Use of [(η-C$_5$R$_5$)M]$^+$ fragments (M = Fe, R = H; M = Ru, R = H, Me) for synthesis of cationic clusters. X-Ray structure of [RuRh$_3$(η-C$_5$Me$_5$)(η-C$_5$H$_5$)$_3$(μ_3-CO)$_3$]PF$_6$

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Abstract

Tetrahedral cationic clusters [MRh$_3$(η-C$_5$R$_5$)(η-C$_5$H$_5$)$_3$(μ_3-CO)$_3$]PF$_6$ (M = Fe, R = H; M = Ru, R = H, Me) were synthesized by reaction of [Fe(η-C$_5$H$_5$)(η-Arene)]PF$_6$ or [Ru(η-C$_5$R$_5$)(MeCN)$_3$]PF$_6$ with Rh$_3$(η-C$_5$H$_5$)$_3$(μ-CO)$_3$. Their structure was confirmed by IR and NMR spectroscopy as well as by an X-ray diffraction study of [RuRh$_3$(η-C$_5$Me$_5$)(η-C$_5$H$_5$)$_3$(μ_3-CO)$_3$]PF$_6$.

Introduction

Cationic clusters of transition metals are rare as compared with neutral and anionic clusters. Especially rare are cationic clusters of middle transition metals. The most common methods of synthesis of such compounds are oxidation of neutral clusters [1] and protonation of neutral clusters [2,3].

$$M_xL_y \xrightarrow{\ -n \cdot e^-\ } \left[M_xL_y\right]^{n+}$$

$$M_xL_y \xrightarrow{\ +n \cdot H^+\ } \left[M_xL_yH_n\right]^{n+}$$
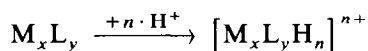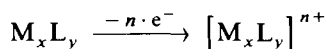
Besides protons other cationic unsaturated particles may also be used in addition reactions. Thus Mingos et al. have used [Au(PR$_3$)]$^+$ species in reactions with Pt$_3$(PR$_3'$)$_3$(μ-CO)$_3$ and have obtained [AuPt$_3$(PR$_3$)(PR$_3'$)$_3$(μ-CO)$_3$]$^+$ [4,5]. We prepared clusters [MRh$_3$(η-C$_5$R$_5$)(η-C$_5$H$_5$)$_3$(μ_3-CO)$_3$]$^+$ by addition of [M(η-C$_5$R$_5$)]$^+$ (M = Fe, R = H; M = Ru, R = H, Me) * to the neutral cluster Rh$_3$(η-C$_5$H$_5$)$_3$(μ-CO)$_3$ (1), which possesses basic properties and can easily be protonated [9]. [M(η-C$_5$R$_5$)]$^+$ particles were used for the first time by us for synthesis of clusters **.

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* For generation of these particles we used the methods developed by Mann et al. [6–8].
** For preliminary communication see ref. 10.

It should be noted that these particles, unlike [Au(PR$_3$)]$^+$, are not isolobal to proton.

Results and discussion

It was shown that irradiation of the solution of the cationic cyclopentadienyl-areneiron complex by visible light in the presence of **1** leads to the mixed FeRh$_3$ cluster **2**:
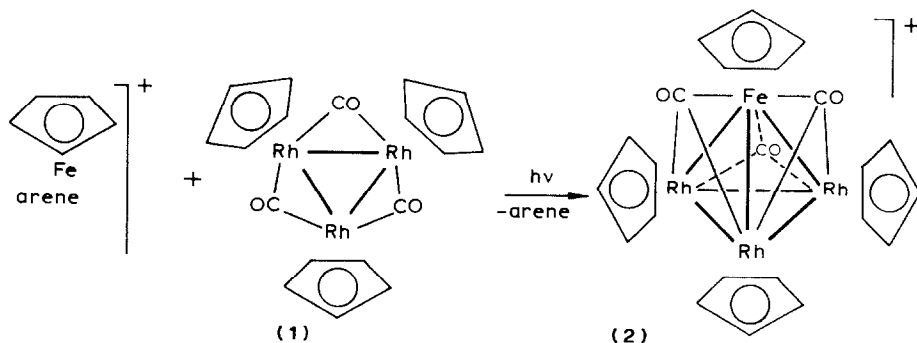
Arene = C$_6$H$_5$NO$_2$, C$_6$H$_6$, p-C$_6$H$_4$Me$_2$

It is noteworthy that the choice of arene in the [Fe(η-C$_5$H$_5$)(η-Arene)]PF$_6$ greatly influences the yield of the product. Thus, in the case of p-xylene, yield is 6%, for benzene it rises to 24% and for nitrobenzene it reaches 65%.

