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Synthesis of the first 30-electron triple-decker complexes of the iron group metals with cyclopentadienyl ligands. X-Ray structure of $[(\eta\text{-}C_5H_5)Ru(\mu,\eta\text{-}C_5Me_5)Ru(\eta\text{-}C_5Me_5)]PF_6$

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Abstract

The first 30-electron triple-decker complexes of the iron group metals $[(\eta\text{-}C_5R_5)M(\mu,\eta\text{-}C_5Me_5)M'(\eta\text{-}C_5Me_5)]PF_6$ were synthesized by reaction of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ or $[Ru(\eta\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me) with decamethylmetallocenes $M'(\eta\text{-}C_5Me_5)_2$ (M′ = Fe, Ru, Os). The pentamethylcyclopentadienyl ligand η-bonded to both metal atoms is the middle deck in these sandwich compounds. Their structure was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy as well as by an X-ray diffraction study of $[(\eta\text{-}C_5H_5)Ru(\mu,\eta\text{-}C_5Me_5)Ru(\eta\text{-}C_5Me_5)]PF_6$.

Introduction

The triple-decker complexes of transition metals have attracted particular interest for the past 15 years. The first complex of this type, viz. 34-electron cation $[(\eta\text{-}C_5H_5)Ni(\mu,\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]^+$ was prepared by Werner and Salzer in 1972 [1,2]. Further development of this field was mainly connected with the use of boron-containing heterocyclic ligands, which readily yield triple-decker as well as multiple-decker complexes [3–5]. However, all attempts [6–8] to prepare other members of this class of compounds with a central cyclopentadienyl ligand were unsuccessful although mass spectrometry data suggested that ions of the type $[MM'(C_5H_5)_3]^+$ (M = M′ = Ni, Fe, Cr; M = Ni, M′ = Fe) were formed from the corresponding metallocenes [9,10] or from $[Fe(\eta\text{-}C_5H_5)(\mu_3\text{-}CO)]_4$ [11] by electron impact.

In 1976 Hoffmann et al. published the results of extended Hückel molecular orbital calculations from which were predicted two series of stable triple-decker

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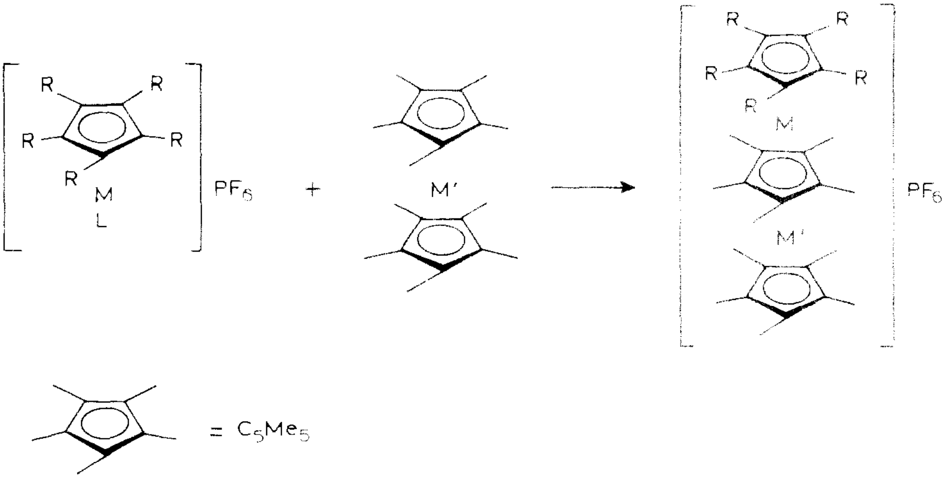
sandwich structures, containing 30 and 34 valence electrons [12]. It was thus surprising that 30-electron triple-decker complexes with cyclopentadienyl ligand as a central unit had not been prepared until now, although, according to these calculations, they should be more stable than 34-electron complexes.

We have prepared the first such complexes with iron group metals * by interaction of electron rich decamethylmetallocenes with cationic complexes $[M(\eta\text{-}C_5R_5)L]PF_6$:



$(M = Fe\ ;\ R = H\ ;\ L = C_6H_6\ ;\ M' = Fe,\ Ru,\ Os\ ;$

$M = Ru\ ;\ R = H,\ Me\ ;\ I = (MeCN)_3\ ;\ M' = Ru,\ Os\ )$

It is noteworthy that earlier attempts to use strong proton acids in reactions with decamethylmetallocenes for the preparation of triple-decker sandwiches gave in the case of decamethylnickelocene only the stable protonation product $[Ni(\eta\text{-}C_5Me_5)(\eta\text{-}C_5Me_5H)]^+$ [8], and in the case of decamethylferrocene the oxidation product $[Fe(\eta\text{-}C_5Me_5)_2]^+$ [14].

