

Synthesis and characterization of the $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)(\text{CO})_2]_2$ and $\text{Ru}_6(\mu_3\text{-H})(\eta^2\text{-}\mu_4\text{-CO})_2(\mu\text{-CO})(\text{CO})_{12}(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)$ complexes

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The reaction of $\text{Ru}_3(\text{CO})_{12}$ with tetramethyltrifluoromethylcyclopentadiene at various ratios of the reagents was studied. Refluxing of $\text{Ru}_3(\text{CO})_{12}$ with a sixfold excess of tetramethyltrifluoromethylcyclopentadiene in octane in an inert atmosphere gave a complex, which is, according to X-ray diffraction data, a dimer, $\text{trans-}[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)(\text{CO})_2]_2$. The reaction under the same conditions but starting from $\text{Ru}_3(\text{CO})_{12}$ and $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ in 2 : 1 molar ratio gave a hexaruthenium cluster $[\text{Ru}_6(\mu_3\text{-H})(\eta^2\text{-}\mu_4\text{-CO})_2(\mu\text{-CO})(\text{CO})_{12}(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)]$, which was characterized by IR as well as ^1H , ^{13}C , and ^{19}F NMR spectroscopy. According to X-ray diffraction data, an Ru_4 tetrahedron, in which two edges are bound by additional "bridging" Ru atoms, constitutes the frame of this compound. This complex has one ($\eta^5\text{-C}_5\text{Me}_4\text{CF}_3$) ligand, as well as one ($\mu_3\text{-H}$) and two ($\eta^2\text{-}\mu_4\text{-CO}$) groups.

Key words: hexaruthenium cluster, pentamethylcyclopentadiene, tetramethyltrifluoromethylcyclopentadiene, synthesis, X-ray diffraction study, IR spectra, ^1H , ^{13}C , and ^{19}F NMR spectra.

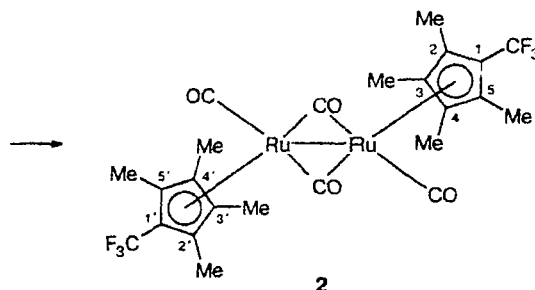
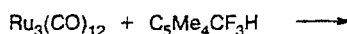
The study of the reaction of $\text{Ru}_3(\text{CO})_{12}$ with cyclopentadienes was started over 25 years ago, when it was shown^{1–3} that, depending on conditions, these reactions give different products. The most thorough study was performed in Ref. 2, in which the reagent ratio was varied over a broad range, from an equimolar ratio to a 30-fold excess of cyclopentadiene (refluxing in heptane, in an inert atmosphere, or in the presence of oxygen). As a result, the $[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ dimer and the $\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2\text{Ru}(\text{CO})_4$ trinuclear complex, as well as the four-nuclear $\text{Ru}_4\text{H}_4(\text{CO})_{12}$ hydride, were identified. In Ref. 3, a threefold excess of pentamethylcyclopentadiene was used in this reaction, and it was shown that refluxing for 4 h in decane gives the $[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]_2$ dimer (1).

Results and Discussion

We recently⁴ studied the reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{C}_5\text{Me}_5\text{H}$ (1.7 mol) with refluxing for 5 h in octane. It gave a new hexanuclear ruthenium complex, $\text{Ru}_6(\mu_3\text{-H})(\eta^2\text{-}\mu_4\text{-CO})_2(\mu\text{-CO})(\text{CO})_{12}(\eta^5\text{-C}_5\text{Me}_5)$, which was isolated from the reaction mixture by chromatography. When nickelocene was used as a donor of the C_5Me_5 ligand (at a $\text{Ru}_3(\text{CO})_{12}$ to NiCp_2 ratio of 1 : 1.25), a hexanuclear cluster of similar structure was also obtained. The structure of these two hexanuclear clusters was confirmed by X-ray diffraction analysis.⁴

In this work, we used the reaction of $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$ with the aim of obtaining new analogous hexanuclear ruthenium complexes. First, an excess of $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ was used. At a $\text{Ru}_3(\text{CO})_{12}$ to $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ ratio of 1 : 6, refluxing in octane for 2 h gave a new dimer, $[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)]_2$ (2), in 35% yield (Scheme 1).^{*} This dimer is an analog of known dimers with C_5H_5 and C_5Me_5 ligands.^{2,3}

Scheme 1



Reagents and conditions: 6 mmol of $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ per 1 mol of $\text{Ru}_3(\text{CO})_{12}$, refluxing in octane (124 °C), 2 h, Ar.

^{*} While this paper was being prepared for publication, a paper⁵ on the synthesis of dimer 2 appeared.

