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Ferrocene compounds

XX *. Synthesis and reactions of some ferrocene fulvenes

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Abstract

Reaction of several aroylferrocenes (**1**) with cyclopentadienide (from cyclopentadiene and sodium in ethanol) has given 6-aryl-6-ferrocenylfulvenes (**2**) in 53–69% yields. Similarly, starting from 1,1′-diaroylferrocenes (**5**), the corresponding bisfulvenes **6** have been obtained in *ca.* 70% yields. Upon standing, in solution or as solids the fulvenes **2** or **6** give equilibrated mixtures with the corresponding dimers **3** and **7** and oligomers **8**. Addition of acrylonitrile to the ferrocene fulvenes gave the *endo*-isomers **4** in 49–57% yields and mixtures of *endo*- and *exo*-bisadducts **10** in 56–75% yields.

1. Introduction

With an ease that depends on the nature of the substituents in position 6, fulvenes undergo dimerization of the Diels–Alder type; the products are those formed by [4 + 2]-addition at an endocyclic double bond of fulvene rather than at an exocyclic one. For example, 6-phenyl-6-(α-pyridyl)fulvene was found to undergo rapid dimerization [2]. Uebersax *et al.* [3] showed that the case of thermal dimerization of the fulvenes decreases sharply in the series fulvene > 6-methylfulvene > 6,6-dimethylfulvene, the products being preponderantly those of *endo*-[4 + 2]-cycloaddition. The two methylfulvene dimers were obtained under equilibration with the starting monomers in solutions above room temperature.

On the basis of frontier MO calculations Houk *et al.* [4] have suggested similarities in reactivity between fulvene and cyclopentadiene since their HO orbitals are approximately equal in energy. In Diels–Alder reaction with dienes, for steric reasons (exocyclic double bond), fulvene reacts preferentially as a dienophile rather than as a diene.

The kinetics, thermodynamics, and stereochemistry of reactions of fulvenes with various dienophiles depend on the nature of the substituents of both reactants. For example, Kresze [5] has found that the equilibrium constant at 20°C for the reaction of 6,6-diarylfulvenes with TCNE increased with change in the substituents in the aryl groups in the following sequence: $m\text{-NO}_2 < p\text{-Cl} < p\text{-Br} < \text{H} < p\text{-OCH}_3$. Houk [4] explained this increasing reactivity of an electron-deficient dienophile with electron-rich fulvenes in terms of a decrease in the energy separating the fulvene HOMO-alkene LUMOs, resulting in stronger interactions between these frontier orbitals. Siegel [6] found that depending on the nature of the substituents in mono- or *gem*-disubstituted alkenes, reactions with 6,6-diphenylfulvenes gave mixtures of *endo*- and *exo*-adducts, in which the *endo*-isomers usually predominate.

Some metallocene-substituted monofulvenes and heteroannularly substituted bisfulvene derivatives have been prepared [7–10] starting from ferrocene or cymantrene carbonyl compounds. 6-Ferrocenylfulvene

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and its bisfulvene analogue were found to dimerize (or polymerize) rapidly in solution [9]. 6-Ferrocenyl-6-methylfulvene and the corresponding bis-fulvene are not so unstable but they also undergo cycloaddition [8]. 6-Cymantrenyl-6-phenylfulvene has been found to undergo dimerization, in contrast to 6-ferrocenyl-6-phenylfulvene in which the donor ferrocenyl substituent stabilizes the fulvene [10].

