# Synthesis, Structure, and Some Reactions of the Cluster Complex $[(\mu-H)_2Fe_5(\mu_3-Se)_2(CO)_{14}]$

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**Abstract**—In the reaction of Na<sub>2</sub>Se with  $[Fe(CO)_5]$  in isopropanol with subsequent acidification with HCl, which is used to synthesize  $[(\mu-H)_2Fe_3(\mu_3-Se)(CO)_9]$  (**II**), the cluster  $[(\mu-H)_2Fe_5(\mu_3-Se)_2(CO)_{14}]$  (**I**) was detected. In assumption that compound **I** could serve as a suitable synthon for preparing the bulky heterometallic clusters, its reactions with the Rh-containing complexes were studied. The reaction of **I** with  $[Rh(CO)_2Cp^*]$  (Cp\* is pentamethylcyclopentadienyl) was found to give a mixture of the products. The main reaction products were isolated and their structures were determined:  $[Fe_2Rh(\mu_3-Se)_2(CO)_6Cp^*]$ ,  $[Fe_2Rh(\mu_3-Se)(\mu-CO)(CO)_3Cp_2^*]$ ,  $[Fe_2Rh_2(\mu_4-Se)(\mu-CO)_4(CO)_2Cp_2^*]$ . Potassium hydride treatment of **II** with subsequent addition of  $[Cp*Rh(CH_3CN)_3](CF_3SO_3)_2$  leads to the well-known cluster complex  $[Fe_3Rh(\mu_4-Se)(CO)_9Cp^*]$ . A set of the reaction products indicates that the  $\{Fe_5Se_2\}$  core cannot be used as one-piece "building block" in the synthesis of heterometallic clusters.

**DOI:** 10.1134/S1070328408100060

The target synthesis of the transition metal heteroelement cluster complexes is still being urgent due to the increasing interest in diverse functional materials with preset composition and structure. Of special interest are the large heterometallic cluster complexes—the potential precursors of the highly ordered nanoparticles, some of which have already showed themselves as promising objects in the design of the high-capacity magnetic stores [1].

The chemistry of iron chalcogenide carbonyl clusters has been well studied in terms of a subsequent molecular design of the heteronuclear derivatives. Thus, dichalcogenide complexes  $[Fe_3(\mu_3-Q)_2(CO)_9]$ ,  $[Fe_3(\mu_3-Q)(\mu_3-Q')(CO)_9],$  $[Fe_2(\mu-Q_2)(CO)_6],$ and  $[Fe_2(\mu-QQ')(CO)_6]$  (Q, Q' = S, Se, Te) have been under study for several decades [2, 3]. The sulfide cluster  $[(\mu-H)_2Fe_3(\mu_3-S)(CO)_9$  has been also studied thoroughly [4], and suitable methods of synthesizing its analogs  $[(\mu-H)_2Fe_3(\mu_3-Q)(CO)_9]$  (Q = Se, Te) have been developed later on, which allowed their systematic study [5-7]. They were shown to be suitable synthons for synthesizing a number of heteroelement clusters containing several transition metals and/or p elements (scheme 1; hereinafter the ligands CO are designated by dashes) [8–13].

The above scheme illustrated huge potentialities and the high synthetic potential of the  $[(\mu-H)_2Fe_3(\mu_3-Q)(CO)_9]$  clusters. However, while expecting to obtain the largest possible cluster aggregates of the nanoparticle sizes, it seems reasonable to use the clusters with a higher nuclearity as the "building blocks". This work is devoted the experimental varification of the possibility of preparing the large heterometallic cluster complexes from diselenide complex  $[(\mu-H)_2Fe_5(\mu_3-Se)_2(CO)_{14}]$  (I), which is formed together with  $[(\mu-H)_2Fe_3(\mu_3-Se)(CO)_9]$  (II) in the reaction of sodium selenide with iron pentacarbonyl in isopropanol with subsequent acidification with HCl.

## EXPERIMENTAL

The synthesis and isolation of the reaction products were performed in the atmosphere of inert gas in the standard Schlenk apparatus. The solvents were dehydrated and degassed by boiling and refluxing in the atmosphere of inert gas using the corresponding dehydrating agents [14]. The dissolved oxygen was removed from water and HCl (in the form of azeotrope) by refluxing in a slow argon flow. The Merck silica gel (0.063–0.200 mm) was used in a column chromatography. The following starting reagents were synthesized by the known procedures: [Rh(CO)<sub>2</sub>Cp\*] [15],  $[\dot{R}h(CH_3CN)_3Cp^*](CF_3SO_3)_2$ by analogy with  $[Rh(CH_3CN)_3Cp^*](BF_4)_2$  [16]. The remaining reagents were used as received.

The <sup>1</sup>H NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.133 MHz at room temperature. The TMS signals were used as the internal standard when recording the NMR spectra.



Scheme 1.

The IR spectra of solutions were recorded on a Bruker IFS28 spectrometer.

Mass spectra were measured on a Varian MAT 711 instrument with the electronic impact ionization 70eV.