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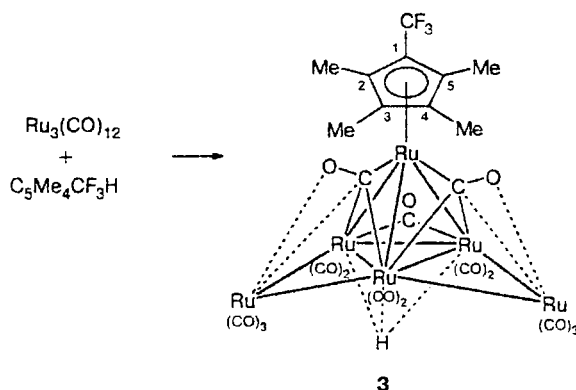
It was also shown by X-ray diffraction analysis (see below) that in the crystal, this dimer has a *trans*-configuration and contains two bridging carbonyl groups. Dimer **2** is stable in the crystalline state but changes on storage in solutions. For example, the metal carbonyl region of the IR spectrum (in CH_2Cl_2) of a freshly prepared solution of **2** crystals contains $\nu(\text{CO})$ absorption bands at 1950 and 1764 cm^{-1} characteristic of terminal and bridging CO groups, respectively. Two new $\nu(\text{CO})$ bands appear at 2048 and 2002 cm^{-1} when a solution of compound **2** in CH_2Cl_2 is stored, in addition to the bands at 1950 and 1764 cm^{-1} ; this indicates the presence of only terminal CO groups. The ^{19}F NMR spectrum of a freshly prepared solution of compound **2** in CH_2Cl_2 contains one signal of the CF_3 group at δ 25.07 corresponding to the *trans*-bridged isomer. When this solution is stored, the second signal at δ 23.71 appears in the spectrum. The integral intensity of this signal increases with time, and only one signal of the CF_3 group at δ 23.71 remains in the spectrum. This signal corresponds to the isomer containing no bridging CO groups. The IR spectrum of this solution after dilution has the same bands with $\nu(\text{CO})$ 2048 and 2002 cm^{-1} corresponding to terminal CO groups. The ^1H NMR spectrum (in CDCl_3) contains signals at δ 2.04 (6 H, $\alpha\text{-CH}_3$, $^5J_{\text{HF}} = 1$ Hz) and δ 1.72 (6 H, $\beta\text{-CH}_3$). The ^{13}C NMR spectra recorded at room temperature often show averaging of the signals of bridging and terminal carbonyls since the exchange of these groups is comparable with the NMR time scale (unlike in IR spectra, where the positions of terminal and bridging $\mu_4\text{-CO}$, $\mu_3\text{-CO}$, and $\mu_2\text{-CO}$ groups are in most cases distinctly different under these conditions). However, ^{13}C NMR signals can be observed in some cases for the ruthenium complexes studied; these signals can be assigned both to the terminal CO group ($\delta \approx 185\text{--}215$) and to bridging $\mu_2\text{-CO}$ ($\delta \approx 215\text{--}230$) and $\mu_4\text{-CO}$ ($\delta \approx 285\text{--}315$) groups.

We did not study the transformations of compound **2** in solutions, since our principal interest was focused on the possibility of the synthesis of hexanuclear complexes. However, we do not rule out that the observed changes could be caused by the possibility of transformation of the *trans*-bridged complex **2** to a "nonbridged" isomer,* which is less stable and can undergo further irreversible transformations. The irreversibility of changes occurring in the system is confirmed by the fact that the IR spectrum of the solid compound obtained upon concentrating a solution stored for some period of time contains only $\nu(\text{CO})$ bands at 2002 and 2048 cm^{-1} .

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ at a 2 : 1 reagent ratio gave a totally different result (Scheme 2). After refluxing the reaction mixture in octane for 5 h, its chromatography on SiO_2 gave the previously

unknown cluster **3** in 12% yield.** Its structure was confirmed by X-ray diffraction analysis (see below).

Scheme 2



Reagents and conditions: 1.0 mol of $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ per 2 mol of $\text{Ru}_3(\text{CO})_{12}$, refluxing in octane (124 $^\circ\text{C}$), 5 h, Ar.

The IR spectrum of complex **3** contains $\eta^2\text{-}\mu_4\text{-CO}$ bands at 1300–1500 cm^{-1} , which have been observed previously.^{4,7} The ^1H NMR spectrum (CDCl_3) contains signals at δ 2.16 (br.s., $\alpha\text{-CH}_3$), δ 1.85 ($\beta\text{-CH}_3$), and a $\mu_3\text{-H}$ hydride proton signal at δ -24.94, whose ratio of integral intensities was 6 : 6 : 1, respectively. The ^{13}C NMR spectrum (CDCl_3) of cluster **3** contains a signal of the C atom in the $\eta^2\text{-}\mu_4\text{-CO}$ group (δ 284.43 (2 C)) and a signal of the $\mu\text{-CO}$ -group (δ 213.07 (1 C)); there are also signals from 12 terminal carbonyl groups (see Experimental).

