

REACTION OF METALLOCENYL THIOKETONES WITH $C_5H_5^-$ AND $[(C_5H_5)Fe(CO)_2]^-$ ANIONS. PREPARATION AND CRYSTAL STRUCTURES OF DIMERIC CYMANTRENYLPHENYLFULVENE DERIVATIVES

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Summary

Ferrocenyl- and cymantrenyl-phenylthioketone react with $C_5H_5^-$ or $[(C_5H_5)Fe(CO)_2]^-$ anions forming ferrocenyl- and cymantrenyl-phenylfulvene. The latter readily undergoes a Diels–Alder dimerization or a cycloaddition with a starting thioketone or analogous ketone. Crystal structures of two dimeric products were established.

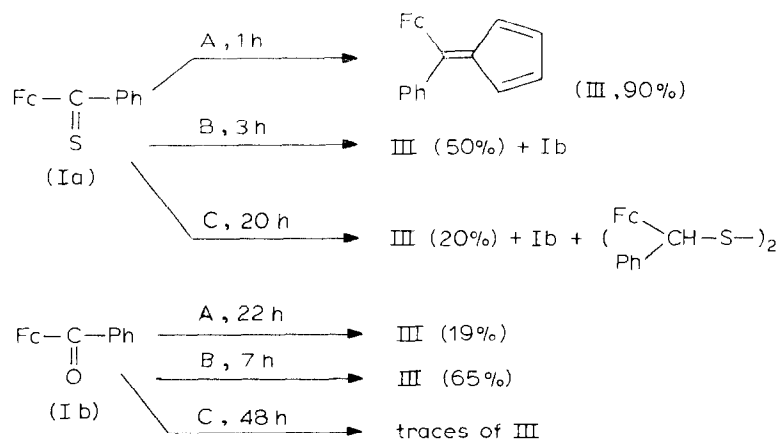
Introduction

Alper et al. [1] have found that diarylthioketones interact with $[CpM(CO)_n]^-$ anions ($M = Fe$, $n = 2$; $M = Mo$ or W , $n = 3$) yielding diarylfulvenes, diaryldisulphides and neutral dimers corresponding to these anions. The reaction proceeds in both organic and aqueous media under conditions of interphase catalysis. However, yields of fulvenes are low and only slightly increase with interphase catalysis [2].

It was interesting to perform a similar reaction with metallocenyl thioketones and thus to obtain fulvenes with a metallocenyl substituent at the exocyclic, i.e. C_6 atom. Such fulvenes are useful for preparation of a novel class of bi-nuclear transition metal complexes by coordination of another metal atom to the fulvene moiety. Some 6-ferrocenylfulvenes have been prepared earlier, using different methods [3–6].

As the starting species in the reaction mentioned above we have chosen ferrocenylphenylthioketone (Ia) and cymantrenyl-phenylthioketone (IIa), prepared by some of us earlier [7] and differing from each other in the electronic properties of the substituents (donor ferrocenyl vs. acceptor cymantrenyl). Herein we report the

* Deceased.



SCHEME 1. Fc = ferrocenyl; methods A, B and C see Experimental.

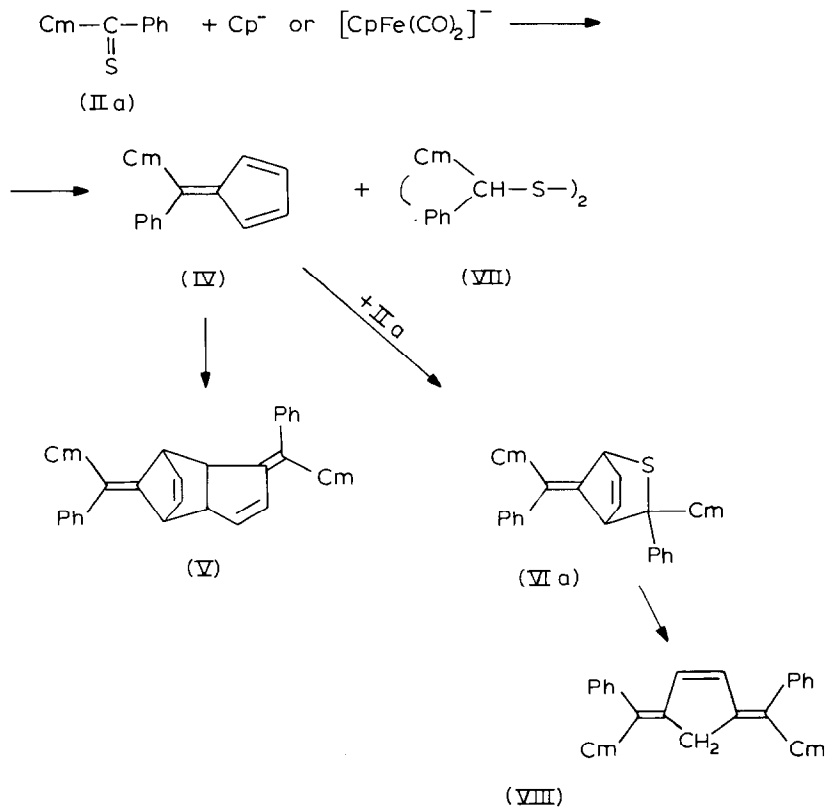
reactions of Ia and IIa and their oxygen analogues Ib and IIb with cyclopentadienyl Cp^- and $[\text{CpFe}(\text{CO})_2]^-$ anions generated from cyclopentadiene and $[\text{CpFe}(\text{CO})_2]_2$ respectively.