Results and discussion

Irradiation of the cationic cyclopentadienylbenzeneiron complex with visible light in the presence of decamethylmetallocenes $M(\eta\text{-}C_5Me_5)_2$ (M = Fe, Ru, Os) in CH_2Cl_2 leads to di-iron, iron-ruthenium and iron-osmium triple-decker cationic complexes (see Scheme 1).

The analogous di-ruthenium and ruthenium-osmium triple-decker compounds were prepared by reaction of both decamethylruthenocene and decamethylosmocene with the acetonitrile complexes of ruthenium $[Ru(\eta\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me) in refluxing nitromethane (see Scheme 2).

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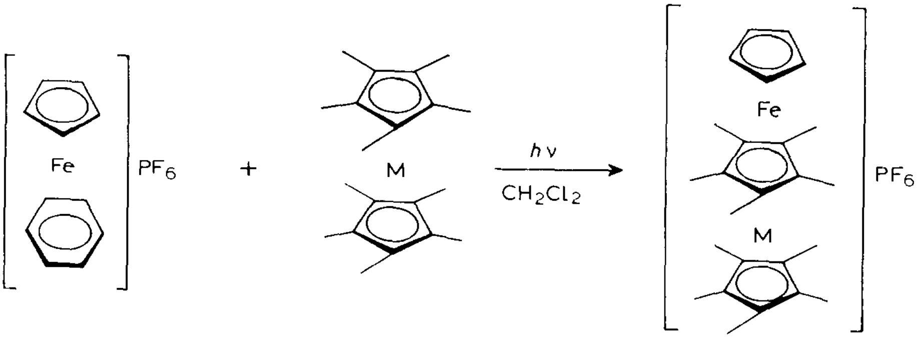
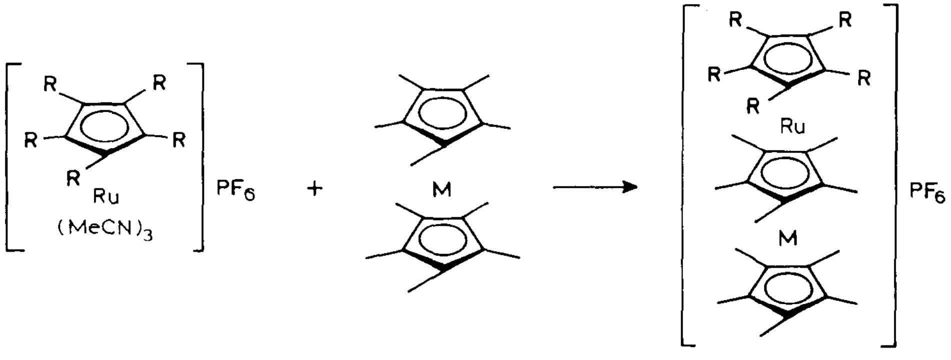
* For preliminary communication see Ref. 13.



(**1**, M = Fe;
2, M = Ru;
3, M = Os)

Scheme 1

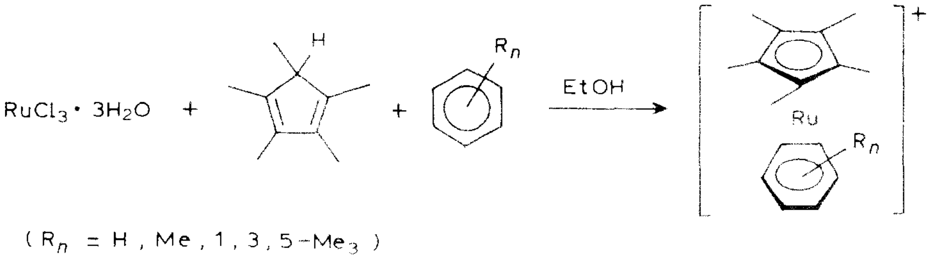
It is noteworthy that for these reactions we used the methods developed by Mann et al. [15–21] for the generation of the coordinatively unsaturated fragments $[M(\eta\text{-}C_5R_5)]^+$ (M = Fe, R = H; M = Ru, R = H, Me). The starting iron complex $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ was prepared by the method of Nesmeyanov and Vol'kenau [22,23]. The starting acetonitrile ruthenium complexes $[Ru(\eta\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me) were prepared by UV-irradiation of the corresponding benzene compounds $[Ru(\eta\text{-}C_5R_5)(\eta\text{-}C_6H_6)]PF_6$ in acetonitrile [17,21]. For the preparation of pentamethylcyclopentadienylbenzene ruthenium cationic complex as well as of other arene complexes of this type we have developed the direct synthetic method based on interaction of ruthenium chloride with a mixture of the