The use of nitrobenzene complex is also convenient due to the high speed of the reaction * and the simplicity with which product can be separated from the reaction mixture, arising from the low solubility of the nitrobenzene complex in CH$_2$Cl$_2$. Using benzene or p-xylene complexes, the product **2** can only be separated by chromatography; see Experimental.

An attempt to prepare the analogous Ru-containing cluster using nitrobenzene

(3, R=H ; 4, R=Me)

(1)

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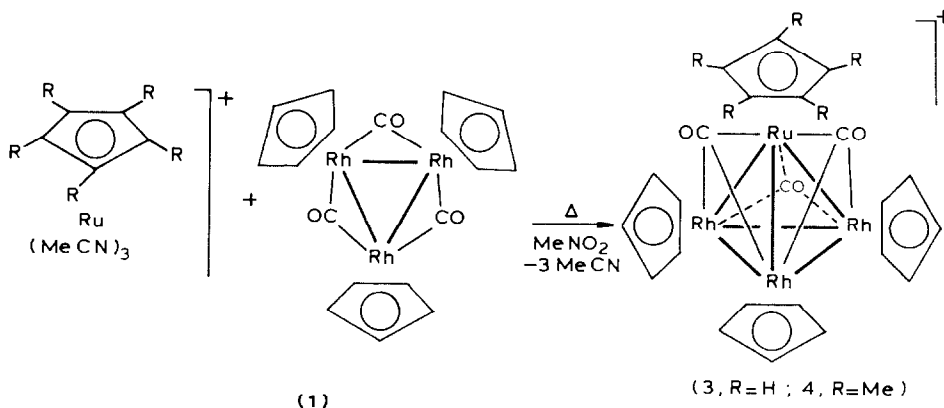
* It should be noted that the change of colour of solution from yellow-green to emerald-green is a useful guide for following the course of the reaction.

complex $[Ru(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_5NO_2)]PF_6$ was not successful. However, using the method of Mann [7,8] we prepared $RuRh_3$ clusters **3** and **4** from **1** and complexes $[Ru(\eta\text{-}C_5R_5)(MeCN)_3]PF_6$ (R = H, Me) by refluxing in nitromethane *.

Besides clusters **3** and **4** in both cases we obtained one and the same compound **5** for which on the basis of spectral data and elemental analysis ** we proposed the distorted octahedron structure of $[Rh_6(\eta\text{-}C_5H_5)_6(\mu_3\text{-}CO)_2](PF_6)_2$.

(5)
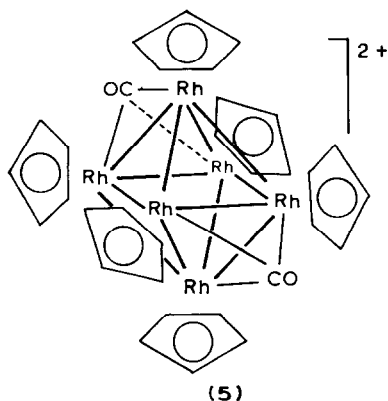
The compounds **2–4** are deep in colour. They are stable in the solid state in air and also in solution in the case of **3** and **4**. The compound **2** is photosensitive in solution. Irradiation with visible light leads to the initial cluster **1**:

(2)   (1)
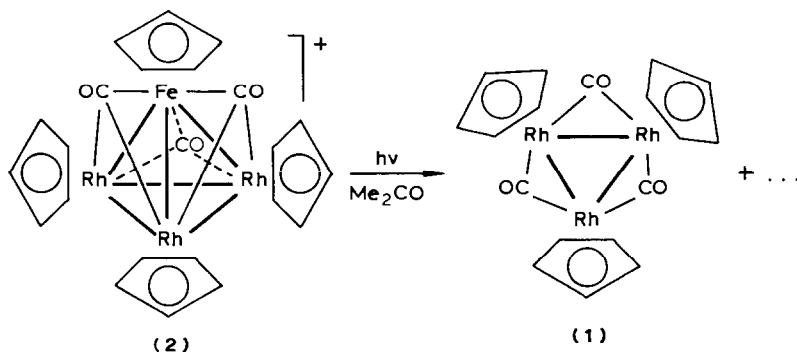
In this respect cluster **2** is similar to the arene complexes $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}arene)]^+$, which liberate arene under irradiation [6,11,12].

