

The X-ray structure of $\text{Fe}(\text{fulvene})_2$: The missing link in the direct synthesis of ansa- and Cp^i -metallocenes ($\text{Cp}^i = \text{C}_5\text{H}_4\text{CHMe}_2$)

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Abstract

The compound (ethene)₂(toluene)iron (**1**) is prepared by cocondensation of iron and toluene and subsequent treatment with ethene. Reaction of (**1**) with 6,6-dimethylfulvene leads to the known products ansa-ferrocene and 1,1'-bis(isopropyl)ferrocene. Reaction of (**1**) with 6,6-diphenylfulvene (**2**) gives 1,1'-bis(benzhydryl)ferrocene (**3**). The intermediate in the formation of (**3**), bis(diphenylfulvene)iron (**4**) was isolated. (**4**) was characterized by MS and a X-ray structure determination and its structure compared with the structure of the free ligand (**2**). The structure of (**4**) was also determined by DFT-ab-initio calculations. © 1997 Elsevier Science S.A.

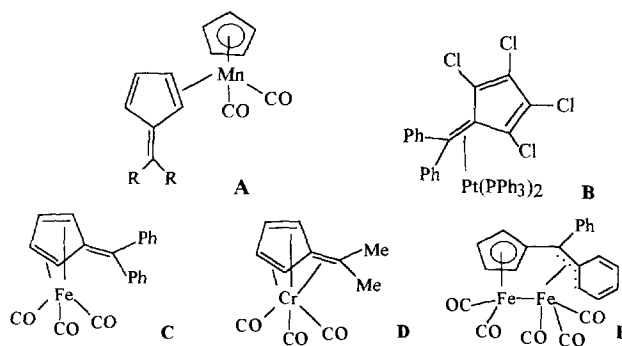
Keywords: Cocondensation; Fulvenes; Iron; Bis(fulvene)iron; Reaction mechanism; Ab-initio calculation

1. Introduction

Fulvenes with their cross-conjugated π -systems build a class of very interesting organic ligands that form a great number of organometallic compounds if coordinated towards a metal center.

Because of the number of double bonds in the fulvenes, there is a great variety in binding modes in these organometallic compounds. It can be coordinated in η^2 , η^4 , η^6 or in the case of an aromatic substituent on the exocyclic double bond, even η^8 . The following compounds give examples for the different bonding modes. Compound **A** shows η^2 -coordination on an endocyclic double bond [1]. Compound **B** is η^2 -coordinated on the exocyclic double bond [2]. η^4 -bonding appears in compound **C** [3]. Compound **D** has a η^6 -coordination [4]. In compound **E** the exocyclic phenyl substituent of the fulvene is part of the coordinating π -system to give η^8 -coordination [5].

Compound **A** and **B** can be regarded as ene-complexes of the metal centers, whereas compounds **C** and **D** are diene- or triene-complexes. Compounds **C** and **D** will be used later to discuss the structure of $\text{Fe}(\text{fulvene})_2$. Compound **E** shows that fulvenes can also coordinate to dinuclear complexes. (Scheme 1)



Scheme 1.

Although there are many compounds containing one or more fulvene ligands, very little about compounds containing only fulvene as ligands is known. E.O. Fischer et al. described the synthesis of the cationic bis(6,6-diphenylfulvene)-complexes of Co (**F**), Rh and Ir [6,7]. These compounds were isolated as PF_6^- -salts and characterized by NMR- and IR spectroscopy. (Fig. 1)

In a later work, Behrens et al. tried to reproduce these results to get material for structural investigations but were not successful [8]. The only product they were able to isolate was the cobaltocenium salt **G** which is formed by hydrogen abstraction from the solvent.

This hydrogen abstraction appears also in a proposed reaction mechanism that Tan et al. made for the coon-

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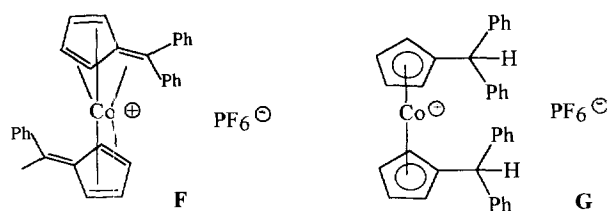


Fig. 1.