(**4a**, M = Ru, R = H;
4b, M = Ru, R = Me;
5, M = Os, R = H)

Scheme 2

ligands, pentamethylcyclopentadiene and arene, in refluxing alcohol [24]:



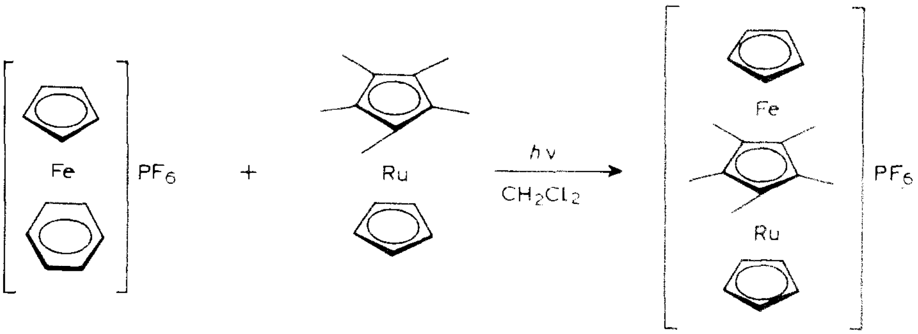
The new triple-decker complexes **1**–**5** are coloured crystalline solids of varying stability. The iron-containing triple-decker complexes **1**–**3** are stable only in an inert atmosphere in the solid state or in methylene chloride solution, but decompose rapidly in solvents of higher polarity. The rate of decomposition in air seems to decrease in order Os > Fe > Ru.

Di-ruthenium (**4a**, **4b**) and ruthenium-osmium (**5**) complexes are air-stable in the solid state, and in CH_2Cl_2, Me_2CO or $MeNO_2$ solution. Complex **4a** is so stable that it remains unchanged in the refluxing $C_6H_6/MeNO_2$ mixture, i.e. the exchange of ruthenocene fragment for benzene does not occur.

These data demonstrate that stability of triple-decker complexes depends primarily on the nature of the metals. Another important factor defining stability of such compounds is the degree to which the cyclic ligands are methylated. In the triple-decker complexes **1**–**5** two or three of the cyclopentadienyl rings are pentamethylated. The analogous complex wherein only one cyclopentadienyl ligand is pentamethylated was also synthesised. The known pentamethylruthenocene [25] was prepared by a simpler method, by the reaction of complex $[Ru(\eta\text{-}C_5Me_5)Cl_2]_x$ with cyclopentadiene in the presence of zinc dust:

$$[Ru(\eta\text{-}C_5Me_5)Cl_2]_x + C_5H_6 \xrightarrow[EtOH]{Zn} Ru(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)$$

Further reaction of the pentamethylruthenocene with cationic cyclopentadienylbenzeneiron complex then gives the unstable triple-decker complex wherein only the central ligand is pentamethylated:



This complex decomposes instantly in air. No triple-decker complexes were obtained from similar reactions with the parent metallocenes $M(\eta\text{-}C_5H_5)_2$ (M = Fe, Ru, Os).

Table 1

Analytical data for, colour of the complexes $[(\eta\text{-C}_5\text{R}_5)\text{M}(\mu,\eta\text{-C}_5\text{Me}_5)\text{M}'(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$

Complex	M	M′	R	Colour	Found (calc)(%)			
					C	H	P	Fe
1	Fe	Fe	H	blue-green	48.96 (48.26) [a]	6.01 (5.72) [a]	5.26 (4.88) [a]	16.38 (17.60) [a]
2	Fe	Ru	H	lilac	43.14 (43.23) [b]	5.33 (5.16) [b]	4.61 (4.29) [b]	8.90 (7.73) [b]
3	Fe	Os	H	lilac			4.33 (4.26)	7.02 (7.69)
4a	Ru	Ru	H	yellow-orange	43.91 (43.98)	5.12 (5.17)	4.55 (4.54)	
4b	Ru	Ru	Me	yellow-orange	48.31 (47.86)	6.03 (6.03)	4.12 (4.11)	
5	Ru	Os	H	yellow-orange			3.90 (4.01)	

[a] Calculated for $[\text{Fe}_2(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)_2]\text{PF}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$. [b] Calculated for $[\text{FeRu}(\text{C}_5\text{H}_5)(\text{C}_5\text{Me}_5)_2]\text{PF}_6 \cdot \text{CH}_2\text{Cl}_2$.