Results and discussion

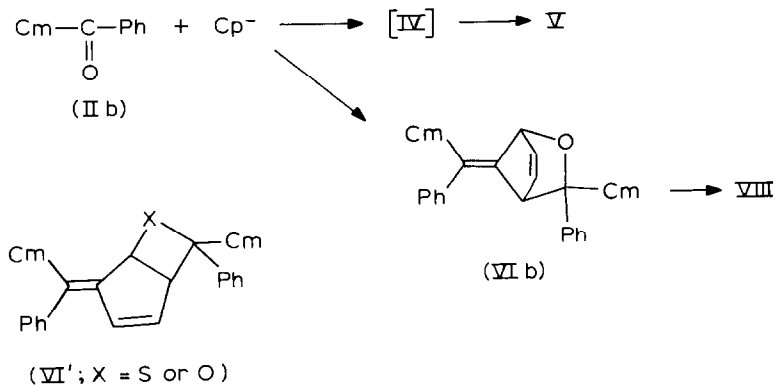
We have found that the reaction is governed by the nature of the metallocenyl substituent and is strongly affected by the reaction conditions (medium, reagent ratio, nature of the anion, etc.). Thus, an interphase-catalyzed interaction of Ia with the Cp^- anion (method A, Scheme 1) gives ferrocenylfulvene (III) in the almost stoichiometric yield, while in non-aqueous solutions (method B, Scheme 1) the yield does not exceed 50% even with a longer reaction time. A still lower yield (ca. 20%) was observed in the reaction of Ia with $[\text{CpFe}(\text{CO})_2]^-$ (method C, Scheme 1). In the latter case, besides III, benzoylferrocene (Ib), bis(ferrocenylphenylmethyl)disulphide and some other products were obtained. Ib reacts with both anions less readily and with lower yields of III (Scheme 1).

IIa reacts with Cp^- (generated from cyclopentadiene in the presence of alkaline reagents) or with $[\text{CpFe}(\text{CO})_2]^-$ (obtained from dimeric $[\text{CpFe}(\text{CO})_2]_2$ under interphase catalysis conditions) in a quite different way. Instead of expected cymantrenylphenylfulvene (IV) we isolated its dimer V and a product (VIa) of cycloaddition between IV and IIa. In some experiments bis(cymantrenylphenylmethyl)disulphide (VII) and triene VIII were also obtained, Scheme 2. Cymantrenylphenylketone (IIb) reacts with the Cp^- anion similarly, yielding no fulvene IV but its dimer V, a product (VIb) by addition of IIb to IV, and VIII, Scheme 3. The yields and relative amounts of the products strongly depend on the reaction conditions. Particularly, an excess of thioketone or ketone (II) in the reaction mixture increases the yield of the cycloaddition product VI, while an excess of the anion yields the dimer V as a major product.

The novel complexes V, VIa and b and VIII were characterized by elemental analysis, IR, ^1H NMR and mass spectra (Tables 1, 7). The structures of V and VIII were elucidated by an X-ray single crystal diffraction study.



SCHEME 2. Cm = cymantrenyl.

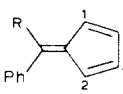
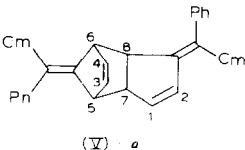
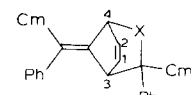
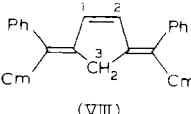
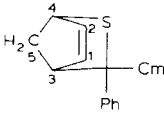


SCHEME 3. Cm = cymantrenyl.

Complex V (Fig. 1) is a dimer of IV formed by the Diels–Alder condensation of cyclopentadiene rings (via the formation of C(17)–C(17') and C(20)–C(18') bonds) into a tricyclic “dicyclopentadiene” system with the C(18)=C(19) and C(19')=C(20') double bonds. A similar dimerization of 6,6-dimethylfulvene has been reported earlier [8]. In Fig. 1 the left half, designated A, of molecule V has a diene-like

TABLE 1

¹H NMR SPECTRA OF III–VI, VIII AND IX (ppm, from TMS, (CD₃)₂CO standard)

	Multiplicity, intensity		
	Ph	Cp	Other protons
	III: 7.2–7.5(m, 5H)	4.17 (s, 5H) 4.51 (t, 2H) 4.54 (t, 2H)	5.78 (dt, 1H)– 6.34 (dt, 1H) 6.61 (dt, 1H) 7.10 (dt, 1H) } 1,2,3,4
R = Fc (III), Cm (IV)	IV: 7.0–7.6(m, 5H)	5.07 (t, 2H) 5.27 (t, 2H)	5.69 (ddd,1H) 6.39 (ddd,1H) 6.57 (ddd,1H) 6.80 (ddd,1H) } 1,2,3,4
	V: 7.0–7.5(m,10H)	3.9(br.s,1H) 4.0(br.s,1H) 4.33(br.m,1H) 4.50 (m, 2H)	6.68 (d, 1H) 1 5.93 (br.d,1H) 2 } J _{1,2} 5.6Hz 5.78 (dd, 1H) 6.00 (dd, 1H) } 3,4 J _{3,4} 5.6Hz
	VIa ^b :	4.58(br.s,1H) 4.63(br.s,1H) 4.73(br.s,1H)	2.98 (br.s,1H) 2.75 (br.s,1H) } 7,8 3.15 (br.s,2H) 5,6 6.72 (dd) } 1,2 J(HH) 5.6 Hz 5.94 (dd) }
X = S (VIa), O (VIb)	VIb: 7.2–7.4(m,10H)	4.6–5.37 ^c (m, 9H)	6.29 (dd,1H) 1 5.77 (dd,1H) 2 } J 5.5 Hz 6.65 (dd,1H) 3
	VIII: 7.2–7.5(m,10H)	5.11 (t, 4H) 5.00 (t, 4H)	6.09 (s, 2H) 1,2 3.90 (br.s,2H) 3
IX: 7.1–7.7 (m,5H)	5.20 (m, 1H) 4.77 (m, 1H) 4.51 (m, 1H) 4.45 (m, 1H)	5.78 (dd,1H) 1 4.15 (br.m,1H) 4 3.75 (br.m,1H) 3	
			2.30(br.d,1H) } AB system of 1.88(dt, 1H) } protons 5. J _{AB} 20 Hz

^a In CS₂, CD₃OD as an outer standard, re-calculated to TMS. ^b Signals of V were observed, indicating the decomposition of VIa during spectral study. ^c Proton 4 signal is in the same range.

five-membered ring, and the right half designated B, has a dienophilic one. The atoms belonging to the A and B moieties have unprimed and primed indices respectively.

Molecule VIII (Fig. 2) is situated on a crystallographic twofold axis passing through C(20) and the midpoint of C(17)–C(17') bond. The atoms related by this axis with the reference atoms are primed.