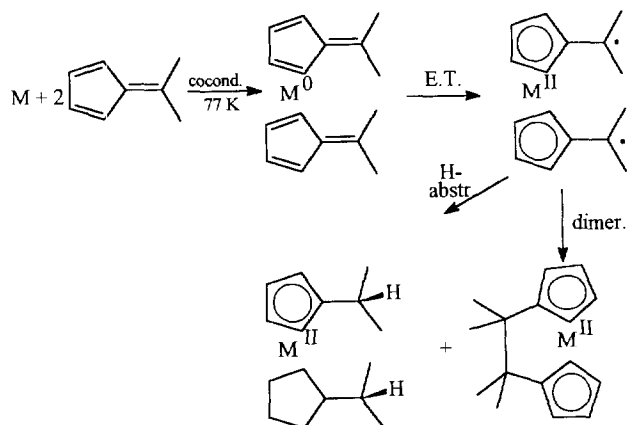
densation of metal atoms with fulvenes [9]. They reacted iron atoms with 6,6-dimethylfulvene and isolated a mixture of the (tetramethylethano)-bridged ansa-ferrocene and the 1,1'-bis(isopropyl)ferrocene. Scheme 2 shows the proposed mechanism for this reaction.

Our paper presents evidence that the postulated intermediate $M^0(\text{fulvene})_2$ has been isolated and characterized.

2. Results and discussion

In order to avoid problems of the direct metal-fulvene cocondensation, as there are difficulties in separating products from reactants and oligomerisation of the ligand 6,6-dimethylfulvene (in mass spectra we detected dimers, trimers, tetramers and pentamers of the fulvene) we were looking for another way of reacting iron atoms with fulvenes. We used the compound bis(η^2 -ethene) $_2(\eta^6$ -toluene)iron (1) because it is a highly-reactive solvated form of iron atoms which is easy to prepare and to handle. This compound is also a starting material for many iron complexes [10,11]. (1) is prepared by cocondensation of iron atoms with toluene at 77 K and warming to 196 K under an atmosphere of ethene (Fig. 2)

The used cocondensation apparatus is described elsewhere [12]. After being filtered through alumina, the solution can be stored at 196 K and its content of iron determined by simply titrating an oxidized part of the



Scheme 2.

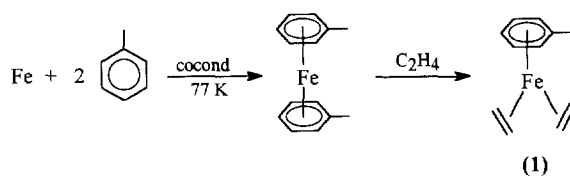


Fig. 2.

solution.

Reaction of (1) with two equivalents of 6,6-dimethylfulvene yields the expected mixture of ansa-ferrocene and 1,1'-bis(isopropyl)ferrocene (see Scheme 2 above).

Reaction of (1) with two equivalents of 6,6-diphenylfulvene (2) leads to the formation of 1,1'-bis[(diphenyl)methyl]ferrocene (3).

Formation of the corresponding ansa-ferrocene compound is not possible in this case because of the steric hindrance of the phenyl substituents on the exo-methylene-group. Force field calculations showed that the hypothetical bridging C–C bond between the cyclopentadienyl rings would be about 190 pm in length [13]. (Fig. 3)

During this reaction, that was carried out by adding a solution of (2) to the solution of (1) both in toluene at 196 K and allowing to warm up slowly to ambient temperature, dark red crystals grew on the wall of the used Schlenk-tube just above the solvent level. It was very little material isolated, however one of the crystals was suitable for an X-ray crystal structure determination. The rest of the material was used to measure high-resolution mass spectra.

