¹H-NMR (CDCl₃): 7.36 (m, 2H), 7.08 (m, 2H), 4.59 (m, 2H), 4.26 (m, 2H), 4.01 (s, 5H), 2.31 (s, 3H).

3.1.12. 4-Tetradecyloxyphenylferrocene

Orange solid (84%, m.p. 93 °C). ¹H-NMR (CDCl₃): 7.37 (m, 2H), 6.82 (m, 2H), 4.54 (m, 2H), 4.24 (m, 2H), 4.01 (s, 5H), 3.94 (t, 2H), 1.78 (m, 2H), 1.43 (m, 2H), 1.25 (m, 20H), 0.87 (t, 3H). Anal. Found: C, 75.99; H, 9.00. Calc. for C₃₀H₄₂FeO: C, 75.94; H, 8.92%.

3.1.13. 2-Thienylferrocene

Orange–red solid (90%, m.p. 121–122 °C, lit. 116–118 °C [21]). ¹H-NMR (CDCl₃): 7.71 (m, 1H), 6.98 (m, 1H), 6.90 (m, 1H), 4.55 (m, 2H), 4.25 (m, 2H), 4.07 (s, 5H).

3.1.14. 3-Trifluoromethylphenylferrocene

Orange–red solid (96%, m.p. 96 °C, lit. 97.5–98 °C [20]). ¹H-NMR (CDCl₃): 7.64 (m, 2H), 7.39 (m, 2H), 4.66 (m, 2H), 4.35 (m, 2H), 4.03 (s, 5H).

Table 5

Selected dihedral angles (°) for dimethyl (Z)-2,3-di(ferrocenyl)-2-butenedioate

C(29)–C(28)–C(2)–C(3)	152.4(4)	C(4)–C(5)–C(47)–C(46)	139.7(5)
C(3)–C(2)–C(28)–Fe(2)	119.8(4)	Fe(4)–C(47)–C(5)–C(4)	130.5(4)
C(2)–C(3)–C(34)–C(33)	44.9(6)	C(51)–C(50)–C(4)–C(5)	37.4(6)
C(2)–C(3)–C(34)–Fe(3)	133.4(4)	Fe(5)–C(50)–C(4)–C(5)	126.2(4)
C(6)–C(2)–C(3)–C(8)	5.6(6)	C(10)–C(4)–C(5)–C(12)	2.9(6)
C(28)–C(2)–C(3)–C(34)	8.7(7)	C(47)–C(5)–C(4)–C(50)	6.0(4)
C(3)–C(2)–C(6)–O(2)	122.3(5)	O(5)–C(10)–C(5)–C(4)	129.1(5)
C(2)–C(3)–C(8)–O(4)	126.4(5)	O(8)–C(12)–C(4)–C(5)	120.6(5)

3.1.15. 2-Trifluoromethylphenylferrocene

Orange–red solid (60%, m.p. 52 °C, lit. 80–82 °C [22]). ¹H-NMR (CDCl₃): 8.03 (m, 1H), 7.58 (m, 1H), 7.49 (m, 1H), 7.30 (m, 1H), 4.55 (m, 2H), 4.30 (m, 2H), 4.14 (s, 5H). Anal. Found: C, 61.99; H, 3.85. Calc. for C₁₇H₁₃F₃Fe: C, 61.85; H, 3.97%.

3.1.16. 2,4-Dinitrophenylferrocene

Black solid (96%, m.p. 162 °C, lit. 160 °C [23]). ¹H-NMR (CDCl₃): 8.32 (m, 1H), 8.27 (m, 1H), 7.91 (m, 1H), 4.58 (m, 2H), 4.52 (m, 2H), 4.12 (s, 5H).

3.1.17. 2-Ethoxycarbonylphenylferrocene

Orange–red solid (85%, m.p. 51–52 °C). ¹H-NMR (CDCl₃): 7.79 (m, 1H), 7.47 (m, 1H), 7.40 (m, 1H), 7.23 (m, 1H), 4.44 (m, 2H), 4.26 (m, 2H), 4.17 (q, 2H), 4.07 (s, 5H), 1.17 (t, 3H). Anal. Found: C, 68.46; H, 5.71. Calc. for C₁₉H₁₈FeO: C, 68.29; H, 5.43%.

3.1.18. 3-Pyridylferrocene

Orange–red solid (84%, m.p. 57 °C, lit. 57–59 °C [24]). ¹H-NMR (CDCl₃): 8.74 (m, 1H), 8.42 (m, 1H), 7.72 (m, 1H), 7.21 (m, 1H), 4.66 (m, 2H), 4.37 (m, 2H), 4.05 (s, 5H).