Synthesis of cluster I. To a solution of Na<sub>2</sub>Se in 100 cm<sup>3</sup> of isopropanol prepared in situ from the amorphous selenium (1.99 g, 0.025 mol) and NaBH<sub>4</sub> (2.13 g, 0.056 mol), 13 cm<sup>3</sup> of Fe(CO)<sub>5</sub> (18.98 g, 0.097 mol) was added at room temperature. The mixture was stirred for 12 h and then refluxed until liberation of CO terminated (for another 12 h). Then, the mixture was cooled, filtered through a glass filter G3, and 600 cm<sup>3</sup> of a 5% HCl solution was added to the filtrate. The mixture obtained was allowed to stay overnight. The liquid was decanted from the black precipitate formed and then, the latter was washed with 60 cm<sup>3</sup> of water, 30 cm<sup>3</sup> of methanol, and dried in a vacuum. The resulting precipitate, containing I, II, and  $[Fe_3(\mu_3-Se)_2(CO)_9]$ , was stored in the atmosphere of argon at  $-12^{\circ}$ C. For every subsequent experiment, some portion of this mixture was used to prepare freshly isolated specimen of cluster I. For this reason, ~0.25 g of the precipitate was dissolved in several cm<sup>3</sup> of toluene and them, ~3 cm<sup>3</sup> of silica gel was added and the solvent was removed in a vacuum. The obtained mixture was applied onto a column with silica gel (d = 2 cm, l = 30 cm) and chromatographed. The fraction order was as follows: (hexane eluent) red-brown zone [Fe<sub>3</sub>( $\mu_3$ -Se)<sub>2</sub>(CO)<sub>9</sub>], small quantities; broun zone,  $[Fe_3(\mu_3-Se)_2(CO)_9]$ ; green zone, [Fe<sub>3</sub>(CO)<sub>12</sub>], small quantities, identified from IR spectrum; (toluene eluent) dark brown zone, (after concentration and cooling to  $-12^{\circ}$ C, ~0.105 g of the crystalline product was obtained).

For I: <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>;  $\delta$ , ppm): –39.69 (2H,  $\mu$ -H).

IR (n-hexane; v(CO), cm<sup>-1</sup>): 2098 w, 2068 s, 2059 w. sh, 2026 s, 2012 m, 2002 w. sh.

Mass spectrum (m/z ( $I_{rel}$ , %)): 832 (1.0) [M<sup>+</sup>]; 804 (0.7) [M<sup>+</sup>–CO]; 776 (0.7) [M<sup>+</sup>–2CO]; 748 (0.6) [M<sup>+</sup>– 3CO]; 720 (0.5) [M<sup>+</sup>–4CO]; 692 (1.2) [M<sup>+</sup>–5CO]; 664 (0.9) [M<sup>+</sup>–6CO]; 636 (1.5) [M<sup>+</sup>–7CO]; 608 (2.7) [M<sup>+</sup>– 8CO]; 580 (2.0) [M<sup>+</sup>–9CO]; 552 (1.9) [M<sup>+</sup>–10CO]; 524 (2.4) [M<sup>+</sup>–11CO]; 501 (8) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>]; 473 (6) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–CO]; 445 (6) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–2CO]; 440 (5) [M<sup>+</sup>–14CO]; 417 (3.1) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–3CO]; 387 (4.3) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–4CO–2H]; 359 (12) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–5CO–2H]; 331 (11) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>– 6CO–2H]; 303 (6) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–7CO–2H]; 247 (15) [H<sub>2</sub>Fe<sub>3</sub>Se(CO)<sup>+</sup><sub>9</sub>–9CO–2H]; 28 (100) [CO<sup>+</sup>].

**Reaction of I with KH and** [Rh(CH<sub>3</sub>CN)<sub>3</sub>Cp\*](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>. To a vessel, which contained a mixture of the solid starting compounds, i.e., I (0.213 g, 0.255 mmol) and KH (0.020 g, 0.5 mmol) and was cooled with a liquid nitrogen, ~10 cm<sup>3</sup> of THF was condensed. Then, the vessel was slowly heated in air to room temperature. The mixture was stirred immediately after the solvent melted and the stirring was continued for 24 h at room temperature. Then the mixture was heated on a water bath at 55°C and stirred at this temperature until the liberation of hydrogen terminated (~1.5 h). On cooling to room temperature, the reaction mixture was filtered through a glass filter G3, and the precipitate was washed with THF ( $15 \text{ cm}^3$ ), and the filtrates were poured together. The solution thus obtained was frozen with a liquid nitrogen, and [Rh(CH<sub>3</sub>CN)<sub>3</sub>Cp\*](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (0.168, 0.255 mmol) was added to a vessel. Then, the vessel was slowly heated in air to room temperature. The stirring was started immediately after the solvent melted and was continued for 24 h at room temperature. The reaction solution was filtered and concentrated to dryness in a vacuum. The solid residue was extracted with 20 cm<sup>3</sup> or toluene and 10 cm<sup>3</sup> of methylene chloride. The extracts were combined and concentrated in a vacuum. The remaining solid was dissolved in 3 cm<sup>3</sup> of methylene chloride and the solution was filtered. Then, hexane  $(10 \text{ cm}^3)$  was poured over this solution. After the layers were mixed fully at 0°C, the dark red crystals of the above-mentioned compound  $[Fe_3Rh(\mu_4-Se)(CO)_9Cp^*]$  (III) [9] were obtained. The yield was 0.150 g (80% on conversion to the starting Rh complex).