This structure determination showed the isolated compound to be the postulated bis(fulvene)iron intermediate (4) (see Scheme 2 above).

It is also the first reported structurally characterized transition metal bis-fulvene compound and the first neutral transition metal compound containing fulvene ligands only.

The isolation of this compound is a proof for the mechanism proposed by McGlinchey et al. [9] that the initial step in the reaction of metal atoms with fulvenes to form ansa- or bis-substituted ferrocenes is the formation of a complex of the metal and two molecules of fulvene in which the metal center is still in oxidation state 0. The following step is the electron transfer from metal center to the 5-membered rings to give the metallocene compound with the metal in oxidation state +II and two cyclopentadienyl rings that can now either form the ansa-bridge or undergo hydrogen abstraction (see Scheme 2 above).

In further experiments we were not able to obtain (4) from solution so one might say that (4) reacts to (3) immediately if dissolved in toluene. An attempt to follow the formation of (4) by low temperature NMR or ESR spectroscopy was prevented by the fact that solu-

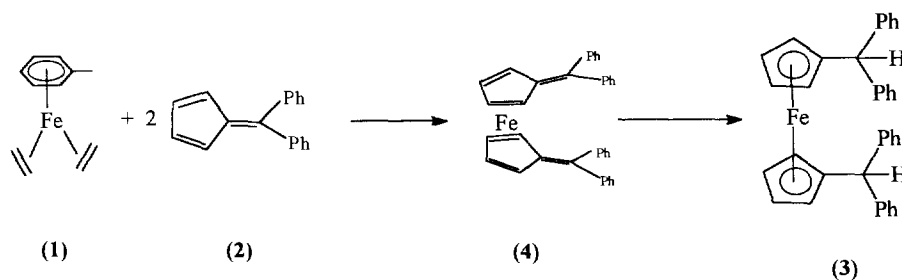


Fig. 3.

tions of (1) always contain certain amounts of elementary iron due to partly decomposition, giving way to extreme line broadening in NMR.

3. Structural investigations

The X-ray structures of the iron-bis-fulvene compound as well as the structure of the free ligand 6,6-diphenylfulvene were determined in order to compare bond lengths and angles.

In the iron-fulvene compound the fulvene ligands coordinate through their 5-membered rings towards the iron center. The exo-methylene groups are located eclipsically, so that both rings are not coplanar any more because of the steric hindrance of the large phenyl-substituents on the exo-methylene groups. The metal-ring perpendiculars form an angle of 150° .

Uncomplexed fulvenes have a planar system of the six carbon atoms that form the skeleton. There is, as it is a diene-like structure, a clear alteration of single and double bonds in the ring [14,15].

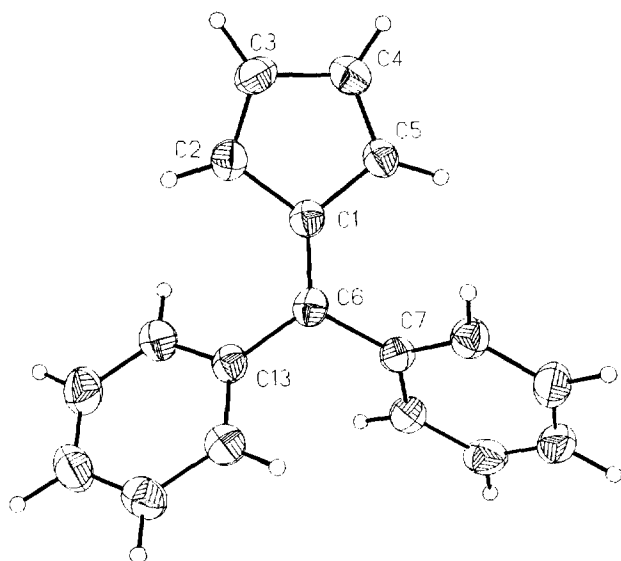
The structure of 6,6-diphenylfulvene follows these structural rules. (2) crystallizes with $Z = 4$ in $P\bar{1}$, it

forms two independent molecules in the unit cell that differ by the torsion angle of the phenyl rings towards the five membered ring by 5° . (Scheme 3, Table 1, Scheme 4, Table 2)

