(C_5H_5)Co-Induced Head-Head Coupling of Dimethylfulvene: Formation, Molecular Structure and Electrochemistry of (1,1,2,2-Tetramethyl-1,2-ethanediyl)bis(cobaltocene)☆

Hubert Wadepohl*[a], Claus-Wilhelm von der Lieth[b], Franz-Josef Paffen[a], and Hans Pritzkow[a]

Anorganisch-Chemisches Institut der Universität Heidelberg[a],
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Deutsches Krebsforschungszentrum, Zentrale Spektroskopie[b],
Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany

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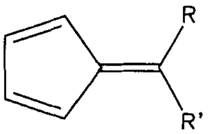
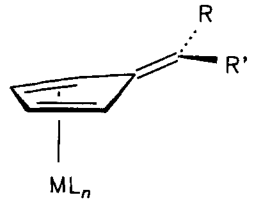
Head-head coupling of a dimethylfulvene ligand occures in the reaction of 6,6-dimethylpentafulvene (**1a**) with $[(C_5H_5)Co(C_2H_4)_2]$ (**7**) to give (1,1,2,2-tetramethyl-1,2-ethanediyl)bis(cobaltocene) (**8a**). In contrast, the mononuclear η^4-fulvene complexes **3b**, **c** are obtained from 6-ethyl-6-methyl- (**1b**) and 6,6-diethylfulvene (**1c**) and **7**. The crystal structures of **8a** and the corresponding bis(ferrocene) **9a** have been determined. The electrochemical behaviour of **8a** and **9a** shows $8a^+$, $8a^-$, and $9a^+$ to be localised mixed-valence species. Molecular mechanics calculations have been performed on the title complex and related derivatives.

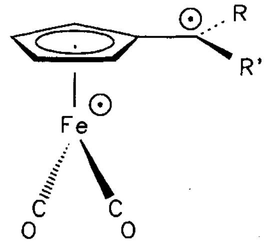
6,6-Diaryl derivatives of pentafulvenes **1** have been reported to react with 14-valence electron (VE) organometallic fragments to give mononuclear complexes with η^4-coordinated fulvene ligands. For example, **2**[1,2], **3**[3–5], **4**[4], and **5**[2] have been prepared and structurally characterised by X-ray crystallography. When fulvenes with small substituents on C-6 are treated with iron carbonyls, a variety of mono- and dinuclear complexes are formed[6,7]. A key step in these reactions was thought to be loss of carbon monoxide from **2** to give the hypothetical intermediate **6**[6]. The range of products formed (mainly by dimerisation of, or hydrogen abstraction by the fulvene ligands) has been taken as an indication of **6** to be a diradical.



1	R	R'
a	Me	Me
b	Me	Et
c	Et	Et
d	Ph	Ph



	ML$_n$
2	$Fe(CO)_3$
3	$Co(\eta-C_5H_5)$
4	$Rh(\eta^5-C_9H_7)$
5	Ni(1,5-cod)



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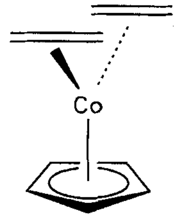

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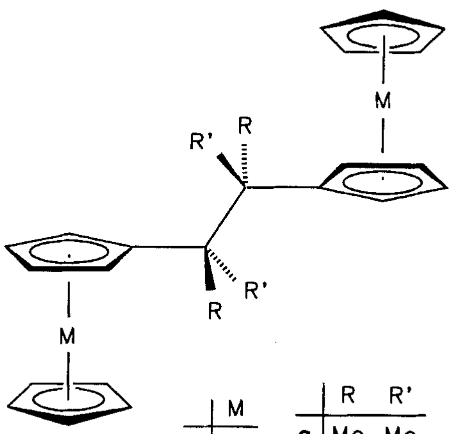


