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# Fragmentation and 1,2-Addition Reactions upon Action of Methyllithium on Coupling Products of Ferrocenecarbaldehyde with Dibenzoylmethane

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**Abstract:** 2-Ferrocenylmethylidene-1,2-diphenylpropanedione (**3**), 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione (**4**), and 2,4-dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (**5**) react with MeLi to undergo fragmentation and 1,2-addition or only 1,2-addition at the carbonyl group. Dehydration of intermediate tertiary alcohols affords α-methylstyrene (**6**), 3-ferrocenyl-1-phenylprop-2-enone (**7**), 3,5-diferrocenyl-1-phenyl-4-(1-phenylvinyl)cyclohexene (**8**), 3-ferrocenylmethylidene-2,4-diphenylpenta-1,4-diene (**9**), 2-benzoyl-1-ferrocenyl-3-phenylbuta-1,3-diene (**10**), 2-benzoyl-1-ferrocenyl-3-methylindene (**11**), 4-ferrocenyl-2-methyl-2,6-diphenyl-3,4-dihydro-2*H*-pyran (**19**), and (*Z,Z*)-2,4-dibenzoyl-1,3-diferrocenyl-5-phenylhexa-1,4-diene (**21**), isolated by chromatography. The spatial structures of ferrocenyldihydropyran (**19**) and diferrocenylhexadiene (**21**) were established by X-ray diffraction analysis.

**Keywords:** 1,2-Addition; (*Z,Z*)-2,4-dibenzoyl-1,3-diferrocenyl-5-phenylhexa-1,4-diene; 4-ferrocenyl-2-methyl-2,6-diphenyl-3,4-dihydro-2*H*-pyran; 2-ferrocenylmethylidene-1,2-diphenylpropanedione; Fragmentation

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## INTRODUCTION

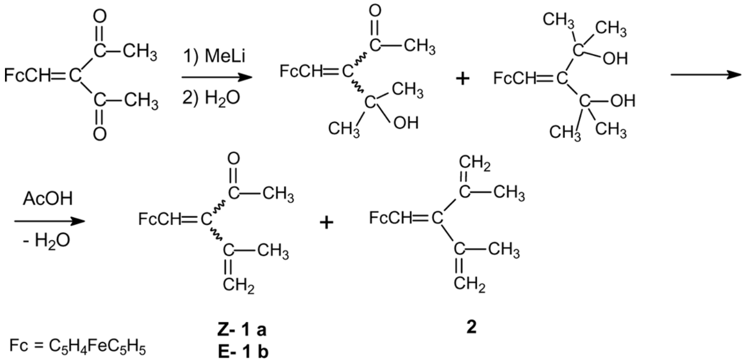
Cross-conjugated trienes with a linear backbone containing ferrocenyl substituents in the molecule are virtually unexplored. In our communications,[1,2] we reported the synthesis of cross-conjugated *Z*- and *E*-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes (**1a,b**) and 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene (**2**) by the reaction of methyllithium with 3-ferrocenylmethylidenepentane-2,4-dione, followed by dehydration of the resulting tertiary alcohols (Scheme 1).

Polyene compounds of the ferrocene series with terminal methylene groups[3,4] have gained recently prominence by virtue of their exciting structure, chemical reactivity, and potential use as molecular building blocks[5] and in the realm of supramolecular chemistry[6,7] as redox switching receptors.[8]

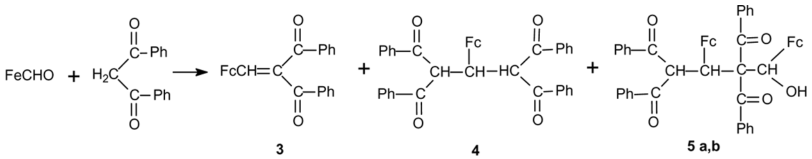
Ferrocenyl-substituted trienes of the types **1** and **2** described by us previously[1,2] are highly reactive compounds. We studied their protonation, cycloaddition, proton- and cation-catalyzed dimerization, and cyclodimerization.

Studies on the possibilities of an access to the linear cross-conjugated polyenes with lateral ferrocenyl and aryl substituents and investigations into their chemical and electrochemical properties is an important task for synthetic and theoretical organic chemistry and polymer chemistry.

With the aim of synthesizing aryl(ferrocenyl)-substituted cross-conjugated trienes and polyenes, we have carried out coupling of ferrocenecarbaldehyde with dibenzoylmethane and investigated the reactions of the resulting products with methyllithium.



*Scheme 1.* Synthesis of *Z*- and *E*-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes (**1a,b**) and 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene (**2**).



*Scheme 2.* Reaction of ferrocenecarbaldehyde with dibenzoylmethane.

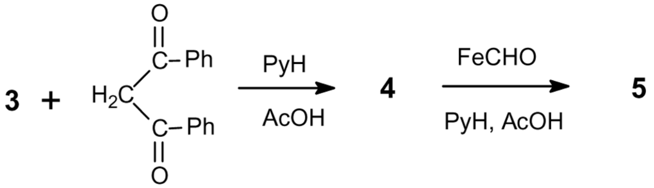
## RESULTS AND DISCUSSION

The reaction of ferrocenecarbaldehyde with dibenzoylmethane afforded three coupling products: 2-ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione (**3**, ~42%), 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione (**4**, ~20%), and 2,4-dibenzoyl-3-ferrocenyl-2-[ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (**5**, ~13%) (Scheme 2).

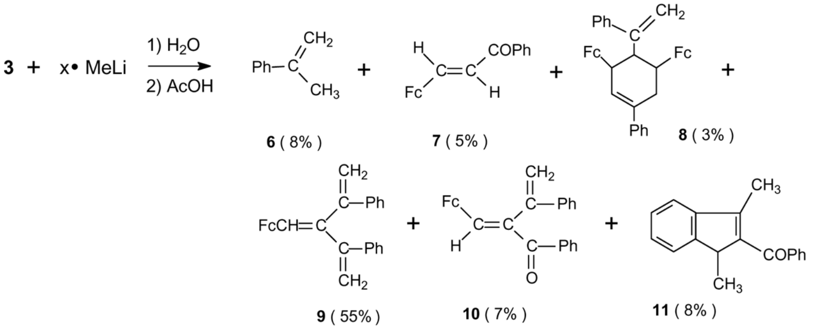
These coupling products were isolated by column chromatography on alumina (Brockmann activity III, see Experimental section). Their structures were established based on the data from mass spectrometry, IR, and $^{1}$H and $^{13}$C NMR spectroscopy. According to the data from $^{1}$H NMR spectroscopy, hydroxytetraone (**5**) represented a mixture of two diastereomers (**5a** and **5b**) in a ratio of ~1:1, which could not be separated by chromatography.