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* An attempt to use milder conditions (20–80°C) led to formation of a complex product mixture, which did not contain clusters **3** and **4**. It is likely that formation of these clusters demands generation from $[Ru(\eta\text{-}C_5R_5)(MeCN)_3]^+$ of the highly reactive species $[Ru(\eta\text{-}C_5R_5)]^+$ (which are probably solvated by $MeNO_2$).

** This compound is not soluble in ether or CH_2Cl_2 and only moderately soluble in acetone or $MeNO_2$. In the ^1H NMR spectrum one singlet is observed. In the IR spectrum only bands of μ_3-CO groups of cationic clusters are present (see Table 1). Unfortunately, crystals suitable for X-ray diffraction study were not obtained by us.
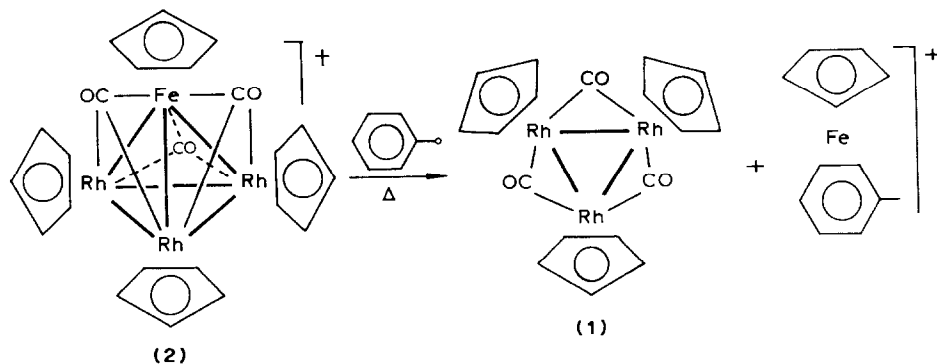
Table 1

Spectra of compounds studied

Compound	IR spectrum $\nu(CO)$, CH_2Cl_2	^1H NMR spectrum $\delta(^1H)$, acetone-d_6	^{13}C NMR spectrum $\delta(^{13}C)$, acetone-d_6
2	1748m, 1718vs	6.00 (s, 15H, C_5H_5Rh)	93.22 (s, C_5H_5Fe)
		5.16 (s, 5H, C_5H_5Fe)	90.13 (s, C_5H_5Rh)
3	1748m, 1714vs	5.97 (s, 15H, C_5H_5Rh)	99.35 (s, C_5H_5Ru)
		5.80 (s, 5H, C_5H_5Ru)	94.16 (s, C_5H_5Rh)
4	1748m, 1716vs	5.89 (s, 15H, C_5H_5Rh)	108.79 (C_5Me_5Ru)
		1.88 (s, 15H, C_5Me_5Ru)	94.00 (C_5H_5Rh)
			8.32 (C_5Me_5Ru)
5	1740m ^{a}, 1710vs	5.87 (s, C_5H_5Rh)	

^{a} In $MeNO_2$.

The cluster **2** is also thermally reactive. Thus, its refluxing in arene gives $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]^+$ and **1**, for example:

Thus, the triangular cluster **1** and arenes can substitute for each other in complexes with $[Fe(\eta\text{-}C_5H_5)]^+$ fragment.

In the ^1H NMR spectra of **2-4** (see Table 1), signals in the field of the cyclopentadienyl protons are observed. For **4** the signal $\delta = 1.88$ ppm of the methyl group is also observed. Intensities are in accordance with proposed structures.

The ^{13}C NMR spectra reproduce this picture. Unfortunately, signals of carbon atoms of μ_3-CO groups were not observed *.

In the IR spectra of **2-4** two bands in the field of μ_3-CO groups of cationic clusters are observed ($\nu = 1750$–1745 and 1720–1710 cm^{-1}) **. It should be noted that the bands of μ_3-CO groups for compounds **2-4** are practically coincident. This is however not surprising since a similar picture is also often observed for mono- and di-nuclear complexes.