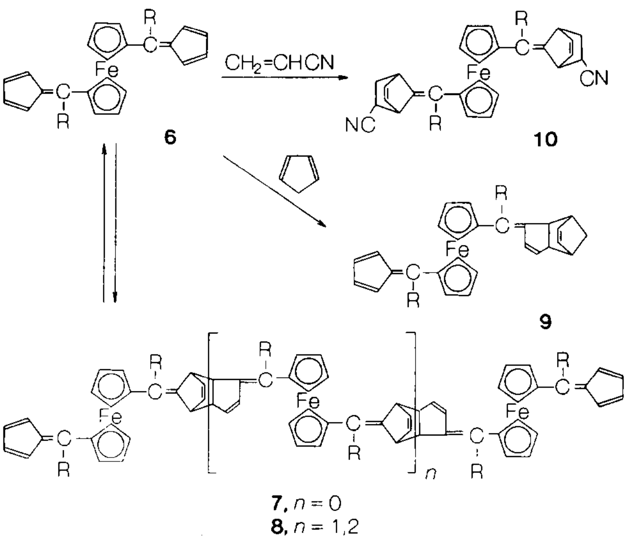
2. Results and discussion

We first examined the dependence of the ease of formation and dimerization or oligomerization of 6-aryl-6-ferrocenylfulvenes (**2**) and their bisfulvene analogues **6** on the character of the aryl groups. Condensation of *m*- and *p*-substituted aryl ferrocenyl ketones **1** with 3.5 molar equivalents of cyclopentadiene in an ethanolic solution of KOH gave 12–27% of **2** (Method A, [10]) (Scheme 1). Better yields (53–69%) and much purer products were obtained by the action of 5 molar equivalents of cyclopentadiene and 10 molar equivalents of Na in absolute ethanol on aroylferrocene **1** (Method B [9]).

A similar procedure gave the bisfulvenes **6** in *ca.* 70% yield from the corresponding 1,1′-diaroylferrocenes (**5**) (Scheme 2).

Attempts to condense the *o*-substituted aroylferrocenes with cyclopentadiene were unsuccessful, probably for steric reasons.

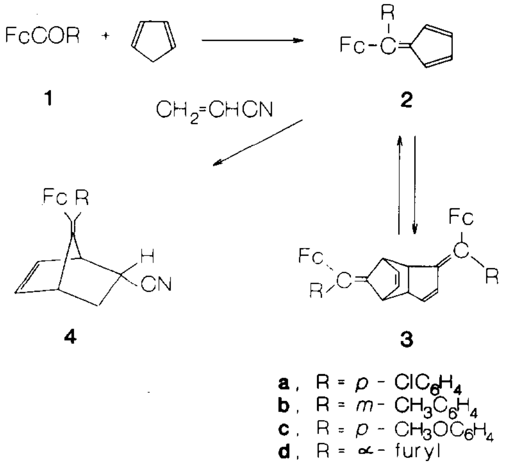
The IR spectra of compounds **2** and **6** showed characteristic weak bands at 3040–3090 (ν(CH)) and strong bands at 1570–1590 cm^{-1} (ν(C=C)). In the ^1H NMR spectra signals from the ferrocene and aromatic protons appear at the usual positions; the cyclopentadiene resonances are at *ca.* 7.0, 6.6, 6.4 and 5.7 ppm [for H(4), H(3), H(5), and H(2), respectively] [6,10]. The UV absorption maxima are at *ca.* 270, 330 and 490 nm.



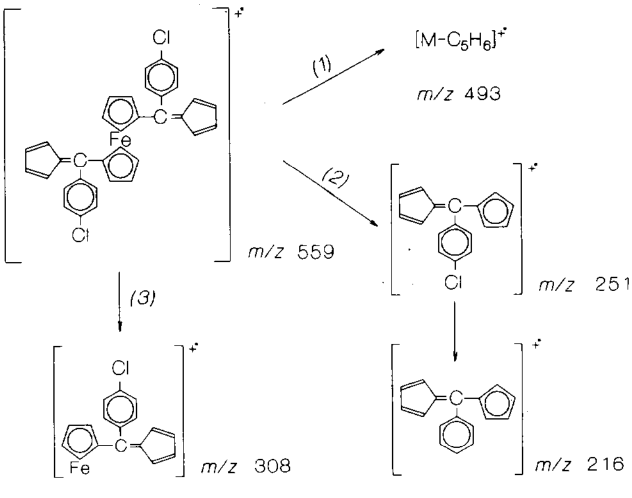
Scheme 2.

Typical fragmentation pathways (1–3) in the mass spectra of bisfulvenes are shown in Scheme 3.