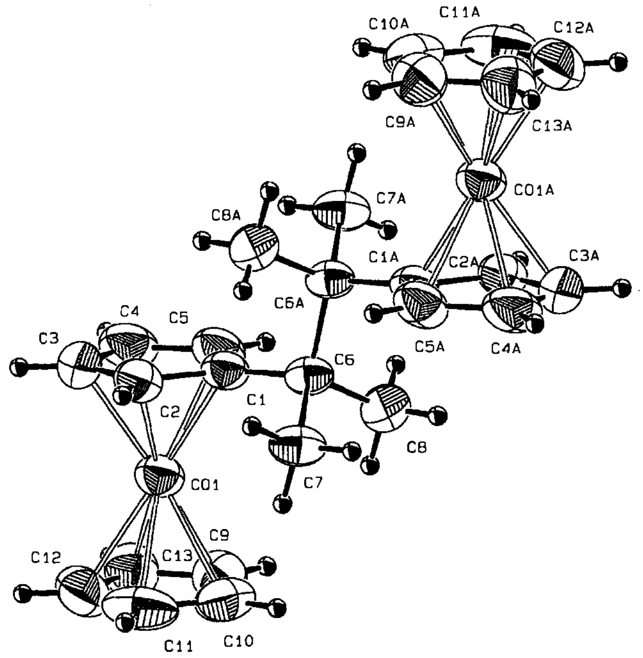
	M
8	Co
9	Fe

	R	R'
a	Me	Me
b	Me	Et
a	Et	Et

In contrast to the reaction of 6,6-diphenylfulvene (**1d**)[3,4] no η^4-fulvene complex could be isolated when 6,6-dimethylfulvene (**1a**) was treated with the Jonas reagent $[(\eta-C_5H_5)Co(C_2H_4)_2]$ (**7**) as a source of $(\eta-C_5H_5)$Co fragments. Instead, the title compound **8a** was obtained (10–20% yield after chromatography and recrystallisation). In marked contrast, from **7** and **1b** or **1c** the mononuclear η^4-fulvene complexes **3b** and **3c**, respectively, were obtained in high yield.

The single-crystal X-ray structure analysis of **8a** (Figure 1) shows that head-head coupling of two $[(\eta-C_5H_5)$Co(6,6-dimethylfulvene)] moieties has taken place. Due to steric congestion in the bis(cobaltocenyl)-substituted dimethylbutane, the central carbon-carbon bond C6–C6A is somewhat elongated[8]. An *anti* conformation is

Figure 1. Molecular structure of **8a**[29]; selected bond lengths [Å] and angles [°]: Co1−C1 2.135(4), Co1−C2...C5 2.092(5)...2.100(5), Co1−C9...C10 2.094(5)...2.101(5), C1−C6 1.528(5), C6−C7 1.541(5), C6−C8 1.534(5), C6−C6A 1.600(7); C1−C6−C6A 109.2(3), C1−C6−C7 109.7(4), C1−C6−C8 109.4(3), C7−C6−C8 107.5(3); the corresponding parameters of **9a** are: Fe1−C1 2.073(2) Fe1−C2...C5 2.034(2)...2.045(2), Co1−C9...C13 2.034(2)...2.045(3), C1−C6 1.525(3), C6−C7 1.535(3), C6−C8 1.536(3), C6−C6A 1.599(3); C1−C6−C6A 108.9(2), C1−C6−C7 109.9(2), C1−C6−C8 109.3(2), C7−C6−C8 107.2(2)



attained around this bond. The planar C_5H_4R and C_5H_5 rings are slightly non-parallel [angle between the normals 1.3(3)°].

Complex **8a** is paramagnetic. The ^{1}H-NMR resonances of the ring protons are broad and strongly shifted to high field. There is little influence of the molecular paramagnetism on the resonances of the methyl protons. This is consistent with observations on substituted mononuclear cobaltocene derivatives[9].

With aqueous hydrochloric acid in air, **8a** is oxidised quantitatively to the diamagnetic bright yellow dication **8a**$^{2+}$, which has been isolated as the chloride [**8a**]Cl_2 and the hexafluorophosphate [**8a**]$[PF_6]_2$. The cyclic voltammogram of **8a** (Figure 2, Table 1) shows two reversible double waves, which correspond to two successive one-electron oxidations and reductions, respectively. The small separation between the two anodic (ΔE^0 = 160 mV) and the two cathodic waves (ΔE^0 = 130 mV) is characteristic[10] of the lack of a significant electronic interaction between the two metal centres. Hence, both the mixed valence **8a**$^-$ and **8a**$^+$ belong to the localised valence class I or class II according to Robin and Day[11].