Reaction of I with [Rh(CO)<sub>2</sub>Cp\*]. Preparation of [Fe<sub>2</sub>Rh( $\mu_3$ -Se)<sub>2</sub>(CO)<sub>6</sub>Cp\*] (IV), [Fe<sub>2</sub>Rh( $\mu_3$ -Se)( $\mu_3$ -CO)(CO)<sub>6</sub>Cp\*] (V), [FeRh<sub>2</sub>( $\mu_3$ -Se)( $\mu$ -CO)(CO)<sub>3</sub>Cp<sup>\*</sup><sub>2</sub>] (VI), and [Fe<sub>2</sub>Rh<sub>2</sub>( $\mu_4$ -Se)( $\mu$ -CO)<sub>4</sub>(CO)<sub>2</sub>Cp<sup>\*</sup><sub>2</sub>] (VII). To

a mixture of the solid reagents I (0.211 g, 0.254 mmol) and [Rh(CO)<sub>2</sub>Cp\*] (0.077 g, 0.262 mmol), 5 cm<sup>3</sup> of toluene was added on stirring. The mixture was stirred for 4 days at room temperature. After that, the solution contained a number of the reaction products (TLC control). The reaction solution was concentrated to dryness in a vacuum. The residue was dissolved in 6 cm<sup>3</sup> of  $CH_2Cl_2$ ,  $\sim 5$  cm<sup>3</sup> of silica gel was added, and the solvent was removed in a vacuum after thorough stirring. The obtained mixture was applied to a silica gel (the column d = 2, l = 30 cm) and chromatographed. The order of zones was as follows: (hexane-toluene (5:1) as eluent) the dark brown zone containing the traces of  $[Fe_3(\mu_3 Se_{2}(CO)_{9}$ , I,  $[Fe_{3}(CO)_{12}]$ , and II; the red zone, IV (after recrystallization from a toluene-hexane mixture, only several crystals of the product were obtained); the light yellow zone, the negligible amount of unidentified compound; the green zone, the negligible amount of unidentified compound; (hexane-toluene (1:1) as eluent) the dark red zone, V (after recrystallization from hexane, the yield was 0.064 g (40% on conversion to the starting Rh complex)); the light brown zone, the negligible amount of unidentified compound; (hexanetoluene (2:3) as eluent) the red zone, VI (with very low yield; after crystallization from hexane, only several crystals were obtained); (hexane-toluene (1:7) as eluent) the brown zone, VII (in very low yield; on crystallization from toluene, only several crystals of the solvate VII  $\cdot$  C<sub>7</sub>H<sub>8</sub> were formed); (toluene as eluent) pale red-brown lengthy zone, the negligible amount of unidentified compound.

For **IV**: IR (*n*-hexane: v(CO), cm<sup>-1</sup>): 2067 w, 2051 s, 2026 s, 2009 w, 1984 s, 1968 s.

Mass spectrum (m/z ( $I_{rel}$ , %)): 676 (3) [M<sup>+</sup>]; 648 (26) [M<sup>+</sup>–CO]; 620 (27) [M<sup>+</sup>–2CO]; 592 (11) [M<sup>+</sup>–3CO]; 564 (8) [M<sup>+</sup>–4CO]; 536 (20) [M<sup>+</sup>–5CO]; 508 (100) [M<sup>+</sup>–6CO]; 373 (27) [M<sup>+</sup>–6CO–Cp<sup>\*</sup>].

For V: IR (*n*-hexane; v(CO), cm<sup>-1</sup>): 2060 s, 2026 s, 2001 s, 1980 m, 1973 w, sh.

<sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>; δ, ppm): 1.94 (15 H, CH<sub>3</sub>, s).

Mass spectrum (*m*/*z* (*I*<sub>отн</sub>, %)): 626 (24) [M<sup>+</sup>]; 598 (12) [M<sup>+</sup>–CO]; 570 (19) [M<sup>+</sup>–2CO]; 542 (15) [M<sup>+</sup>–3CO]; 514 (24) [M<sup>+</sup>–4CO]; 486 (44) [M<sup>+</sup>–5CO]; 458 (92) [M<sup>+</sup>–6CO]; 430 (100) [M<sup>+</sup>–7CO].

For VI: IR (CH<sub>2</sub>Cl<sub>2</sub>; v(CO), cm<sup>-1</sup>): 2039 s, 2001 m, 1966 s.

Mass spectrum: 723 (5) [M<sup>+</sup>]; 695 (3.5) [M<sup>+</sup>–CO]; 667 (3) [M<sup>+</sup>–2CO]; 639 (4) [M<sup>+</sup>–3CO]; 611 (28) [M<sup>+</sup>– 4CO]; 28 (100) [CO<sup>+</sup>].

For **VII**: mass spectrum (*m*/*z* (*I*<sub>OTH</sub>, %)): 835 (6) [M<sup>+</sup>]; 751 (10) [M<sup>+</sup>–3CO]; 723 (5) [M<sup>+</sup>–4CO]; 695 (40) [M<sup>+</sup>– 5CO]; 667 (57) [M<sup>+</sup>–6CO]; 112 (100) [Fe(CO)<sup>+</sup><sub>2</sub>].