The relevant geometrical parameters of molecules V and VIII are listed in Tables 2 and 3.

Cymantrenylphenylethylene moieties of V and VIII have similar geometry and conformation. The bond distances and angles in cymantrenyl residues are unexceptional [9,10]. In both halves of molecule V the C(3) atom of an Mn(CO)₃ group is eclipsed by the C(5) atom of a cyclopentadienyl ring, while C(1) and C(2) are

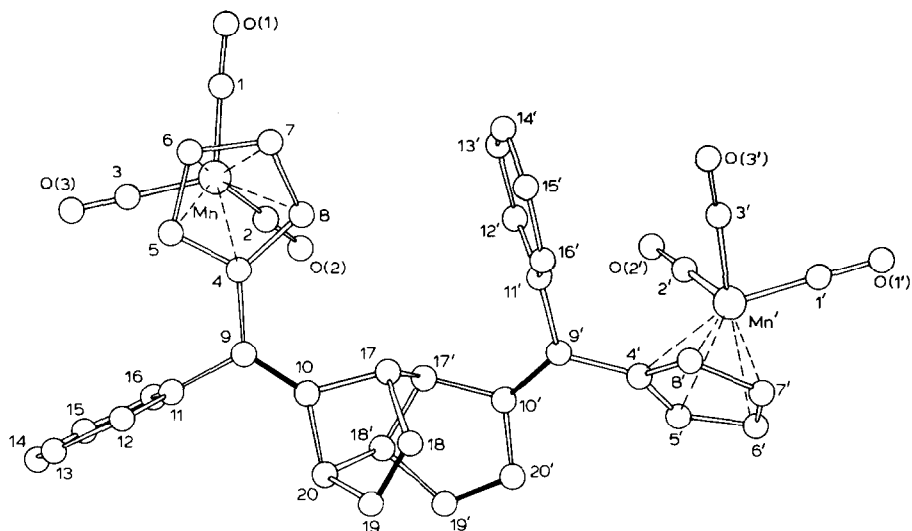


Fig. 1. Molecular structure of V (double bonds blackened, hydrogen atoms omitted).

situated above C(6)–C(7) and C(4)–C(8) bonds with C(1) being almost in *trans* position to C(4). In molecule VIII the C(3) atom lies above the C(5)–C(6) bond while C(1) and C(2) are rotated by 15° and 10° from C(4) and C(7) respectively. Systematic lengthening of cyclopentadienyl C–C bonds *cis* to CO groups and shortening of *trans* bonds, predicted by MO calculations [10], are not observed in V and VIII.

All the Ph and Cp-rings in V and VIII are planar. The Ph-plane is inclined to the coordination plane of the C(9) atom by 84.6°(V, A), 69.4°(V, B), 84.4°(VIII), and the

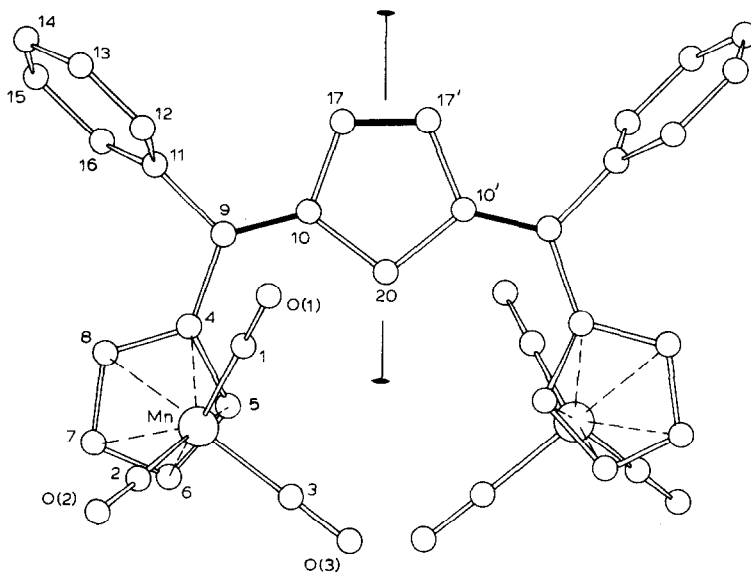


Fig. 2. Molecular structure of VIII (double bonds blackened, hydrogen atoms omitted).

TABLE 2
BOND DISTANCES (Å)

Bond	V (A)	V (B)	VIII	Bond	V (A)	V (B)	VIII
Mn–C(1)	1.783(4)	1.801(4)	1.798(6)	C(4)–C(9)	1.484(5)	1.473(5)	1.476(5)
Mn–C(2)	1.789(4)	1.789(4)	1.782(7)	C(9)–C(10)	1.323(5)	1.333(5)	1.344(5)
Mn–C(3)	1.802(4)	1.786(4)	1.805(5)	C(9)–C(11)	1.495(5)	1.496(5)	1.490(5)
Mn–C(4)	2.158(4)	2.159(3)	2.173(6)	C(10)–C(17)	1.523(5)	1.517(5)	1.453(5)
Mn–C(5)	2.142(4)	2.123(4)	2.152(5)	C(10)–C(20)	1.523(5)	1.466(5)	1.513(5)
Mn–C(6)	2.141(4)	2.125(4)	2.147(7)	C(11)–C(12)	1.383(5)	1.393(5)	1.38(1)
Mn–C(7)	2.129(4)	2.139(4)	2.132(9)	C(11)–C(16)	1.383(6)	1.394(5)	1.388(9)
Mn–C(8)	2.128(4)	2.144(4)	2.138(8)	C(12)–C(13)	1.376(6)	1.386(5)	1.383(7)
Mn–Cp ^a	1.767	1.764	1.779	C(13)–C(14)	1.371(6)	1.377(6)	1.38(1)
O(1)–C(1)	1.147(5)	1.145(5)	1.137(8)	C(14)–C(15)	1.373(6)	1.370(6)	1.35(1)
O(2)–C(2)	1.150(5)	1.154(5)	1.158(9)	C(15)–C(16)	1.374(6)	1.392(6)	1.388(7)
O(3)–C(3)	1.147(5)	1.151(5)	1.139(6)	C(17)–C(18)	1.509(5)	1.560(5)	–
C(4)–C(5)	1.415(5)	1.429(5)	1.438(6)	C(18)–C(19)	1.333(5)	1.493(5)	–
C(5)–C(6)	1.421(5)	1.414(6)	1.409(7)	C(19)–C(20)	1.517(6)	1.336(5)	–
C(6)–C(7)	1.407(5)	1.422(6)	1.391(7)	C(17)–C(17')	1.574(5)		1.328(5)
C(7)–C(8)	1.408(5)	1.404(6)	1.423(6)	C(20)–C(18')	1.592(5)		–
C(4)–C(8)	1.442(5)	1.437(5)	1.421(6)				

^a Cp is the cyclopentadienyl ring centroid.