Figure 2. Cyclic voltammograms of **9a** (top, in CH_2Cl_2) and **8a** (bottom, in 1,2-dimethoxyethane); supporting electrolyte Bu_4NPF_6; scan rate 100 mV/s

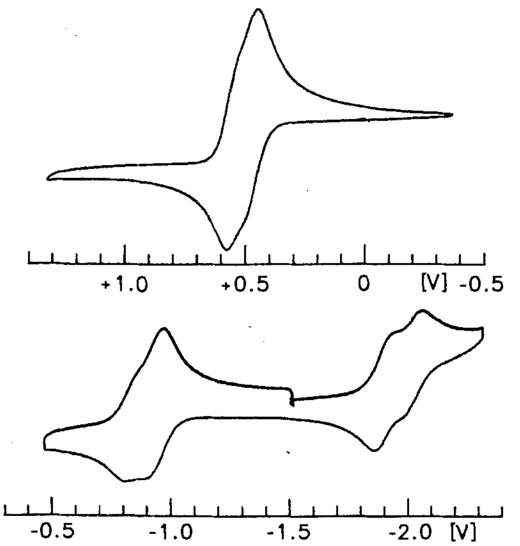


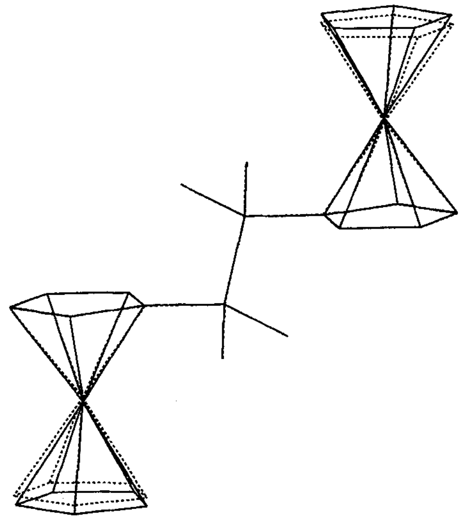
Table 1. Redox potentials for complexes **8a** and **9a** [E^0 in V vs. SCE (ΔE_p in mV)]; supporting electrolyte Bu_4NPF_6

	-2/-1	-1/0	0/+1	+1/+2
8a[a]	-2.08 (144)	-1.95 (128)	-0.92 (88)	-0.76 (82)
9a[b]			0.46 (40)	0.54 (40)

[a] In 1,2-dimethoxyethane. – [b] In CH_2Cl_2.

A large number of dinuclear complexes have been prepared in which two ferrocenyl moieties are connected to each other by an organic "spacer"[12]. The interaction between the redox active centres in such molecules has been studied intensively[12] Therefore, it has been of interest to compare the structure and redox properties of **8a** with those of the diiron analogue **9a**. Although **9a** is a known compound[13], its crystal structure and redox behaviour have not been previously reported[14]. We therefore have prepared **9a** by published methods[13] and have determined its crystal and molecular structure. Crystals of **8a** and **9a** are isomorphous, and the geometries of both molecules are very similar. There are only minor differences within the metallocenyl units, mainly affecting metal carbon bonds (Figure 3). As expected, these are longer in the cobaltocenyl groups of **8a** than in the ferrocenyl groups of **9a**.

Figure 3. Superposition of the molecules of **8a** (solid lines) and **9a** (dashed lines)



Compound **9a** has been found to give two barely resolved anodic waves in the cyclic voltammogram with a peak separation of 80 mV (Figure 2, Table 1). (1,2-Ethanediyl)bis(ferrocene), another bis(ferrocene) compound with a saturated dicarbon bridge between the two C_5H_4 rings, is oxidised at 0.37 V[15]. The two one-electron steps of this oxidation could just be resolved into two waves about 40 mV apart by using differential pulse polarography[15]. Clearly, in **8a**, **9a** and (1,2-ethanediyl)bis(ferrocene) the interaction between the two redox active centres is only very small.

