

**SYNTHESIS OF TRIFERROCENYLBENZENES BY TANTALUM(V)-CATALYZED CYCLOTRIMERIZATION OF ETHYNYLFERROCENE. THE CRYSTAL STRUCTURE OF 1,3,5-TRIFERROCENYL BENZENE**

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Exclusive, high-yield formation of the cyclotrimers of ethynylferrocene (**1**) was observed when TaCl<sub>5</sub> in benzene was employed as catalyst. Analysis of the resulting isomer mixture by means of HPLC and <sup>1</sup>H NMR revealed the presence of 1,3,5-triferrocenylbenzene (*sym-2*) and 1,2,4-triferrocenylbenzene (*asym-2*) in the ratio of 4 : 6. A small amount of pure *sym-2* isomer was isolated, and its solid-state structure was established by single-crystal X-ray diffraction. The molecules of *sym-2* possess a distorted up-up-down arrangement of the ferrocenyl groups attached to the benzene ring.

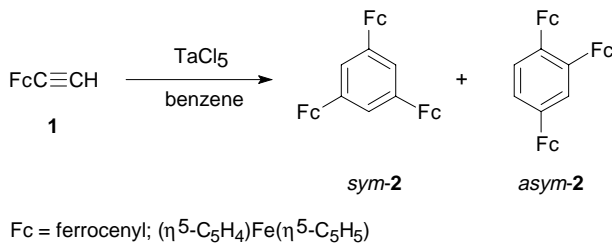
**Key words:** Metallocenes; Ferrocene derivatives; Ethynylferrocene; Cyclotrimerization; X-Ray structure; Tantalum(V).

Acetylenes as a starting material in organic and polymer chemistry are a very powerful tool for a variety of ingenious syntheses. Among these, transformations of acetylenes induced by metathesis catalysts (based mainly on Mo, W, Nb and Ta) are of particular importance<sup>1</sup>. The metathesis-type reactions of acetylenes fall into three groups: (i) metathesis polymerization, (ii) cyclotrimerization, and (iii) transalkylidation (true metathesis, *i.e.*, an apparent exchange of carbon atoms between a pair of triple bonds). The first reaction serves as a route to highly desirable oligo- and polyacetylenes<sup>2</sup>. Cyclotrimerization and transalkylidation are important paths to trisubstituted benzenes and symmetrical acetylenes with internal triple bond, respectively.

Transformations of metallocene-bearing acetylenes into polymers and/or oligomers has attracted great attention in the last period because these polyenes should exhibit enhanced optical non-linearity<sup>3,4</sup>. In addition, incorporation of metallocene moieties into polymer or oligomer chains might desirably tune further properties of these materials such as electrical conductivity, magnetic behaviour, and thermal stability. A straightforward

ward approach to the preparation of metallocene-containing polyenes is a polymerization of ethynylferrocene (**1**), likely one of the most easily accessible metallocene substituted acetylenes. However, except for the recent successful polymerization of **1** catalyzed by Schrock-type carbenes of the general formula  $[\text{Mo}(=\text{NAr})(=\text{CHC}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)\{\text{OC}(\text{CF}_3)_2\text{CH}_3\}_2]$  ( $\text{Ar} = \text{aryl}$ ) which yields well defined soluble poly(ethynylferrocene)<sup>3</sup>, other attempts to polymerize **1** were much less successful. Polymerization of **1** with classical radical initiators or Ziegler–Natta catalysts gave mostly mixtures of poorly defined insoluble polymers, linear low-molecular weight oligomers, and cyclotrimers<sup>5,6</sup>. By a proper selection of conditions, the yield of cyclotrimers was considerably enhanced with  $\text{TiCl}_4$ -based catalyst<sup>7</sup>. However, there is a serious discrepancy in the literature concerning the  $\text{TiCl}_4$ -catalyzed cyclotrimerization of **1**. While Schlögl *et al.* reported 1,2,4-triferrocenylbenzene to be the only product<sup>8,9</sup>, Nakashima *et al.*<sup>7</sup> described the presence of both possible 1,2,4- and 1,3,5-isomers as evidenced by  $^1\text{H}$  NMR. In general, the difficulties in a controlled polymerization of **1** are ascribed to a high electron-donating character of the ferrocenyl group which makes the acetylenic triple bond very reactive.