3.1.19. 1,4-Diferrocenylbenzene

¹H-NMR (CDCl₃): 7.38 (s, 4H), 4.63 (m, 4H), 4.30 (m, 4H), 4.04 (s, 10H) [10b].

3.1.20. 4-Chloro-6-ferrocenylquinoline

Orange–red solid (92%, m.p. 137 °C). ¹H-NMR (CDCl₃): 8.69 (d, 1H), 8.18 (d, 1H), 8.03 (d, 1H), 7.91 (dd, 1H), 7.44 (d, 1H), 4.79 (m, 2H), 4.41 (m, 2H), 4.05 (s, 5H). Anal. Found: C, 65.52; H, 4.33; N, 3.84. Calc. for C₁₉H₁₄ClFeN: C, 65.65; H, 4.06; N, 4.03%.

3.1.21. 4-Hydroxyphenylferrocene

¹H-NMR (CDCl₃): 7.34 (m, 2H), 6.76 (m, 2H), 4.84 (s, 1H), 4.54 (m, 2H), 4.25 (m, 2H), 4.02 (s, 5H) [20].

3.1.22. 4-Ferrocenylacetophenone

Orange–red solid (m.p. 175–176 °C, lit. 173–174 °C [20]). ¹H-NMR (CDCl₃): 7.86 (m, 2H), 7.51 (m, 2H), 4.72 (m, 2H), 4.40 (m, 2H), 4.04 (s, 5H), 2.58 (s, 3H).

3.2. Suzuki coupling of bromoarylferrocenes with 4-tolylboronic acid

3.2.1. General procedure

In a flask equipped with reflux condenser and gas inlet 0.150 mmol of bromoarylferrocene, 0.165 mmol 4-tolylboronic acid, 0.450 mmol K₂CO₃ were dissolved in 3 ml of THF and 1 ml of water under Ar atmosphere. Pd(PPh₃)₄ (6.0 μmol, 4 mol%) was added and the solution was stirred at reflux for 24 h. Solvents were evaporated in vacuum and the residue was purified by

column chromatography on silica with benzene–hexane mixture as eluent.

3.2.2. 4-Ferrocenyl-4'-methylbiphenyl

Orange solid (64%, m.p. 181 °C). ¹H-NMR (CDCl₃): 7.49 (m, 6H), 7.23 (m, 2H), 4.69 (m, 2H), 4.35 (m, 2H), 4.08 (s, 5H), 2.38 (s, 3H). Anal. Found: C, 78.25; H, 5.97; Fe, 15.72. Calc. for C₂₃H₂₀Fe: C, 78.42; H, 5.72; Fe, 15.85%.

3.2.3. 4-Ferrocenyl-4''-methyl-[1,1';4',1'']terphenyl

Orange solid (68%, m.p. (dec.) > 270 °C). ¹H-NMR (CDCl₃): 7.64 (m, 4H), 7.53 (m, 4H), 7.41 (m, 2H), 7.26 (m, 2H), 4.84 (m, 2H), 4.49 (m, 2H), 4.19 (s, 5H), 2.39 (s, 3H). Anal. Found: C, 81.58; H, 5.63; Fe, 12.69. Calc. for C₂₉H₂₄Fe: C, 81.32; H, 5.65; Fe, 13.04%.

3.3. The reaction of bis(ferrocenyl)mercury with acid chlorides

3.3.1. General procedure

In a flask equipped with reflux condenser and gas inlet 70 mg Fc₂Hg (0.12 mmol), ArCOCl (0.28 mmol), 74 mg NaI (0.48 mmol), and 4 ml dry Me₂CO were placed. Pd(MeCN)₂Cl₂ (1.3 mg, 4.8 μmol, 4 mol%) was added to the reaction mixture. After stirring at room temperature (the course of reaction was followed by TLC), the mixture was passed through a pad of silica, and evaporated in vacuum. The product was purified by column chromatography (silica, benzene as eluent).

3.3.2. Benzoylferrocene

Orange–red solid (96%, m.p. 104–105 °C, lit. 108–109 °C [25]). ¹H-NMR (CDCl₃): 7.87 (m, 2H), 7.49 (m, 3H), 4.89 (m, 2H), 4.58 (m, 2H), 4.20 (s, 5H).

3.3.3. 4-Chlorobenzoylferrocene

Orange–red solid (98%, m.p. 119 °C, lit. 121–122 °C [25]). ¹H-NMR (CDCl₃): 7.84 (m, 2H), 7.43 (m, 2H), 4.86 (m, 2H), 4.59 (m, 2H), 4.19 (s, 5H).