2,4-Dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione (**4**) was also synthesized by the Michael coupling of 2-ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione (**3**) with dibenzoylmethane, and 2,4-dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (**5**) was obtained by aldol condensation of compound **4** with ferrocenecarbaldehyde (Scheme 3).

Compound **3** was intended to be employed for the synthesis of cross-conjugated ferrocenyl(diphenyl)triene, while compounds **4** and **5** were intended for the synthesis of polyenes. To this end, the reactions of these compounds with methyllithium have been investigated.



*Scheme 3.* Preparation of 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione and 2,4-dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione.



***Scheme 4.*** Reaction of 2-ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione with methyllithium.

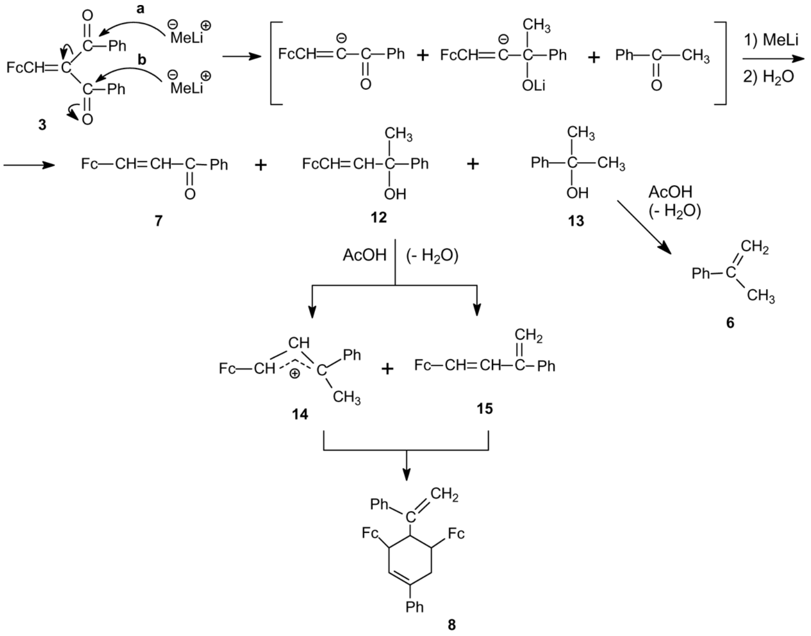
2-Ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione (**3**) was made to react with excess of methyllithium; the reaction mixture was quenched with water and concentrated, and the residue was treated with glacial acetic acid to give compounds (**6**–**11**) isolated by column chromatography on alumina (Scheme 4).

Obviously, compounds **6**, **7**, and **8** result from fragmentation (a) and 1,2-addition (b) reactions that occur under the action of methyllithium on ferrocenylmethylidene(dibenzoyl)methane **3** (Scheme 5).

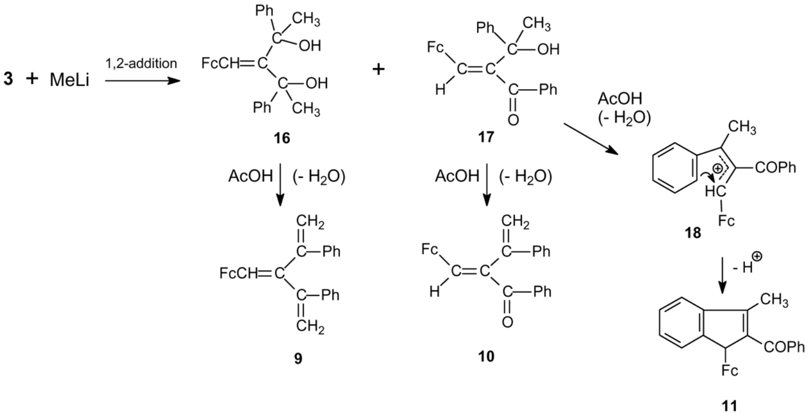
3,5-Diferrocenyl-1-phenyl-4-(1-phenylvinyl)cyclohexene (**8**) represents a cyclodimer of 1-ferrocenyl-phenylbuta-1,3-diene (**15**); this is formed upon cationic cycloaddition of allylic cation **14** to diene **15** (Scheme 5). The mechanism of cationic cycloaddition to ferrocenylbuta-1,3-dienes and the effect of stereoelectronic factors have been studied in detail earlier.[9] It is noteworthy that cyclodimer **8** is formed as a single diastereomeric ($^1$H NMR data) despite the presence of three stereogenic centers. The physicochemical characteristics of compound **8** and $^1$H NMR spectroscopic data totally coincide with those reported earlier.[9]

Compounds **9** and **10** resulted from the classical 1,2-addition of methyllithium to the carbonyl group followed by dehydration of tertiary alcohols **16** and **17** in an acidic medium (Scheme 6).

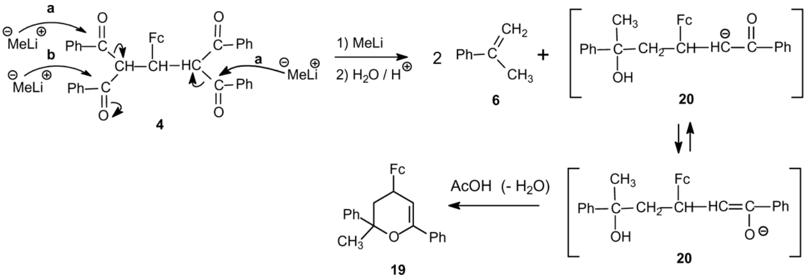
2-Benzoyl-1-ferrocenyl-3-methylindene (**11**) is the intramolecular alkylation product of the phenyl ring in the intermediate 2-benzoyl-1-ferrocenyl-3-methyl-3-phenylallyl cation (**18**) (Scheme 6). To confirm the proposed reaction pathways (Schemes 5 and 6), we performed chromatographic separation of reaction products of compound **3** with methyllithium following aqueous workup. The following products were isolated: 2-phenylpropan-2-ol (**13**), chalcone (**7**), 4-ferrocenyl-2-phenylbut-3-en-2-ol (**12**), diol (**16**), and hydroxyketone (**17**). The latter was



***Scheme 5.*** Plausible mechanism for the formation of compounds **6**–**8** from the reaction of 2-ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione **3** with methyllithium.