X-ray diffraction analysis of I, IV–VI. VII  $\cdot$  C<sub>7</sub>H<sub>8</sub>. The crystallographic parameters and summary of data collection are presented in Table 1. The absorption correction for I, V was applied using the azimuthal scanning curves and integration with account for the crystal faceting, respectively; in the rest cases, it was applied empirically on the basis of the intensities of the equivalent reflections. The structures were solved by the direct method and refined by the full-matrix leastsquares method in anisotropic approximation for nonhydrogen atoms. The calculations were performed with the SHELXL-97 program package [17]. The hydrogen atoms were refined geometrically. The main bond lengths for I, IV–VI, VII  $\cdot$  C<sub>7</sub>H<sub>8</sub> are listed in Table 2. The coordinates of atoms, the thermal parameters, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Center (No. 677881-677885).

# **RESULTS AND DISCUSSION**

The reaction of sodium selenide with  $[Fe(CO)_5 \text{ in}]$  isopropanol was used as a suitable method for synthesizing cluster **II** [7]. The above reaction requires prolonged heating and gives several iron chalcogenide forms in a solution. The addition of a 5% HCl solution leads to the precipitation of a mixture of the products, of which only three compounds were identified previously, i.e.,  $[Fe_3(\mu_3-Se)_2(CO)_9]$ ,  $[Fe_3(CO)_{12}]$ , and **II**. The components of the mixture, except for **II**, were present in insignificant amounts and therefore, the isolation and purification of the latter compound by extraction with a

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raianietei	Ι	IV	V	VIVII $\cdot C_7H_8$ 723.11927.11MonoclinicTriclinic $P_{2_1/n}$ $P_{1}$ 11.950(2)8.6904(9)14.737(3)9.9396(12)14.978(3)20.839(2)9090.680(14)99.98(3)96.958(13)9096.761(13)2598.0(9)1773.7(3)421.8491.73614249203.234 (MoK $_{\alpha}$ )2.782 (MoK $_{\alpha}$ )STOE IPDS, 203.0(2)STOE IPDS, 213.0(2)54.3048.10 $-15 \le h \le 15$ $-9 \le h \le 9$ $-13 \le k \le 18$ $-11 \le k \le 11$ $-18 \le l \le 19$ $-23 \le l \le 23$ 11201105585473, 0.06965263, 0.054944213451300358 $R_1 = 0.0789$ $wR_2 = 0.1132$ $R_1 = 0.0789$ $wR_2 = 0.2600$ 0.9741.048 $-0.746/1.205$ $-1.046/4.683$					
М	831.33	675.81	624.86	723.11	927.11				
Crystal system	Monoclinic	Rhombic	Rhombic	Monoclinic	Triclinic				
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	P212121	P212121	<i>P</i> 2 <sub>1</sub> / <i>n</i>	$P\overline{1}$				
a, Å	9.3907(12)	9.1018(18)	9.062(3)	11.950(2)	8.6904(9)				
b, Å	27.383(4)	12.452(3)	13.518(4)	14.737(3)	9.9396(12)				
<i>c</i> , Å	9.5903(10)	18.886(4)	17.386(5)	14.978(3)	20.839(2)				
α, deg	90	90	90	90	90.680(14)				
β, deg	106.446(9)	90	90	99.98(3)	96.958(13)				
γ, deg	90	90	90	90	96.761(13)				
<i>V</i> , Å <sup>3</sup>	2365.2(5)	2140.4(7)	2129.8(11)	2598.0(9)	1773.7(3)				
Ζ	4	4	4	4	2				
$\rho$ (calcd.), g/cm <sup>3</sup>	2.335	2.097	1.949	1.849	1.736				
<i>F</i> (000)	1584	1296	1216	1424	920				
$\mu$ (radiation), mm <sup>-1</sup>	6.137 (MoK <sub>α</sub> )	5.528 (MoK <sub>α</sub> )	19.244 (Cu <i>K</i> <sub>α</sub> )	3.234 (MoK <sub>α</sub> )	2.782 (MoK <sub>α</sub> )				
Crystal size, mm	$0.40 \times 0.32 \times 0.16$		$1.17 \times 0.12 \times 0.10$						
Diffractometer T, K	Nonius CAD4, Room temperature	STOE IPDS, 193.0(2)	Syntex P2 <sub>1</sub> , room temperature	STOE IPDS, 203.0(2)	STOE IPDS, 213.0(2)				
$2\theta_{\text{max}}$ , deg	49.92	47.86	140.0	54.30	48.10				
Range of reflection indices	$0 \le h \le 11$	$-8 \le h \le 10$	$-2 \le h \le 11$	$-15 \le h \le 15$	$-9 \le h \le 9$				
	$0 \le k \le 32$	$-14 \le k \le 14$	$0 \le k \le 16$	$-13 \le k \le 18$	$-11 \le k \le 11$				
	$-11 \leq l \leq 10$	$-19 \le l \le 21$	$0 \le l \le 21$	$-18 \le l \le 19$	$-23 \le l \le 23$				
Measured reflections	4410	6840	2940	11201	10558				
Independent reflection, $R_{\rm int}$	4149, 0.0519	3268, 0.0492	2633, 0.0707	5473, 0.0696	5263, 0.0549				
Reflections with $I \ge 2\sigma(I)$	1999	3101	2335	4421	3451				
Refined parameters	325	250	259	300	358				
<i>R</i> -factors for $I \ge 2\sigma(I)$	$R_1 = 0.0319$ $wR_2 = 0.0567$	$R_1 = 0.0366$ $wR_2 = 0.1021$	$R_1 = 0.0502$ $wR_2 = 0.1177$	$R_1 = 0.0438$ $wR_2 = 0.1096$	$R_1 = 0.0789$ $wR_2 = 0.2481$				
<i>R</i> -factors for all reflections	$R_1 = 0.1035$ $wR_2 = 0.0727$	$R_1 = 0.0386$ $wR_2 = 0.1042$	$R_1 = 0.0556$ $wR_2 = 0.1231$	$R_1 = 0.0519$ $wR_2 = 0.1132$	$R_1 = 0.1069$ $wR_2 = 0.2600$				
GOOF on $F^2$	0.728	1.091	1.075	0.974	1.048				
Residual electronic density (min/max, $e \text{ Å}^{-3}$ )	-0.444/0.474	-0.692/0.521	-1.543/1.433	-0.746/1.205	-1.046/4.683				

