Russian Chemical Bulletin, International Edition, Vol. 54, No. 8, pp. 1813—1818, August, 2005

Replacement of Fe atoms by Ru in a carbidocarbonyl cluster $[Fe_6C(CO)_{16}]^{2-}$. Structures of reaction products

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The reaction of the carbidocarbonyl cluster $[Fe_6C(CO)_{16}]^{2-}$ with ruthenium(IV) hydroxochloride $Ru(OH)Cl_3$ was studied. At 90—100 °C, the reaction gave products of replacement of Fe atoms by Ru in the $[Fe_6C(CO)_{16}]^{2-}$ cluster along with degradation products. Treatment of the replacement products with $FeCl_3$ afforded the $[Fe_{2.96}Ru_{3.04}C(CO)_{17}]$ compound (**1**), which was characterized by X-ray diffraction analysis. The crystals of cluster **1** are composed of two types of octahedral molecules (**1a** and **1b**) in a ratio of 2 : 1. Molecules **1a** are in general positions, and molecules **1b** are located on twofold axes. In both molecules, the Fe and Ru atoms are disordered over four of six positions.

Key words: crystal structure, heterometallic carbidocarbonyl clusters, ruthenium, iron.

Heterometallic clusters are important members in a series of transition metal compounds and are of particular interest for the stereochemistry and materials science.[1,2] Heterometallic carbidocarbonyl clusters[1—4] occupy a special place among these promising compounds. More than 90 such clusters containing from one to four different metals (Fe, Co, Ni, Cr, W, Rh, Pd, Pt, Cu, and Ru)[1—4] have been synthesized and characterized.

We have developed procedures for the synthesis of such clusters with specified geometry for a wide range of metals. The most promising method for the preparation of such clusters is based on the indirect replacement of vertices in a metal polyhedron. This process generally involves the removal of a vertex from the metal core followed by the addition of another metal at this position.[1,5—9] The synthetic potential of this method is far from being exhausted. Hence, we continued studies of transmetallation of $[Fe_6C(CO)_{16}]^{2-}$, extended our investigation to a wider range of metallating systems, and gave greater attention to the conditions of this complex reaction accompanied by oxidative degradation of the starting cluster and products of its transmetallation.

In the present study, we investigated the reaction of the carbidocarbonyl cluster $[Fe_6C(CO)_{16}]^{2-}$ with ruthenium(IV) hydroxochloride $Ru(OH)Cl_3$. We isolated products of replacement of Fe by Ru in the $[Fe_6C(CO)_{16}]^{2-}$ cluster along with the earlier described[10,11] derivatives of oxidative degradation products, the clusters $(\mu\text{-H})Ru_2Fe_2PdC(CO)_{12}(\eta^3\text{-}C_{10}H_{15})$ and $Fe_3RuPd_2C(CO)_{12}(\eta^3\text{-}C_{10}H_{15})_2$.

Results and Discussion

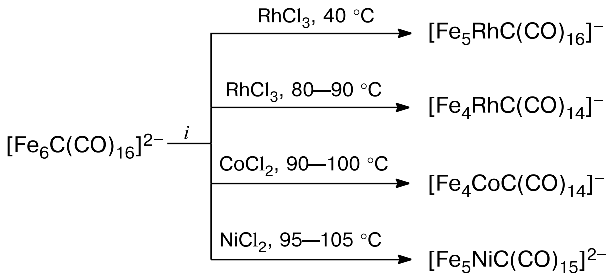
To perform successful replacement of one metal with another, a combination of the following two conditions is required: redox interaction of the metal carbonyl anion with metal chloride and simultaneous carbonylation of the resulting zero-valent metal.[12—15]

Studies in organometallic chemistry showed that binary halides of both main-group and transition metals are most reactive in transmetallation reactions.[16,17] Earlier, we have studied the reactions of the cluster anions $[Fe_6C(CO)_{16}]^{2-}$ and $[Fe_5C(CO)_{14}]^{2-}$ with a number of transition metal halides.[12,17,18] It was found that these dianions, like other metal carbonyls, can reduce transition metal halides.