***Scheme 6.*** Mechanism for the formation of compounds **9**–**11** from the reaction of 2-ferrocenyl-methylidene-1,3-diphenylpropane-1,3-dione **3** with methyllithium.



*Scheme 7.* Plausible mechanism for the formation of compound **19** from the reaction of 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione **4** with methyllithium.

isolated as a nonseparable mixture of two diastereomeric forms in a ratio of 2:1; their configurations could not be determined.

We also found that 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione (**4**) reacts with an excess of methyllithium to afford α-methylstyrene (**6**) and 4-ferrocenyl-2-methyl-2,6-diphenyl-3,4-dihydro-2$H$-pyran (**19**). Scheme 7 depicts a tentative reaction pathway.

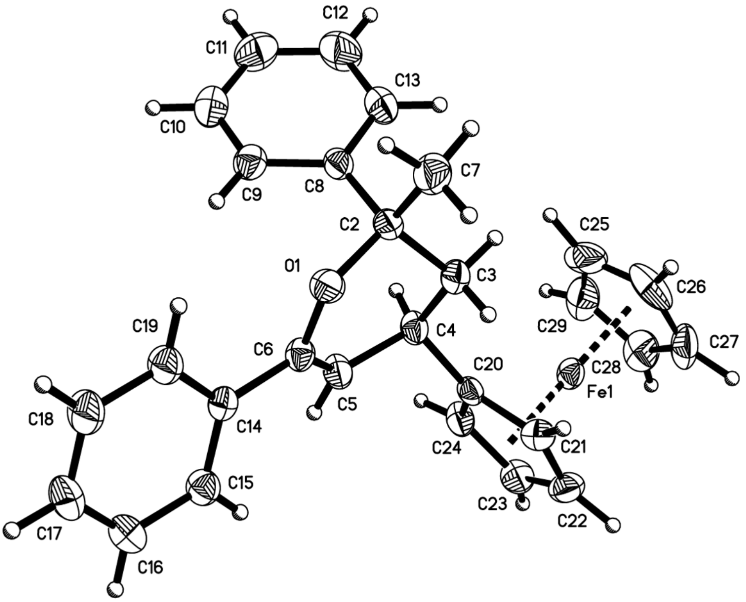


*Figure 1.* Structure of **19** as determined by X-ray crystallography.

**Table 1.** Selected bond lengths and bond angles for **19** and **21**

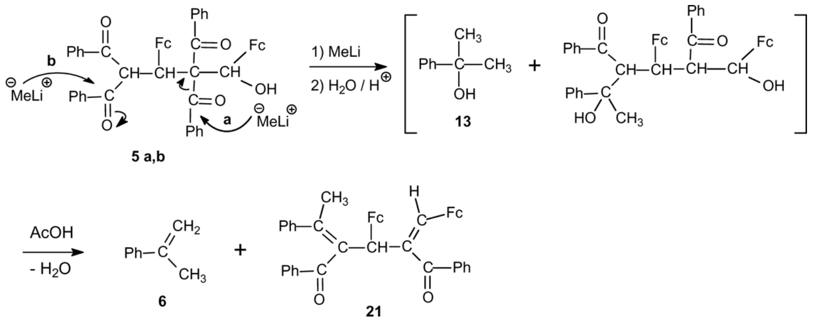
| Bond | Length r (Å) | Bond | Angles, ω (°)– |
|---|---|---|---|
| | **19** | | |
| O(1)–C(2) | 1.449(3) | C(2)–O(1)–C(6) | 117.29(19) |
| C(2)–C(3) | 1.538(3) | C(3)–C(2)–O(1) | 108.1(2) |
| C(3)–C(4) | 1.498(3) | C(2)–C(3)–C(4) | 112.1(2) |
| C(4)–C(5) | 1.509(3) | C(3)–C(4)–C(5) | 108.2(2) |
| C(5)–C(6) | 1.321(3) | C(4)–C(5)–C(6) | 124.2(2) |
| O(1)–C(6) | 1.375(3) | C(5)–C(6)–O(1) | 122.6(2) |
| C(6)–C(14) | 1.481(3) | C(5)–C(6)–C(14) | 125.4(2) |
| C(2)–C(8) | 1.521(3) | C(7)–C(2)–C(8) | 111.1(2) |
| C(2)–C(7) | 1.510(3) | C(3)–C(4)–C(20) | 114.0(2) |
| C(4)–C(20) | 1.520(3) | C(3)–C(2)–C(7) | 110.6(2) |
| | **21** | | |
| C(1)–O(1) | 1.194(6) | O(1)–C(1)–C(2) | 121.2(5) |
| C(1)–C(2) | 1.493(7) | C(1)–C(2)–C(3) | 115.0(4) |
| C(2)–C(3) | 1.541(6) | C(2)–C(3)–C(4) | 113.4(4) |
| C(3)–C(4) | 1.546(7) | C(3)–C(4)–C(5) | 117.3(4) |
| C(4)–C(5) | 1.498(7) | C(4)–C(5)–O(2) | 121.9(5) |
| C(5)–O(2) | 1.218(6) | C(4)–C(39)–C(40) | 124.2(5) |
| C(4)–C(39) | 1.322(6) | C(2)–C(16)–C(17) | 128.4(5) |
| C(2)–C(16) | 1.338(6) | C(1)–C(2)–C(16) | 123.6(5) |
| C(16)–C(17) | 1.467(7) | C(2)–C(3)–C(6) | 113.3(4) |
| C(1)–C(27) | 1.506(7) | C(4)–C(5)–C(33) | 117.2(5) |

The reaction seems to involve two processes, namely, fragmentation (a) and 1,2-addition (b) to the carbonyl group. The transient enediol (**20**) undergoes cyclization in an acidic medium to afford dihydropyran (**19**).