In contrast to a previous report [10], we observed that during the preparation of violet monofulvenes **2** some yellow dimers **3** were formed. (They can be separated by TLC.) Brief heating of a DMSO solution of the dimers **3** at 100°C caused *retro*-Diels–Alder conversion into monomers. Upon longer standing, either in solution or as crystals, monomers or dimers equilibrate. Similarly, in the synthesis of bisfulvenes in addition to monomers **6**, dimeric products **7**, along with small quantities of oligomers **8**, were obtained. The base peaks, in the mass spectra of dimers **3** and **7** appear at *m/z* values corresponding to the parent



Scheme 1.



Scheme 3.

peaks of monomers **2** and **6**, respectively. Attempts to observe the molecular ions of dimers by recording spectra at lower temperatures with an ionizing voltage of 10–75 eV were unsuccessful, presumably because of the ease of thermal conversion of dimers to monomers. When the reaction products were kept, the proportion of oligomers had increased after a few days. Upon heating the solution of the oligomers in DMSO at 100°C for 4–5 min, de-oligomerization into **6** occurred. The degree of polymerization of materials **7** and **8** was determined by gel permeable chromatography (GPC); the oligomers were predominantly dimers, with smaller amounts of trimers and tetramers.

In addition to the compounds described in the preparation of bisfulvenes **6**, red-violet products with higher R_F value were isolated. On the basis of mass, IR and ^1H NMR spectra, we suggest for these the "dicyclopentadiene" structure **9**. In the light of Houk's results [4], we assumed that addition of fulvene (as dienophile) to cyclopentadiene (as diene) had occurred. The alternative structure (analogous to compound **10**), formed by the fulvene acting as a diene, must also be considered.

In a typical experiment, 70% of monomer **6a**, 15% of the dicyclopentadiene compounds **9a**, 12% of dimer **7a**, and 3% of oligomer **8a** were isolated from the reaction mixture.

Attempts to measure the rates of *retro*-Diels–Alder reactions of dimers **3** and **7** were made by means of UV spectroscopy. Solutions of samples in DMSO were kept at 50–60°C and the spectra recorded over a period of 15–40 min. Unfortunately, the positions of the peaks of the reactants and products were too close to allow a rate measurement.

2.1. *Adducts of ferrocene fulvenes*

Furdik *et al.* [8] studied the addition of maleimides on 6-ferrocenylfulvene, 6-ferrocenyl-6-methylfulvene and 1,1'-bis(α-cyclopentadienylideneethyl)ferrocene by means of IR spectroscopy, and found that monofulvenes gave *endo*-adducts. In the case of bisfulvene, depending on the solvent used and the nature of the *N*-substituent in the reagent, two isomers were formed, to which stereochemistries were not assigned. The bulk of the ferrocenyl groups accounts for the sterically more favourable *endo*-addition.

We examined the action of acrylonitrile (AN) and methacrylonitrile on several of the above-mentioned mono-, **2**, and bis-fulvenes, **6**. Attempted additions of 2–4 molar of ratios of the reagents with [6] or without solvents were unsuccessful. Only after prolonged standing of monofulvenes **2** with 10 molar proportions of AN or bisfulvenes **6** with 20–30 molar proportions of AN were **4** (49–57%) and **10** (56–75%) formed at room temperature. Under neither set of conditions did methacrylonitrile react with ferrocenylfulvenes, probably owing to steric interaction of the methyl group of the reagents with bulky ferrocenyl and aryl substituents of the fulvenes.

As mentioned above, Houk found [4], that the ease of reaction of AN (an electron-deficient alkene) rises with electron release in substituents on the aryl groups of arylfulvenes in the sequence: $p\text{-ClC}_6H_4 < m\text{-CH}_3C_6H_4 < \alpha$-furyl. (The corresponding Hammett constants, σ^+, are 0.11, -0.1 and -0.9, respectively). The electron-releasing ferrocenyl group ($\sigma^+ = -1.31$) will increase the rate of reaction.

The additions to monofulvenes **2a**, **2b** and **2d** take place in 7, 12 and 4 days, respectively. The high reactivity of **2d** is in accordance with the above reasoning; the unexpectedly low reactivity of **2b** is probably due to steric hindrance by the *m*-methyl group. All the reactions are stereoselective, in each case only one of four possible isomers (arising from the presence of two different substituents on the exocyclic fulvene carbon) is formed.