The structures of complexes **2-4** were finally confirmed by an X-ray diffraction study of compound **4**.

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* This may be due to fast motion of CO groups.
** For example in the related $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-CO})_4]^{+\cdot}$ cluster the band of μ_3-CO is observed at 1700 cm^{-1} [13,14].

X-Ray crystal structure of 4

Cation **4** is shown in Fig. 1, and the most important bond distances and angles are listed in Table 2. The heterometallic tetrahedral core of **4** has small, but significant trigonal distortions with mean Ru–Rh bond distances of 2.696 and mean basal Rh–Rh bond distances of 2.616 Å.

The pentamethylated C_5Me_5 ligand at the Ru vertex is almost coplanar with the Rh_3 triangle (corresponding dihedral angles in the two indepedent molecules **4A** and **4B** being 2.0 and 3.8° respectively). Three $RuRh_2$ faces of the cluster are symmetrically bridged by μ_3-CO ligands with main $Ru–C_{(CO)}$ and $Rh–C_{(CO)}$ bond distances of 2.107 and 2.078 Å, respectively.

Carbonyl CO fragments in **4** are slightly (by 5–15°) deviated from being normal to corresponding triangular faces, towards the basal Rh_3 face. The stoichiometry of **4** corresponds to 60 valence electrons in the metal tetrahedron in accordance with EAN rule. All metal–metal bonds in **4** are therefore single.

Large values of thermal parameters of C atoms in cyclopentadienyl ligands together with the substantial scattering of C–C bond distances all point to these ligands being in rotational disorder. However, the atomic positions corresponding to the second orientation were partially revealed (4 atoms out of 5) only in the C_5Me_5 ligand at the Ru(1) vertex in the indepedent molecule **4A**. Based on trigonal symmetry of the cluster, one can suggest that the C_5Me_5 fragment is located in a disordered occupancy pattern over three positions, but the present precision of our knowledge of the structure does not allow us to confirm or reject this suggestion.

The tetrahedral Ru and Rh clusters (both homo- and heteronuclear) studied so far mostly have metal–metal bond distances between 2.70 and 2.80 Å (as, for example, in $Rh_4(CO)_{12}$ with an average Rh–Rh distance of 2.73 Å [15]). Deviations from this interval are typical in hydride clusters, where the lengths of M–M bonds,
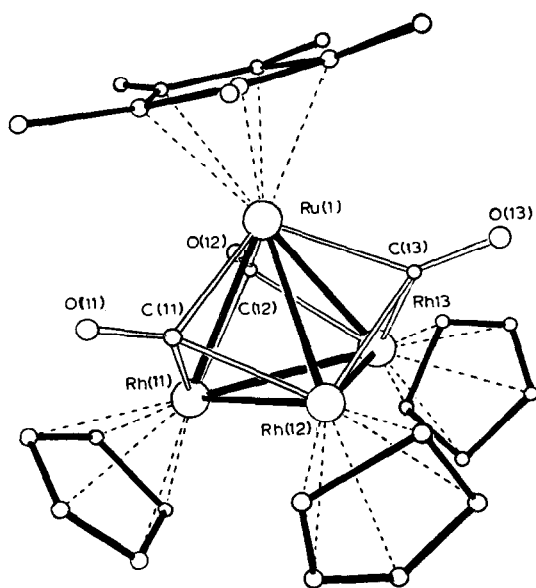

Fig. 1. Cation **4A** (H atoms are not shown).