The structure of binuclear complex **2** is shown in Fig. 1. The bond lengths and some of the bond angles are listed in Tables 1 and 2. The molecule occupies a specific position in the crystallographic inversion center and is characterized by a *transoid* arrangement of the cyclopentadienyl and carbonyl ligands with respect to the Ru–Ru bond. The geometry of complex **2** is close to that found for analogous complex **1** containing the pentamethylcyclopentadienyl ligand.⁸ An interesting feature observed in such binuclear complexes (see the references cited in Ref. 8) is the distortion of the η^5 -coordination symmetry of the ligand caused by the dependence of the Ru– C_{Cp} distance on the π -acceptor ability of pseudo-*trans*-ligands. For example, the shortest Ru– C_{Cp} distance is observed for the atom located *trans* to the Ru–Ru bond (which corresponds to the C(7) atom in Fig. 1). The atoms which lie opposite the Ru– $\text{CO}_{\text{bridge}}$ bonds (the C(3) and C(6) atoms) are more distant from the ruthenium atom, and the atoms located opposite the Ru– CO_{term} bonds (the C(4) and C(5) atoms) form even longer Ru– C_{Cp} bonds. Such a distri-

* Such transformations have been reported in the literature⁶ for the $\text{Cp}[\text{Ru}(\text{CO})_2]_2$ complex, where $\text{Cp} = \text{C}_5\text{Me}_5$.

** It should be noted that during the chromatographic separation of complexes **2** and **3**, a difficultly separable mixture of $\text{Ru}_3(\text{CO})_{12}$ and ruthenium carbonyl hydrides is eluted first.

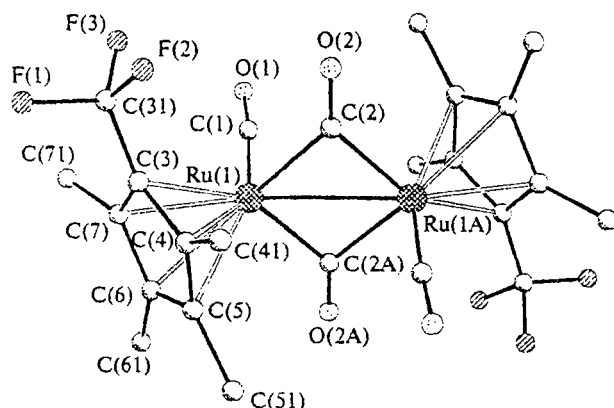


Fig. 1. Structure of complex 2.

bution of the majority of bond lengths is also observed in complex 2. However, a significant feature of its geometry is that the distance between the Ru atom and the CF_3 -substituted carbon atom in the Cp ring is noticeably shorter (Ru(1)—C(3) 2.231(3) Å; for comparison, an equivalent Ru(1)—C(6) bond length is 2.309(3) Å; these bond length in complex 1 are nearly the same). Such a noticeable shortening of the Ru—C CF_3 bond agrees well with that observed previously⁹ in $\{\text{C}_5(\text{CF}_3)\text{Me}_4\}\text{Fe}(\text{C}_5\text{H}_5)$ (4), in which the Fe—C CF_3 distance (2.007(6) Å) is also, on average, 0.05 Å shorter than the other Ru—C Cp bonds.

The main geometric parameters of hexanuclear cluster 3 (Fig. 2) are presented in Tables 1 and 2. In the crystal, the molecule occupies a specific position on the symmetry plane that passes through the Ru(1) and Ru(2) atoms and the middle of the Ru(3)—Ru(3A) bond. The metal frame constitutes a tetrahedron, whose two adjacent edges are bound by additional Ru(4) and Ru(4A) atoms. The Ru(4) atom is shifted by 0.427 Å from the tetrahedron base plane in the direction opposite to the Ru(2) atom; the angle between the Ru(1)Ru(3)Ru(3A) and Ru(1)Ru(3)Ru(4)

planes is 10.2°. The cluster contains three types of carbonyl ligands: 12 terminal groups (mean C=O bond length 1.129 Å), one μ_2 -bridging group (C(32)—O(32) 1.129(11) Å), and two relatively rare μ_4 groups. Each of these groups forms a bond with the Ru(4) and Ru(4A) atoms, which is naturally described as η^2 -coordination; the C=O bonds in these groups are elongated considerably (C(11)—O(11) 1.263(6) Å). The μ_3 -hydride ligand directly revealed in cluster 3 (see Experimental) is located below the base of the metal tetrahedron; the H(1) atom is shifted by 0.88 Å from the Ru(1)Ru(3)Ru(3A) plane, and the Ru(1)—H(1) and Ru(3)—H(1) distances are 1.76(6) and 1.89(7) Å, respectively.