The structure of the 30-electron triple-decker compounds **1**–**5** was confirmed by elemental analysis (Table 1), ^{1}H and ^{13}C {^{1}H} NMR spectra (Table 2) as well as by an X-ray diffraction study of complex **4a**.

The ^{1}H NMR data (Table 2) show that the signals of unsubstituted cyclopentadienyl ring protons are in the range of $\delta = 3.87$–4.50 ppm and those of the methyl group protons of the central and terminal rings are in the regions of $\delta = 2.17$–2.70 and 1.43–1.56 ppm respectively. The assignment of signals was made on the basis of ^{1}H NMR spectrum of the permethylated complex **4b**, which showed two peaks at $\delta = 2.17$ and 1.55 ppm with an integral intensity ratio 1/2.

It should be noted that the signals of the central ring methyl groups are shifted downfield by 0.62–1.23 ppm relative to the terminal ring methyl groups. This shift

Table 2

^{1}H and ^{13}C NMR data for the complexes $[(\eta\text{-C}_5\text{R}_5)\text{M}(\mu,\eta\text{-C}_5\text{Me}_5)\text{M}'(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$ (in $\text{CD}_2\text{Cl}_2/\text{SiMe}_4$)

Complex	M	M′	R	^{1}H NMR, δ (ppm) [a]			^{13}C NMR, δ (ppm) [a]				
				η-C$_5$H$_5$	η-C$_5$Me$_5$	μ,η-C$_5$Me$_5$	η-C$_5$H$_5$	η-C$_5$Me$_5$	μ,η-C$_5$Me$_5$	η-C$_5$*Me*$_5$	μ,η-C$_5$*Me*$_5$
1	Fe	Fe	H	3.87	1.51	2.69	71.92	79.15	69.14	13.28	8.29
2	Fe	Ru	H	4.09	1.43	2.56	72.36	84.88	71.15	13.68	9.18
3	Fe	Os	H	4.13	1.47	2.70	72.16	81.95	63.58	13.46	9.68
4a	Ru	Ru	H	4.45	1.52	2.51	74.14	84.73	74.29	14.40	9.26
4b	Ru	Ru	Me	–	1.55	2.17	–	84.89	72.52	11.92	9.36
5	Ru	Os	H	4.50	1.56	2.64	73.74	82.05	67.07	14.32	9.76

[a] All signals are singlets.

can be explained by the deshielding effect of the central ring bonded to two positively charged metal atoms. A similar difference between the signals of the methyl group protons of the central and terminal cyclopentadienyl rings was observed earlier by Werner et al. in the case of the 34-electron nickel complex $[(\eta\text{-}C_5H_4Me)Ni(\mu,\eta\text{-}C_5H_4Me)Ni(\eta\text{-}C_5H_4Me)]^+$ [2].

The $^{13}C\{^1H\}$ NMR spectra are also consistent with the structure of triple-decker complexes **1**–**5**. It is interesting to note that the methyl group signals of the central ring in $^{13}C\{^1H\}$ NMR spectra are shifted upfield relative to the signals of methyl groups of the terminal rings. However, the opposite pattern is observed for the ring carbons of pentamethylcyclopentadienyl ligands.

The nature of metal atoms has no significant influence on the signal positions the largest effect was shown by osmium. At the same time the position of signals of similar groups is strongly dependent on the ring position (central or terminal).

The X-ray diffraction study confirmed the structure of complex **4a** to be a triple-decker sandwich compound and its geometry was in good agreement with that found for the nickel complex $[(\eta\text{-}C_5H_5)Ni(\mu,\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]BF_4$ [26,27]. The structure of the complex **4a** cation is shown in Fig. 1; the cation lies in a special position on the mirror plane through the C(1), C(4), C(7), C(11) and C(14) atoms. Unfortunately the intense thermal motion of the ions in the crystal or, perhaps their disorder, prevented the geometrical parameters from being obtained with sufficient accuracy, so that detailed discussion was deemed unnecessary. Nevertheless some