Table 2

Bond lengths (Å) in cluster **4**

	Cation **4A**		Cation **4B**
Ru(1)–Rh(11)	2.699(1)	Ru(2)–Rh(21)	2.695(1)
Ru(1)–Rh(12)	2.698(1)	Ru(2)–Rh(22)	2.683(1)
Ru(1)–Rh(13)	2.694(1)	Ru(2)–Rh(23)	2.704(1)
Rh(11)–Rh(12)	2.619(1)	Rh(21)–Rh(22)	2.617(1)
Rh(11)–Rh(13)	2.613(2)	Rh(21)–Rh(23)	2.620(1)
Rh(12)–Rh(13)	2.614(2)	Rh(22)–Rh(23)	2.611(1)
Ru(1)–C(11)	2.086(8)	Ru(2)–C(21)	2.092(8)
Ru(1)–C(12)	1.994(13)	Ru(2)–C(22)	1.999(10)
Ru(1)–C(13)	2.127(8)	Ru(2)–C(23)	2.170(8)
Rh(11)–C(11)	2.12(2)	Rh(21)–C(21)	2.11(1)
Rh(12)–C(11)	2.08(2)	Rh(21)–C(22)	2.08(1)
Rh(11)–C(12)	2.15(1)	Rh(22)–C(21)	2.09(1)
Rh(13)–C(12)	2.15(1)	Rh(23)–C(22)	2.04(1)
Rh(12)–C(13)	2.06(1)	Rh(22)–C(23)	2.17(1)
Rh(13)–C(13)	2.09(1)	Rh(23)–C(23)	2.15(1)
Ru(1)–C(111)	2.24(1)	Ru(2)–C(211)	2.22(1)
Ru(1)–C(112)	2.26(1)	Ru(2)–C(212)	2.27(1)
Ru(1)–C(113)	2.03(5)	Ru(2)–C(213)	2.21(1)
Ru(1)–C(114)	2.30(2)	Ru(2)–C(214)	2.21(1)
Ru(1)–C(115)	2.21(2)	Ru(2)–C(215)	2.22(1)
Rh(11)–C(121)	2.19(1)	Rh(21)–C(221)	2.24(1)
Rh(11)–C(122)	2.30(1)	Rh(21)–C(222)	2.25(1)
Rh(11)–C(123)	2.16(1)	Rh(21)–C(223)	2.15(1)
Rh(11)–C(124)	2.21(1)	Rh(21)–C(224)	2.20(2)
Rh(11)–C(125)	2.11(1)	Rh(21)–C(225)	2.21(1)
Rh(12)–C(131)	2.31(2)	Rh(22)–C(231)	2.21(1)
Rh(12)–C(132)	2.18(1)	Rh(22)–C(232)	2.19(1)
Rh(12)–C(133)	2.25(2)	Rh(22)–C(233)	2.26(1)
Rh(12)–C(134)	2.32(1)	Rh(22)–C(234)	2.28(1)
Rh(12)–C(135)	2.30(2)	Rh(22)–C(235)	2.21(1)
Rh(13)–C(141)	2.22(1)	Rh(23)–C(241)	2.18(1)
Rh(13)–C(142)	2.23(1)	Rh(23)–C(242)	2.24(1)
Rh(13)–C(143)	2.19(2)	Rh(23)–C(243)	2.24(1)
Rh(13)–C(144)	2.17(1)	Rh(23)–C(244)	2.27(1)
Rh(13)–C(145)	2.27(1)	Rh(23)–C(245)	2.22(1)
Ru(1)–C(111R) [a]	2.12(4)	C(21)–O(21)	1.18(1)
Ru(1)–C(112R) [a]	2.19(1)	C(22)–O(22)	1.25(1)
Ru(1)–C(113R) [a]	2.35(4)	C(23)–O(23)	1.16(1)
Ru(1)–C(114R) [a]	2.20(4)	C–C(Cp*)	1.32–1.47(3)
Ru(1)–C(115R) [a]	2.23(2)	C–C(Cp)	1.21–1.60(2)
C(11)–O(11)	1.19(1)	C–C(Me)	1.51–1.63(2)
C(12)–O(12)	1.19(1)		
C(13)–O(13)	1.23(1)		
C–C(Cp*)	0.93–1.94(5)		
C–C(Cp)	1.20–1.67(3)		
C–C(Me)	1.42–1.74(4)		

[a] Second orientation of Cp* ligand (unrevealed in **4B** molecule).

connected with μ-H bridges, lie mostly between 2.9 and 3.1 Å [16,17]. The existence of μ_n-CO ligands usually has no influence on metal–metal bond distances [18].