The fulvene rings in the bis-fulvene-iron compound show some distortion from the diene-like structure. The bond lengths C(2)–C(3), C(3)–C(4) and C(4)–C(5) are of about the same, while bonds C(1)–C(5) and C(1)–C(2) being markedly longer. The exocyclic bond C(1)–C(6) has a value of 140.8 pm, that is in between a single and a double bond. This shows, that there is a certain amount of coordination of the exocyclic double bond towards the iron center. The length of the exocyclic bond of tricarbonyl-fulvene-iron **C** is 135.7 pm, showing that there is certainly no influence of the iron center to the double bond. In compound **D**, tricarbonyl-fulvene-chromium, the exocyclic bond is longer than in the free ligand, that shows that there is coordination to the metal center. This becomes also clear by the fact that the exocyclic bond is bent out of the plane of the five-membered ring towards the chromium center by 31° . This angle also leads to a short distance between metal center and exocyclic carbon that is about 253 pm. In (4) the exocyclic C(6) stays in the plane of the fulvene ring, so that the compound can be regarded as a “real” fulvene complex and not some kind of ferrocene derivative. Distances from iron center to C(6) and C(24) are about 329 pm and are noncoordinative.

Another way of describing the bonding in (4) is the formation of a biradicalic compound in which iron is in oxidation state +II coordinated to two substituted cyclopentadienyl rings that are formed by the reduction of the fulvene. The exocyclic carbons bear single electrons, as shown in Fig. 4.

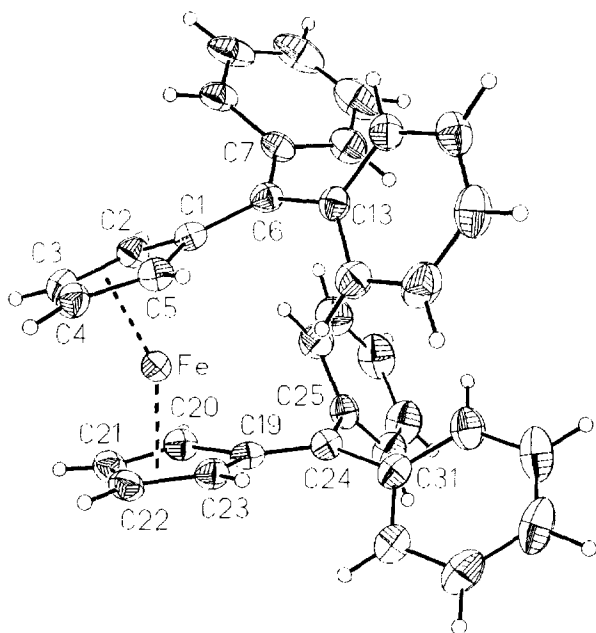
This view of the bonding is enhanced by the fact that ligands present in this formulation of the structure,



Scheme 3. ORTEP plot of 6,6-diphenylfulvene (2).

Table 1
Selected bond lengths of (2) [Å]

C(1)–C(6)	1.356(3)	C(1)–C(5)	1.466(3)
C(1)–C(2)	1.471(3)	C(2)–C(3)	1.337(3)
C(3)–C(4)	1.454(3)	C(4)–C(5)	1.341(3)
C(6)–C(13)	1.483(3)	C(6)–C(7)	1.492(3)



Scheme 4. ORTEP plot of bis-diphenylfulvene-iron (4).