Previously,^{4,7} the structure of three analogous complexes of general formula $\text{Ru}_6(\mu_3\text{-H})(\eta^2\text{-}\mu_4\text{-CO})_2(\mu\text{-CO})(\text{CO})_{12}(\eta^5\text{-C}_5\text{R}'_4\text{R}'')$, where $\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$,⁷ $\text{R}' = \text{R}'' = \text{H}$ or Me ,⁴ was determined and discussed. In view of this, we are not going to dwell on a description of the structure of this cluster, but will only note the differences coming from a change of the R' and R'' ligands in the Cp ligand. For example, the Ru—C Cp distances in cluster 3 ($\text{R}' = \text{Me}$, $\text{R}'' = \text{CF}_3$) are clearly non-equivalent, unlike those in the three clusters mentioned above. In particular, the distance to the carbon atom bound with the trifluoromethyl group (Ru(2)—C(01) 2.207(8) Å) is noticeably smaller than the two other crystallographically independent Ru—C Cp distances (Ru(2)—C(02) 2.272(5) and Ru(2)—C(03) 2.246(5) Å). The short Ru—C distance for the trifluoromethyl-substituted atom of the Cp ring can be explained by distortion of the Cp ligand planarity (unlike in dimers 2 and 1, all of whose Cp rings are virtually planar) observed as the shift of the C(01) atom from the plane of the other four ring atoms by 0.077 Å in the direction toward the Ru(2) atom.

Thus, considerable shortening of the distance from the metal atom to the CF_3 -bound atom of the Cp ring in comparison with the other M—C Cp bonds should be noted first of all for complexes 2, 3, and 4. The degree of this shortening is almost the same in all of the

Table 1. Bond lengths (*d*) in complexes 2 and 3

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å	Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
Complex 2							
Ru(1)—C(1)	1.872(3)	C(3)—C(7)	1.456(4)	Ru(1)—Ru(3)	2.8491(8)	F(1)—C(04)	1.363(12)
Ru(1)—C(2A)	2.043(3)	C(3)—C(31)	1.492(4)	Ru(2)—C(11)	1.938(5)	F(2)—C(04)	1.336(8)
Ru(1)—C(2)	2.056(3)	C(4)—C(5)	1.440(4)	Ru(2)—C(01)	2.207(8)	O(11)—C(11)	1.263(6)
Ru(1)—C(3)	2.231(3)	C(4)—C(41)	1.502(4)	Ru(2)—C(03)	2.246(5)	O(12)—C(12)	1.138(10)
Ru(1)—C(7)	2.245(3)	C(5)—C(6)	1.431(4)	Ru(2)—C(02)	2.272(5)	O(13)—C(13)	1.147(10)
Ru(1)—C(6)	2.309(3)	C(5)—C(51)	1.500(4)	Ru(2)—Ru(3)	2.8472(8)	O(31)—C(31)	1.127(8)
Ru(1)—C(4)	2.314(3)	C(6)—C(7)	1.440(4)	Ru(3)—C(31)	1.893(6)	O(32)—C(32)	1.129(11)
Ru(1)—C(5)	2.329(3)	C(6)—C(61)	1.514(4)	Ru(3)—C(33)	1.914(6)	O(33)—C(33)	1.121(8)
Ru(1)—Ru(1A)	2.7621(10)	C(7)—C(71)	1.507(4)	Ru(3)—C(32)	2.133(7)	O(41)—C(41)	1.121(8)
F(1)—C(31)	1.333(4)	Complex 3				O(42)—C(42)	1.131(7)
F(2)—C(31)	1.336(4)	Ru(1)—C(12)	1.884(7)	Ru(3)—C(11)	2.212(5)	O(43)—C(43)	1.126(9)
F(3)—C(31)	1.352(5)	Ru(1)—C(13)	1.907(8)	Ru(3)—Ru(3A)	2.7199(9)	C(01)—C(02)	1.429(7)
O(1)—C(1)	1.151(4)	Ru(1)—C(11)	2.230(5)	Ru(3)—Ru(4)	2.7664(8)	C(01)—C(04)	1.477(12)
O(2)—C(2)	1.185(4)	Ru(1)—Ru(2)	2.7750(10)	Ru(4)—C(43)	1.882(7)	C(02)—C(03)	1.438(8)
C(3)—C(4)	1.441(4)	Ru(1)—Ru(4)	2.8294(7)	Ru(4)—C(42)	1.923(6)	C(02)—C(05)	1.489(9)
				Ru(4)—C(41)	1.928(6)	C(03)—C(03A)	1.418(11)
				Ru(4)—O(11)	2.135(4)	C(03)—C(06)	1.489(8)
				Ru(4)—C(11)	2.299(5)		