The structure of compound **19** as 4-ferrocenyl-2-methyl-2,6-diphenyl-3,4-dihydro-2*H*-pyran was established by X-ray diffraction analysis of single crystals obtained by crystallization from $CH_2Cl_2$; it was confirmed by $^1H$ and $^{13}C$ NMR spectroscopic data. The general view of molecule **19** is shown in Fig. 1. The central six-membered ring in molecule **19** adopts the half-chair conformation; its main geometric parameters are given in Table 1. The mean Fe-C distance is equal to 2.035 Å; the mean C-C bond length in the cyclopentadienyl rings is equal to 1.402 Å.

It turned out that the reaction of methyllithium with 2,4-dibenzoyl-3-ferrocenyl-2-[ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (**5**) was also accompanied by fragmentation (a) and 1,2-addition (b) processes.(*Z,Z*)-2,4-Dibenzoyl-1,3-diferrocenyl-5-phenylhexa-1,4-diene (**21**) was obtained as the main reaction product (Scheme 8).

According to data from $^1H$ NMR spectroscopy, it was isolated as a single geometric isomer with *Z,Z* configurations of the double bonds.



***Scheme 8.*** Plausible mechanism for the formation of compound **21** from the reaction of 2,4-dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione **5** with methyllithium.

The structure of this compound was established by X-ray diffraction analysis of single crystals obtained by crystallization from $CH_2Cl_2$; it was confirmed by data from mass, IR, and $^1H$ and $^{13}C$ NMR spectroscopy. The general view of molecule **21** is shown in Fig. 2. The main geometric parameters are given in Table 1.

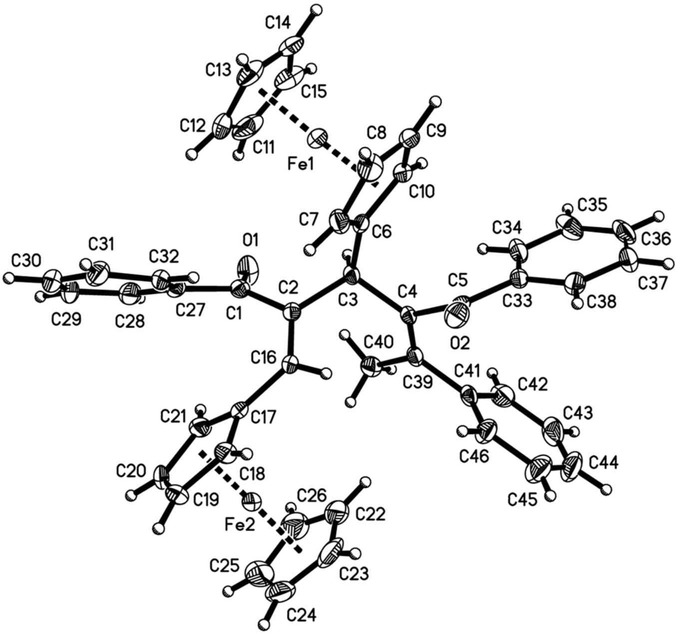


***Figure 2.*** Structure of **21** as determined by X-ray crystallography.

It is noteworthy that the reactions of methyllithium with the coupling products of ferrocenecarbaldehyde with dibenzoylmethane, which are accompanied by simultaneous fragmentation and 1,2-addition, occur with high diastereoselectivity. The major reaction products (**8**, **19**, and **21**) were isolated in single diastereomeric or geometrical forms. The formation of small amounts of other isomeric products cannot be ruled out; however, they have not been detected.

## CONCLUSIONS

The results of the present work demonstrate that the ability of the coupling products of ferrocenecarbaldehyde with dibenzoylmethane to undergo simultaneous fragmentation with abstraction of the benzoyl fragments under the action of methyllithium and 1,2-addition of the latter to the remaining carbonyl groups makes these compounds convenient starting materials for the synthesis of ferrocene-containing substances that are otherwise accessible only with difficulty. Of particular interest is a new method of synthesis of ferrocenyl(diphenyl)-3,4-dihydro-2*H*-pyran (**19**) as a representative of potentially biologically active compounds. Synthesis of 2,4-dibenzoyl-1,3-diferrocenyl-5-phenylhexa-1,4-diene (**21**) is also worth noting, as it opens new prospects for application in the field of electrochemistry and physical optics and provides a new and simple access to bridged heterocyclic structures. In our opinion, the ability to undergo fragmentation under the action of organolithium compounds together with their 1,2-addition to the carbonyl groups is of general character and is typical of other coupling products of aromatic aldehydes with 1,3-diaryl-β-diketones. These reactions are promising as new and simple methods of synthesis of diarylbuta-1,3-dienes, cross-conjugated trienes, and triaryldihydro-2*H*-pyrans, 2,4-diacylhexa-1,4-dienes.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$, with $Me_4Si$ as the internal standard. The IR spectra were measured on a Specord IR-75 instruments for KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). Elementar Analysen systeme GmbH was used for elemental analyses. All the solvents were dried according to standard procedures and were freshly distilled before use. Column chromatography and thin-layer chromatography (TLC) were carried out on alumina (Brockmann activity III). The following reagents were purchased from Aldrich: dibenzoylmethane, 98%; ferrocenecarboxaldehyde, 98%; methyllithium, 1.6 M solution in diethyl ether; acetic acid, glacial, 99.99%; piperidine, 99%; and pyridine, 99%.

## Condensation of Ferrocenecarboxaldehyde with Dibenzoylmethane

A mixture of FcCHO (4.3 g, 0.02 mol), dibenzoylmethane (6.72 g, 0.03 mol), piperidine (1 mL), pyridine (1 mL), and AcOH (2 mL) in dry benzene (100 mL) was refluxed for 6 h. The reaction mixture was washed with 5% HCl to remove the amines, and the organic layer was concentrated to dryness. Diethyl ether (100 mL) was added to the residue, and the precipitate was filtered off and dried on a filter to give 2-ferrocenylmethylidene1,3-diphenylpropan-1,3-dione (**3**). The ethereal filtrate was concentrated, and the residue was chromatographed on $Al_2O_3$ (hexane–dichloromethane, 1:1) to give 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentan-1,5-dione (**4**) and 2,4-dibenzoyl-3-ferricenyl-2-[(ferrocenyl) -hydroxymethyl]-1,5-diphenylpentane-1,5-dione (**5a,b**).