TABLE 3
BOND ANGLES (°)

Angle	V (A)	V (B)	VIII	Angle	V (A)	V (B)	VIII
C(1)MnC(2)	93.7(2)	95.0(2)	91.1(3)	C(4)C(8)C(7)	108.1(3)	109.2(3)	108.6(5)
C(1)MnC(3)	93.1(2)	91.8(2)	92.1(3)	C(4)C(9)C(10)	123.1(3)	123.5(3)	124.6(5)
C(2)MnC(3)	91.8(2)	91.5(2)	93.8(3)	C(4)C(9)C(11)	115.9(3)	116.8(3)	115.0(4)
CpMnC(1)	123.4	125.7	124.4	C(10)C(9)C(11)	121.0(3)	119.7(3)	120.3(5)
CpMnC(2)	122.0	122.0	124.4	C(9)C(10)C(17)	133.0(3)	124.5(3)	125.9(5)
CpMnC(3)	124.1	122.0	122.0	C(9)C(10)C(20)	130.3(3)	129.4(3)	128.3(4)
MnC(1)O(1)	178.9(4)	179.5(4)	178.4(6)	C(17)C(10)C(20)	96.3(3)	106.1(3)	105.8(4)
MnC(2)O(2)	177.9(4)	176.7(3)	178.5(5)	C(9)C(11)C(12)	120.1(3)	119.4(3)	120.2(5)
MnC(3)O(3)	178.6(4)	178.2(3)	176.6(6)	C(9)C(11)C(16)	121.2(3)	122.4(3)	121.9(5)
C(5)C(4)C(8)	106.4(3)	105.6(3)	106.1(5)	C(12)C(11)C(16)	118.7(4)	118.2(3)	117.9(5)
C(5)C(4)C(9)	125.5(3)	127.1(3)	123.2(5)	C(11)C(12)C(13)	120.7(4)	120.6(4)	121.7(6)
C(8)C(4)C(9)	128.1(3)	127.3(3)	130.7(5)	C(12)C(13)C(14)	120.5(4)	120.4(4)	119.1(6)
C(4)C(5)C(6)	109.2(3)	109.7(3)	108.5(5)	C(13)C(14)C(15)	118.8(4)	119.8(4)	120.2(6)
C(5)C(6)C(7)	107.5(3)	107.2(3)	108.6(6)	C(14)C(15)C(16)	121.4(4)	120.4(4)	120.7(6)
C(6)C(7)C(8)	108.8(3)	108.3(3)	108.1(6)	C(11)C(16)C(15)	119.9(4)	120.5(4)	120.4(6)
Angle	V	Angle	V	Angle	VIII		
C(10)C(17)C(18)	100.6(3)	C(17)C(17')C(10')	115.3(3)	C(10)C(17)C(17')	111.7(5)		
C(10)C(17)C(17')	97.7(3)	C(17)C(17')C(18')	102.8(3)	C(10)C(20)C(10')	105.1(3)		
C(18)C(17)C(17')	107.2(3)	C(10')C(17')C(18')	106.2(3)				
C(17)C(18)C(19)	108.0(3)	C(20)C(18')C(17')	103.1(3)				
C(18)C(19)C(20)	108.0(3)	C(20)C(18')C(19')	117.7(3)				
C(10)C(20)C(19)	100.1(3)	C(17')C(18')C(19')	103.1(3)				
C(10)C(20)C(18')	97.4(3)	C(18')C(19')C(20')	112.9(3)				
C(19)C(20)C(18')	106.1(3)	C(10')C(20')C(19')	111.8(3)				

Cp-plane by 22.4(V, A), 39.8(V, B) and 18.2°(VIII). Therefore, C(9)=C(10) double bonds have no π -conjugation with phenyls and a rather weak π -interaction with Cp rings. In fact, the C(9)–C(Cp) bond distances are comparable with the standard non-conjugated C(sp^2)–C(sp^2) single bond length of 1.476 Å [11], while the C(9)–C(Ph) bonds are still longer (1.490–1.496 Å).

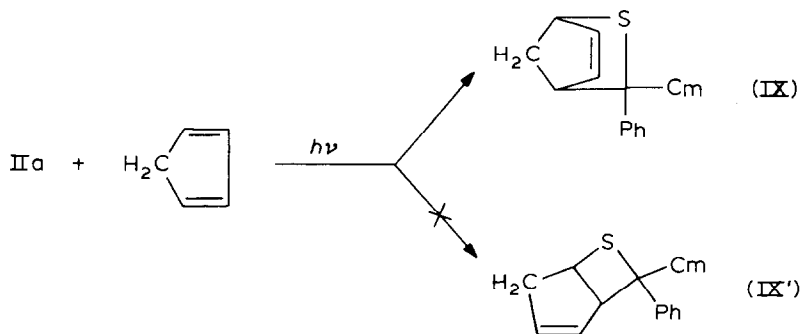
Bulky substituents at C(9) cause a torsion of the C(9)=C(10) double bond by 6.1(V, A), 1.7(V, B) and 6.3°(VIII).

The dicyclopentadiene system in V is, as usual, very strained, bond angles being strongly distorted (96–113° at sp^2 , and 97–118° at sp^3 -hybridized carbons). The C(17)–C(17') and C(20)–C(18') bonds formed on dimerization of IV are longer by 0.04 and 0.06 Å (i.e., by 8 and 12 σ) than the standard C(sp^3)–C(sp^3) single bond (1.535 Å) [11]. This lengthening is consistent with the lability of these bonds manifested by a partial re-monomerization of V in solution (see below). The conjugation between C(9')=C(10') and C(19')=C(20') double bonds (the C(9')C(10')C(20')C(19') torsion angle is 177.6(6)°) causes a shortening of the C(10')–C(20') single bond to 1.466(5) Å.