Compounds **8a** and **9a** are fairly strained hexasubstituted ethane derivatives. Such compounds have attracted organic chemists for a long time, and many derivatives have been synthesised[16]. In 2,3-diorganyl-2,3-dimethylbutanes the lengths of the central carbon carbon bond range from 1.58 to 1.64 Å[16]. It has been stated that force-field methods ("molecular mechanics") are well suited to determine the structural parameters and preferred conformations of such molecules[16a]. We wanted to test whether the stability of **3b** and **3c** with respect to dimerisation was due to excess steric stress, which would be imposed on the central carbon carbon bond in the dimers.

Therefore, we have conducted molecular mechanics calculations on **8a**–**c** using Allinger's MM2 force-field[17] with later additions[16b]. Since this force field is not parameterised for metal π complexes[18], the internal geometry of the metallocenyl units has been restrained by assigning large force constants to the CC, MC distances, CMC angles, and HCCC torsion angles. This approach treats the metallocenyl groups essentially as large rigid substituents. For comparison, the calculations on **8a** have been performed with two different geometries for the cobaltocenyl substituents (Table 2). In all cases, conformational space has been searched by molecular dynamics simulations.

Table 2. Selected calculated and observed structural parameters (distances in Å, angles in °) for **8a**–**c**

	8a[a]	**8a**[b]	**8a**[c]	**8a**[d]	**8b**[c]	**8c**[c]
C1-C6	1.528	1.521	1.517	1.512	1.525	1.536
C6-C6A	1.600	1.598	1.591	1.579	1.606	1.701
C6-C7	1.541	1.550	1.549	1.550	1.550	1.558, 1.575
C6-C8	1.534	1.550	1.549	1.550	1.563[e]	1.556, 1.564
C1-C6-C6A-C1A	180	180.0	179.3	179.3	171.4	162.4
C2-C1-C6-C6A	3.2	0.6	1.6	0.7	5.0	1.0, 15.5
Co1-C1-C6	128.7	123.0	122.0	127.7	122.0	124, 125
C1-C6-C6A	109.2	107.8	108.0	109.6	107.2	107

[a] Experimental values from crystal structure. – [b] Internal geometry of the cobaltocenyl groups restricted to d_{CC} = 1.42 Å, d_{CoC} = 2.09 Å, C_5H_5 and C_5H_4R rings parallel and eclipsed. – [c] Internal geometry of the cobaltocenyl groups taken from the crystal structure of **8a**. – [d] As [c], but angle Co1–C1–C6 restrained to 128.7° [using a force constant of 125 kcal · mol^{-1} · (°)$^{-2}$]. – [e] C–C_{ethyl}.

In the minimum-energy structures the central carbon carbon (C6–C6A) bond lengths are 1.598 and 1.591 Å for **8a**, close to the one found in the crystal structure (Table 2). As can be seen from Table 2, there are problems with the bond C1–C6, which joins one of the "aromatic" carbon atoms of the cobaltocenyl group to the organic part of the molecules. This holds true for both the bond length (calculated too short) and the bending out of the plane of the cyclopentadienyl ring (calculated to small). Also, the carbon-carbon distances to the methyl groups have been calculated to be somewhat longer (1.550 Å) than the experimental values (mean 1.538 Å). Going from **8a** to the hypothetical dimerisation product of **3b**, (1,2-diethyl-1,2-dimethyl-1,2-ethanediyl)bis(cobaltocene) (**8b**), and of **3c**, (1,1,2,2-tetraethyl-1,2-ethanediyl)bis(cobaltocene) (**8c**), the steric stress increases considerably. This is illustrated by a lengthening of the C6–C6A and C6–C_{ethyl} bonds (Table 2).

The question remains how **8a** is formed from **1a** and **7**. It has been known for a long time that certain fulvenes (e.g. **1a**) reductively dimerise at C-6 when treated with very electropositive metals[19]. This reaction has been utilised extensively for the synthesis of *ansa*-metallocenes[20]. In the present case, the complex **3a** with a neutral η^4-fulvene ligand is a likely intermediate. During the dimerisation, two even-electron metal centres (in **3a**, formally Co^I) are transformed into odd-electron species (formally Co^{II} in **8a**), with concurrent formal reduction of the bridging ligand. In the similar reaction of $[(Me_3P)_2Fe(\eta\text{-}C_6H_6)]$ with **1a** or 6-methyl-6-phenylfulvene to give ethano-bridged *ansa*-ferrocenes[21], the two electrons which are formally required for the reduction of the fulvenes are supplied by the same metal centre.