Reactions of AN with bisfulvenes **6a** and **6b** took 20 and 40 days, respectively. These results are consistent with the above arguments. As previously observed [8], in these reactions only bisadducts **10**, (*i.e.* no monoadducts) were formed. From inspection of molecular models of **10** it can be seen that there is a possibility of forming 4 racemates and 4 *meso*-products, which are related as diastereoisomers or structural isomers. Addition of AN to **6b** gave two isomeric products **10b**, which were separated by TLC and shown to have *endo*- and *exo*-configuration. Addition of AN to **6a** gave a single product, probably the *exo*-isomer **10a**.

The stereochemistries of products **4** and **10** were assigned on the basis of ^1H NMR spectroscopy. The *exo*-proton in the 2-position of the *endo*-isomers is less shielded than the *endo*-hydrogen atom of the *exo*-isomers, and therefore shifted further downfield [6]. Thus the signals at δ 2.12–2.29 were attributed to the H(2)-protons of the *endo*-isomers, and peaks at δ 1.56–1.25 ppm to H(2)-protons of the *exo*-isomers. The stereochemistry of these adducts will be more closely studied in subsequent work.

It is noteworthy that reactions of AN with oligomeric bisfulvenes **8** gave the monomeric adducts **10** after 20–40 days, showing that the adducts are much more stable than the oligomeric materials **8**.

3. Experimental details

The melting points were determined with a Büchi apparatus and are uncorrected. The IR spectra were

TABLE 1. Physical constants and IR and UV spectral data for [aryl(cyclopentadienylidene)methyl]ferrocene (**2**) and of 1,1′-bis[aryl(cyclopentadienylidene)methyl]ferrocene (**6**)

Compound	Aryl	Formula (molecular weight)	Yield (%) Method A (Method B)	m.p. [a] (°C)	Analysis Found (calcd.) (%)		IR spectra (cm^{-1})		UV spectra (nm)		
					C	H	ν(CH)Fc(Me)	ν(C=C)			
2a	*p*-Chlorophenyl	$C_{22}H_{17}ClFe$ (372.7)	15 (58)	110–112	71.24 (70.90)	4.28 (4.60) [b]	3085m	1580b	270	308	469
2b	*m*-Tolyl	$C_{23}H_{20}Fe$ (352.3)	12 (53)	Resin	78.19 (78.41)	5.92 (5.73)	3090w (2910m)	1590s 1570b	271	324	485
2c	*p*-Methoxyphenyl	$C_{23}H_{20}FeO$ (368.3)	27	69–72	75.39 (75.00)	5.55 (5.49)	3085w (2920m)	1585b	273	330	488
2d	α-Furyl	$C_{20}H_{17}FeO$ (329.2)	21 (69)	65–68	73.24 (72.97)	5.41 (5.20)	3095w	1573s 1542s	271	328	489
6a	*p*-Chlorophenyl	$C_{34}H_{24}Cl_2Fe$ (559.3)	(72)	152–153	73.32 (73.00)	4.09 (4.33) [c]	3060w	1576s	271	330	493
6b	*m*-Tolyl	$C_{36}H_{30}Fe$ (518.5)	(68)	88–89	83.48 (83.38)	6.21 (5.84)	3040w (2905m)	1570s	270	336	496

[a] Recrystallized from ethanol. [b] Cl: found 9.93, calcd. 9.51%. [c] Cl: found 12.54, calcd. 12.68%.

recorded as KBr pellets or liquid films with a Perkin-Elmer 257 Grating Infrared Spectrophotometer. The UV spectra (in dioxane) were recorded with a Hewlett Packard 8452 A spectrophotometer. The ^1H NMR spectra were recorded on a Varian EM 360 or Varian Gemini 300 spectrometer with tetramethylsilane as internal standard. The mass spectra were obtained with a Shimadzu GCNS-QP 1000 spectrometer. Degrees of polymerization of oligomers were determined by gel permeable chromatography (GPC) on a 500 A PL gel column (Varian 8500 pump, tetrahydrofuran as eluent). Reaction products were purified by preparative TLC on silica gel (Merck, Kieselgel 60 HF_{254}) or by recrystallization from ethanol. Aroylferrocenes (**1a–1d**), *o*-chlorobenzoylferrocene and 1,1′-diaroylferrocenes (**5a–5d**) were prepared by acylation of ferrocene [11–13].