Rh–Ru and Rh–Rh distances in cluster **4** agree well with this general rule. The
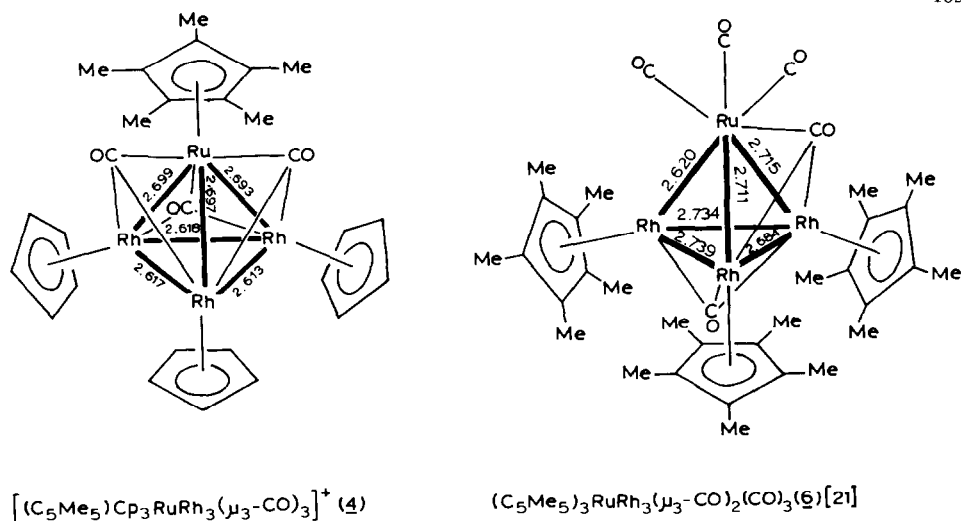
$[(C_5Me_5)Cp_3RuRh_3(\mu_3-CO)_3]^+$ (**4**) $(C_5Me_5)_3RuRh_3(\mu_3-CO)_2(CO)_3$(**6**)[21]

Fig. 2. M–M bond lengths in clusters **4** (average distances in two independent cations 4A and 4B) and **6** [19].

closest structural analogue of **4** is the mixed-metal tetrahedral cluster $(CO)_3RuRh_3$-$(\mu_3-CO)_2(C_5Me_5)_3$ (**6**) [19]. Molecules of **4** and **6** are shown in Fig. 2. **6** differs from **4** by the replacement of the C_5Me_5 ligand at the Ru vertex by three terminal CO ligands and by the replacement of each unsubstituted C_5H_5 ligand at Rh atoms by pentamethylated C_5Me_5. The coordination of triangular faces of the $RuRh_3$ tetrahedron by two μ_3-CO ligands in **6** is less symmetrical than that achieved by three triply-bridging carbonyls in **4**, the former structure displaying noticeable non-equivalence in M–M bond distances.

The above distortions of the metal framework in **4** and **6** may in principle have either a sterical or an electronic basis. Since the less symmetrical and more sterically crowded molecule of **6** is more distorted, sterical reasons for this effect seem to be more likely. To test this hypothesis we calculated the optimised geometry of **4** by the molecular mechanic (MM) theory.

The most important bond lengths in **4**, calculated within an MM framework, are compared with their experimental values in Table 3. The calculated values are in good quantitative agreement with the experimental, clearly showing the sterical basis for the distortion of the metal core. Minimal van der Waals energy of the ligand environment was reached by the elongation of three metal–metal edges at their apex with the larger C_5Me_5 ligand, to 2.698 Å, and the shortening of three other M–M edges between basal vertices with smaller C_5H_5 ligands to 2.634 Å from

Table 3

Experimental (X-ray) and calculated (MM) bond lengths of **4**

	d_{X-ray}	d_{calc}
Ru–Rh	2.69_7	2.70
Rh–Rh	2.61_6	2.63
M–C(CO)	2.09_4	2.10
Ru–C(Cp)	2.22_5	2.19
Rh–C(Cp)	2.21_8	2.24

the common initial value of 2.66 Å (note, that all MM parameters of Ru and Rh atoms in the cluster core were defined as equal). The key role in the distortions of the cluster, according to MM calculations, is played by the existence of three coordinated and one empty triangular faces in tetrahedron. In earlier MM calculations of $[CrFe_3(CO)_{14}]^{2-}$ heteronuclear cluster only qualitative agreement between calculated and X-ray data has been reached, although the same conclusion of the influence of ligand environment on M–M distances has been drawn [20].