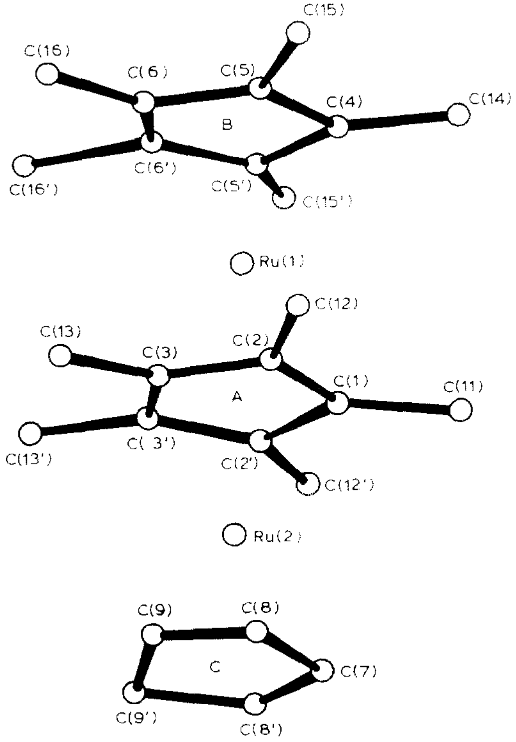


Fig. 1. The structure of the cation $[(\eta\text{-}C_5H_5)Ru(\mu,\eta\text{-}C_5Me_5)Ru(\eta\text{-}C_5Me_5)]^+$.

main features of the structure can still be mentioned.

The cyclopentadienyl ring planes A, B and C (see Fig. 1) are, in fact parallel to each other, the dihedral angles A/B, A/C and B/C being equal to 2.3, 2.0 and 2.4° respectively. In contrast to the nickel complex in which the two neighbouring cyclopentadienyl rings are in the eclipsed conformation and the third ring is staggered relative to the other two, in complex **4a** all cyclopentadienyl ligands are eclipsed. This is remarkable if one takes into account that each of the A and B rings has five methyl substituents which should in general add to the relative instability of the eclipsed conformation. It should be mentioned, however, that the cyclopentadienyl rings in the crystal structure of decamethylruthenocene, in contrast to decamethylferrocene [28] and in agreement with the theoretical predictions for metallocenes, are also in the eclipsed conformation (see ref. 25 and references therein).

The Ru–C distances (2.11–2.26 Å) agree well with the values found in ruthenocene [29] and decamethylruthenocene [25] (the averaged values are 2.186 and 2.174 Å respectively). In the complex **4a** as well as in the nickel triple-decker (vide supra) the distances from the metal atoms to the central cyclopentadienyl ring plane (Ru(1)–A 1.87, Ru(2)–A 1.77 Å) are longer than the metal–terminal ring plane distances (Ru(1)–B and Ru(2)–C 1.75 Å), the difference between the Ru(1)–A and Ru(2)–A distances in **4a**, is increased owing to mutual repulsion by the methyl groups on each of the A and B rings in the eclipsed conformation.

In spite of the very large variation in the observed endocyclic C–C and exocyclic C–C(Me) bond lengths, the suggestion that **4a** is a triple-decker sandwich, still holds. The triple-decker structure of the complexes **1–5** can then be inferred from the similarity of their NMR spectra to that of **4a**.

Experimental

All reactions were carried out under argon, except for the case of iron-containing triple-decker complexes, reaction products were worked-up in air. CH_2Cl_2 was washed successively with conc. H_2SO_4, water, and aqueous Na_2CO_3 solution, dried over K_2CO_3, and distilled from K_2CO_3, and then from P_2O_5 under argon. $MeNO_2$ was dried over $CaCl_2$ and distilled under argon. All other solvents and reagents were of reagent grade and were used as received. The compounds were prepared by published methods: pentamethylcyclopentadiene [30], $Fe(\eta\text{-}C_5Me_5)_2$ [31], $Os(\eta\text{-}C_5Me_5)_2$ [25], $[Ru(\eta\text{-}C_5Me_5)Cl_2]_x$ [32], $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ [23], $[Ru(\eta\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me) [17,21]. The syntheses of known $Ru(\eta\text{-}C_5Me_5)_2$ [25,32,33], $Ru(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)$ [25], and the cation $[Ru(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]^+$ [21,24,34,35] (as the PF_6^- salt) were improved and are given below. ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker WP 200 SY spectrometer with $SiMe_4$ as internal reference.

Preparation of $Ru(\eta\text{-}C_5Me_5)_2$

A solution of $RuCl_3 \cdot 3H_2O$ (1.044 g, 4 mmol) in a mixture of ethanol (40 ml) and water (20 ml) was refluxed for 1 h. To this solution was added pentamethylcyclopentadiene (1.4 g, ca. 10 mmol) and the mixture was refluxed with stirring for 8 h. After cooling to room temperature, the solid product was filtered off and washed with cold acetone (ca. 5 ml). The solid was dissolved in hexane (or light petroleum) and eluted through a short alumina column (10–15 cm). The solvent was removed in vacuo and the residue was recrystallized from acetone (−20 °C). Yields, 55–60%. Anal. Found: C, 64.26; H, 8.20. $C_{20}H_{30}Ru$ calc: C, 64.66; H, 8.14%. ^1H NMR ($CDCl_3$): δ 1.64 (s).