3.1. [Aryl(cyclopentadienylidene)methyl]ferrocene (2)

(A) The aroylferrocene (**1**) (1.3 mmol) was dissolved in 15 ml of ethanol and 2 g of KOH and 0.4 ml (4.8 mmol) of freshly distilled cyclopentadiene was added. The mixture was stirred for 2–4 h at room temperature then poured into ice-water. The mixture was shaken with ether containing some dichloromethane and the organic layer was washed with water until neutral then dried with Na_2SO_4, and evaporated *in vacuo* to a small

TABLE 2. ^1H NMR spectral data for ferrocene fulvenes **2** and **6**

Compound	Aromatic protons			Cyclopentadiene protons				Ferrocene protons			CH_3
				H(4)	H(3)	H(5)	H(2)	Substituted ring		Unsubstituted ring	
2a	7.43 (2,d)	7.33 (2,d)		7.06 (1,dt)	6.59 (1,dt)	6.33 (1,dt)	5.73 (1,dt)	4.53 (4,dt)		4.18 (5,s)	–
2b	7.40–7.31 (4,m)			7.16 (1,m)	6.71 (1,m)	6.40 (1,m)	5.86 (1,m)	4.63 (2,d)	4.22 (2,d)	4.28 (5,s)	2.52 (3,s)
2c	7.30 (2,d)	6.99 (2,d)		7.11 (1,dt)	6.57 (1,dt)	6.31 (1,dt)	5.81 (1,dt)	4.51 (4,dd)		4.17 (5,s)	3.88 (3,s)
2d	7.83 (1,dt)	6.88 (1,d)	6.45 (1,m)	6.85 (1,m)	6.66 (1,m)	6.56 (1,m)	6.45 (1,m)	4.58 (4,dt)		4.21 (5,s)	–
6a	7.52–7.20 (8,m)			6.91 (2,dt)	6.57 (2,dt)	6.36 (2,dt)	5.71 (2,dt)	4.58 (4,t)	44 (4,t)	–	–
6b	7.41–7.30 (8,m)			6.92 (2,dt)	6.53 (2,dt)	6.30 (2,dt)	5.73 (2,dt)	4.52 (4,t)	4.42 (4,t)	–	2.36 (6,s)

TABLE 3. Molecular weights, IR and UV spectral data for dimers **3** and **7** and dicyclopentadiene derivatives **9**

Compound	Aryl	Formula	Molecular weight Found (calcd.)	IR spectra (cm^{-1}) ν(CH)Fc	ν(CH)aliphatic	ν(C=C)	UV spectra (nm)		
3a	*p*-Chlorophenyl	$C_{44}H_{34}Cl_2Fe_2$	373 (745.4)	3050m	2908m 2840m	1580b			
3d	α-Furyl	$C_{40}H_{34}Fe_2O_2$	329 (658.4)	3095w	2910w 2840w	1573s 1542s			
7a	*p*-Chlorophenyl	$C_{68}H_{48}Cl_4Fe_2$	559 (1118.6)	3085w	2960m 2920m	1576s	274	314	518
7b	*m*-Tolyl	$C_{72}H_{60}Fe_2$	518 (1037.0)	3060w	2950w 2910m	1571s	276	324	496
9a	*p*-Chlorophenyl	$C_{39}H_{30}Cl_2Fe$ [a]	625 (625.4)	3065w	2960w 2910m	1575s	269	328	490
9b	*m*-Tolyl	$C_{41}H_{36}Fe$ [b]	584 (584.6)	3045w	2950w 2905m	1570s	270	331	486

[a] Analysis (found (calcd.) (%)): C, 75.21 (74.90); H, 4.66 (4.84); Cl, 11.65 (11.34). [b] Analysis (found (calcd.) (%)): C, 84.25 (84.24); H, 6.53 (6.21).

volume. The residue was subjected to TLC on silica gel with petroleum ether/benzene (4:1, v/v) as eluent and subsequent recrystallization from ethanol.