## Data

**2-Ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione (3)**: violet crystals, yield 4.2 g (50%), mp 203–204 °C. IR (KBr): 819, 848,1102, 1480, 1645, 1668, 1695, 1712, 1820, 3030 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 4.18$ (s, 5H, $C_5H_5$), 4.29 (m, 2H, $C_5H_4$), 4.40 (m, 2H, $C_5H_4$), 7.46–8.01 (m, 10H, 2 $C_6H_5$). MS (EI, 70 eV): $m/z = 420$ $[M]^+$. Anal. calcd for $C_{26}H_{20}FeO_2$: C, 74.30; H, 4.80; Fe, 13.29. Found: C, 74.21; H, 4.97; Fe, 13.44.

**2,4-Dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione (4)**: orange powder, yield 2.6 g (20%), mp 242–244°C. IR (KBr): 798, 829, 835,1100, 1467, 1688, 1720, 2921, 3024 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 3.32$ (d, $J = 7.2$ Hz, 2 H, 2 CH), 4.12 (t, $J = 7.2$ Hz, 1 H, CH), 4.04 (s, 5 H, $C_5H_5$), 4.17 (m, 2H, $C_5H_4$), 4.32 (m, 2H, $C_5H_4$). MS (EI, 70 eV): $m/z = 644$ $[M]^+$. Anal. calcd for $C_{41}H_{32}FeO_4$: C, 76.40; H, 5.00; Fe, 8.67. Found: C, 76.59; H, 5.13; Fe 8.48.

**2,4-Dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (5a,b)**: orange powder, yield 2.21 g (13%), two diastereomers (~1:1), mp 303–305 °C. IR (KBr): 806, 811, 839, 1106, 1444, 1663, 1722, 2929, 3004, 3332 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 1.98$ (bs, 1 H, OH), 2.13 (bs, 1 H, OH), 3.16 (d, $J = 6.9$ Hz, 1 H, CH), 3.31 (d, $J = 6.3$ Hz, 1 H, CH), 4.17 (d, $J = 6.9$ Hz, 1 H, CH), 4.28 (d, $J = 6.3$ Hz, 1 H, CH), 4.00 (s, 5 H, $C_5H_5$), 4.06 (s, 5 H, $C_5H_5$), 4.08 (s, 5 H, $C_5H_5$), 4.11 (s, 5 H, $C_5H_5$), 4.14 (m, 2H, $C_5H_4$), 4.21 (m, 4H,

$C_5H_4$), 4.24 (m, 2H, $C_5H_4$), 4.29 (m, 2H, $C_5H_4$), 4.35 (m, 2H, $C_5H_4$), 5.34 (s, 1 H, CH), 5.42 (s, 1 H, CH). MS (EI, 70 eV): $m/z = 858$ $[M]^+$. Anal. calcd for $C_{52}H_{42}Fe_2O_5$: C, 72.74; H, 4.93; Fe, 13.01. Found: C, 72.57; H, 5.05; Fe, 12.87.

### Condensation of 2-Ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione (3) with Dibenzoylmethane

A mixture of (**3**) (1.3 g, 0.003 mol), dibenzoylmethane (0.67 g, 0.003 mol), piperidine (0.3 mL), pyridine (0.3 mL), and AcOH (0.6 mL) in dry benzene (100 mL) was refluxed for 6 h. The reaction mixture was washed with 5% HCl to remove the amines, and the organic layer was concentrated. Ethanol (50 mL) was added to the residue, and the precipitate was filtered off and dried on a filter to give 2,4-dibenzoyl-3-ferrocenyl-1,5-diphenylpentane-1,5-dione (**4**): yield 1.18 g (61%), orange powder, mp 242–243 °C.

### 2,4-Dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (5a,b)

Analogous to the previous procedure, the reaction of **4** (0.65 g, 0.001 mol) with ferrocenecarboxaldehyde (0.32 g, 0.0015 mol) (0.1 mL piperidine, 0.1 mL pyridine, 0.2 mL AcOH) in 50 mL of dry benzene and subsequent workup afforded compound (**5a,b**): yield 0.42 g (49%), orange powder, mp 304–306 °C.

### Reaction of 2-Ferrocenylmethylidene-1,3-diphenylpropane-1,3-dione (3) with Methyllithium

#### Method A

Ethereal solution of MeLi (1.6 *M*, 30 mL) was added dropwise with stirring to a solution of compound **3** (2.95 g, 7 mmol) in dry benzene (100 mL) in an inert dry atmosphere at ambient temperature. The reaction mixture was stirred for 3 h and quenched with water (50 mL). The organic layer was separated, washed with water (2 × 20 mL), and dried with $Na_2SO_4$. The solvent was distilled off in vacuo. Glacial acetic acid (50 mL) was added to the residue, and the mixture was boiled under reflux for 5 min and cooled. Then it was diluted with benzene (50 mL) and washed with water (2 × 20 mL) and 5% aq. $NaHCO_3$. The solvent was distilled off in vacuo, and the residue was chromatographed on a column with alumina (Brockmann activity III) in hexane to yield compounds **6**–**11**.

## Data

**α-Methylstyrene (6)**: colorless oil, yield 0.7 g (8%), $n_D^{20}$ 1.5381.

**3-Ferrocenyl-1-phenyl-2-propenone (7)**: violet crystals, yield 0.11 g (5%), mp 139 °C.[10] IR (KBr): 700, 986, 1108, 1566, 1647, 1703, 3064 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 4.23$ (s, 5 H, $C_5H_5$), 4.54 (m, 2 H, $C_5H_4$), 4.66 (m, 2 H, $C_5H_4$), 7.13 (d, $J = 15.3$ Hz, 1 H, CH=), 7.75 (d, $J = 15.3$ Hz, 1 H, CH=), 7.52 (m, 3 H, $C_6H_5$), 7.97 (m, 2 H, $C_6H_5$). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 69.32$, 71.81 ($C_5H_4$), 70.23 ($C_5H_5$), 79.74 ($C_{ipso}$Fc), 119.63, 128.34 (2 CH=), 128.49, 132.31, 146.73 ($C_6H_5$), 138.98 ($C_{ipso}$), 190.52 (C=O). MS (EI, 70 eV): $m/z = 316$ $[M]^+$. Anal. calcd. for $C_{19}H_{16}FeO$: C, 72.17; H, 5.10; Fe, 17.66. Found: C, 72.29; H, 5.03; Fe, 17.82.