Table 1. The crystallographic parameters and summary of data collection for compound I, IV–VI, VII  $\cdot$  C<sub>7</sub>H<sub>8</sub>

Bond	<i>d</i> , Å	Angle	ω, deg	Bond	<i>d</i> , Å	Angle	ω, deg
	Ι				1.145(17)	132.5(12)	
Se(1)–Fe(1)	2.3471(14)	Fe(2)Fe(1)Fe(3)	59.89(4)			VI	
Se(1)–Fe(2)	2.3162(15)	Fe(2)Fe(1)Fe(4)	153.31(6)	Rh(1)–C(1)	2.019(5)	Rh(1)Fe(1)Rh(2)	60.73(2)
Se(1)–Fe(3)	2.2931(15)	Fe(2)Fe(1)Fe(5)	120.77(6)	Rh(1)–Se(1)	2.3835(7)	Fe(1)Rh(2)Rh(1)	59.27(2)
Se(2)–Fe(1)	2.3461(14)	Fe(4)Fe(1)Fe(3)	128.15(6)	Rh(1)–Fe(1)	2.6588(9)	Fe(1)Rh(1)Rh(2)	60.00(3)
Se(2)–Fe(4)	2.3155(14)	Fe(4)Fe(1)Fe(5)	60.17(4)	Rh(1)–Rh(2)	2.6983(7)	Rh(1)Se(1)Rh(2)	68.873(19)
Se(2)–Fe(5)	2.2988(15)	Se(2)Fe(1)Se(1)	88.96(5)	Rh(2)–C(1)	1.997(5)	Fe(1)Se(1)Rh(1)	69.01(3)
Fe(1)–Fe(2)	2.6639(16)	Se(1)Fe(1)Fe(4)	106.68(5)	Rh(2)–Se(1)	2.3880(7)	Fe(1)Se(1)Rh(2)	69.52(2)
Fe(1)–Fe(3)	2.6783(16)	Se(1)Fe(1)Fe(5)	142.37(6)	Rh(2)–Fe(1)	2.6786(9)	Se(1)Fe(1)Rh(1)	56.82(3)
Fe(1)–Fe(4)	2.6673(16)	Se(2)Fe(1)Fe(2)	102.58(5)	Fe(1)–Se(1)	2.3088(11)	Se(1)Fe(1)Rh(2)	56.63(2)
Fe(1)–Fe(5)	2.6700(16)	Se(2)Fe(1)Fe(3)	142.71(6)	C(1)–O(1)	1.186(5)	O(1)C(1)Rh(2)	138.1(4)
Fe(2)–Fe(3)	2.6667(17)	C(21)Fe(2)Fe(3)	101.9(3)	C(2)–O(2)	1.148(7) O(1)C(1)Rh(1)		134.5(4)
Fe(2)–H(1)	1.41(7)	C(31)Fe(3)Fe(2)	100.3(3)		V	$\mathbf{H} \cdot \mathbf{C}_7 \mathbf{H}_8$	
Fe(3)–H(1)	1.48(7)	Fe(3)Fe(2)H(1)	23(3)	Rh(1)–Se(1)	2.5031(18)	Fe(2)Rh(1)Fe(1)	61.20(7)
Fe(4)–Fe(5)	2.6755(17)	Fe(2)Fe(3)H(1)	22(3)	Rh(1)–Fe(2)	2.598(2)	Fe(1)Rh(2)Fe(2)	61.56(7)
Fe(4)–H(2)	1.47(7)	Fe(5)Fe(4)H(2)	30(3)	Rh(1)–Fe(1)	2.606(2)	Fe(1)Se(1)Fe(2)	68.31(9)
Fe(5)–H(2)	1.57(7)	Fe(4)Fe(5)H(2)	28(3)	Rh(2)–Se(1)	2.490(2)	Rh(2)Se(1)Rh(1)	117.39(7)
Se(1)–Se(2)	3.288 (8)	C(11)Fe(1)C(12)	88.8(4)	Rh(2)–Fe(1)	2.584(2)	Rh(2)Fe(1)Rh(1)	110.58(8)
		IV		Rh(2)–Fe(2)	2.592(2)	Rh(2)Fe(1)Fe(2)	59.37(7)
Rh(1)-Se(2)	2.4040(10)	Fe(2)Rh(1)Fe(1)	82.11(4)	Se(1)–Fe(1)	2.359(3)	Rh(1)Fe(1)Fe(2)	59.25(7)