For example, heating of rhodium trichloride with $[Fe_6C(CO)_{16}]^{2-}$ in diglyme leads to the replacement of the Fe atom with Rh giving rise to heterometallic clusters[18—21] (Scheme 1). In the octahedral cluster, the replacement of iron occurs under milder conditions compared to that in the tetragonal-pyramidal cluster. Apparently, the former reaction performed at high temperature involves both the replacement of iron by rhodium and thermal degradation of the initially formed Fe_5Rh cluster.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1761—1766, August, 2005.

Scheme 1



i. Diglyme.

Cobalt(II) chloride does not react with $[Fe_6C(CO)_{16}]^{2-}$ in diglyme at <60 °C. At 90—100 °C, the reaction produces the heterometallic cluster $[Fe_4CoC(CO)_{14}]^-$ (see Scheme 1).[12,19] During the reaction, the oxidation state of the cobalt atom formally changes from 2+ to 0 followed by its carbonylation. An important role of the redox step in these processes is confirmed by the fact that the reaction does not occur in the $[Fe_6C(CO)_{16}]^{2-}$—$Co_2(CO)_8$ system containing no oxidizing agent under the same and even more drastic conditions, and the starting iron cluster is recovered.[16] The possibility of carbonylation of the reduced Co atom with iron carbonyls was demonstrated using the reaction of $CoCl_2$ with $Fe(CO)_5$ as an example. However, the latter reaction occurs rather efficiently only at >60 °C to form[16,22] the $[FeCo_3(CO)_{12}]^-$ cluster.

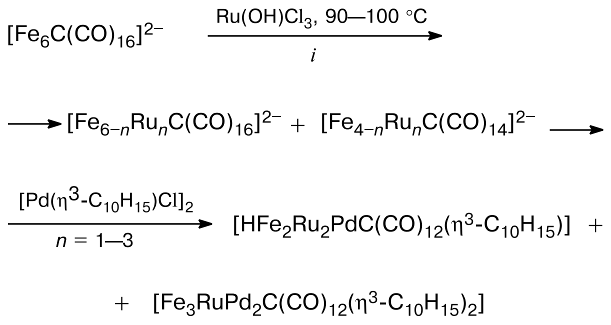
At 90—100 °C, the reaction of $[Fe_6C(CO)_{16}]^{2-}$ with $CoCl_2$, like that with $RhCl_3$, involves the following two processes: replacement of one metal with another and thermal degradation. The difference in the reactions occurring at lower temperatures is apparently determined primarily by the difference in the ability of these metals to undergo carbonylation in diglyme. For example, carbonylation of Rh occurs already at 25 °C, whereas this reaction with the Co compound proceeds efficiently only at 80—100 °C. However, the cluster containing the Fe_4Co core is most stable under these conditions.

Nickel(II) chloride, like cobalt(II) chloride, reacts with $[Fe_6C(CO)_{16}]^{2-}$ in diglyme at 95—105 °C only. Heating for 4—5 h afforded the heterometallic cluster $[Fe_5NiC(CO)_{15}]^{2-}$ in 25—40% yield (see Scheme 1).[12,18] Under these drastic conditions, the reaction with nickel(II) chloride gives the most stable cluster with the Fe_5Ni core, whereas the reaction with cobalt(II) chloride produces the cluster containing the Fe_4Co core.

Analysis of the published data and results of our investigations showed that transmetallation occurs under milder conditions with metallating reagents belonging to the second transition period. In the present study, we examined the possibility of using ruthenium(IV) oxochloride $RuOHCl_3$ in the synthesis of heterometallic clusters.

The reaction of the $[Fe_6C(CO)_{16}]^{2-}$ cluster with ruthenium(IV) hydroxochloride produces a mixture of replacement products. In some experiments, we detected up to ten or even more products. The replacement reactions are accompanied by oxidative degradation giving rise to clusters containing a tetragonal-pyramidal or butterfly metal core or deeper degradation products.[10,11] These mixtures are difficult to separate into individual components. We treated the purified reaction mixture with an excess of $[(\pi\text{-}C_3H_5)PdCl]_2$ or $[(\pi\text{-}\beta\text{-}C_{10}H_{15})PdCl]_2$. Scheme 2 shows the products of this reaction, which have been isolated and characterized.