**3,5-Diferrocenyl-1-phenyl-4-(1-phenylvinyl)cyclohexene (8)**: orange crystals, yield 0.13 g (3%), mp 186–187 °C.[9] $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 2.23$ (dd, $J = 10.5$, 15.9 Hz, 1 H, $CH_2$), 2.69 (dd, $J = 5.7$, 15.9 Hz, 1 H, $CH_2$), 2.81 (m, 1 H, $CH^5$), 3.21 (dd, $J = 11.4$, 12.9 Hz, 1 H, $CH^4$), 3.50 (dd, $J = 1.8$, 11.4, 12.9 Hz, 1 H, $CH^3$), 4.12 (s, 5 H, $C_5H_5$), 4.18 (s, 5 H, $C_5H_5$), 3.77 (m, 1 H, $C_5H_4$), 3.82 (m, 1 H, $C_5H_4$), 3.96 (m, 2 H, $C_5H_4$), 3.99 (m, 1 H, $C_5H_4$), 4.03 (m, 2 H, $C_5H_4$), 4.08 (m, 1 H, $C_5H_4$), 5.11 (s, 1 H, $CH_2$=), 5.33 (s, 1 H, $CH_2$=), 6.74 (d, $J = 1.8$ Hz, 1 H, CH=), 6.52 (m, 2 H, $C_6H_5$), 6.92–7.64 (m, 8 H, $C_6H_5$). MS (EI, 70 eV): $m/z = 656$ $[M]^+$. Anal. calcd. for $C_{42}H_{40}Fe_2$: C, 76.84; H, 6.14; Fe, 17.02. Found: C, 76.71; H, 6.23; Fe, 16.88.

**3-Ferrocenylmethylidene-2,4-diphenylpenta-1,4-diene (9)**: orange powder, yield 1.6 g (55%), mp 124–125 °C. IR (KBr): 758, 821, 846, 996, 1101, 1049, 1186, 1225, 1335, 1606, 1649, 2967, 3085 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 4.02$ (s, 5 H, $C_5H_5$), 4.12 (m, 2 H, $C_5H_4$), 4.28 (m, 2 H, $C_5H_4$), 5.04 (d, $J = 1.2$ Hz, 1 H, $CH_2$=), 5.23 (d, $J = 1.2$ Hz, 1 H, $CH_2$=), 5.26 (d, $J = 1.5$ Hz, 1 H, $CH_2$=), 5.90 (d, $J = 1.5$ Hz, 1 H, $CH_2$=), 6.21 (s, 1 H, CH=), 7.28–7.44, 7.63–7.68 (m, 10 H, 2 $C_6H_5$). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 68.95$ ($C_5H_5$), 69.13, 69.66 ($C_5H_4$), 81.16 ($C_{ipso}$Fc), 115.87, 115.94 (2 $CH_2$=), 127.19 (CH=), 126.25, 127.77, 128.01, 128.52, 129.05, 130.64 (2 $C_6H_5$), 138.68, 139.18, 142.17, 146.25, 150.24 (5 C). MS (EI, 70 eV): $m/z = 416$ $[M]^+$. Anal. calcd. for $C_{28}H_{24}Fe$: C, 80.77; H, 5.81; Fe, 13.42. Found: C, 80.64; H, 5.98; Fe, 13.64.

**2-Benzoyl-1-ferrocenyl-3-phenylbuta-1,3-diene (10a,b)**: orange powder, yield 0.2 g (7%), (*Z,E*)-isomers (~1:1), mp 132–133 °C. IR

(KBr): 812, 824, 883, 895, 1002, 1030, 1050, 1105, 1180, 1251, 1340, 1425, 1606, 1658, 1699, 1713, 2929, 2963, 3091 $\mathrm{cm}^{-1}$. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta = 4.11$ (s, 5 H, $C_5H_5$), 4.19 (s, 5 H, $C_5H_5$), 3.95 (m, 2 H, $C_5H_4$), 4.16 (m, 2 H, $C_5H_4$), 4.29 (m, 2 H, $C_5H_4$), 4.42 (m, 2 H, $C_5H_4$), 4.97 (d, 1 H, $J = 1.2$, $CH_2$=), 5.04 (d, 1 H, $J = 0.9$, $CH_2$=), 5.18 (d, 1 H, $J = 1.2$, $CH_2$=), 5.26 (d, 1 H, $J = 0.9$, $CH_2$=), 6.34 (s, 1H, CH=), 6.67 (s, 1H, CH=), 6.89–7.63 (m, 20 H, 4 $C_6H_5$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 68.86$, 68.91, 69.85, 70.24 (2 $C_5H_4$), 69.49, 69.66 (2 $C_5H_5$), 79.89, 80.04 (2 $C_{ipso}$Fc), 114.11, 116.17 (2 $CH_2$=), 124.45, 124.59 (2 CH=), 126.45, 126.58, 127.12, 127.36, 127.54, 128.43, 128.51, 128.69, 129.18, 129.72, 131.14, 131.19 (4 $C_6H_5$), 136.58, 136.63, 138.45, 138.71, 139.11, 139.36, 141.21, 141.83 (8 C), 199.87, 201.08 (2 C=O). MS (EI, 70 eV): $m/z = 418$ $[M]^+$. Anal. calcd. for $C_{27}H_{22}FeO$: C, 77.52; H, 5.30; Fe, 13.35. Found: C, 77.67; H, 5.18; Fe, 13.49.

**2-Benzoyl-1-ferrocenyl-3-methylinden (11)**: orange powder, yield 0.25 g (8%), mp 127–128 °C. IR (KBr): 791, 846, 1103, 1054, 1190, 1253, 1345, 1606, 1649, 1667, 2979, 3083 $\mathrm{cm}^{-1}$.

$^{1}$H NMR (300 MHz, $CDCl_3$): $\delta = 2.27$ (s, 3 H, $CH_3$), 4.15 (s, 5 H, $C_5H_5$), 3.93 (m, 1 H, $C_5H_4$), 4.00 (m, 1 H, $C_5H_4$), 4.08 (m, 1 H, $C_5H_4$), 4.21 (m, 1 H, $C_5H_4$), 4.06 (s, 1 H, CH), 6.93–7.38 (m, 9 H, $C_6H_4$, $C_6H_5$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 18.94$ ($CH_3$), 36.38 (CH), 69.59 ($C_5H_5$), 67.93, 68.01 ($C_5H_4$), 93.11 ($C_{ipso}$Fc), 127.27, 127.70, 128.34, 129.15, 131.69 ($C_6H_4$, $C_6H_5$), 126.90, 135.97, 137.98, 141.65, 142.84 (5 C), 200.62 (C=O). MS (EI, 70 eV): $m/z = 418$ $[M]^+$. Anal. calcd. for $C_{27}H_{22}FeO$: C, 77.52; H, 5.30; Fe, 13.35. Found: C, 77.40; H, 5.42; Fe, 13.17.