The same result was obtained when "ruthenium blue" solution, generated by a published procedure [36] was used.

The use of 2-methoxyethanol in place of aqueous ethanol gave no yield improvement.

Preparation of $Ru(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)$

A mixture of $[Ru(\eta\text{-}C_5Me_5)Cl_2]_x$ (0.614 g), freshly distilled cyclopentadiene (ca. 5 ml) and ethanol (ca. 10 ml) was stirred until the initial material had dissolved to give a deep green solution (ca. 3 h). Zinc dust (ca. 0.5 g) was gradually added and the reaction mixture was stirred for 1 h. The mixture was evaporated to dryness in vacuo. The residue was extracted with hexane and eluted through a short alumina column. The solvent was evaporated in vacuo and the solid was recrystallized from methanol (−20 °C) to give very pale yellow crystals. Yields 70–75%. Anal. Found: C, 59.54; H, 6.80. $C_{15}H_{20}Ru$ calc: C, 59.78; H, 6.69%. ^1H NMR ($CDCl_3$): δ 1.95 (s, 15H, C_5Me_5), 4.16 (s, 5H, C_5H_5).

Preparation of $[Ru(\eta\text{-}C_5Me_5)(\eta\text{-}C_6H_6)]PF_6$

A solution of $RuCl_3 \cdot 3H_2O$ (2.088 g, 8 mmol) in ethanol (100 ml) was refluxed for ca. 1 h. Benzene (20 ml) and pentamethylcyclopentadiene (2.2 g, ca. 16 mmol) were added and the reaction mixture was refluxed for 8–12 h. The mixture was evaporated to dryness in vacuo. The residue was then washed with ether, dissolved in water (ca. 50 ml), and the solution filtered into a solution of NH_4PF_6 (1.6 g, 10 mmol) in water (ca. 10 ml). The precipitate which was filtered off, was washed with water and dissolved in acetone. The solution was then filtered through a short alumina column (ca. 10 cm) and eluted with acetone. After the solvent had been removed in vacuo, the residue was washed with three 10 ml portions of ethanol, and then with ether to give a colourless crystalline solid. Yields 70–75%. Anal. Found: C, 41.41; H, 4.65; P, 6.57. $C_{16}H_{21}F_6PRu$ calc: C, 41.83; H, 4.61; P, 6.74%. ^1H NMR (CD_3COCD_3): 2.07 (s, 15H, C_5Me_5), 6.03 (s, 6H, C_6H_6). If necessary the product can be recrystallized from $MeNO_2$/EtOH mixture.

Preparation of $[(\eta\text{-}C_5H_5)Fe(\mu,\eta\text{-}C_5Me_5)M(\eta\text{-}C_5Me_5)]PF_6$ *(1, M = Fe; 2, M = Ru; 3, M = Os)*

To a mixture of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ (0.172 g, 0.5 mmol) and $M(\eta\text{-}C_5Me_5)_2$ (M = Fe, Ru, Os) (0.5 mmol) was added dichloromethane (ca. 40 ml). The mixture was degassed by bubbling of argon through it for 15 min and then irradiated by visible light (300 W tungsten lamp) from a distance of 5–10 cm for 5–8 h with stirring and internal cooling with cold water. The solvent was evaporated in vacuo and the residue was washed with hexane to remove unchanged decamethylmetallocene. The product was extracted from the residue with dichloromethane/hexane (1/1) mixture thus separating it from the starting $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$. The extract was filtered into an approximately equal volume of hexane. The resulting solid was reprecipitated by hexane from a solution in dichloromethane/hexane (3/4) mixture. Yields ca. 50–60%.

The complex $[(\eta\text{-}C_5H_5)Fe(\mu,\eta\text{-}C_5Me_5)Ru(\eta\text{-}C_5H_5)]PF_6$ can be prepared similarly using pentamethylruthenocene but in this case much more rigorous exclusion of air and moisture is essential.