Scheme 2



i. Diglyme.

We isolated the products of replacement of the Fe atoms by Ru in the $[Fe_6C(CO)_{16}]^{2-}$ cluster along with derivatives of oxidative degradation products, *viz.*, the earlier described[10,11] $(\mu\text{-}H)Ru_2Fe_2PdC(CO)_{12}(\eta^3\text{-}C_{10}H_{15})$ and $Fe_3RuPd_2C(CO)_{12}(\eta^3\text{-}C_{10}H_{15})_2$ clusters. Treatment of the replacement products with $FeCl_3$ afforded the $[Fe_{2.96}Ru_{3.04}C(CO)_{17}]$ compound (**1**), which was characterized by X-ray diffraction.

The reaction of $[Fe_6C(CO)_{16}]^{2-}$ with $Ru(OH)Cl_3$ in diglyme in the presence of methanol at 90—100 °C for 90 min produced a mixture, which was analyzed by TLC (dichloromethane as the eluent). Several cluster compounds were detected (spots with $R_f^1 = 0.1$, $R_f^2 = 0.15$, $R_f^3 = 0.3$, and $R_f^4 = 0.5$ as well as one spot at the start). After isolation of a mixture of clusters as tetraalkylammonium salts by fractional crystallization from acetone—isopropyl alcohol and isopropyl alcohol—hexane mixtures, we isolated two solid fractions (**A** and **B**). The IR spectrum (CH_2Cl_2) provides evidence that the fraction **A** contains, apparently, dianionic clusters ($\nu(CO)/cm^{-1}$: 2100 (sh), 2040 (sh), 2015 (sh), 1965 (s), 1780 (w)), because dianionic clusters are known[8,10] to be characterized by an intense peak at 1950—1965 cm^{-1}. Analysis by TLC showed that the fraction **A** is a mixture of two clusters.

Presumably, the fraction **A** is a mixture of the octahedral clusters $[Et_4N]_2[Fe_{6-n}Ru_nC(CO)_{16}]$ (n = 2—3) formed by the direct replacement of one metal by another. This is confirmed by the fact that treatment of the fraction **A** with an aqueous $FeCl_3$ solution afforded uncharged cluster **1**. In the reaction of $[Fe_6C(CO)_{16}]^{2-}$ with $RuCl_3(OH)$ at high temperature (100—105 °C), the presumed octahedral clusters $[Et_4N]_2[Fe_4Ru_2C(CO)_{16}]$ and $[Et_4N]_2[Fe_5RuC(CO)_{16}]$ undergo oxidative degradation, and these clusters are absent in the final reaction mixture.