Rh(1)-Se(1)	2.4057(10)	Se(1)Rh(1)Se(2)	81.48(3)	Se(1)–Fe(2)	2.359(3)	Rh(2)Fe(2)Rh(1)	110.58(9)
Rh(1)–Fe(2)	2.6575(13)	Se(1)Fe(1)Se(2)	83.24(5)	Fe(1)–Fe(2)	2.649(3)	Rh(2)Fe(2)Fe(1)	59.07(7)
Rh(1)–Fe(1)	2.6872(13)	Se(1)Fe(2)Se(2)	83.29(4)	Rh(1)–C(22)	2.516(16)	Rh(1)Fe(2)Fe(1)	59.55(7)
Fe(1)–Se(2)	2.3564(14)	Fe(1)Se(1)Fe(2)	95.79(5)	Fe(1)–C(22)	1.797(19)	Fe(1)C(22)Rh(1)	72.2(6)
Fe(1)–Se(1)	2.3699(15)	Fe(1)Se(2)Fe(2)	96.14(5)	Rh(2)–C(23)	2.415(18)	Fe(1)C(23)Rh(2)	74.8(7)
Fe(2)–Se(1)	2.3617(14)	C(1)Fe(1)Se(1)	87.5(3)	Fe(1)–C(23)	1.752(19)	Fe(2)C(24)Rh(1)	75.8(7)
Fe(2)–Se(2)	2.3621(14)	C(1)Fe(1)Se(2)	156.8(3)	Rh(1)-C(24)	2.388(18)	Fe(2)C(25)Rh(2)	72.4(7)
V				Fe(2)–C(24)	1.766(17)	O(22)C(22)Fe(1)	167.4(14)
Rh(1)–Fe(1)	2.6373(17)	Fe(2)Fe(1)Rh(1)	60.34(5)	Rh(2)–C(25)	2.52(2)	O(21)C(21)Fe(1)	178(2)
Rh(1)–Fe(2)	2.6506(19)	Fe(1)Fe(2)Rh(1)	59.84(6)	Fe(2)–C(25)	1.73(2)	O(22)C(22)Rh(1)	120.3(12)
Fe(1)–Fe(2)	2.637(3)	Fe(1)Rh(1)Fe(2)	59.82(6)	Fe(1)–C(21)	1.80(2)	O(23)C(23)Fe(1)	163.0(16)
Rh(1)-Se(1)	2.3824(12)	Fe(1)Se(1)Rh(1)	67.90(5)	Fe(2)–C(26)	1.770(19)	O(23)C(23)Rh(2)	121.8(13)
Fe(1)–Se(1)	2.3396(18)	Fe(2)Se(1)Rh(1)	68.48(5)	C(21)–O(21)	1.11(3)	O(24)C(24)Fe(2)	161.3(15)
Fe(2)–Se(1)	2.328(2)	Fe(2)Se(1)Fe(1)	68.80(7)	C(22)–O(22)	1.14(2)	O(24)C(24)Rh(1)	122.2(12)
Rh(1)–C(1M)	2.020(11)	Se(1)Rh(1)Fe(1)	55.28(5)	C(23)–O(23)	1.18(2)	O(25)C(25)Fe(2)	168.5(17)
Fe(1)–C(1M)	2.124(13)	Se(1)Rh(1)Fe(2)	54.79(5)	C(24)–O(24)	1.18(2)	O(25)C(25)Rh(2)	119.1(13)
Fe(2)–C(1M)	2.164(12)	O(1M)C(1M)Rh	132.9(10)	C(25)–O(25)	1.21(2)	O(26)C(26)Fe(2)	177.7(19)
C(1M)–O(1M)	1.187(13)	O(1M)C(1M)Fe(1)	135.1(10)	C(26)–O(26)	1.16(2)	C(21)Fe(1)Fe(2)	157.8(7)

Table 2.	The main	bond l	lengths	and	bond	angles	in <b>I</b>	, IV-	-VI,	VII ·	$\mathrm{C_7H_8}$	
Table 2.	The main	bond	lengths	and	bond	angles	1n <b>I</b> ,	, 1V-	-VI,	VII ·	$C_7H_8$	

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hot hexane and crystallization on cooling did not cause difficulties.