Recently we tested classical metathesis catalyst systems based on  $\text{WOCl}_4$  and tungsten aryloxo complexes which are very efficient for polymerizations of a wide spectrum of monosubstituted acetylenes<sup>10,11</sup>. Unfortunately, the results obtained for monomer **1** were similar to those outlined above for Ziegler–Natta catalysts. However, we have found that cyclotrimers of **1** were formed in a markedly high yield in this reaction. The question has thus arisen whether a selective cyclotrimerization of **1** can be performed with a Ta-based metathesis catalyst. For this purpose, tantalum(V) chloride was chosen since it is known to polymerize internal acetylenes but only cyclotrimerize terminal acetylenes<sup>12</sup>. In this paper, we report a successful cyclotrimerization of **1** with  $\text{TaCl}_5$  (Scheme 1) as well as characterization of the reaction products including the X-ray structure determination of 1,3,5-triferrocenylbenzene.



SCHEME 1

## EXPERIMENTAL

### Materials

Ethynylferrocene (**1**) was prepared as reported<sup>13,14</sup> from acetylferrocene. Tantalum pentachloride (Aldrich, 99.99%) was used as obtained. Benzene (Lachema, Czech Republic) was purified as described elsewhere<sup>15</sup>.

### Techniques

Size exclusion chromatography (SEC) was performed using a TSP chromatograph (Thermo Separation Products, Florida, U.S.A.) fitted with a series of two columns (Mixbed B and C, Polymer Laboratories, Bristol, U.K.) calibrated by polystyrene standards. Conditions: room temperature, tetrahydrofuran as the eluent (flow rate  $0.7 \text{ cm}^3 \text{ min}^{-1}$ ), spectrophotometric UV detection at 254 nm. HPLC analyses were carried out at room temperature using LiChrospher WP 300 column ( $25 \times 0.4 \text{ cm}$ , Merck) starting with 50%  $\text{CH}_3\text{CN}$  in water (v/v) and increasing acetonitrile concentration linearly up to 100%  $\text{CH}_3\text{CN}$  during 120 min; flow rate  $1 \text{ cm}^3 \text{ min}^{-1}$ ; spectrophotometric detection at 254 nm. The samples were injected as solutions in  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{CN}$  (3 : 1, v/v) presaturated with water.  $^1\text{H}$  NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (399.95 MHz) in  $[\text{C}^2\text{H}]\text{Cl}_3$  solutions at 21 °C using tetramethylsilane as internal standard. IR spectra were measured on an FT IR ATI Mattson Genesis instrument in Nujol mulls in the range of 400–4 000  $\text{cm}^{-1}$ . Mass spectra were obtained on a VG-7070E spectrometer (electron impact mode, 70 eV, direct inlet at 235 °C). Exact mass (HR MS) was determined by peak matching method using perfluorokerosene as a mass-scale calibrant.

### Cyclotrimerization of **1**

Using the standard vacuum break-seal technique, a solution of ethynylferrocene (**1**; 420 mg, 2.0 mmol) in benzene ( $1 \text{ cm}^3$ ) was mixed with 16 mM benzene solution of  $\text{TaCl}_5$  ( $5 \text{ cm}^3$ , 80  $\mu\text{mol}$ ; molar ratio **1** : catalyst = 25). After standing for 24 h at room temperature, the reaction was quenched by addition of methanol ( $2 \text{ cm}^3$ ) and the resulting mixture evaporated to dryness. SEC of the crude product showed only two sharp peaks of elution volume corresponding to unseparated trimers and unreacted monomer, respectively; no polymer was detected.

To remove a catalyst residue, the crude product was extracted with toluene ( $100 \text{ cm}^3$ ) and filtered. The filtrate was washed with 3 M aqueous HCl ( $25 \text{ cm}^3$ ), saturated aqueous  $\text{NaHCO}_3$  ( $25 \text{ cm}^3$ ) and water ( $50 \text{ cm}^3$ ). After drying ( $\text{MgSO}_4$ ), evaporation provided a mixture of isomers *sym*-**2** and *asym*-**2** as an orange solid (322 mg, 79% isolated yield). IR spectrum of the mixture showed the absence of terminal acetylenic groups. For  $\text{C}_{30}\text{H}_{36}\text{Fe}_3$  (630.2) calculated: 68.62% C, 4.80% H; found: 68.71% C, 4.70% H.