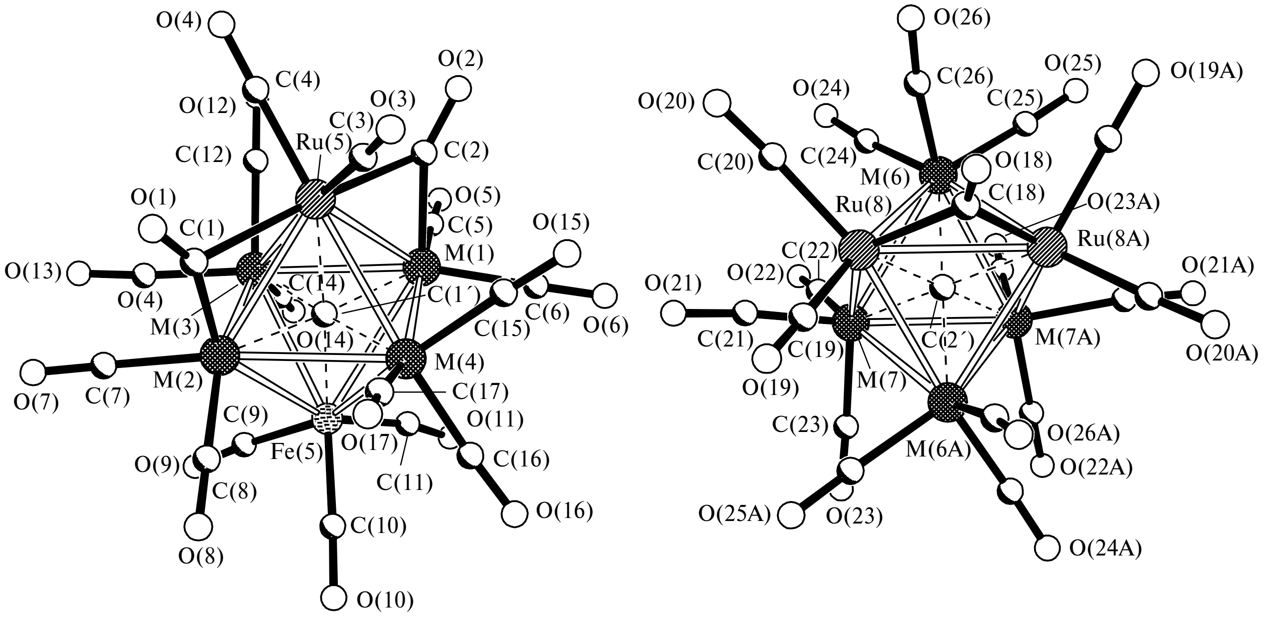
At 90—100 °C, the reaction also gave predominantly degradation products. The percentage of the fraction **B** was approximately estimated as ~60%. The addition of $[(\pi\text{-}L)PdCl]_2$ (L = η^3-$C_{10}H_{15}$ or η^3-C_3H_5) to the butterfly clusters $[Et_4N][HFe_nRu_mC(CO)_{12}]$ ($n + m = 4$) afforded considerable amounts of doubly or even more substituted products. The bridged-butterfly $HFe_2Ru_2PdC(CO)_{12}(\eta^3\text{-}C_{10}H_{15})$ cluster (**2**) was prepared in 29% yield, whereas the yield of $Fe_3RuPd_2C(CO)_{12}(\eta^3\text{-}C_{10}H_{15})_2$ (**3**) was ~5%. Analogous results were obtained in the reaction of $[(C_3H_5)PdCl]_2$ with the fraction **B** (30 and 5%, respectively).

The structures and chiroptical properties of clusters **2** and **3** have been considered in detail in our studies.[10,11] Here we described a procedure for their synthesis to give a more complete insight into transmetallation that occurs in the reaction of $[Fe_6C(CO)_{16}]^{2-}$ with $Ru(OH)Cl_3$. The results of this and earlier investigations[10,11] confirm that transmetallation with metallating agents belonging to the second transition period occurs under milder conditions, and the products of replacements in the octahedral cluster are more stable than those with elements of the first transition period.

The crystals of compound **1** contain two crystallographically independent molecules (**1a** and **1b**) in a ratio of 2 : 1. Molecules **1a** lie in general positions, whereas molecules **1b** are located on twofold axes (Fig. 1). Selected geometric parameters (bond lengths and bond angles) for molecules **1a** and **1b** are given in Table 1. Both molecules **1a** and **1b** are carbon-centered octahedral heterometallic (Fe and Ru) clusters of the general formula $M_6C(CO)_{17}$.

In both molecules, four of six vertices of the metal core are occupied by both Fe and Ru atoms (in Fig. 1, these disordered positions are denoted by M). However, the character of disorder in molecule **1a** differs substantially from that in molecule **1b**. In molecule **1a**, four disordered M atoms lie in a single plane, and the completely ordered Fe(5) and Ru(5) atoms are in *trans* positions with respect to each other. In molecule **1b**, the completely ordered Ru(8) and Ru(8a) atoms related by a twofold axis are in the *cis* arrangement with respect to each other. The crystallographic axis passes through the bridging carbonyl group, the central carbide atom, and the midpoints of the Ru(8)—Ru(8a) and M(7)—M(7a) bonds.

The arrangement of the carbonyl groups in molecule **1a** differs from that in **1b**. In molecule **1a**, two carbonyl groups are bridging and other 15 carbonyl groups are terminal, whereas only one carbonyl group, C(18)—O(18), is bridging in molecule **1b**. Compound **1** is isostructural with the $Ru_6C(CO)_{17}$ cluster studied earlier. The unit cell parameters of the second crystal modification of the latter are very similar to those found for cluster **1**, and both crystals are described by the same space group. In addition, this crystal modification of the $Ru_6C(CO)_{17}$ cluster



1a **1b**

Fig. 1. Molecular structures of **1a** and **1b**. Positions partially occupied by both the Fe and Ru atoms are denoted by M(1)—M(7).