Several routes are feasible for the dimerisation of **3a**. First, **3a** could be a diradical which undergoes a Wurtz-type coupling at the exocyclic fulvene carbon C-6. This is unlikely in view of the diamagnetism of **3b** and **3c**. Another pathway could be $\eta^5 \rightarrow \eta^3$ C_5H_5 ring slippage in **3a** to give a 16-VE diradical species $[(\eta^3\text{-}C_5H_5)Co(1-5\text{-}\eta\text{-}6,6\text{-dimethylfulvene})]$ (**3a'**), which then again could couple at C-6. So far, no evidence has been found for cyclopentadienyl or indenyl ring slippage in any stable fulvene complex with a $(C_5H_5)M$ or $(C_9H_7)M$ fragment (M = Co, Rh). As a third possibility, frontier-orbital-controlled intermolecular coupling of **3a** could take place[22], similar to the dimerisation of singlet methylene[23].

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Experimental

All operations were carried out under purified nitrogen (BASF R3-11 catalyst) by using Schlenk techniques. Solvents were dried by conventional methods. The complexes $[(C_5H_5)Co(C_2H_4)_2]$ (**7**)[24], 2,3-diferrocenyl-2,3-dimethylbutane [= (1,1,2,2-tetramethyl-1,2-ethanediyl)bis(ferrocene)] (**9a**)[13] and the fulvenes 6,6-R,R'-C_6H_4 (**1a**, R = R' = Me[25]; **1b**, R = Me, R' = Et[26]; **1c**, R = R' = Et[26]) were prepared as described in the literature. – NMR: Bruker AC 200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C). – MS: Finnigan MAT 8230. – Electrochemistry: EG & G PARC Model 173 potentiostat and Model 175 Universal Programmer; working electrode: glassy carbon. – Elemental analyses: Mikroanalytisches Labor Beller, Göttingen.

8a: A solution of 530 mg (5.0 mmol) of 6,6-dimethylfulvene (**1a**) in 20 ml of petroleum ether was added dropwise to a petroleum ether (40 ml) solution of 900 mg (5.0 mmol) of **7** at –40°C. The black solution was slowly warmed to room temp., deposited on a short (3 · 2 cm) column of deactivated alumina (5% H_2O) and washed with petroleum ether. Pure **8a** was eluted from the column with toluene. Single crystals were obtained by recrystallisation from toluene at –25°C (250 mg, 0.54 mmol, 11%), m.p. 177°C. – ^1H NMR (CD_2Cl_2): δ = 2.23 (br. s, 12H, CH_3), –42.5 (br. s, 4H, CH), –51.0 (br. s, 10H, C_5H_5), –57.5 (br. s, 4H, CH). – EI MS (70 eV), *m/z* (%): 460 (7) $[M]^+$, 230 (100) $[M^+/2, M^{2+}]$. – $C_{26}H_{30}Co_2$ (460.4): calcd. C 67.83, H 6.57; found C 67.88, H 6.56.

3b *and* **3c**: A solution of the fulvene (5–6 mmol) in 20 ml of petroleum ether was added dropwise to an equimolar amount of **7** in petroleum ether (40–50 ml) at –40°C. The black solution was slowly warmed to room temp. and filtered. After removal of solvent from the filtrate in vacuo the products **3b** and **3c**, respectively, were obtained as very air-sensitive brown oils (yields 80–90%). – **3b**: ^1H NMR (C_6D_6): δ = 5.12 (m, 2H, CH), 4.48 (s, 5H, C_5H_5), 3.71

(m, 2H, CH), 1.51 (s, 3H, CH$_3$), 1.06 (t, 3H, CH$_3$), 0.86 (q, 2H, CH$_2$). – **3c**: ^{1}H NMR (C$_6$D$_6$): δ = 5.13 (br, 2H, CH), 4.47 (s, 5H, C$_5$H$_5$), 3.71 (br, 2H, CH), 1.95 (q, 4H, CH$_2$), 1.09 (t, 6H, CH$_3$). – ^{13}C NMR (C$_6$D$_6$): δ = 106.3, 79.4, 77.0, 52.8, 25.9, 13.4. – Due to the extreme sensitivity of **3b** and **3c**, reproducible C,H analyses could not be obtained.