The cyclopentene ring in VIII is planar. The C(9)=C(10) and C(9')=C(10') bonds, coplanar with it, are conjugated with the endocyclic C(17)=C(17') bond. Therefore the C(10)–C(17) single bond is shortened to 1.453(5) Å. Nevertheless, all the double bonds in V and VIII are localized.

¹H NMR spectra of V and VIII are consistent with their solid state structures. The spectrum of V exhibits olefinic and tertiary proton signals (average δ of 6.37 and 3.36 ppm, respectively) in a 1/1 ratio. The spectrum of VIII exhibits, besides phenyl and two Cp-ring proton signals, only two signals at 6.09 ppm (two olefinic protons) and 3.90 ppm (methylene group), confirming a high symmetry of the molecule.

There is some ambiguity concerning the structure of VI, as the cycloaddition of IIa or IIb to IV can proceed either via the butadiene moiety of the fulvene ring (1,4-addition, shown in Schemes 2 and 3), or via one of its double bonds (1,2-addition, leading to an alternative structure VI'). The former route seems more probable, since IV dimerizes into V unequivocally via 1,4-addition. To clarify this problem, we prepared from IIa and cyclopentadiene a complex (Scheme 4) which may be either a 1,4-(structure IX) or a 1,2-adduct (structure IX'). Nevertheless, its ¹H NMR spectrum (Fig. 3) exhibits splitting of the proton signals in positions 1, 2



SCHEME 4

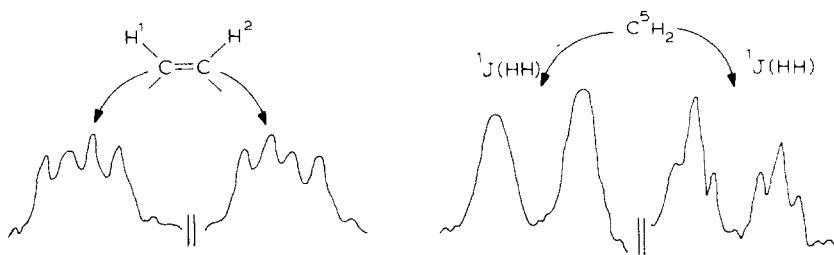


Fig. 3. ^1H NMR spectra of IX (atom numbering see Table 1).

and 5, confirming the structure as IX. The similarity of $\text{CH}=\text{CH}$ group signals in the ^1H NMR spectra of VI and IX is evidence for the 1,4-addition structure of VI. It is noteworthy that accumulation spectra of both VIb and VIII exhibit weak additional signals which can be attributed to another isomer. This suggestion needs, however, further investigation.

Surprisingly the mass spectrum of V exhibits no molecular ion of the dimer, but an ion of the monomer IV and some fragmentation products of the latter (Table 1), indicating easy splitting of V into IV. We attempted to perform such re-monomerization by chemical means. When V was heated to 100°C in dimethylsulphoxide, integral intensities of the dimer signals in its ^1H NMR spectrum decreased. Simultaneously several new peaks appeared, their multiplicity and relative intensities being consistent with the structure of IV (Table 1).

The fulvene ring proton signals of III and IV have chemical shifts usual for pentafulvenes [5]. These signals of IV lie in a slightly higher field compared to III (average δ 6.36 vs 6.46 ppm), but the difference is small.

Thus, the interaction of metallocenyl thioketones with the cyclopentadienyl anion gives pentafulvenes, whose reactivity depends on the nature of a metallocenyl moiety. An acceptor cymantrenyl substituent at the exocyclic carbon atom makes the fulvene reactive both as diene and dienophile (in the Diels-Alder dimerization and cycloaddition with thioketone or ketone). In contrast, a donor ferrocenyl substituent stabilizes the fulvene and prevents the mentioned reactions. The stereoselectivity of both dimerization and cycloaddition reactions is also noteworthy, as in each case only one of several possible (caused by two different substituents at the exocyclic fulvene carbon) isomers is formed.

Experimental

^1H NMR spectra were recorded with a Bruker WP-200 SY spectrometer (200 MHz, 0.2 Hz/channel sweep), IR spectra with a UR-20 spectrometer and mass spectra with an AEI MS-30/DS-50 instrument.

X-ray diffraction experiments were performed with 4-circle autodiffractometers and the calculations were carried out with an Eclipse S/200 computer using INEXTL programmes [12]. Crystal data and experimental details are presented in Table 4. Both structures V and VIII were solved by conventional Patterson and Fourier methods and refined by least squares (block-diagonal for V, full matrix for VIII) in anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms in VIII were refined isotropically and in V they are included as fixed contributions in

TABLE 4
CRYSTAL DATA AND EXPERIMENTAL DETAILS

Compound	V	VIII
Formula	C ₄₀ H ₂₆ Mn ₂ O ₆	C ₃₅ H ₂₂ Mn ₂ O ₆
<i>a</i> (Å)	10.259(7)	24.509(2)
<i>b</i> (Å)	10.848(8)	9.5540(5)
<i>c</i> (Å)	14.685(10)	20.812(2)
α (°)	98.47(6)	90
β (°)	92.03(5)	143.502(4)
γ (°)	98.99(6)	90
<i>V</i> (Å ³)	1594(3)	2898.6(4)
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	4
<i>d</i> (calcd) g cm ⁻³	1.48	1.49
Diffractometer	Syntex P2 ₁	Hilger & Watts
Radiation	graphite-monochromated Mo- <i>K</i> _α	
Temperature (°C)	-80	+20
Scan mode	θ/2θ	θ/2θ
θ _{max} (°)	20	30
No. of independent reflections with <i>I</i> ≥ 2σ	2557	1783 ^a
Weighting scheme	<i>w</i> _F = σ _F ⁻²	<i>w</i> _F = σ _F ⁻²
<i>R</i>	0.030	0.038
<i>R</i> _w	0.029	0.033

^a Except 2 rejected low-angle reflections, affected by extinction.

calculated positions (assuming C(*sp*²)-H bond distances of 1.00 Å, C(*sp*³)-H of 1.05 Å, *B*_{iso} by 1 Å² greater than *B*_{iso}^{eq} of the corresponding carbon atom). Final positional and thermal atomic parameters are listed in Tables 5, 6.