### Characterization of *sym*-**2**

Unfortunately, the isomer mixture could not be simply separated by preparative chromatography (column chromatography or TLC). On the other hand, the mixture could be possibly separated by preparative HPLC as documented by analytical HPLC used for quantitative analysis (Fig. 1). The information on the quantitative composition of the mixture can be also easily derived from  $^1\text{H}$  NMR signals of the aromatic protons  $\text{C}_6\text{H}_3\text{Fe}_3$ . The cyclopentadienyl (Cp) region is not suitable for the purpose due to an insufficient resolution of signals.  $^1\text{H}$  NMR (relative signal intensities for both isomers given); *sym*-**2**: 7.44 s, 0.4 H. *Asym*-**2** (numbered as 1,2,4-triferrocenylbenzene): 7.35 dd, 0.6 H,  $J(\text{H-5}, \text{H-6}) = 7.9$ ,  $J(\text{H-3}, \text{H-5}) = 1.9$  (H-5); 7.65 d, 0.6 H,  $J(\text{H-5}, \text{H-6}) = 7.9$  (H-6); 7.88 d, 0.6 H,  $J(\text{H-3}, \text{H-5}) = 1.9$

(H-3). The quantitative analysis by either  $^1\text{H}$  NMR or HPLC gave the same ratio *sym-2* : *asym-2* of 4 : 6.

On the other hand, a small amount of pure *sym-2* as well-developed orange needles was obtained by gas-phase diffusion of methanol into a toluene solution of the mixture. That was also used as standard for HPLC analysis. Mass spectrum, *m/z* (rel. abund., %): 632 (11), 631 (45), 630 (100,  $\text{M}^+$ ), 629 (9), 628 (19), 443 (4), 316 (4), 315.5 (17), 315 (38,  $\text{M}^{2+}$ ), 314 (8), 121 (6,  $[\text{C}_5\text{H}_5\text{Fe}]^+$ ). HRMS, measured (calculated) *m/z*: 630.0408 (630.0396),  $\text{C}_{36}\text{H}_{30}\text{Fe}_3$ .

### X-Ray Crystallography

A crystal of *sym-2* grown as described above was glued to a glass fiber by epoxy cement. The diffractions were measured at 296(1) K on an Enraf-Nonius CAD 4-MACH III diffractometer using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) and  $\theta$ - $2\theta$  scan. Since the measurement was carried out at the  $\psi$ -angle minimizing an intensity distortion due to the crystal shape (needle), no further absorption correction was applied. Accurate cell parameters were determined by least squares from 25 centered diffractions with  $\theta$  angle in the range of 13.5–16°. The structure was solved by direct methods (SIR92, ref.<sup>16</sup>) and refined by full-matrix least squares on  $F^2$  (SHELXL93, ref.<sup>17</sup>). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were first defined geometrically and then freely isotropically refined. Relevant crystallographic parameters are given in Table I, the selected geometrical parameters are presented in Table II. Additional crystallographic data are available from the Cambridge Crystallographic Data Centre.

### RESULTS AND DISCUSSION

An attempted polymerization of **1** with W-based catalysts led to the formation of polymer-linear oligomer-cyclotrimer mixture (as deduced from SEC). The use of  $\text{TaCl}_5$  as a catalyst in benzene produces directly a polymer-free mixture of cyclotrimers *sym-2* and *asym-2* in the 4 : 6 ratio in 79% yield after purification. The procedure described above produces both isomers under very mild conditions. The isomer mixture is well soluble in dichloromethane, chloroform, tetrahydrofuran, toluene and insoluble in methanol or water. The retention characteristics of both isomers are very similar (see

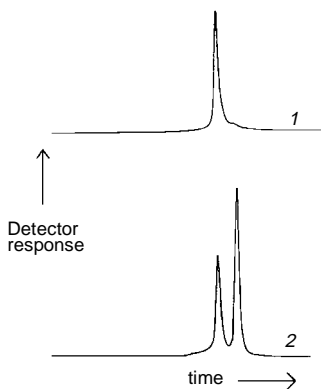


FIG. 1  
HPLC traces recorded for pure *sym-2* (1) and purified mixture of isomers (2). See Experimental for details

Fig. 1); therefore, the mixture could not be simply separated (*e.g.*, by preparative chromatography). Notwithstanding, on slow gas-phase diffusion of methanol into a toluene solution of the mixture, the more symmetrical isomer, *sym-2*, crystallizes as clusters of well-developed crystals.