*Preparation of $[(\eta\text{-}C_5R_5)Ru(\mu,\eta\text{-}C_5Me_5)M(\eta\text{-}C_5Me_5)]PF_6$ (**4a**, M = Ru, R = H; **4b**, M = Ru, R = Me; **5**, M = Os, R = H)*

Nitromethane (5–10 ml) was degassed by bubbling of argon through it for 10 min and then was added to a mixture of $[Ru(\eta\text{-}C_5H_5)(MeCN)_3]PF_6$ (0.217 g, 0.5 mmol) and $M(\eta\text{-}C_5Me_5)_2$ (M = Ru, Os) (0.5 mmol), and the mixture was refluxed for 0.5 h (M = Ru) or 4 h (M = Os). The solvent was then evaporated in vacuo and the residue was washed with ether to remove unchanged decamethylmetallocene. The residue was chromatographed on an alumina column (15–20 cm) with acetone as eluent and, the yellow band was collected. The volume of the resultant solution was reduced in vacuo and ether was slowly added to give yellow-orange microcrystals. Yieds: ca. 80% (M = Ru), ca. 60% (M = Os).

Complex **4b** (ca. 50%) was prepared similarly by heating a mixture of $[Ru(\eta\text{-}C_5Me_5)(MeCN)_3]PF_6$ and $Ru(\eta\text{-}C_5Me_5)_2$ in $MeNO_2$ at reflux for 8 h.

The complexes **4**–**5** can be recrystallized from ethanol.

*X-ray structural study of complex **4a***

Crystals of **4a** were obtained by recrystallization from nitromethane/ethyl acetate mixture. The crystals are orthorhombic, at 20 °C *a* 8.632(4), *b* 21.612(3), *c*

Table 3

Atomic coordinates and equivalent isotropic temperature factors for complex 4a.

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Ru(1)	0	0.71998(3)	0.501	3.39(1)
Ru(2)	0	0.55153(3)	0.5013(2)	4.50(2)
P	0	1.0010(5)	0.7506(9)	6.67(7)
F(1)	−0.1647(9)	0.9789(5)	0.7428(9)	17.0(3)
F(2)	0	0.9849(8)	0.645(1)	20.5(6)
F(3)	0	0.9378(6)	0.796(1)	16.8(6)
F(4)	0	0.995(1)	0.8517(8)	15.7(7)
F(5)	0	1.0667(6)	0.763(2)	21.3(9)
C(1)	0	0.6330(5)	0.5831(7)	4.5(3)
C(2)	−0.1313(9)	0.6350(3)	0.5310(9)	8.9(4)
C(3)	−0.090(2)	0.6351(4)	0.4427(8)	8.5(3)
C(4)	0	0.7977(6)	0.603(1)	6.2(4)
C(5)	−0.126(1)	0.8021(4)	0.5415(8)	6.4(3)
C(6)	−0.091(1)	0.8043(4)	0.4502(5)	5.3(2)
C(7)	0	0.4700(6)	0.580(1)	7.1(4)
C(8)	0.138(1)	0.4665(3)	0.535(1)	8.7(4)
C(9)	0.077(1)	0.4687(4)	0.440(1)	9.4(3)
C(11)	0	0.6272(9)	0.684(1)	22(2)
C(12)	−0.292(1)	0.6348(5)	0.566(2)	27.3(9)
C(13)	−0.190(3)	0.6366(7)	0.360(1)	31.0(4)
C(14)	0	0.7936(8)	0.705(1)	10.5(8)
C(15)	−0.302(2)	0.8013(6)	0.589(1)	10.8(5)
C(16)	−0.193(2)	0.8143(6)	0.3758(9)	11.6(4)

14.732(2) Å, V 2748.5 Å^3, $Z = 4$, d (calc.) 1.652 g/cm^3, space group $Cmc2_1$, both cation and anion lie in special positions on the mirror plane. Unit cell parameters and the intensities of 1044 reflections with $F^2 \geqslant 3\sigma$ were measured with an Enraf–Nonius CAD4 four-circle automatic diffractometer (+20 °C, λ Mo-K_α, graphite monochromator, scan speed ratio $\omega/\theta = 1.2/1$, $\theta \leqslant 28°$).

The structure was solved by the direct method, the Ru atoms were located in the E-synthesis, and all the other non-hydrogen atoms were found in the subsequent F- and D-syntheses. The structure was refined by the full-matrix least-squares technique at first to an isotropic and then to an anisotropic approximation. Although the refinement converged to rather low discrepancy factors $R = 0.034$, $R_w = 0.041$, the scatter of the chemically equivalent bond lengths proved to be very large and the temperature factors of a number of light atoms (the fluorine atoms of the anion and the methyl group carbon atoms) became very high (up to 30 Å^2). Attempts to resolve the possible disorder as well as to solve the structure in the centrosymmetric space group $Cmcm$ (assuming the disorder of the cation) to give better results failed. The difficulties in the refinement of the structure of **4a** may be the result of the peculiarities of the crystal packing which is made up of the nearly spherical PF_6^- anions and cylindrical $[(\eta\text{-}C_5H_5)Ru(\mu,\eta\text{-}C_5Me_5)Ru(\eta\text{-}C_5Me_5)]^+$ cations. Both types of ions may be involved in some kind of rotational motion in crystal, although this rotation is perhaps not completely free.