Starting complexes I and II were prepared as described in [7,13,14]. Cyclopentadiene was distilled immediately before experiments. All reactions were carried out under nitrogen.

Method A: interphase-catalysed reaction with Cp⁻

(a) *Ia*. The mixture of *Ia* (0.25 g, 0.82 mmol), cyclopentadiene (0.3 ml, 3.6 mmol), KOH (2 g) in water (2 ml) benzene (2 ml) and 18-crown-6 (0.02 g, 0.1 mmol) was stirred for 1 h at room temperature, poured into water and extracted with hexane/benzene (5/1). The layers were separated, the organic part was washed with water to neutral reaction and dried with MgSO₄, then evaporated in vacuo to 1 ml and chromatographed on a silica gel column. The product III was eluted with hexane/benzene (5/1) and re-crystallized from acetone (0.25 g, 90%, m.p. 99–100°C).

Ib under the same conditions but for 22 h, gives III with a 19% yield.

(b) *IIa*. The mixture of *IIa* (0.39 g, 1.2 mmol), cyclopentadiene (0.1 ml, 1.2 mmol), KOH (2 g) in water (2 ml)/benzene (2ml) and 18-crown-6 (0.02 g, 0.1 mmol) was stirred for 3 h and then treated as above. The products were separated by thin layer chromatography on silica gel using benzene as an eluent. The first zone yielded V (0.17 g, 40%, ν(CO) in CH₂Cl₂ at 1955 and 2035 cm⁻¹) and the second zone gave VIa (0.16 g, 20%, ν(CO) in hexane at 1952 and 2030 cm⁻¹). The latter was impossible to purify from traces of V and VII, therefore its elemental analysis was

TABLE 5

ATOMIC COORDINATES ($\times 10^4$, for Mn $\times 10^5$) AND THERMAL FACTORS $B_{\text{iso}}^{\text{eq}} = 1/3 \sum_{ij} B_{ij} a_i^* a_j^* (a_i a_j) (\text{\AA}^2)$ IN THE STRUCTURE V

Atom	x	y	z	$B_{\text{iso}}^{\text{eq}}$	Atom	x	y	z	$B_{\text{iso}}^{\text{eq}}$
Mn	16070(6)	77854(5)	10496(4)	2.04(2)	Mn'	82024(6)	64482(5)	53127(4)	1.83(2)
O(1)	-253(3)	5444(3)	1057(2)	4.8(1)	O(1')	8933(3)	4906(3)	6683(2)	4.2(1)
O(2)	1773(3)	8521(3)	3063(2)	5.5(1)	O(2')	5404(3)	6295(2)	5731(2)	3.3(1)
O(3)	-489(3)	9313(3)	828(2)	4.7(1)	O(3')	7618(3)	4239(2)	3857(2)	3.2(1)
C(1)	467(4)	6367(4)	1058(3)	3.0(1)	C(1')	8643(4)	5505(3)	6151(3)	2.6(1)
C(2)	1689(4)	8216(4)	2277(3)	3.4(1)	C(2')	6506(4)	6329(3)	5584(3)	2.1(1)
C(3)	315(4)	8705(4)	909(3)	3.1(1)	C(3')	7835(4)	5094(3)	4437(3)	2.3(1)
C(4)	3497(4)	8882(3)	867(2)	1.6(1)	C(4')	8242(4)	8029(3)	4571(3)	1.6(1)
C(5)	2698(4)	8667(3)	35(3)	2.0(1)	C(5')	9324(4)	7377(3)	4351(3)	2.0(1)
C(6)	2378(4)	7346(3)	-274(3)	2.3(1)	C(6')	10131(4)	7415(3)	5159(3)	2.6(1)
C(7)	2976(4)	6735(3)	370(3)	2.2(1)	C(7')	9559(4)	8103(3)	5898(3)	2.6(1)
C(8)	3656(4)	7654(3)	1076(3)	2.0(1)	C(8')	8412(4)	8470(3)	5546(3)	1.9(1)
C(9)	4032(4)	10137(3)	1406(2)	1.5(1)	C(9')	7170(4)	8202(3)	3931(2)	1.4(1)
C(10)	5087(4)	10337(3)	1986(3)	1.7(1)	C(10')	6667(4)	9268(3)	3973(2)	1.3(1)
C(11)	3325(4)	11196(3)	1239(3)	1.6(1)	C(11')	6629(4)	7098(3)	3211(2)	1.6(1)
C(12)	3618(4)	11823(4)	499(3)	2.6(1)	C(12')	5356(4)	6454(3)	3269(3)	2.1(1)
C(13)	2958(4)	12784(4)	328(3)	3.6(2)	C(13')	4829(4)	5431(3)	2609(3)	2.9(1)
C(14)	1996(4)	13136(4)	889(3)	3.1(1)	C(14')	5567(5)	5021(4)	1894(3)	3.3(2)
C(15)	1704(5)	12512(4)	1623(3)	3.5(2)	C(15')	6821(5)	5640(4)	1826(3)	3.0(1)
C(16)	2353(4)	11550(4)	1803(3)	2.9(1)	C(16')	7350(4)	6689(3)	2470(3)	2.2(1)
C(17)	6018(4)	9481(3)	2274(3)	1.7(1)	C(17')	5607(4)	9489(3)	3297(2)	1.5(1)
C(18)	7330(4)	10343(3)	2309(3)	2.0(1)	C(18')	5383(4)	10878(3)	3591(3)	1.7(1)
C(19)	7123(4)	11529(3)	2543(3)	2.0(1)	C(19')	6332(4)	11335(3)	4410(2)	1.8(1)
C(20)	5661(4)	11494(3)	2684(3)	1.7(1)	C(20')	7032(4)	10459(3)	4609(2)	1.6(1)

unsatisfactory. Found: C, 62.34; H, 3.98; Mn, 14.76; S, 3.71. $\text{C}_{35}\text{H}_{22}\text{Mn}_2\text{O}_6\text{S}$, calcd.: C, 61.76; H, 3.23; Mn, 16.18; S, 4.71%. The third zone yielded traces of VII ($\nu(\text{CO})$ in CH_2Cl_2 at 1945 and 2030 cm^{-1}). Found: C, 56.12; H, 3.04; Mn, 17.26; S, 9.18. $\text{C}_{30}\text{H}_{20}\text{O}_6\text{Mn}_2\text{S}_2$ calcd.: C, 55.38; H, 3.08; Mn, 16.92; S, 9.85%.