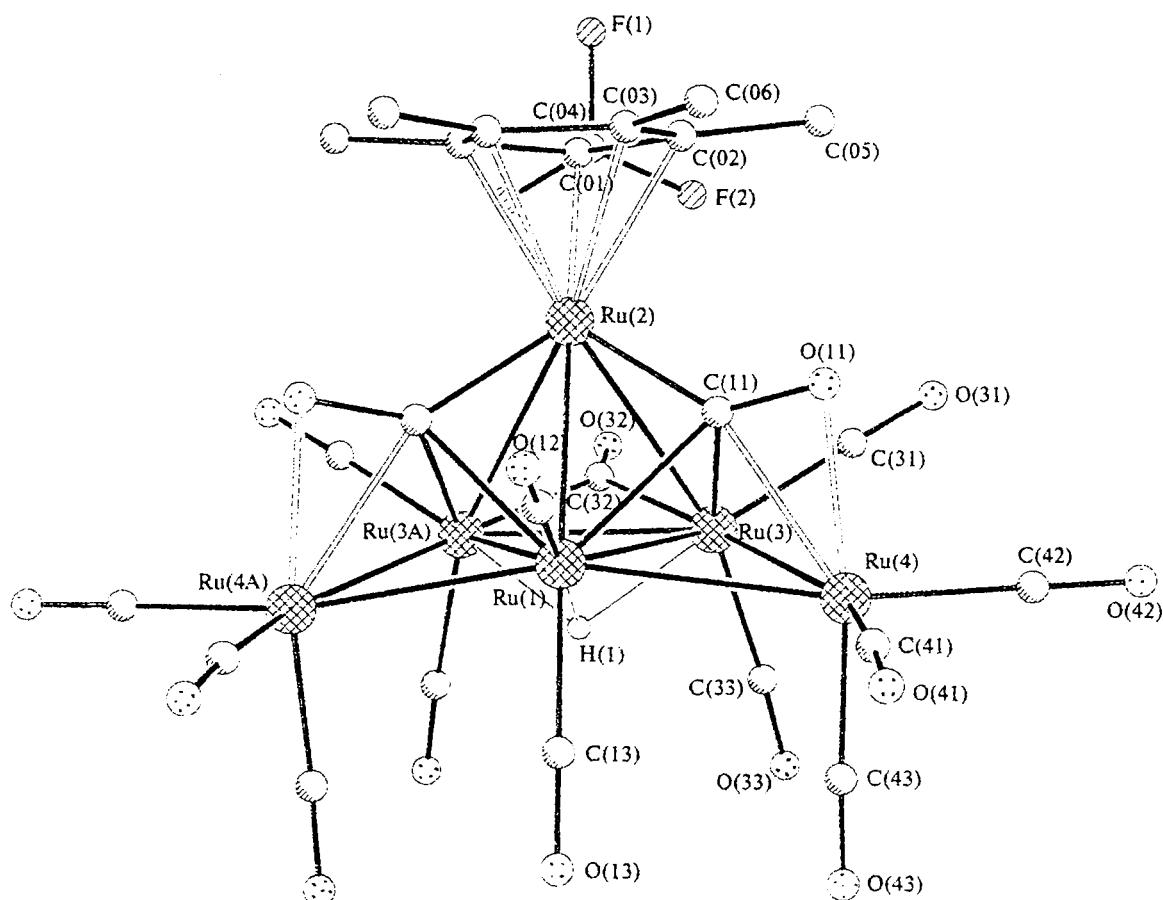


Fig. 2. Structure of cluster 3.