All calculations were performed with a PDP-II/23PLUS computer using the SDP-PLUS program package [37]. The final atomic coordinates and their equivalent isotropic temperature factors are given in Table 3.

References

1 H. Werner and A. Salzer, Synth. Inorg. Met.-Org. Chem., 2 (1972) 239.
2 A. Salzer and H. Werner, Angew. Chem., Int. Ed. Engl., 11 (1972) 930.
3 R.N. Grimes, Coord. Chem. Rev., 28 (1979) 47.
4 W. Siebert, Adv. Organomet. Chem., 18 (1980) 301.
5 G.E. Herberich, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 1, p. 381.
6 H. Werner, Angew. Chem., Int. Ed. Engl., 16 (1977) 1.
7 H. Werner, J. Organomet. Chem., 200 (1980) 335.
8 H. Werner and Th. Dernberger, J. Organomet. Chem., 198 (1980) 97.
9 E. Schumacher and R. Taubenest, Helv. Chim. Acta, 47 (1964) 1525.
10 J. Müller and K. Fenderl, Chem. Ber., 104 (1971) 2199.
11 R.B. King, J. Chem. Soc., Chem. Commun., (1969) 436.
12 J.W. Lauher, M. Elian, R.H. Summerville and R. Hoffmann, J. Am. Chem. Soc., 98 (1976) 3219.
13 A.R. Kudinov and M.I. Rybinskaya, Dokl. Akad. Nauk SSSR, 293 (1987) 1173.
14 A.Z. Kreindlin and M.I. Rybinskaya, unpublished results.
15 T.P. Gill and K.R. Mann, Inorg. Chem., 19 (1980) 3007.
16 T.P. Gill and K.R. Mann, J. Organomet. Chem., 216 (1981) 65.
17 T.P. Gill and K.R. Mann, Organometallics, 1 (1982) 485.
18 A.M. McNair, J.L. Schrenk and K.R. Mann, Inorg. Chem., 23 (1984) 2633.
19 A.M. McNair, D.C. Boyd and K.R. Mann, Organometallics, 5 (1986) 303.
20 A.M. McNair and K.R. Mann, Inorg. Chem., 25 (1986) 2519.
21 J.L. Schrenk, A.M. McNair, F.B. McCormick and K.R. Mann, Inorg. Chem., 25 (1986) 3501.
22 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Tetrahedron Lett., (1963) 1725.
23 A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova, and L.S. Polkovnikova, Koord. Khim., 1 (1975) 1252.
24 V.S. Kaganovich, A.R. Kudinov and M.I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1986) 492.

25 M.O. Albers, D.C. Liles, D.J. Robinson, A. Shaver, E. Singleton, M.B. Wiege, J.C.A. Boeyens and D.C. Levendis, Organometallics, 5 (1986) 2321.
26 E. Dubler, M. Textor, H.R. Oswald and A. Salzer, Angew. Chem., Int. Ed. Engl., 13 (1974) 135.
27 E. Dubler, M. Textor, H.R. Oswald and G.B. Jameson, Acta Crystallogr. B, 39 (1983) 607.
28 D.P. Freyberg, J.L. Robbins, K.N. Raymond and J.C. Smart, J. Am. Chem. Soc., 101 (1979) 892.
29 P. Seiler and J.D. Dunitz, Acta Crystallogr. B, 36 (1980) 2946.
30 R.S. Threlkel and J.E. Bercaw, J. Organomet. Chem., 136 (1977) 1.
31 R.B. King and M.B. Bisnette, J. Organomet. Chem., 8 (1967) 287.
32 T.D. Tilley, R.H. Grubbs and J.E. Bercaw, Organometallics, 3 (1984) 274.
33 U. Koelle and A. Salzer, J. Organomet. Chem., 243 (1983) C27.
34 M. Stebler-Röthlisberger, A. Salzer, H.B. Bürgi and A. Ludi, Organometallics, 5 (1986) 298.
35 N. Oshima, H. Suzuki and Y. Moro-oka, Inorg. Chem., 25 (1986) 3407.
36 A. Endo, K. Shimizu, G.P. Sato and M. Mukaida, Chem. Lett., (1984) 437.
37 B.A. Frenz, in H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld and G.C. Bassi (Eds.), Computing in Crystallography, Delft University Press, Delft, 1978, p. 64.