## Method B

Analogously, a solution of compound **3** (2.10 g, 5 mmol) in dry benzene (70 mL) was treated with methyllithium (1.6 M solution in diethyl ether, 20 mL) for 3 h at ~20 °C and quenched with water (20 mL), and the organic layer was washed with water and concentrated. Column chromatography of the residue on alumina (Brockmann activity III) in hexane–benzene (2:1) afforded compounds **7, 2, 13, 16, and 17**.

## Data

**2-Phenyl-2-propanol (13)**: colorless oil, yield 0.48 g (22%), mp 32–34 °C.

**3-Ferrocenyl-1-phenyl-2-propenone (7)**: violet crystals, yield 0.08 g (7%), mp 139 °C.

**1-Ferrocenyl-3-phenyl-1-buten-3-ol (12)**: orange powder, yield 0.5 (30%), mp 132–134 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 1.66$ (s, 3 H, $CH_3$), 1.96 (bs, 1 H, OH), 4.08 (s, 5 H, $C_5H_5$), 4.18–4.30 (m, 4 H, $C_5H_4$), 6.10 (d, 1 H, $J = 16.0$ Hz, CH=), 6.40 (d, 1 H, $J = 16.0$ Hz, CH=), 7.20–7.42 (m, 5 H, Ph). MS (EI, 70 eV): $m/z = 332$ $[M]^+$. Anal. calcd. for $C_{20}H_{20}FeO$: C, 72.30; H, 6.07; Fe, 16.81. Found: C, 72.26; H, 6.01; Fe, 16.77.

**2-Benzoyl-1-ferrocenyl-3-phenyl-1-buten-3-ol (17a,b)**: orange powder, yield 0.22 g (10%), (*Z,E*)-isomers ($\sim$1:1), mp 211–212 °C. IR (KBr): 810, 1101, 1157, 1264, 1445, 1529, 1645, 1714, 2930, 3090, 3340–3450 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 1.92$ (s, 3 H, $CH_3$), 1.98 (s, 3 H, $CH_3$), 2.75 (bs, 1 H, OH), 2.89 (bs, 1 H, OH), 4.14 (s, 5 H, $C_5H_5$), 4.19 (s, 5 H, $C_5H_5$), 4.25 (m, 2 H, $C_5H_4$), 4.28 (m, 4 H, $C_5H_4$), 4.32 (m, 2 H, $C_5H_4$), 6.49 (s, 1 H, CH=), 6.56 (s, 1 H, CH=), 7.11–7.52 (m, 10 H, 2 Ph). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 27.46$ ($CH_3$), 29.14 ($CH_3$), 68.89, 68.95, 69.78, 69.83 (2 $C_5H_4$), 69.30, 69.41 (2 $C_5H_5$), 72.47, 72.56 (2 C-OH), 80.31, 80.67 (2 $C_{ipso}$Fc), 124.89, 125.40 (2 CH=), 138.97, 139.32, 144.34, 145.59 (4 $C_{\mathrm{ipso}}$), 208.12, 210.22 (2 C=O). MS (EI, 70 eV): $m/z = 436$ $[M]^+$. Anal. calcd. for $C_{27}H_{24}FeO_2$: C, 74.32; H, 5.54; Fe, 12.80. Found: C, 74.56; H, 5.39; Fe, 12.71.

**3-Ferrocenylmethylidene-2,4-diphenylpentan-2,4-diol (16a,b)**: orange powder, yield 1.47 g (65%), two diastereomers ($\sim$2:1), mp 224–226 °C. IR (KBr): 788, 848, 1104, 1163, 1247, 1451, 1533, 1641, 1667, 2923, 3079, 3334–3445 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$) for **16a**: $\delta = 1.87$ (s, 3 H, $CH_3$), 1.96 (s, 3H, $CH_3$), 2.99 (bs, 2 H, OH), 3.99 (s, 5 H, $C_5H_5$), 3.88 (m, 2 H, $C_5H_4$), 3.96 (m, 1 H, $C_5H_4$), 4.13 (m, 1 H, $C_5H_4$), 6.44 (s, 1 H, CH=), 7.19–7.60 (m, 10 H, 2 Ph). $^1$H NMR (300 MHz, $CDCl_3$) for **16b**: $\delta = 1.71$ (s, 3 H, $CH_3$), 1.79 (s, 3H, $CH_3$), 2.45 (bs, 2 H, OH), 4.05 (s, 5 H, $C_5H_5$), 3.20 (m, 1 H, $C_5H_4$), 3.49 (m, 1 H, $C_5H_4$), 4.24 (m, 2 H, $C_5H_4$), 6.69 (s, 1 H, CH=), 7.40–7.92 (m, 10 H, 2 Ph). MS (EI, 70 eV): $m/z = 452$ $[M]^+$. Anal. calcd. for $C_{28}H_{28}FeO_2$: C, 74.34; H, 6.24; Fe, 12.35. Found: C, 74.23; H, 6.35; Fe, 12.21.

## Reaction of 2,4-Dibenzoyl-3-ferrocenyl-1,5-diphenylpentan-1,5-dione (4) with MeLi

A solution of MeLi (1.6 M solution in diethyl ether, 10 mL) was added dropwise in an inert atmosphere to a stirred solution of compound **4** (0.97 g, 0.0015 mol) in dry benzene (50 mL) at 20 °C for 30 min. The mixture was stirred for an additional 6 h, and the excess of MeLi was quenched by addition of water (50 mL). The organic layer was separated, dried with $Na_2SO_4$, and concentrated. The residue was chromatographed on $Al_2O_3$ (hexane–ether, 4:1) to give 0.22 g (62%) of the α-methylstyrene (**6**) as a colorless oil ($n_D^{20}$ 1.5382), and 0.52 g (80%) of the 4-ferrocenyl-2-methyl-2,6-diphenyl-3,4-dihydro-2H-pyran **(19)**.