The X-ray structure determination confirms the structure of the *sym-2* isomer (Fig. 2). The three ferrocenyl groups linked directly to the substituted benzene ring in the 1, 3,

TABLE I  
Crystallographic data for *sym-2*

Formula unit	C <sub>36</sub> H <sub>30</sub> Fe <sub>3</sub>
<i>M</i> , g mol <sup>-1</sup>	630.15
Crystal system; space group	orthorhombic; <i>Pbca</i> (No. 61)
<i>a</i> , Å	14.360(1)
<i>b</i> , Å	10.845(2)
<i>c</i> , Å	34.882(2)
<i>V</i> , Å <sup>3</sup> ; <i>Z</i>	5 432(1); 8
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.54
<i>F</i> (000)	2 592
Crystal size, mm <sup>3</sup>	0.15 × 0.19 × 0.73
Colour, habit	orange, bar
<i>μ</i> , mm <sup>-1</sup>	1.61
2θ range	2.3–48.0°
<i>hkl</i> range	0→16; 0→12; 0→39
Diffractions collected; <i>R</i> (σ) <sup>a</sup> , %	4 287; 3.4
Diffractions unique	4 268
Diffractions observed; <i>F<sub>o</sub></i> ≥ 4σ( <i>F<sub>o</sub></i> )	3 137
Standard diffractions	3 monitored every 1 h
Variations in standards, %	2.5
Weighting scheme; <i>w</i> <sub>1</sub> , <i>w</i> <sub>2</sub> <sup>b</sup>	0.0304, 88.5908
Number of parameters	472
<i>R</i> <sub>all</sub> ( <i>F</i> ); <i>R</i> <sub>obs</sub> ( <i>F</i> ) <sup>a</sup> , %	6.9; 3.4
<i>wR</i> <sub>all</sub> ( <i>F</i> <sup>2</sup> ); <i>wR</i> <sub>obs</sub> ( <i>F</i> <sup>2</sup> ) <sup>a</sup> , %	11.7; 7.7
GOF <sub>all</sub> <sup>a</sup>	1.06
(Δ/σ) <sub>max</sub>	0.002
Δρ, e Å <sup>-3</sup>	0.34; -0.37

$$^a R(F) = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}, wR(F^2) = \frac{\sum[(w(F_o^2 - F_c^2)^2)/(w(F_o^2)^2)]^{1/2}}{\sum F_o^2}$$

$$\text{GOF} = \left[ \frac{\sum(w(F_o^2 - F_c^2)^2)/(N_{\text{diffs}} - N_{\text{params}})}{\sum F_o^2} \right]^{1/2}, R(\sigma) = \frac{\sum \sigma(F_o^2)}{\sum F_o^2}$$

$$^b \text{Weighting scheme: } w = [\sigma^2(F_o^2) + w_1P^2 + w_2P]^{-1}; P = [\max(F_o^2) + 2F_c^2]/3.$$

and 5 positions are in a general up-up-down arrangement but with different deviation of the substituted Cp-rings from the benzene plane. The distortion increases in the order: Fc5(7°) < Fc1(14°) < Fc3(28°), the corresponding dihedral angles of the substituted cyclopentadienyl and benzene ring planes being given in parentheses (*cf.* Table II). On the other hand, no distortion occurs at the C(C<sub>6</sub>H<sub>3</sub>)–C(Fc) bond as demonstrated by a very short perpendicular distance of the Cp-carbon directly bonded to the benzene least-square plane [maximum 0.080(6) Å for C(50)] and C(C<sub>6</sub>H<sub>3</sub>)–C(C<sub>6</sub>H<sub>3</sub>)–C(Fc) angles close to 120°. All three ferrocenyl groups in *sym-2* exhibit eclipsed conformation

TABLE II

Selected bond lengths (Å), bond angles and dihedral angles of l. s.-planes<sup>a</sup> (°) for *sym-2*