3.3.4. 4-Bromobenzoylferrocene

Orange–red solid (18%, m.p. 121–122 °C, lit. 123–124 °C [25]). ¹H-NMR (CDCl₃): 7.76 (m, 2H), 7.59 (m, 2H), 4.86 (m, 2H), 4.59 (m, 2H), 4.18 (s, 5H).

3.3.5. 4-Ferrocenylbenzoylferrocene

Orange–red solid (81%, m.p. 195 °C). ¹H-NMR (CDCl₃): 7.85 (m, 2H), 7.54 (m, 2H), 4.92 (m, 2H), 4.71 (m, 2H), 4.97 (m, 2H), 4.39 (m, 2H), 4.21 (s, 5H), 4.06 (s, 5H). Anal. Found: C, 67.96; H, 5.12. Calc. for C₂₇H₂₂Fe₂O: C, 68.39; H, 4.68%.

3.3.6. 2-Furoylferrocene

Orange–red solid (98%, m.p. 80 °C, lit. 80 °C [26]). ¹H-NMR (CDCl₃): 7.64 (m, 1H), 7.32 (m, 1H), 6.57 (m, 1H), 5.14 (m, 2H), 4.61 (m, 2H), 4.19 (s, 5H).

3.3.7. (*E*)-Cinnamoylferrocene

Orange–red solid (38%, m.p. 136 °C, lit. 139–140 °C [27]). ¹H-NMR (CDCl₃): 7.78 (d, *J* = 15.8 Hz, 1H), 7.64 (m, 2H), 7.41 (m, 2H), 7.12 (d, *J* = 15.8 Hz, 1H), 4.90 (m, 2H), 4.58 (m, 2H), 4.20 (s, 5H).

3.4. Dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate

In a flask equipped with reflux condenser and gas inlet 70 mg Fc₂Hg (0.12 mmol), 34 mg dimethyl acetylenedicarboxylate (0.24 mmol), 74 mg NaI (0.48 mmol), 2 ml dry THF, and 2 ml dry Me₂CO were placed under Ar atmosphere. After heating to reflux a catalyst (12 μmol, 10 mol%) was added to the reaction mixture. The mixture was stirred at reflux (the course of reaction was followed by TLC), passed through a pad of silica, and evaporated in vacuum. The product was purified by column chromatography (silica, benzene as eluent), (72%, m.p. 173–174 °C). ¹H-NMR (CDCl₃): 4.21 (m, 4H), 4.17 (m, 4H), 4.03 (s, 10H), 3.87 (s, 6H). ¹³C-NMR (CDCl₃): 167.83, 132.99, 77.41, 70.22, 69.28, 68.82, 51.85. Anal. Found: C, 59.62; H, 5.09; Fe, 22.36. Calc. for C₂₆H₂₄Fe₂O₄: C, 60.97; H, 4.72; Fe, 21.81%.

3.5. Dimethyl (*Z*)-2,3-di(4-methoxyphenyl)-2-butenedioate

Obtained similarly (40%, white–yellow oil). ¹H-NMR (CDCl₃): 7.01 (m, 4H), 6.71 (m, 4H), 3.80 (s, 6H), 3.74 (s, 6H). ¹³C-NMR (CDCl₃): 168.85, 159.45, 137.34, 131.20, 126.81, 113.72, 55.14, 52.60. Anal. Found: C, 67.41; H, 5.66. Calc. for C₂₀H₂₀O₆: C, 67.83; H, 6.04%.

3.6. X-ray diffraction study of dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate

Crystal data and the number of reflections collected are given in Table 4. A red irregular crystal was used with CAD-4 diffractometer (Mo–K_α radiation, graphite monochromator). The intensities were collected by using the ω -scan mode in the range $2\theta < 52^\circ$. Throughout the data collection, intensities of three standard reflections were measured every 2 h as a check of stability of the crystal. Absorption correction was not applied. A total of 8808 independent reflections ($R_{\text{int}} = 0.022$) were measured, among which 6111 were accepted as observable [$F > 4\sigma(F)$] and were used in solution and structure refinement.

The structure was solved by direct methods (SHELX-97) and full-matrix least-squares procedures were applied for refinement. All the non-hydrogen atoms were refined with anisotropy thermal parameters. The positions of the hydrogen atoms were calculated (for cycles as external bisectors C–C*–C) and riding model refinement was used. Refinement led to the final residuals $R = 0.051$, $R_w = 0.012$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 158165 for compound dimethyl (*Z*)-2,3-di(ferrocenyl)-2-butenedioate. 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 www: <http://www.ccdc.cam.ac.uk>).

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