On the other hand, it was established previously that in the reaction of K<sub>2</sub>Se with  $[Fe(CO)_5]$  in DMF, which resulted predominantly in the salt of the deprotonated form II, i.e.,  $[Fe_3(\mu_3-Se)(CO)_9]^{2-}$ , gave also insignificant amount of the cluster  $[Fe_5(\mu_3-Se)_2(CO)_{14}]^{2-}$ , identified in [6] as a salt  $[PPh_4]_2[Fe_5(\mu_3-Se)_2(CO)_{14}]$ , whose acceptable quantity can be obtained on lowering the reaction temperature and reducing the synthesis time. Since the anion  $[Fe_5(\mu_3-Se)_2(CO)_{14}]^{2-}$ , in principle, is of interest as a large "building block" fro the synthesis of heterometallic clusters, we performed a detailed study of the above-mentioned mixture of the solid product obtained on acidification and suggested that it can contain the protonated form of the anion  $[Fe_5(\mu_3-Se)_2(CO)_{14}]^{2-}$ . Indeed, in addition to  $[Fe_3(\mu_3-Se)_2(CO)_9]$ ,  $[Fe_3(CO)_{12}]$ , and **II**, the mixture contained cluster I in perceptible amounts (scheme 2) that could be isolated by chromatography as individual compound.



The cluster I core represents two tetrahedra  $\{Fe_3Se\}$ with a shared vertex, i.e., the Fe(1) atom (Fig. 1). The tetrahedra have a skewed conformation relative to the mutual location of the Se atoms. The bridging H atoms lie at the opposite bonds Fe–Fe, which lead to the characteristic elongation of the corresponding bonds Fe-Fe. All the Fe-Fe bond lengths in I are equal to 2.66 - 2.68A. The situation is different in  $[Fe_5(\mu_3-Se)_2(CO)_{14}]^{2-}$ : the four central bonds Fe–Fe are 2.64–2.66 Å, but Fe(2)–Fe(3) and Fe(4)–Fe(5) (the same numbering as in Fig. 1) are noticeably shorter, i.e., ~2.60 Å [6]. The bridging H atoms are asymmetric and deviate to different sides from the corresponding plane  $Fe_3$ . The H(1) atom deviates from the F(1)Fe(2)Fe(3) plane toward the Se(1) atom (the angles Fe91)Z(1)H(1) 168°), while H(2) deviates form the Se(2) atom (the angle Fe(1)Z(2)H(2)  $152^{\circ}$ ).<sup>1</sup>

However, the <sup>1</sup>H NMR spectrum of I in  $CD_2Cl_2$  contains only one singlet signal with the negative chemical shift ( $\delta$ ) corresponding to the bridging hydrogen, i.e., the asymmetry of the H atoms observed in X-ray diffraction only occurs in the solid.

When studying compound **II** by the standard methods [7], cluster I was obtained in negligible amounts, but it increases with the reduction in the reaction time. However, in some experiments, after acidification of the precipitate, cluster I was formed in quantities comparable with **II**, but its yields were unstable, and it is still unclear what was the reason for this. Moreover, in a solution, compound I turned unstable and gradually (for several days) decomposed with the formation of **II**, which is insoluble dark precipitate, and  $[Fe_3(\mu_3-Se)_2(CO)_9]$  in small quantities. Compound I is more stable in a solid state and can be stored in the atmosphere of argon at  $-12^{\circ}$ C for a week without noticeable decomposition. Nevertheless, the elemental analysis of I did not give satisfactory results. Taking this fact into account, we used a freshly prepared specimen of compound I for recording the spectra and in the subsequent experiments.

The most probable approach to the design of heterometallic clusters based on compound I core was assumed to be the interaction of a neutral complex I or its anionic form with the electrohpilic compounds of transition metals or p elements. The distance between two Se atoms in molecule I Se...Se is 3.29 Å (3.21 Å in the dianionic form [6]). This suggests the possibility of the bidentate coordination of the Se atoms to one metal atom or to two other atoms located at a distance of a bond. This coordination was supposed to be the emf of the interaction between I and the electrophilic agents, at least, at the first step.

For cluster **II** and its sulfide and telluride analogs, it was illustrated by a number of examples that the most successful approach to the synthesis of heterometallic derivatives is the following. By the reaction with KH, complex **II** and its analogs are deprotonated and converted to K<sub>2</sub>[Fe<sub>3</sub>( $\mu_3$ -Q)(CO)<sub>9</sub>] (Q = S, Se, Te), which is then reacted with the electrophilic agents. For example, the subsequent treatment of compound **II** with KH and then with [Rh(CH<sub>3</sub>CN)<sub>3</sub>Cp\*](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> results in the addition of the fragment {RhCp\*}<sup>2+</sup> to [Fe<sub>3</sub>( $\mu_3$ -Se)(CO)<sub>9</sub>]<sup>2-</sup> and formation of heterometallic cluster **III** [9].

It is particular this variant that was used for compound I. It turned out hat in this case, too, the subsequent treatment with KH and  $[Rh(CH_3CN)_3Cp^*](CF_3SO_3)_2$  gave the same product III in a high yield (scheme 3).

 $<sup>^{1}</sup>$ Z(1) and Z(2) are the midpoints of the bonds Fe(2)–Fe(3) and Fe(3)–Fe(4), respectively.



Thus, the reaction causes degradation of cluster I. This is likely to occur at the stage of the treatment with KH, i.e., under the conditions required for completion of the deprotonation reaction, and compound **III** formed is actually the product of the interaction of the cluster  $[Fe_3(\mu_3-Se)(CO)_9]^{2-}$  obtained in a solution with  $[Rh(CH_3CN)_3Cp^*](CF_3SO_3)_2$ . An attempt to vary the time and temperature of the synthesis in reasonable limits do not bring radical changes, and, in any case, compound **III** is a sole heterometallic cluster being formed. The above result doubts the possibility of the design of heterometallic clusters containing the core of compound I completely.