(B) Sodium (920 mg, 40 mmol) was dissolved in 30 ml of absolute ethanol and 1.65 ml (20 mmol) of cyclopentadiene were added during 10 min. After 20 min, a solution of 4 mmol of aroylferrocene (**1**) in 20 ml of ethanol was added, and the mixture stirred for 30 min at room temperature and then refluxed for 2–3 h. The usual work-up and purification by TLC gave the fulvenes **2** as violet oils or as resins that solidified on standing (Tables 1 and 2).

3.2. 5,5,10,10-Bis[aryl(ferrocenyl)methylene]tricyclo-[5.2.1.0^{2,6}]deca-3,8-dien (3)

During the preparation of fulvenes **2** some yellow dimers **3** were formed and these were separated by TLC (Tables 3 and 4).

3.3. 7,7-[Aryl(ferrocenyl)methylene]bicyclo[2.2.1]hept-5-ene-2-carbonitrile (4)

A solution of 1 mmol of fulvene **2** in 10 mmol of freshly distilled acrylonitrile was kept for 4–12 days at room temperature. Removal of the excess of the nitrile

TABLE 4. ^{1}H NMR spectral data for dimers **3** and **7** and of cyclopentadiene derivatives **9**

Compound	Aromatic protons	Cyclopentadiene protons H(4)	H(3)	H(5)	H(2)	Dicyclopentadiene protons Vinyl H(3) H(4)	H(8) H(9)	Methine H(1) H(2) H(6) H(7)	Methylene H(10)	Ferrocene protons		CH_3
3d [a]	7.75–7.51 (m)	–	–	–	–	6.95 (d)	5.89 (m)	3.50–3.20 (m)	–	4.25 (m)	4.01 (m)	
7a	7.53–7.18 (16,m)	6.94 (2,m)	6.60 (2,m)	6.40 (2,m)	5.62 (2,m)	5.91 (4,m)	5.72 (4,m)	3.6–3.2 (4,m)	–	4.50–4.10 (16,m)		
7b	7.21–7.15 (16,m)	6.91 (2,m)	6.62 (2,m)	6.30 (2,m)	5.60 (2,m)	5.94 (4,m)	5.69 (4,m)	3.5–3.1 (4,m)	–	4.40–4.10 (16,m)		2.41 (12,s)
9a	7.49–7.18 (8,m)	6.93 (1,m)	6.57 (1,dm)	6.33 (1,dt)	5.56 (1,m)	6.05 (2,dd)	5.75 (2,t)	3.52–3.10 (4,m)	1.36 (2,m)	4.39 (4,m)	4.10 (4,m)	–
9b	7.31–7.14 (8,m)	6.95 (1,m)	6.61 (1,dm)	6.30 (1,ddd)	5.61 (1,m)	6.03 (2,dd)	5.73 (2,m)	3.4–3.0 (4,m)	1.39 (2,m)	4.39 (4,m)	4.06 (4,m)	2.37 (6,s)

[a] Dimer **3d** rapidly equilibrates in solution with monomer **2d**, so that the signals from the corresponding cyclopentadiene protons are also present.

TABLE 5. Physical constants and IR spectral data for adducts **4** and **10**

Compound	Aryl	Formula (molecular weight calcd.)	Yield (%)	m.p. [a] (°C)	Analysis (found (calcd.) (%))			IR spectra (cm^{-1})			
					C	H	N	ν(CH)Fc	ν(CH) aliph.	ν(C≡N)	ν(C=C)
endo- **4a**	*p*-Chlorophenyl	$C_{25}H_{20}ClFeN$ (425.7)	57	91–93	70.91 (70.52)	4.53 (4.74)	3.32 (3.29) [b]	3070w	2900s 2840m	2215m	1575m
endo- **4b**	*m*-Tolyl	$C_{26}H_{23}FeN$ (405.3)	53	58–60	76.76 (77.05)	5.99 (5.72)	3.13 (3.46)	3060w	2950w 2900w	2221s	1570m
endo- **4d**	α-Furyl	$C_{23}H_{20}FeNO$ (382.3)	49	72–74	72.10 (72.26)	5.32 (5.27)	3.51 (3.66)	3090m	2910s 2850w	2222s	1580m
"*exo*"- **10a**	*p*-Chlorophenyl	$C_{40}H_{30}Cl_2FeN_2$ (665.4)	56	147–148	71.15 (72.20)	4.55 (4.54)	4.63 (4.21) [c]	3070w	2915s 2860m	2218m	1592m
"*endo*"- **10b**	*m*-Tolyl	$C_{42}H_{36}FeN_2$ (624.6)	51	110–114	81.00 (80.76)	5.66 (5.81)	4.52 (4.49)	3050w	2955w 2910m	2220s	1575m
"*exo*"- **10b**	*m*-Tolyl	$C_{42}H_{36}FeN_2$ (624.6)	24	78–80	80.54 (80.76)	6.11 (5.81)	4.62 (4.49)	3065m	2930m 2860w	2225m	1603s