Energy barriers to rotation of cyclopentadienyl ligands in **4** around the normals drawn to their planes, according to MM data, are about 0.2 kcal/mol. This very low value agrees well with the observed rotational disorder of Cp ligands in the crystal structure of **4**. Since the energy of thermal motion of atoms at the temperature of X-ray study ($kT = 0.3$ kcal/mol) is comparable with this barrier, the difficulties in the localization of the second orientation of Cp ligands in **4** may serve as indirect confirmation of the dynamical nature of the observed disorder.

Experimental

All reactions were carried out under argon, and reaction products were worked up in air. All solvents were dried by conventional techniques and were distilled under an atmosphere of dry argon. The compounds $1 \cdot \frac{1}{2}CH_2Cl_2$ [21], [Fe(η-C_5H_5)(η-C_6H_6)]PF$_6$, [Fe(η-C_5H_5)(η-$C_6H_4Me_2$)]PF$_6$ [22], [Fe(η-C_5H_5)(η-C_6H_5 NO$_2$)]PF$_6$ [23], [Ru(η-C_5H_5)(MeCN)$_3$]PF$_6$ [7] and [Ru(η-C_5Me_5)(MeCN)$_3$]PF$_6$ [8] were prepared by literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker WP 200SY spectrometer with SiMe$_4$ as internal reference. IR spectra were recorded on UR-20 spectrophotometer.

1. Synthesis of 2

(a) From p-xylene- or benzeneiron complexes. 0.315 g (0.5 mmol) of $1 \cdot \frac{1}{2}CH_2Cl_2$ and 0.5 mmol of cyclopentadienylareneiron complex were dissolved in 200 ml of CH$_2$Cl$_2$ and irradiated by visible light (250 W luminescence lamp) for 3 h (considerable increase of irradiation time leads to decreased yields because of photosensitivity of product **2**). After that the solution was evaporated and the remaining solid was chromatographed on an alumina column (2 × 60 cm) with acetone/ether (1 : 1) mixture. The emerald-green band was collected and the solvent was removed in vacuo. The purity of the product was controlled by ^{1}H NMR spectroscopy. If the product contains admixture of initial areneiron complex the chromatography should be repeated. Yields: 23% (from benzene complex), 6% (from *p*-xylene complex).

(b) From nitrobenzene complex. 0.195 g (0.5 mmol) of [Fe(η-C_5H_5)(η-$C_6H_5NO_2$)]PF$_6$ was dissolved in 5 ml of MeNO$_2$ and then $1 \cdot \frac{1}{2}CH_2Cl_2$ (0.315 g, 0.5 mmol) and CH$_2$Cl$_2$ (200 ml) were added. The mixture was irradiated with visible light (250 W luminescence lamp) for 1 h. Even after 5 min the solution begins to change from yellow-green to the emerald-green colour of the product. The solution was evaporated to a small volume, ether was added and the resulting precipitate was filtered off. This solid was extracted by CH$_2$Cl$_2$ and precipitation by ether was repeated. The resulting dark-green solid was dried *in vacuo*. Yield 65%. Anal. Found: C, 32.35; H, 2.44; P, 3.45. $C_{23}H_{20}F_6FeO_3PRh_3$ calcd.: C, 32.35; H, 2.37; P, 3.63%.

2. Synthesis of 3 (or 4) and 5

0.315 g (0.5 mmol) of $1 \cdot \frac{1}{2}CH_2Cl_2$ and 0.5 mmol of $[Ru(\eta-C_5R_5)(MeCN)_3]PF_6$ (R = H, Me) were placed in 10 ml of $MeNO_2$ and refluxed for 1 h. 20 ml of ether were added and the resulting solid was filtered off. This solid was extracted by CH_2Cl_2 and the solution obtained was chromatographed on an alumina column (2 × 30 cm) with acetone/ether (1 : 1) mixture. The deep-violet band was collected, the solvent was evaporated to a small volume and ether was added. The solid was filtered off and dried *in vacuo*. 3: Yield 43%. Anal. Found: C, 30.17; H, 2.38; P, 3.32. $C_{23}H_{20}F_6O_3PRuRh_3$ calcd.: C, 30.72; H, 2.25; P, 3.45%. 4: Yield 24%. Anal. Found: C, 34.72; H, 2.93; P, 3.21. $C_{28}H_{30}F_6O_3PRuRh_3$ calcd.: C, 34.70; H, 3.12; P, 3.20%. The remaining solid on the filter was extracted by $MeNO_2$. Ether was added to the extract and dark-brown precipitate was filtered and dried *in vacuo*. Yields of 5: 6% in the case of synthesis of 3 or 10% in the case of synthesis of 4. Anal. Found: C, 28.55; H, 2.22; P, 4.81. $C_{32}H_{30}F_{12}O_2P_2Rh_6$ calcd.: C, 28.39; H, 2.23; P, 4.57%.