Table 2. Main bond angles (ω) in complexes 2 and 3

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Complex 2		Complex 3			
C(1)—Ru(1)—C(2A)	93.05(12)	C(6)—Ru(1)—Ru(1A)	135.90(7)	Ru(3)—Ru(4)—Ru(1)	61.20(2)
C(1)—Ru(1)—C(2)	91.56(12)	C(4)—Ru(1)—Ru(1A)	111.77(7)	O(11)—C(11)—Ru(2)	138.1(4)
C(2A)—Ru(1)—C(2)	95.28(11)	C(5)—Ru(1)—Ru(1A)	110.74(7)	O(11)—C(11)—Ru(3)	124.6(4)
C(1)—Ru(1)—C(3)	110.71(12)	O(1)—C(1)—Ru(1)	176.3(3)	Ru(2)—C(11)—Ru(3)	86.4(2)
C(2A)—Ru(1)—C(3)	151.62(10)	O(2)—C(2)—Ru(1A)	137.8(2)	O(11)—C(11)—Ru(1)	125.8(4)
C(2)—Ru(1)—C(3)	99.22(11)	O(2)—C(2)—Ru(1)	137.5(2)	Ru(2)—C(11)—Ru(1)	83.2(2)
C(1)—Ru(1)—C(7)	94.27(12)	Ru(1A)—C(2)—Ru(1)	84.72(11)	Ru(3)—C(11)—Ru(1)	79.8(2)
C(2A)—Ru(1)—C(7)	128.45(11)	Complex 3		O(32)—C(32)—Ru(3)	140.3(2)
C(2)—Ru(1)—C(7)	135.35(11)	C(11)—Ru(1)—C(11A)	87.5(2)	Ru(3)—C(32)—Ru(3A)	79.2(3)
C(1)—Ru(1)—C(6)	114.41(12)	Ru(2)—Ru(1)—Ru(4)	95.234(14)	C(02A)—C(01)—C(02)	109.2(7)
C(2A)—Ru(1)—C(6)	94.99(10)	Ru(4A)—Ru(1)—Ru(4)	161.21(3)	C(02)—C(01)—C(04)	124.6(4)
C(2)—Ru(1)—C(6)	151.44(10)	Ru(2)—Ru(1)—Ru(3)	60.81(2)	C(04)—C(01)—Ru(2)	130.1(7)
C(1)—Ru(1)—C(4)	147.29(12)	Ru(4A)—Ru(1)—Ru(3)	114.61(2)	C(01)—C(02)—C(03)	106.7(5)
C(2A)—Ru(1)—C(4)	119.20(10)	Ru(4)—Ru(1)—Ru(3)	58.31(2)	C(01)—C(02)—C(05)	128.5(6)
C(2)—Ru(1)—C(4)	90.77(10)	Ru(3A)—Ru(1)—Ru(3)	57.02(2)	C(03)—C(02)—C(05)	124.7(6)
C(1)—Ru(1)—C(5)	150.35(12)	C(11)—Ru(2)—C(11A)	105.5(3)	C(05)—C(02)—Ru(2)	128.1(4)
C(2A)—Ru(1)—C(5)	90.99(10)	Ru(1)—Ru(2)—Ru(3)	60.88(2)	C(03A)—C(03)—C(02)	108.5(3)
C(2)—Ru(1)—C(5)	117.31(10)	Ru(3A)—Ru(2)—Ru(3)	57.06(2)	C(03A)—C(03)—C(06)	124.4(4)
C(1)—Ru(1)—Ru(1A)	93.42(9)	Ru(3A)—Ru(3)—Ru(4)	121.162(14)	C(02)—C(03)—C(06)	126.9(5)
C(2A)—Ru(1)—Ru(1A)	47.83(8)	Ru(3A)—Ru(3)—Ru(2)	61.468(11)	C(06)—C(03)—Ru(2)	126.2(4)
C(2)—Ru(1)—Ru(1A)	47.44(8)	Ru(4)—Ru(3)—Ru(2)	95.02(2)	F(2A)—C(04)—F(2)	106.2(9)
C(3)—Ru(1)—Ru(1A)	140.36(7)	Ru(3A)—Ru(3)—Ru(1)	61.490(12)	F(2)—C(04)—F(1)	104.8(6)
C(7)—Ru(1)—Ru(1A)	171.69(7)	Ru(4)—Ru(3)—Ru(1)	60.49(2)	F(2)—C(04)—C(01)	114.7(5)
		Ru(2)—Ru(3)—Ru(1)	58.31(2)	F(1)—C(04)—C(01)	110.6(9)

mentioned complexes with the CF_3 -substituted ligand and is most probably determined by the electron-withdrawing properties of the trifluoromethyl group (evidently, neither the metal atom nor the nature of other ligands play an important role).

It is important to note in conclusion that, as shown in this work, the reaction of the $\text{Ru}_3(\text{CO})_{12}$ complex with $\text{C}_5\text{Me}_4\text{CF}_3\text{H}$ occurs similarly to the reaction with $\text{C}_5\text{Me}_5\text{H}$, and similar dependences of the product composition on the ratio of reagents are observed in both cases.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Jeol JNM GSX 270 FT NMR instrument, at 270.17 (^1H) and 67.94 (^{13}C) MHz, respectively, and on a Bruker WP-400-SY spectrometer at 400.13 MHz (^1H). ^{19}F NMR spectra were recorded on a Bruker WP-200-SV instrument at 188.312 with TFA as the standard. IR spectra were obtained on a Specord-80 instrument in heptane, hexane, and CH_2Cl_2 solutions, as well as in Vaseline oil.

The $[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)]_2$ complex (2). A mixture of $\text{Ru}_3(\text{CO})_{12}$ (0.5 g, 0.78 mmol) and octane (25 mL) was refluxed for 0.5 h in an argon atmosphere. $\text{C}_5\text{Me}_4\text{CF}_3$ (1.2 mL, 0.89 g, 4.68 mmol) was added, and refluxing was continued for 2 h. After cooling, the solution was decanted. The precipitate was washed with hexane, and the well-shaped crystals were dried *in vacuo* to give 0.232 g (35% with respect to $\text{Ru}_3(\text{CO})_{12}$) of yellow-orange crystals of compound 2. Chromatographic separation of the solution on a column with SiO_2 (230–400 mesh) using a CHCl_3 –hexane mixture with increasing polarity of the eluting mixture gave an additional amount (87 mg) of compound 2. Found (%): C, 41.71; H, 3.48. $\text{C}_{24}\text{H}_{24}\text{O}_4\text{F}_6\text{Ru}_2$. Calculated (%): C, 41.62; H, 3.49. IR (Vaseline oil), ν/cm^{-1} : 1243 and 1166 (CF_3)¹⁰. ^{13}C NMR

(CDCl_3), δ : 224.14 ($\mu_2\text{-CO}$); 201.93 and 196.22 (CO); 128–123 (unresolved quint, CF_3). Two signals in around δ 112 (presumably C(1) and C(1') of Cp rings), 105–103 (C(2, 5), C(2', 5') and C(3, 4), C(3', 4'), Cp); 10.04 ($\text{Me-C}(2, 5, 2', 5')$) and 8.6 ($\text{Me-C}(3, 4, 3', 4')$).