Table 2
Selected bond lengths of (4) [Å]

Fe–C(4)	2.036(3)	Fe–C(21)	2.035(2)
Fe–C(22)	2.036(3)	Fe–C(3)	2.046(3)
Fe–C(5)	2.056(3)	Fe–C(20)	2.063(3)
Fe–C(23)	2.066(2)	Fe–C(2)	2.075(2)
Fe–C(1)	2.201(2)	Fe–C(19)	2.209(2)
C(1)–C(6)	1.408(3)	C(1)–C(2)	1.445(3)
C(1)–C(5)	1.448(3)	C(2)–C(3)	1.406(3)
C(3)–C(4)	1.410(3)	C(4)–C(5)	1.408(3)
C(6)–C(13)	1.465(3)	C(6)–C(7)	1.472(3)
C(7)–C(8)	1.396(3)	C(7)–C(12)	1.396(4)
C(8)–C(9)	1.386(4)	C(9)–C(10)	1.375(5)
C(10)–C(11)	1.375(5)	C(11)–C(12)	1.389(4)
C(13)–C(14)	1.397(3)	C(13)–C(18)	1.404(3)
C(14)–C(15)	1.378(4)	C(15)–C(16)	1.380(4)
C(16)–C(17)	1.383(4)	C(17)–C(18)	1.377(3)
C(19)–C(24)	1.398(3)	C(19)–C(23)	1.451(3)
C(19)–C(20)	1.452(3)	C(20)–C(21)	1.408(4)
C(21)–C(22)	1.417(3)	C(22)–C(23)	1.407(3)
C(24)–C(31)	1.469(3)	C(24)–C(25)	1.482(3)

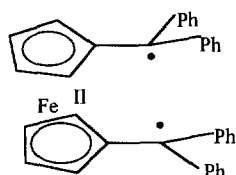


Fig. 4.

Table 3
Calculated and experimental bond lengths of (4) [pm]

Bond	Exptl.	Calc.	Bond	Exptl.	Calc.
Fe–C1	220.1	225.1	C1–C2	144.5	147.2
Fe–C2	207.5	206.6	C2–C3	140.6	143.0
Fe–C3	204.6	204.7	C3–C4	141.0	144.0
Fe–C4	203.6	204.7	C4–C5	140.8	143.0
Fe–C5	205.6	206.6	C5–C1	144.8	147.2
			C1–C6	140.8	137.9

cyclopentadienyldiphenylmethyl radicals, are closely related to the trityl radical which is known to be stable in THF solution at room temperature [16].

The presence of two radical ligands could also explain the staggered position of the bulky substituents of the cp-rings; there could be a certain amount of interaction of the singly occupied orbitals on the exo-carbon atoms the distance between is 434 pm. Proof for this

Table 4
Crystal data and data collection parameters

Compound	(2)	(4)
Chem. formula	C ₁₈ H ₁₄	C ₃₆ H ₂₈ Fe
Mol. mass	230.29	516.43
Cryst size [mm]	0.2 × 0.4 × 0.4	0.1 × 0.4 × 0.8
Cryst system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
<i>a</i> , [Å]	10.0050(10)	10.456(6)
<i>b</i> , [Å]	10.0440(10)	11.054(6)
<i>c</i> , [Å]	14.291(2)	13.557(10)
α , [°]	90.630(10)	82.57(3)
β , [°]	99.810(10)	67.64(3)
γ , [°]	113.260(10)	63.45(2)
<i>V</i> , [Å ³]	1295.2(3)	1294.8(14)
<i>Z</i>	4	2
ρ (calc), [Mg/m ³]	1.181	1.325
μ [mm ⁻¹]	0.067	0.606
<i>F</i> (000)	488	540
2 θ max[°]	45.00	50.06
<i>T</i> , [K]	210	210
Refl. collected	3382	6449
Refl. unique	3382	4567
Refl. observed (4 σ)	2455	3571
<i>R</i> (int.)	0.0000	0.0266
No. variables	438	418
Weighting scheme ^a <i>x/y</i>	0.0472/0.0491	0.0413/0.5229
GOOF	1.020	0.997
<i>R</i> 1(4 σ)	0.0351	0.0325
w <i>R</i> 2 (all data)	0.0805	0.0790
Larg. res. peak [e/Å ³]	0.137	0.291

$$^a w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP; P = (F_o^2 + 2F_c^2)/3.$$

type of bonding would be possible by ESR and magnetic measurements, but these methods would require larger amounts of (4), so there is still work to be done.