[**8a**]$^{2+}$2Cl$^-$ *and* [**8a**]$^{2+}$2[PF$_6$]$^-$: 10 ml of aqueous hydrochloric acid was added to 220 mg (0.48 mmol) of **8a**. Air was passed through the mixture for 30 min. The salt **8a**Cl$_2$ was obtained in quantitative yield after removal of all volatile products in vacuo. – ^{1}H NMR (D$_2$O): δ = 5.46 (s, 10H, C$_5$H$_5$), 5.38 (m, 4H, CH), 5.15 (m, 4H, CH), 1.05 (s, 12H, CH$_3$). – ^{13}C NMR (D$_2$O): δ = 117.9 (C), 83.1 (CH), 84.8 (C$_5$H$_5$), 81.2 (CH), 40.2 [*C*(CH$_3$)$_2$], 23.9 (CH$_3$). – Compound **8a**(PF$_6$)$_2$ was obtained by adding an aqueous solution of NH$_4$PF$_6$ to the reaction mixture after it had turned yellow. An immediately formed yellow precipitate was collected, washed twice with water and recrystallised from acetone.

Crystal-Structure Determination of **8a** *and* **9a**[27]: Complex **8a**: Monoclinic, a = 12.031(16), b = 7.612(8), c = 12.803(17) Å; β = 115.07(6)°; V = 1062.04 Å^3; space group $P2_1/c$; Z = 2; μ(Mo-K_α) = 15.7 cm^{-1}; crystal size 0.1 × 0.4 × 0.7 mm; $2\Theta_{\text{min.}}$ = 3°; $2\Theta_{\text{max.}}$ = 60°; *hkl* range ±16, 10, 18; reflexions measured: 3156; unique: 2948; empirical absorption correction ($T_{\text{min.}}$ = 0.36, $T_{\text{max.}}$ = 0.65); hydrogen atoms were inserted at calculated positions, methyl groups were refined as rigid groups; R = 0.044 [1289 reflexions with $F_o \geqslant 4\sigma(F_o)$]; $wR2$ = 0.118 (on F^2, all reflexions), $w = [\sigma^2(F_o^2) + (0.0403 \cdot P)^2]^{-1}$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$. – **9a**: Monoclinic; a = 11.849(6), b = 7.517(4), c = 12.952(7) Å; β = 115.81(2)°; V = 1038.54 Å^3; space group $P2_1/c$; Z = 2; μ(Mo-K_α) = 14.1 cm^{-1}; crystal size 0.2 × 0.5 × 0.6 mm; $2\Theta_{\text{min.}}$ = 3°; $2\Theta_{\text{max.}}$ = 60°; *hkl* range ±16, 10, 18; reflexions measured: 3251; unique: 3031; empirical absorption correction ($T_{\text{min.}}$ = 0.56, $T_{\text{max.}}$ = 0.80); hydrogen atoms were located from difference Fourier maps and refined with isotropic temperature factors; R = 0.034 [2380 reflexions with $F_o \geqslant 4\sigma(F_o)$]; $wR2$ = 0.094 (on F^2, all reflexions), $w = [\sigma^2(F_o^2) + (0.0468 \cdot P)^2 + 0.20 \cdot P]^{-1}$, $P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$. – All intensity data were measured at ambient temperature on a STOE/Siemens four-circle diffractometer with Mo-K_α radiation (graphite monochromator) in the ω scan mode. The structures were solved by the heavy-atom method and refined by full-matrix least squares based on F^2 (SHELXS-86[28a] and SHELXL-93[28b]).

☆ Dedicated to Professor *Peter Paetzold* on the occasion of his 60th birthday.

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[368/94]