$\text{Ru}_6(\mu_3\text{-H})(\eta^2\text{-}\mu_4\text{-CO})_2(\mu\text{-CO})(\text{CO})_{12}(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)$ cluster (3). A mixture of $\text{Ru}_3(\text{CO})_{12}$ (0.39 g, 0.62 mmol) and octane (25 mL) was refluxed for 0.5 h in an argon atmosphere. $\text{C}_5\text{Me}_4\text{CF}_3$ (0.059 g, 0.31 mmol) was added, and refluxing was continued for 5 h. The octane was evaporated *in vacuo*, and the residue was chromatographed on a column with SiO_2 (70–230 mesh) using a petroleum ether (b.p. 40–60 °C)– CH_2Cl_2 mixture with increasing polarity of the eluent. First, a mixture of the original $\text{Ru}_3(\text{CO})_{12}$ and hydridoruthenium carbonyls (~135 mg) was separated, and then 35 mg (12%) of dark brown crystals of compound 3 and 10 mg of a brown compound were obtained (the structure of the latter compound was not determined). IR (heptane), $\nu(\text{CO})/\text{cm}^{-1}$: 2090 m, 2068 s, 2062 m, 2034 s, 2022 m, 2012 m, 1984 w, 1960 w, 1948 w (term. CO); 1892 w, 1856 w ($\mu\text{-CO}$); 1300–1500 ($\eta^2\text{-}\mu_4\text{-CO}$). ^1H NMR (CDCl_3), δ : 2.16 (br.s, $\alpha\text{-CH}_3$, Cp); 1.85 ($\beta\text{-CH}_3$, Cp); –24.94 ($\mu_3\text{-H}$) with integral intensity ratio 6 : 6 : 1, respectively.

^{13}C NMR (CDCl_3), δ : 284.43 (2 C, $\eta^2\text{-}\mu_4\text{-CO}$); 213.07 ($\mu\text{-CO}$); 204.58, 200.0, 196.60, 191.84 (2 C), 189.75, 189.70 (2 C), 185.67 (2 C), 185.37 (2 C), 12 term. CO groups; 126.40 (q, C-1, Cp, $^2J_{\text{CF}} \leq 82.73$ Hz); 124.19 (q, CF_3 , Cp, $^1J_{\text{CF}_3} = 271.6$ Hz); 107.54 (q, C-1 and C-5, Cp); and 104.85 (q, C-3 and C-4, Cp), the integral intensity ratio is 1 : 1 : 2 : 2, respectively; 29.72 ($\text{Me-C}(3, 4)$) and 9.59 ($\text{Me-C}(2, 5)$), $^4J_{\text{CF}} \leq 3.34$ Hz).

X-ray diffraction study of complexes 2 and 3. The crystals of compound 2 were grown by slow evaporation of the solvent (CHCl_3).

The crystals of compound 3 were grown by slow evaporation of the solvent (a hexane–chloroform mixture).

The crystallographic data and parameters obtained by X-ray diffraction analysis of complexes 2 and 3 are presented in Table 3.

Table 3. Crystallographic data for complexes 2 and 3

Parameter	2	3
Molecular formula	$\text{C}_{24}\text{H}_{24}\text{F}_6\text{O}_4\text{Ru}_2$	$\text{C}_{25}\text{H}_{13}\text{F}_3\text{O}_{15}\text{Ru}_6$
Molecular mass	692.57	1216.77
Crystal syngony	Monoclinic	Monoclinic
Temperature/K	193	293
Space group	$P2_1/n$	$P2_1/m$
$a/\text{\AA}$	8.539(4)	9.581(2)
$b/\text{\AA}$	9.801(4)	17.480(3)
$c/\text{\AA}$	15.089(5)	10.670(2)
β/deg	97.17(3)	111.88(2)
$V/\text{\AA}^3$	1252.9(9)	1658.3(6)
Z	2	2
Calculated density/ g cm^{-3}	1.836	2.437
Absorption coefficient/ cm^{-1}	12.79	27.47
$F(000)$	684	1148
Diffractometer	Syntex $P2_1$	Enraf-Nonius CAD4
Irradiation	Mo-K α	
	graphite monochromator	
$\lambda/\text{\AA}$	0.71073	0.71073
$\theta_{\text{max}}/\text{deg}$	27°	30°

Parameter	2	3
Scan type	$\theta/2\theta$	$\theta/5/3\theta$
Number of independent reflections	2563	4684
Correction for absorption	Not introduced	Introduced using the DIFABS program ¹¹
R_1 (on F)	0.0321	0.0670
Number of reflections with $I > 2\sigma(I)$	2344	3819
wR_2 (on F^2)	0.1098	0.1935
Weighing scheme	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = (F_0^2 + 2 F_c^2)/3$, $a = 0.0659$ $b = 0.7502$	
Number of reflections, used for refinement	2505	4625
GOF	1.047	1.020
Number of refined parameters	211	240
Residual electron density, min/max/ $\text{e} \cdot \text{\AA}^{-3}$	–0.710/0.919	–1.640/1.564