In (4) it is not easy to determine the hapticity of the fulvene ligands. Counting electrons, η^4 -coordination of the cyclic double bonds of the fulvenes leads to a 16 VE-system, whereas η^6 -coordination leads to a 20 VE compound. Regarding the bond lengths, a "half-coordinating" exocyclic double bond may be the best explanation. Metal carbon distances in the ring are about 204 to 207 pm to C(2), C(3), C(4) and C(5), Fe–C(1) distance is 220 pm. This is markedly shorter than the certainly noncoordinating M–C(1) distance in (Fv)Fe(CO)₃ that is about 250 pm [3].

In order to decide between these both possible descriptions of (4) we performed an ab-initio-calculation of the molecule bis(fulvene)iron with the phenyl groups substituted by hydrogen. We used the RI-DFT module [17] of the program package TURBOMOLE [18] and auxiliary SV(P)-basis sets.

The calculated geometry of (4) shows that the description as a bis-fulvene complex is the right one. The calculated distances are very close to those experimentally determined in the X-ray structure analysis.

The SEN (shared electron number) [19,20] as a measure for covalency in the exocyclic bond C1–C6 has a value of 1.91 showing it to be a double bond clearly.

Selected bond lengths are listed in Table 3 and compared to the experimental values.(Table 4)

4. Experimental section

All reactions were carried out under Schlenk-conditions using dried solvents in an atmosphere of dried nitrogen or argon. NMR spectra were recorded in C₆D₆ using a Bruker AC-SC 250 instrument.

Mass spectra were obtained on an Finnigan Mat MS 8230 instrument (EI, 70 eV).

Separation of products was carried out on dried neutral alumina (Fluka) deactivated with 4% H₂O. Diphenylfulvene was purchased from Aldrich. Dimethylfulvene was prepared according to literature methods [21]

4.1. Bis-ethylene toluene iron (1)

5 g Iron atoms were cocondensed with 80 ml of toluene at 77 K and warmed to 196 K under an atmosphere of ethylene. Iron atoms were generated in a resistively heated crucible at about 1200°C. The solution was collected with the internal drain, filtered through neutral alumina and stored at 196 K.

4.2. Reaction of (1) with 6,6-dimethylfulvene

A solution of 2 equivalents fulvene in toluene was added dropwise to the solution of (1) at 196 K and

allowed to warm slowly up to ambient temperature. The solution was filtered through neutral alumina. Removal of solvent yielded the mixture of ansa ferrocene and 1,1' bis-isopropyl ferrocene, products were identified by comparison of their spectroscopic data with literature.

4.3. Reaction of (1) with 6,6-diphenylfulvene (2)

Two equivalents of fulvene (2) in toluene were added to a solution of (1) in toluene at 196 K and allowed to warm up to ambient temperature. After stirring for 48 h the solution was separated on alumina (10 × 2 cm). Elution with toluene gave a yellow band of 6,6-diphenyl-fulvene (2) and a second, orange band of the 1,1' bis(diphenylmethyl)ferrocene (3). ¹H NMR (C₆D₆, ppm): 3.86 (8H, C₅H₄), 4.85 (s, 2H, C₅H₄–CH–(Ph)₂), 7.0–7.2 (m, C₆H₅) ¹³C NMR (C₆D₆, ppm): 52.79 (C6), 59.59 (C4–C3), 70.81 (C2–C5), 90.79 (C1) High Resolution MS for (1): 518.17072 M⁺, calc. 518.16968 High Resolution MS for (4): 516.15107 M⁺, calc. 516.15405.

4.4. Structural investigations

Crystals of (2) were grown from a pentane solution by slowly cooling. X-ray structures were determined with an STOE STADI 4 diffractometer using Mo-K_α-radiation with a graphite monochromator. Data collection was performed with commercial STOE software. Structure solution was carried out with the program package SHELLXTL for PC.

Acknowledgements

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