Atoms	Distances	Atoms	Angles		
C–C (Fc, av.)	1.41(2) <sup>b</sup>	C–C–C (Fc, av.)	108(1) <sup>b</sup>		
Fe–C (Fc, av.)	2.04(1) <sup>b</sup>				
C01–C02	1.390(5)	C02–C01–C06	118.7(3)		
C01–C06	1.394(5)	C01–C02–C03	121.1(3)		
C02–C03	1.396(5)	C02–C03–C04	118.7(3)		
C03–C04	1.391(5)	C03–C04–C05	121.3(3)		
C04–C05	1.396(5)	C04–C05–C06	118.6(3)		
C05–C06	1.383(5)	C01–C06–C05	121.6(3)		
C01–C10	1.474(5)	C02–C01–C10	120.8(3)		
C03–C30	1.475(5)	C06–C01–C10	120.6(3)		
C05–C50	1.475(5)	C02–C03–C30	122.0(3)		
		C04–C03–C30	119.2(3)		
		C04–C05–C50	119.7(3)		
		C06–C05–C50	121.6(3)		
Dihedral angles					
Cp1 vs C <sub>6</sub> H <sub>3</sub>	13.6(2)	Cp1 vs Cp3	20.8(2)	Cp1 vs Cp1'	0.2(3)
Cp3 vs C <sub>6</sub> H <sub>3</sub>	27.5(2)	Cp1 vs Cp5	10.6(3)	Cp3 vs Cp3'	1.7(3)
Cp5 vs C <sub>6</sub> H <sub>3</sub>	7.3(3)	Cp3 vs Cp5	20.2(3)	Cp5 vs Cp5'	1.1(4)

<sup>a</sup> Cp1 plane defined by carbons C10, C11, C12, C13, and C14; Cp1': C15, C16, C17, C18, and C19; Cp3: C30, C31, C32, C33, and C34; Cp3': C35, C36, C37, C38, and C39; Cp5: C50, C51, C52, C53, and C54; Cp5': C55, C56, C57, C58, and C59; C<sub>6</sub>H<sub>3</sub>: C01, C02, C03, C04, C05, C06. <sup>b</sup> 30 entries.

without any deformation of the parallel Cp-rings (Cp, Cp dihedral angle  $< 2^\circ$ ). Similar up-up-down arrangement was observed for tris[( $\eta^6$ -phenylethynyl)tricarbonylchromium(0)] benzene derivative 1,3,5-{Cr(CO)<sub>3</sub>( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>CsC)}<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, ref.<sup>18</sup>. Unlike *sym-2*, the  $\eta^6$ -C<sub>6</sub>H<sub>5</sub> planes are almost perfectly coplanar with the central C<sub>6</sub>H<sub>3</sub> plane in the chromium carbonyl complex. The structure of the related 1,3,5-tris(ferrocenylethynyl)benzene<sup>19</sup> has revealed two eclipsed ferrocenyl groups to adopt perfectly coplanar orientation with respect to the 1,3,5-C<sub>6</sub>H<sub>3</sub> moiety (up-up arrangement) while the third one was staggered and oriented orthogonally. The torsional distortion of the “regular” arrangement of ferrocenyl groups in the case of *sym-2* is caused most likely by steric requirements of bulky ferrocenyl groups which is, however, markedly reduced by an introduction of C<sub>2</sub>-spacer (ethynediyl group) as reflected in the solid-state structures of the organometallics mentioned above.

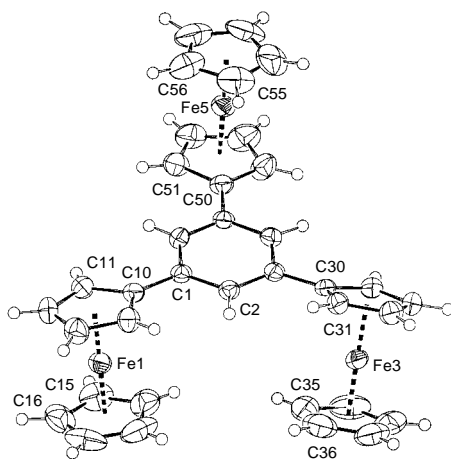


FIG. 2

Perspective view of *sym-2* showing labelling scheme (only pivot and adjacent atoms labelled). Thermal ellipsoids drawn at 50% probability level

No significant intermolecular contacts shorter than the sum of van der Waals radii have been detected within the crystal packing of *sym-2*; the molecules are stacked in normal van der Waals distances forming a molecular crystal lattice.

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