3. Study of photochemical reactivitiy of 2

An NMR sample of 2 in acetone-d_6 was irradiated with sunlight for 2 days. After that according to ^1H NMR spectrum the signals of 2 were absent, but two new signals (with the ratio of intensities (3 : 1) were observed. One ($\delta = 5.62$ ppm) corresponded to 1 and another ($\delta = 6.00$ ppm) corresponded to product of transformation of $[Fe(\eta-C_5H_5)]^+$ particles.

4. Study of thermal reactivity of 2

0.128 g (0.15 mmol) of 2 was placed in 20 ml of toluene and refluxed for 2 h. The solvent was evaporated. According to ^1H NMR spectrum, the solid obtained was a mixture of 1 and $[Fe(\eta-C_5H_5)(\eta-C_6H_5Me)]^+$.

5. X-Ray structural study of 4

X-Ray study of 4 was carried out on Syntax $P2_1$ diffractometer at $-120°C$ ($\lambda(Mo-K_\alpha)$, graphite monochromator, $\theta/2\theta$ scan, $2\theta < 48°$). Crystals of 4 were obtained by recrystallization from an acetone/hexane mixture. 4 forms tetragonal crystals, $a = 31.50(1)$, $c = 13.451(7)$ Å, space group 14, $Z = 16$; 5136 independent reflections measured, 4565 observed reflexions ($I > 2\sigma$) used in calculations.

The structure of 4 was solved by direct methods using the MULTAN program and refined by block diagonal least squares technique in anisitropic approximation. Difference Fourier synthesis revealed the positions of fluorine atoms in one of three PF_6^- anions and of carbon atoms in one C_5Me_5 ligand, which correspond to second orientation of rotationally disordered fragments. The acetone solvate molecule was also revealed to be disordered over two positions. Occupancies and isotropic thermal parameters of atoms in these fragments were refined in subsequent least square cycles. Final results were $R = 0.028$, $R_w = 0.038$ by 4207 reflections with $I > 3\sigma$. Calculations were performed on an Eclipse S/200 computer using INEXTL programs [24]. Atom coordinates and the complete tables of bond distances and bond angles in 4 are deposited in the Cambridge Crystallographic Data Centre *.

Molecular mechanic calculation of the geometry of 4 using the MOLBD3 program

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* Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

Table 4

Standard geometrical parameters and force constants in MM calculations of cluster 4 [a]

	R_r (mdin/Å)	r_0 (Å)		K_0 (mdin/rad)	O_0 (deg)
M–M	6.0	2.66	M–M–M	0.5	60.0
M–C(CO)	2.0	2.09	M–M–C(CO)	0.3	50.0
M–Cp [b]	7.0	1.87	M–C(CO)–M	0.3	80.0
C–Cp [b]	7.0	1.23	M–M–Cp [b]	0.5	145.0
C–C	5.0	1.44	M–Cp–C [b]	0.5	90.0
C–O	12.0	1.20	M–C–O	0.05	133.0
C–H	4.6	1.10	C–C–C(Cp) [b]	0.5	108.0
			C–C–R [c]	0.5	126.0

[a] Parameters of van der Waals interactions see ref. 26. [b] Cp is centroid of cyclopentadienyl ligand. [c] R is a substituent in cyclopentadienyl ring.

[25] was carried out on the ES 1061 computer of the Computing Centre of the Academy of Sciences of the USSR. Mechanical model parameters, listed in Table 4, were chosen as in ref. 26.

The initial geometry for molecular mechanic calculations was taken from X-ray study excluding the M–M bond lengths, for which the average value of 2.66 Å was chosen. Centres of the planar cyclopentadienyl ligands were placed on the prolongations of the straight lines connecting vertices of the metal tetrahedron with the centres of opposite triangular faces. Each Cp plane was fixed normal to the corresponding line. The centres of Cp ligands, to which force constants and geometrical parameters in Table 4 were related, were used as dummy atoms with zero van der Waals radii.

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