Table 1. Selected geometric characteristics of cluster **1***

Bond	*d*/Å
Molecule **1a**	
Ru(5)—M(1)	2.8479(8)
Ru(5)—M(2)	2.7986(8)
Ru(5)—M(3)	2.9201(8)
Ru(5)—M(4)	2.805(1)
Fe(5)—M(1)	2.899(1)
Fe(5)—M(2)	2.767(1)
Fe(5)—M(3)	2.750(1)
Fe(5)—M(4)	2.756(1)
M(1)—M(3)	2.7693(9)
M(3)—M(2)	2.8870(9)
M(2)—M(4)	2.846(1)
M(4)—M(1)	2.768(1)
Ru(5)—C(1´)	2.052(6)
Fe(5)—C(1´)	1.932(7)
M(1)—C(1´)	2.011(6)
M(2)—C(1´)	2.007(6)
M(3)—C(1´)	2.001(6)
M(4)—C(1´)	1.951(6)
Ru(5)—C(1)	2.402(8)
Ru(5)—C(2)	2.175(7)
M(2)—C(1)	1.926(8)
M(1)—C(2)	2.011(7)
Molecule **1b**	
Ru(8)—Ru(8A)	2.8690(9)
Ru(8)—M(6)	2.8396(9)
Ru(8)—M(6A)	2.7797(9)
Ru(8)—M(7)	2.8960(9)
M(6)—M(7)	2.814(1)
M(7)—M(7A)	2.763(1)
Ru(8)—C(2´)	2.065(6)
M(7)—C(2´)	1.954(6)
M(6)—C(2´)	1.9494(8)
Ru(8)—C(18)	2.080(7)

Angle	ω/deg
Molecule **1a**	
O(1)—C(1)—M(2)	153.2(6)
O(1)—C(1)—Ru(5)	127.1(6)
M(2)—C(1)—Ru(5)	79.8(2)
O(2)—C(2)—M(1)	142.9(5)
O(2)—C(2)—Ru(5)	131.8(5)
M(1)—C(2)—Ru(5)	85.4(2)
Molecule **1b**	
O(18)—C(18)—Ru(8)	136.4(2)
Ru(8)—C(18)—Ru(8A)	87.2(3)
O(18)—C(18)—Ru(8)	136.4(2)

* The symmetry code (A): $-x + 1, y, -z - 1/2$.

also contains two crystallographically independent molecules, one of which is located on a twofold axis. However, both independent molecules in the crystal of $Ru_6C(CO)_{17}$, unlike those in the structure of **1**, are structurally identical to **1b**, whereas molecules **1a** are absent.[23—25]

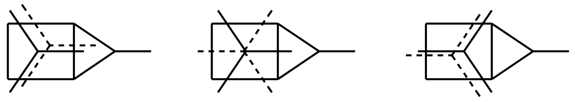
In molecule **1a**, the Ru(5)—M, Fe(5)—M, and M—M distances are in the ranges of 2.7986(8)—2.9201(8), 2.750(1)—2.899(1), and 2.768(1)—2.8870(9) Å, and their average values are 2.843, 2.793, and 2.818 Å, respectively. In molecule **1b**, the Ru(8)—Ru(8a) distance is 2.8690(9) Å, and the average Ru—M and M—M distances are 2.838 and 2.788 Å, respectively. Therefore, the Fe—M bonds involving the completely ordered Fe(5) atom are noticeably shorter than the Ru—M bonds formed by the completely ordered Ru(5), Ru(8), and Ru(8a) atoms in both molecules. The Ru—Ru distances in the $Ru_6C(CO)_{17}$ cluster are in the range of 2.803—2.998 Å.[23]

In both molecules, the carbide C(1´) and C(2´) atoms are located in the vicinity of the geometric centers of the metal octahedra. In molecule **1a**, the Ru(5)—C(1´) and Fe(5)—C(1´) distances are 2.052(6) and 1.932(7) Å, respectively. The M—C(1´) distances are in the range of 1.951(6)—2.011(6) Å. In molecule **1b**, the Ru(8)—C(2´) distance is 2.065(6) Å, and the M—C(2´) distances are in the range of 1.954(6)—1.9494(8) Å. In the $Ru_6C(CO)_{17}$ compound, the corresponding Ru—C distances are in the range of 2.026—2.060 Å.