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3/\text{\AA}^2$) in structures **2** and **3**

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Complex 2					Complex 3				
Ru(1)	5909(1)	-5166(1)	4312(1)	16(1)	Ru(1)	-3971(1)	2500	-5641(1)	24(1)
F(1)	5401(3)	-5939(4)	1379(1)	84(1)	Ru(2)	-2293(1)	2500	-2887(1)	26(1)
F(2)	3331(2)	-5715(3)	2027(1)	51(1)	Ru(3)	-1156(1)	1722(1)	-4651(1)	28(1)
F(3)	4995(3)	-4090(3)	2080(2)	65(1)	Ru(4)	-3764(1)	903(1)	-5969(1)	30(1)
O(1)	6824(3)	-2193(2)	4247(2)	49(1)	F(1)	1357(8)	2500	1248(7)	88(3)
O(2)	2460(2)	-4423(3)	3808(1)	31(1)	F(2)	1537(5)	1889(3)	-421(6)	75(1)
C(1)	6458(4)	-3318(3)	4299(2)	27(1)	O(11)	-3749(4)	996(2)	-3969(4)	33(1)
C(2)	3568(3)	-4692(3)	4333(2)	20(1)	O(12)	-7096(8)	2500	-5573(9)	60(2)
C(3)	5763(3)	-6056(3)	2943(2)	23(1)	O(13)	-5207(8)	2500	-8725(6)	53(2)
C(4)	5223(3)	-7118(3)	3492(2)	24(1)	O(31)	446(7)	384(4)	-2921(7)	75(2)
C(5)	6543(3)	-7455(3)	4145(2)	22(1)	O(32)	1857(7)	2500	-2975(8)	55(2)
C(6)	7877(3)	-6639(3)	4001(2)	22(1)	O(33)	82(6)	1357(4)	-6817(6)	63(1)
C(7)	7410(3)	-5753(3)	3253(2)	22(1)	O(41)	-7124(6)	665(3)	-7494(6)	66(2)
C(31)	4881(4)	-5464(4)	2117(2)	37(1)	O(42)	-2810(6)	-775(3)	-5638(7)	58(1)
C(41)	3658(4)	-7836(4)	3368(3)	36(1)	O(43)	-3278(8)	963(4)	-8594(6)	76(2)
C(51)	6597(5)	-8570(3)	4829(2)	36(1)	C(01)	-779(9)	2500	-742(8)	42(2)
C(61)	9515(4)	-6764(3)	4510(2)	31(1)	C(02)	-1698(6)	1833(3)	-929(5)	34(1)
C(71)	8482(5)	-4831(4)	2804(3)	34(1)	C(03)	-3229(6)	2094(3)	-1361(5)	35(1)
H(41A)	3553(41)	-8405(42)	2825(26)	36(9)	C(04)	880(10)	2500	-125(10)	52(2)
H(41B)	2873(61)	-7269(58)	3283(37)	68(15)	C(05)	-1219(9)	1020(4)	-666(7)	53(2)
H(41C)	3510(40)	-8475(41)	3793(24)	30(9)	C(06)	-4595(8)	1613(4)	-1641(6)	50(2)
H(51A)	6900(62)	-9351(64)	4610(37)	69(15)	C(11)	-3105(6)	1618(3)	-4026(5)	27(1)
H(51B)	5566(55)	-8780(46)	4960(26)	43(10)	C(12)	-5921(8)	2500	-5602(9)	34(2)
H(51C)	7103(52)	-8262(51)	5368(33)	53(12)	C(13)	-4747(9)	2500	-7567(8)	38(2)
H(61A)	10291(65)	-6117(69)	4275(38)	85(17)	C(31)	-164(7)	884(3)	-3556(7)	41(1)
H(61B)	9446(46)	-6769(43)	5147(28)	39(10)	C(32)	621(10)	2500	-3633(9)	39(2)
H(61C)	9898(49)	-7674(51)	4412(31)	52(12)	C(33)	-372(6)	1470(3)	-6006(6)	38(1)
H(71A)	9115(83)	-4475(77)	3248(51)	106(23)	C(41)	-5896(7)	739(3)	-6880(7)	41(1)
H(71B)	7909(52)	-3989(57)	2567(33)	59(13)	C(42)	-3148(6)	-151(3)	-5751(6)	39(1)
H(71C)	9077(85)	-5292(71)	2425(55)	98(23)	C(43)	-3468(7)	959(4)	-7614(7)	45(1)
					H(1)	-2233(117)	2500	-5855(111)	50(9)

Both structures were solved by the direct method and refined with respect to F^2 by full-matrix least squares method in the anisotropic approximation for non-hydrogen atoms. All hydrogen atoms in complex **2** and the μ^3 -hydride atom in complex **3** were found directly and included in refinement in the isotropic approximation. The remaining hydrogen atoms in complex **3** were positioned geometrically and refined using the "riding" model. All calculations were done using the SHELXTL PLUS 5 program complex (gamma-version). The atomic coordinates in complexes **2** and **3** are listed in Table 4.

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