[a] Recrystallized from ethanol. [b] Cl: found 8.49, calcd. 8.33%. [c] Cl: found 10.35, calcd. 10.92%.

in vacuo left an orange solid, which was purified by TLC (Tables 5 and 6).

3.4. *1,1'-Bis[aryl(cyclopentadienylidene)methyl]ferrocene (6)*

The title compounds were prepared according to procedure B used for synthesis of fulvenes **2**, starting from 1 mmol of 1,1'-diaroylferrocene (**5**), 74 mmol of sodium, and 40 mmol of cyclopentadiene (Tables 1 and 2).

3.5. *Oligomers 7, 8 and dicyclopentadiene derivatives 9 of 1,1'-bis[aryl(cyclopentadienylidene)methyl]ferrocene*

In the syntheses of bisfulvenes **6**, violet dimeric products **7** were formed, followed by small quantities of oligomers **8** and purple dicyclopentadiene derivatives **9**. The products were separated by preparative TLC with a mixture of petroleum ether benzene (3 : 1, v/v) as eluent; the following compounds (in order of descending R_F values) were eluted: **9**, **6**, **7** and **8** (Tables 3 and 4).

3.6. *α,α'-(1,1'-Ferrocenylene)bis{7,7-(arylmethylene)bicyclo[2.2.1]hept-5-ene-2-carbonitrile} (10)*

When dark violet solutions of bisfulvenes **6** or their oligomeric products (**7**, **8**) in 20–30 mmol of acrylonitrile were kept at room temperature for 2–3 weeks, orange-red cycloaddition products **10** were obtained (Tables 5 and 6).

TABLE 6. ^1H NMR spectral data for adducts **4** and **10**

Compound	Aromatic protons	Norbornene protons						Ferrocene protons		CH_3
		H(5) H(6)	H(1)	H(4)	H(2)	*exo*-H(3)	*endo*-H(3)	Substituted ring	Unsubstituted ring	
endo- **4a**	7.39–7.00 (4,m)	6.51 (2,m)	3.97 (1,m)	3.10 (1,dt)	2.12 (1,m)	1.52 (1,m)	1.25 (1,m)	4.19 (4,m)	4.03 (5,s)	–
endo- **4b**	7.35–7.25 (4,m)	6.45 (2,m)	3.65 (1,m)	2.95 (1,d)	2.29 (1,m)	1.55 (1,m)	1.26 (1,m)	4.20 (4,m)	4.03 (5,s)	2.34 (3,s)
endo- **4d**	7.43 (1,m) 6.42 (4,m)		3.70 (1,m)	2.90 (1,dt)	2.28 (1,m)	1.57 (1,m)	1.25 (1,m)	4.2 (4,m)	4.04 (5,s)	–
"*exo*"- **10a**	7.90–6.90 (8,m)	6.38 (4,m)			1.56–1.26 (10,m)			4.07 (8,m)	–	–
"*endo*"- **10b**	7.35–6.85 (8,m)	6.42 (4,m)	3.23 (2,d)	2.90 (2,d)	2.17 (2,m)	1.63 (2,dt)	1.32 (2,dt)	4.03 (8,m)	–	2.35 (6,s)
"*exo*"- **10b**	7.77–6.85 (8,m)	6.45 (4,m)	1.52–1.25 (10,m)					4.09 (8,m)	–	2.33 (6,s)

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