(c) *Of IIb*. The mixture of IIb (1.5 g, 4.87 mmol), cyclopentadiene (0.1 ml, 1.2 mmol), KOH (2 g) in water (2 ml)/benzene (2 ml) and 18-crown-6 (0.02 g, 0.1 mmol) was stirred vigorously for 7 h at room temperature, then treated as above and chromatographed on a Al_2O_3 column. V was eluted with hexane/benzene (5/1) and identified by ^1H NMR spectroscopy, as it was difficult to isolate V from IIb. The yield of the raw product is 0.8 g (53%). VIb was eluted with benzene and re-crystallized from hexane (0.1 g, 15%, m.p. 100°C (dec.), $\nu(\text{CO})$ in CH_2Cl_2 at 1945 and 2025 cm^{-1}). Found: C, 63.26; H, 3.34. $\text{C}_{35}\text{H}_{22}\text{Mn}_2\text{O}_7$ calcd.: C, 63.25; H, 3.31%.

Method B; interaction with Cp^- in KOH/ethanol solution

(a) *Ia*. The mixture of Ia (0.25 g, 0.8 mmol), cyclopentadiene (0.3 ml, 3.6 mmol), KOH (2.5 g) and ethanol (20 ml) was stirred for 3 h at room temperature, then poured into water and extracted with benzene. The layers were separated, the organic part was washed with water to neutral reaction and dried with MgSO_4 , then evaporated in vacuo to 1 ml and chromatographed on a silica gel column. III was eluted with hexane/benzene (5/1) and re-crystallized from hexane (0.13 g, 47%, m.p. 98–99°C). Ib (30%) was eluted with benzene.

TABLE 6

COORDINATES ($\times 10^4$, for Mn $\times 10^5$, for H $\times 10^3$) AND THERMAL FACTORS $B_{\text{iso}}^{\text{eq}}$ (for H, B_{iso} , \AA^2) IN THE STRUCTURE VIII

Atom	x	y	z	B
Mn	8611(4)	26503(6)	47732(4)	3.94(5)
O(1)	-530(2)	570(3)	3814(3)	7.1(4)
O(2)	773(2)	3961(3)	5966(3)	6.9(4)
O(3)	-510(2)	4494(4)	2875(3)	8.7(4)
C(1)	5(3)	1389(4)	4188(3)	5.0(4)
C(2)	799(3)	3456(4)	5485(3)	4.8(4)
C(3)	13(3)	3795(5)	3620(4)	5.5(5)
C(4)	1606(2)	1072(4)	4937(3)	3.5(3)
C(5)	2112(3)	1455(5)	5982(3)	4.4(4)
C(6)	2325(3)	2891(5)	6148(4)	5.3(4)
C(7)	1957(3)	3428(5)	5234(4)	5.1(5)
C(8)	1511(2)	2318(4)	4480(3)	4.2(4)
C(9)	1306(2)	-373(3)	4517(3)	3.3(3)
C(10)	635(2)	-719(4)	3469(3)	3.4(3)
C(11)	1767(2)	-1475(4)	5344(3)	3.4(3)
C(12)	1314(3)	-2086(4)	5426(3)	4.9(4)
C(13)	1737(3)	-3062(5)	6217(4)	5.4(5)
C(14)	2630(3)	-3455(5)	6933(3)	4.9(4)
C(15)	3085(3)	-2879(5)	6861(3)	5.3(4)
C(16)	2666(3)	-1880(5)	6080(3)	4.7(4)
C(17)	349(2)	-2132(4)	3036(3)	3.8(3)
C(20)	0	244(6)	1/4	3.7(5)
H(5)	227(2)	83(4)	647(3)	4(1)
H(6)	267(2)	336(4)	680(3)	5(1)
H(7)	197(2)	432(4)	507(3)	5(1)
H(8)	123(2)	243(4)	380(2)	3(1)
H(12)	62(3)	-189(4)	484(3)	6(1)
H(13)	140(2)	-349(4)	630(3)	6(1)
H(14)	291(2)	-400(4)	748(3)	3(1)
H(15)	367(3)	-309(4)	730(3)	6(1)
H(16)	300(2)	-151(4)	605(3)	4(1)
H(17)	56(2)	-291(3)	339(2)	4(1)
H(20)	34(2)	76(4)	246(3)	6(1)

(b) *Ib*. The mixture of *Ib* (0.42 g, 1.42 mmol), cyclopentadiene (0.4 ml, 4.8 mmol), KOH (2.5 g) and ethanol (20 ml) was stirred for 7 h at room temperature and treated as above, yielding *III* (0.3 g, 65%) and unreacted *Ib* (30%).

(c) *IIb*. The mixture of *IIb* (0.4 g, 1.99 mmol), cyclopentadiene (0.3 ml, 3.6 mmol), KOH (2.5 g) and ethanol (20 ml) was stirred at room temperature for 7 h, treated as above and chromatographed on an Al_2O_3 column. *V* was eluted with hexane/benzene (5/1) and re-crystallized from hexane (0.37 g, 80%, m.p. 138–139°C, $\nu(\text{CO})$ in CH_2Cl_2 at 1955 and 2035 cm^{-1}). Found: C, 67.38; H, 3.70; Mn, 15.55. $\text{C}_{40}\text{H}_{26}\text{Mn}_2\text{O}_6$ calcd.: C, 67.42; H, 3.65; Mn, 15.47%.