In molecule **1b**, the bridging carbonyl group is located strictly symmetrically, the Ru(8)—C(18) bond length is 2.080(7) Å, and the Ru(8)—C(18)—O(18) angle is 136.4(2)°. The corresponding parameters in the analogous $Ru_6C(CO)_{17}$ molecules are in the ranges of 2.100(3)—2.070(4) Å and 136.2(1)—138(2)°.

Molecule **1a** contains two bridging carbonyl groups. One of these groups, C(2)—O(2), is almost symmetrical. The Ru(5)—C(2) bond length is rather similar to the M(1)—C(2) bond length (2.175(7) and 2.011(7) Å, respectively). The same is true for the O(2)—C(2)—Ru(5) and O(2)—C(2)—M(1) angles (131.8(5) and 142.9(5)°, respectively). The second bridging group, C(1)—O(1), is strongly asymmetrical. There are significant differences between the corresponding Ru(5)—C(1) and M(2)—C(1) bond lengths (2.402(8) and 1.926(8) Å, respectively) and the O(1)—C(1)—Ru(5) and O(1)—C(1)—M(2) angles (127.1(6) and 153.2(6)°, respectively). The corresponding parameters in the $Ru_6C(CO)_{17}$ molecule vary in the ranges of 2.523(6)—1.946(5) Å and 124.9(4)—156.8(5)°, respectively.

In two crystal modifications of the $Ru_6C(CO)_{17}$ compound, three different molecules have been found earlier.[23—25] These molecules exist in two (*cis—cis* and *cis—trans*) of three possible rotameric forms, which differ in the mutual arrangement of the $M(CO)_3$ fragments above and below the plane of the bridging ligand.



cis—cis *cis—trans* *trans—trans*

In the structure of **1**, both independent molecules exist as *cis—cis* rotamers, in spite of the fact that **1** is isostructural with $Ru_6C(CO)_{17}$.

Experimental

The IR spectra were recorded on a Specord IR-75 spectrophotometer (in CH_2Cl_2 or hexane). Elemental microanalysis was carried out on a CHN-3 C,H,N analyzer (Carlo Erba Strumentione, Italy). The course of the reactions was monitored by TLC (Silufol). All reactions were carried out under argon with the use of dry solvents, which were prepared according to standard procedures.[6] The $[Et_4N]_2[Fe_6C(CO)_{12}]$,[9] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$,[27] and $[Pd(\eta^3\text{-}C_{10}H_{15})Cl]_2$ compounds[28] were synthesized according to known procedures.

Reaction of $[Et_4N]_2[Fe_6C(CO)_{12}]$ with $Ru(OH)Cl_3$. A solution of $Ru(OH)Cl_3$ (0.5 g, 0.222 mmol) in methanol (10 mL) was added to a solution of $[Et_4N]_2[Fe_6C(CO)_{12}]$ (1 g, 1.13 mmol) in diglyme (50 mL) at 25 °C. The reaction mixture was stirred at 90—100 °C for 1.5 h. The methanol was removed at 70 °C. The mixture was cooled and filtered into a saturated aqueous Et_4NBr solution. The precipitate that formed was filtered off, dissolved in acetone (50 mL), and added to a solution of isopropyl alcohol (75 mL). Then the acetone was removed *in vacuo*, and the precipitate (0.22 g) was filtered off (fraction **A**). The filtrate was evaporated *in vacuo* and the precipitate was washed with hexane and recrystallized from a 1 : 2 isopropyl alcohol—hexane mixture at –5 °C. The fraction **B** was obtained in a yield of 0.31 g.