**Compound (19)**: orange crystals, mp 118–119 °C. IR (KBr): 816, 891, 1101, 1148, 1254, 1647, 1673, 2867, 2916, 3032 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, $CH_3$), 2.54 (dd, $J$ = 5.4, 15.3 Hz, 1 H, $CH_2$), 3.05 (dd, $J$ = 8.7, 15.3 Hz, 1 H, $CH_2$), 3.69 (m, 1 H, CH), 4.10 (s, 5 H, $C_5H_5$), 4.14 (m, 2 H, $C_5H_4$), 4.31 (m, 2 H, $C_5H_4$), 6.84 (d, $J$ = 7.2 Hz, 1 H, CH=), 7.03–7.47 (m, 10 H, 2 $C_6H_5$). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 21.24 ($CH_3$), 34.15 ($CH_2$), 43.26 (CH), 58.93 (C), 69.25 ($C_5H_5$), 68.93, 70.12 ($C_5H_4$), 82.03 ($C_{ipso}$Fc), 124.14 (CH=), 126.31, 126.63, 127.10, 127.39, 128.45, 130.14 (2 $C_6H_5$), 138.54, 142.91, 143.67 (3 C). MS (EI, 70 eV): $m/z$ = 434 $[M]^+$. Anal. calcd. for $C_{28}H_{26}FeO$: C, 77.42; H, 6.03; Fe, 12.87. Found: C, 77.23; H, 6.19; Fe, 12.68.

## Reaction of 2,4-Dibenzoyl-3-ferrocenyl-2-[(ferrocenyl)hydroxymethyl]-1,5-diphenylpentane-1,5-dione (5a,b) with MeLi

Analogous to the previous procedure, the reaction of **5a,b** (1.29 g, 0.0015 mol) with MeLi (1.6 M solution in diethyl ether, 10 mL) in 50 mL of dry benzene (20 °C, 10 h) and subsequent workup afforded compound **6**, 0.1 g (55%), and compound (**21**), 0.74 g (67%).

**(*Z,Z*)-2,4-Dibenzoyl-1,3-diferrocenyl-5-phenylhexa-1,4-diene (21)**: violet crystals, mp 242–243 °C. IR (KBr): 819, 888, 1101, 1154, 1248, 1645, 1675, 2883, 2928, 3039 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.87 (s, 3 H, $CH_3$), 3.79 (s, 1 H, CH), 4.04 (s, 5 H, $C_5H_5$), 4.17 (s, 5 H, $C_5H_5$), 3.78 (m, 2 H, $C_5H_4$), 3.89 (m, 2 H, $C_5H_4$), 4.21 (m, 2 H, $C_5H_4$), 4.38 (m, 2 H, $C_5H_4$), 6.64 (s, 1 H, CH=), 7.03–7.79 (m, 15 H, 3 $C_6H_5$). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 20.03 ($CH_3$), 39.22 (CH), 69.13, 69.84 (2 $C_5H_5$), 68.37, 68.91, 70.43, 71.07 (2 $C_5H_4$), 80.11, 80.43 (2 $C_{ipso}$Fc), 123.94 (CH=), 126.33, 126.48, 126.78, 127.23, 127.65, 128.04, 129.61, 130.04, 131.13 (3 $C_6H_5$), 128.78, 136.34, 137.18, 137.92, 138.16, 141.91 (6 C), 203.15, 205.07 (2 C=O). MS (EI, 70 eV): $m/z$ = 734 $[M]^+$. Anal. calcd. for $C_{46}H_{38}Fe_2O_2$: C, 75.22; H, 5.21; Fe, 15.21. Found: C, 75.39; H, 5.06; Fe, 15.38.

## X-ray Crystal Structure Analysis of (19) and (21)

Crystals were obtained from $CH_2Cl_2$. The unit-cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD diffractometer. The structures of compounds were solved by direct methods (SHELXS-97[11]) and refined using full-matrix least squares on $F^2$.

**Crystal data for $C_{28}H_{26}FeO$ (19)**: $M = 434.34\,g{\cdot}mol^{-1}$, triclinic P-1, $a = 7.829(1)$, $b = 10.455(1)$, $c = 14.744(1)$ Å, $\alpha = 73.828(1)°$, $\beta = 82.515(2)°$, $\gamma = 69.288(1)°$, $V = 1083.5(1)$ Å$^3$, $T = 293(2)$ K, $Z = 2$, $\rho = 1.331\,Mg/m^3$, $\lambda$ (Mo–K$\alpha$) = 0.71073 Å, F(000) = 456, absorption coefficient $0.713\,mm^{-1}$, crystal size $0.236 \times 0.21 \times 0.088\,mm^3$, index ranges $-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$, scan range $2.15 \leq \theta \leq 25.02°$, 3836 independent reflections, $R_{int} = 0.0464$, 12934 total reflections, 272 refinable parameters, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0457$, $wR_2 = 0.0658$, R indices (all data) $R_1 = 0.0643$, $wR_2 = 0.0686$, largest difference peak and hole $0.612/-0.230\,e$Å$^{-3}$.

**Crystal data for $C_{46}H_{38}Fe_2O_2$ (21)**: $M = 734.46\,g{\cdot}mol^{-1}$, monoclinic P21/n, $a = 6.219(1)$, $b = 26.756(2)$, $c = 21.105(2)$ Å, $\alpha = 90°$, $\beta = 94.666(2)°$, $\gamma = 90°$, $V = 3500.1(7)$ Å$^3$, $T = 293(2)$ K, $Z = 4$, $\rho = 1.394\,Mg/m^3$, $\lambda$ (Mo–K$\alpha$) = 0.71073 Å, F(000) = 1528, absorption coefficient $0.868\,mm^{-1}$, crystal size $0.648 \times 0.026 \times 0.024\,mm^3$, index ranges $-7 \leq h \leq 7$, $-31 \leq k \leq 31$, $-24 \leq l \leq 25$, scan range $1.80 \leq \theta \leq 25.01°$, 6176 independent reflections, $R_{int} = 0.1488$, 28148 total reflections, 452 refinable parameters, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0724$, $wR_2 = 0.1090$, R indices (all data) $R_1 = 0.1454$, $wR_2 = 0.1252$, largest difference peak and hole $0.497/-0.323\,e$Å$^{-3}$.

**Supplementary material**: crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 649254 for compound **19** and no. 649253 for compound **21**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambrige CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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