Method C; interphase-catalyzed reaction with $[\text{CpFe}(\text{CO})_2]^-$

(a) *Ia*. The mixture of *Ia* (0.3 g, 0.98 mmol), $[\text{CpFe}(\text{CO})_2]_2$ (0.15 g, 0.43 mmol), KOH (2 g) in water (2 ml) benzene (2 ml) solution and 18-crown-6 (0.02 g, 0.1 mmol) was vigorously stirred for 20 h at room temperature, then poured into water

TABLE 7
MASS SPECTRA (70 eV)

Compound	<i>m/z</i>	Ion	<i>m/z</i>	Ion	<i>m/z</i>	Ion
III	338	[P] ⁺	153	[P-Cp-Fe-C ₅ H ₄] ⁺	65	[Cp] ⁺
	273	[P-Cp] ⁺	121	[CpFe] ⁺	56	[Fe] ⁺
	217	[P-Cp-Fe] ⁺	77	[Ph] ⁺		
IV, V ^a	356	[P] ⁺	203	[C ₅ H ₄ Mn(CO) ₃] ⁺	77	[Ph] ⁺
	300	[P-2CO] ⁺	153	[C ₅ H ₄ CPh] ⁺	64	[C ₅ H ₄] ⁺
	272	[P-3CO] ⁺	131	[MnC ₅ H ₄ C] ⁺	55	[Mn] ⁺
	217	[P-3CO-Mn] ⁺	119	[C ₅ H ₄ Mn] ⁺		
	No peak	[P] ⁺	328	[(OC) ₂ MnC ₅ H ₄ C(C ₅ H ₄)Ph] ⁺	120	[CpMn] ⁺
	648	[P-S] ⁺	274	[C ₅ H ₄ MnCHC ₅ H ₅ Ph] ⁺	88	[MnSH] ⁺
VIa	565	[P-S-3CO+H] ⁺	240	[C ₅ H ₄ MnCSPh] ⁺	55	[Mn] ⁺
	480	[P-S-6CO] ⁺	210	[Mn(C ₅ H ₄ CH ₂ Ph)] ⁺		
	367	[P-S-6CO-2Mn-3H] ⁺	153	[C ₅ H ₄ CPh] ⁺		
	664	[P] ⁺	496	[P-6CO] ⁺	210	[C ₅ H ₄ MnCH ₂ Ph] ⁺
	648	[P-O] ⁺	480	[P-6CO-O] ⁺	153	[C ₅ H ₄ PhC] ⁺
	580	[P-3CO] ⁺	367	[P-6CO-O-2Mn-3H] ⁺	120	[CpMn] ⁺
	564	[P-3CO-O] ⁺	304	[P-6CO-O-2Mn-C ₅ H ₄ -2H] ⁺	55	[Mn] ⁺
VIII	No peak	[P] ⁺	370	[P-6CO-2Mn] ⁺	77	[Ph] ⁺
	564	[P-3CO] ⁺	240	[P-6CO-2Mn-2Cp] ⁺	64	[C ₅ H ₄] ⁺
	480	[P-6CO] ⁺	219	[C ₅ H ₄ C(Ph)C ₅ H ₆] ⁺	55	[Mn] ⁺
	425	[P-6CO-Mn] ⁺	152	[PhC≡CCH=C=C=CH ₂] ⁺		
	No peak	[P] ⁺	268	[P-2CO-C ₅ H ₆] ⁺	132	[MnPh] ⁺
IX	362	[P-CO] ⁺	240	[P-3CO-C ₅ H ₆] ⁺	87	[MnS] ⁺
	306	[P-3CO] ⁺	185	[P-3CO-C ₅ H ₆ -Mn] ⁺		
	296	[P-CO-C ₅ H ₆] ⁺	152	[PhC≡CCH=C=C=CH ₂] ⁺		

^a Complex V exhibit peaks of monomer IV only.

and extracted with hexane/benzene (5/1). The layers were separated, the organic part was washed with water to neutral reaction and dried with MgSO_4 , then evaporated in vacuo to 1 ml and chromatographed on a silica gel column. III was eluted with hexane/benzene (5/1) and re-crystallized from hexane (0.06 g, 18%). From the second zone 0.03 g (10%) of Ia was isolated. Then traces of bis[(ferrocenyl)(phenyl)methyl] disulphide were eluted; mass spectrum (m/z); $P^+ - S$ 582, $P^+ - S - \text{Cp}$ 517, $P^+ - S - \text{Cp} - \text{Fe}$ 461, $P^+ - (\text{Ia}) - \text{H}$ 306, etc. From the fourth zone $[\text{CpFe}(\text{CO})_2]_2$ (0.06 g, 40%) was eluted with hexane/benzene (1/1), from the fifth zone Ib (0.1 g, 35%) was eluted with benzene.

(b) *IIa*. A mixture of *IIa* (0.35 g, 1.1 mmol), $[\text{CpFe}(\text{CO})_2]_2$ (0.17 g, 0.48 mmol), KOH (2 g) in water(2 ml)/benzene(2 ml) and 18-crown-6 (0.02 g, 0.1 mmol) was stirred for 5 h and kept for a further 15 h at room temperature, then treated as above and chromatographed on an Al_2O_3 column. V (0.1 g, 25%) was eluted with hexane/benzene (5/1). Then VIII was eluted and re-crystallized from hexane (0.15 g, 43%; $\nu(\text{CO})$ in CH_2Cl_2 at 1950 and 2038 cm^{-1}) Found: C, 64.79; H, 3.26; Mn, 15.73. $\text{C}_{33}\text{H}_{22}\text{Mn}_2\text{O}_6$ calcd.: C, 64.81; H, 3.39; Mn, 16.07%.

Preparation of IX

0.15 g (0.5 mmol) of *IIB* in 2 ml (24.2 mmol) of cyclopentadiene was UV-irradiated (a PRK-4 lamp, 220 W) for 2 h and then 15 ml of benzene was added. The solution was filtered from the precipitate, the solvent was removed in vacuo and the residue chromatographed on a silica gel column. IX was eluted with hexane/benzene (5/1) and re-crystallized from hexane (0.1 g, 55%; m.p. 148–150°C; $\nu(\text{CO})$ in CH_2Cl_2 at 1945 and 2020 cm^{-1}).

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