Reactions of fraction B with $[Pd(\eta^3\text{-}C_{10}H_{15})Cl]_2$ and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$. A 1.5-fold excess of $[Pd(C_{10}H_{15})Cl]_2$ was added to a solution of the fraction **B** (0.31 g) in CH_2Cl_2 (10 mL) at 25 °C. The reaction mixture was stirred for 5 min, the solvent was removed on a rotary evaporator, and the dry residue was chromatographed on SiO_2 using a 4 : 1 hexane—CH_2Cl_2 mixture as the eluent. The fractions **B1** and **B2** (orange and green, respectively) were isolated. After evaporation of the solvent and crystallization from pentane at –5 °C, red crystals of $HFe_2Ru_2PdC(CO)_{12}(\eta^3\text{-}C_{10}H_{15})$ (**2**) and black crystals of $Fe_3RuPd_2C(CO)_{12}(\eta^3\text{-}C_{10}H_{15})_2$ (**3**) were isolated from the fractions **B1** and **B2** in yields of 0.12 (29%) and 0.024 g (4.5%), respectively.

The $HFe_2Ru_2PdC(CO)_{12}(\eta^3\text{-}C_3H_5)$ (**4**) and $Fe_3RuPd_2C(CO)_{12}(\eta^3\text{-}C_3H_5)_2$ (**5**) compounds were synthesized analogously in yields of 0.042 (30%) and 0.006 g (5%), respectively, by the reaction of the fraction **B** (0.793 g) with $[Pd(C_3H_5)Cl]_2$ (0.0375 g) in CH_2Cl_2 followed by chromatography on SiO_2.

X-ray diffraction study of cluster 1. X-ray diffraction data were collected on an automated Bruker SMART CCD diffractometer at 150 K using Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator). Crystals of **1** ($C_{18}Fe_{2.96}O_{17}Ru_{3.04}$, M = 960.90) are monoclinic, space group $P2/c$, a = 23.6815(1) Å, b = 9.1545(1) Å, c = 17.3375(2) Å, β = 98.241(1)°, V = 3719.82(6) Å, Z = 6, d_{calc} = 2.574 g cm^{-3}, μ(Mo-Kα) = 3.574 mm^{-1}, F(000) = 2729. The intensities of 25214 reflections (of which 8121 reflections were independent, R_{int} = 0.0417) were measured using the ω scan mode in the angle range $0.87° < \theta < 27.00°$ ($-30 \le h \le 27$, $-10 \le k \le 11$, $-15 \le l \le 22$). The absorption correction was applied based on the intensities of equivalent reflections.[29] The structure was solved by direct methods using the SHELX-86 program package.[30] In the course of structure refinement, it was found that some positions in the octahedral metal core are occupied by both the Fe and Ru atoms. The refinement of the occupancies of the M(1), M(2), M(3), M(4), M(5), M(6), and M(7) sites resulted in the Fe/Ru ratios of 0.30/0.70, 0.30/0.70, 0.35/0.65, 0.40/0.60, 0.73/0.27, 0.67/0.33, and 0.72/0.28, respectively. Then all atoms were refined anisotropically by the full-matrix least-squares based on F^2 (SHELXL-93[31]) with the use of common positional and thermal parameters for the Fe and Ru atoms occupying the same positions. The final R factors were R_1 = 0.0447 and wR_2 = 0.0969 for 6598 reflections with $I > 2\sigma(I)$, 561 parameters were refined; GOF = 1.115, the residual electron density (e A^{-3}) was $\rho_{\max}/\rho_{\min}$ = 3.590/–1.296.

The crystallographic data for the structure of **1** were deposited with the Cambridge Structural Database (CCDC 232898).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 04-03-32090, 04-03-32311, 04-03-32597, and 05-03-32083), the Council on Grants of the President of the Russian Federation (Program for State Support of Young Scientists, Grant MK-3697.2004.3), the Russian Science Support Foundation, the International Science and Technology Center (ISTC, Grant 1991), and the Programs of the Presidium of the Russian Academy of Sciences "Fundamental Problems of Physics and Chemistry of Nanosized Systems and Nanomaterials" and "Directed Synthesis of Inorganic Compounds with Desired Properties and Design of Functional Materials on Their Basis."

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Received March 3, 2005;
in revised form June 7, 2005