Nevertheless, one more variant of the synthesis of heterometallic derivatives was tried using the neutral protonated form of cluster I in the reaction with  $[Rh(CO)_2Cp^*]$  that resulted in a mixture of a great number of the products formed in a low yield, none of the products being predominant. The most representative components **IV–VII** were isolated from a mixture and their structures were established (scheme 4):



Fig. 1. The structure of cluster complex I (the thermal displacement ellipsoids of 50% probability, also used in Fig. 2–5).



Fig. 2. The structure of cluster complex IV.

Taking into account the tendency of I to a spontaneous decay in a solution, the reaction was performed at room temperature, such that it could occur at reasonable rate and the starting cluster could remain in a solution for the maximum possible time. However, none of the products with the established structure contained the { $Fe_5Se_2$ } fragment completely, only it separate elements were detected.

Molecule **IV** (Fig. 2) represents the tetragonal pyramid with Fe<sub>2</sub>Se<sub>2</sub> base and the Rh atom in the apical vertex. Every Fe atom is coordinated with three terminal CO<sub>t</sub> ligands, while the Rh atom is coordinated with Cp\*. The examples of the above clusters are numerous. For instance, they are the typical products of replacement of the {Fe(CO)<sub>3</sub>} group by the isolobal metal fragment in the compounds [Fe<sub>3</sub>( $\mu_3$ -Q)<sub>2</sub>(CO)<sub>9</sub>] (Q = S, Se, Te) or the products of addition of such a metal fragment to [Fe<sub>2</sub>( $\mu$ -Q<sub>2</sub>)(CO)<sub>6</sub>] (Q = S, Se, Te) [3].

Molecule V (Fig. 3) forms the Fe<sub>2</sub>Rh triangle with the coordinated  $\mu_3$ -ligands, i.e., Se and CO. As in complex **IV**, every Fe atom is coordinated with the CO ligands, while the Rh atom is coordinated with Cp\*. The  $\mu_3$ -CO ligand lies almost symmetrically above the Fe<sub>2</sub>Rh face: the distances M–C(1M) (M = Fe, Rh) differ by about 0.15 Å, the MC(1M)O(1M) angles have close values ~133°–135°. At the same time, the IR spectrum of a solution of this compound does not exhibit the absorption bands in the region of the wave numbers < 1970 cm<sup>-1</sup>. Obviously, the above distinct  $\mu_3$ -coordination of the CO ligand is realized only in a solid, while in a solution, the carbonyl groups show the dynamic behavior.

Molecule VI (Fig. 4) also has the tringle metal core with one coordinated  $\mu_3$ -Se ligand The Fe atom is coordinated with three CO<sub>t</sub> ligands and every Rh atom is coordinated with Cp\*. In addition, the bridging µ-CO ligand is also coordinated to the Rh atoms. As in the case of V, the bridging CO group in the structure of VI lies on the other side of a plane passing through three metal atoms such that the planes Rh(1)Rh(2)C(1) and Rh(1)Rh(2)Fe(1) are almost mutually perpendicular. The C(1) atom is equidistant from the Rh atoms, and the lengths of the Rh-C(1) bonds are almost equal to those of Rh(1)-C(1M) in cluster V, but is remote from the Fe(1) atom at a distance > 2.5 Å. The IR spectrum of a solution of VI, as for cluster V, does not contain the bands which could be assigned to the vibrations of the bridging CO groups.

Molecule VII (Fig. 5) forms a distorted tribonal bipyramid with the  $Fe_2Se$  base and two Rh atoms in the apical vertices. Every Rh atom is coordinated with the Cp\* ligand and every Fe atom is coordinated to one CO<sub>t</sub>



Fig. 3. The structure of cluster complex V.



Fig. 4. The structure of cluster complex VI.

ligand. The rest four CO groups are likely to be coordinated in a half-bridging mode: the distance between the Fe and C atoms is characteristic of the Fe-C bond, but the Rh-C distance is substantially longer (by 0.4 Å on the average) than that in molecules of V and VI. However, in this case, the corresponding fragments Fe–C–O are nonlinear, although the O atoms are shifted significantly toward the Rh atoms: the corresponding FeCO angles are  $160^{\circ}$ – $170^{\circ}$ , the RhCO angles are close to 120°. The analogous location of the carbonyl groups is observed, for example, in the clusters [Fe<sub>3</sub>M( $\mu_4$ -Q)(CO)<sub>9</sub>Cp\*] (Q = Se, Te; M = Rh, Ir), whose cores also represent the trigonal bipyramid with the Fe<sub>2</sub>Q base and the Rh or Ir atoms in the apical vertices [9].

The molecules of heterometallic products **VI–VII** form as a result of different variants of addition of a mononuclear fragment  $\{Rh(CO)_xCp^*\}$  and the frag-

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Fig. 5. The structure of cluster complex VII.

ments of cluster I degradation:  $\{Fe_2Se(CO)_{\nu}\}$  and  $\{FeSe(CO)_{r}\}$ . The monitoring of the reaction course (TLC control) shows that compound II is soon formed in a solution, while compound V, which is the main component in a mixture of the reaction products, predominates among heterometallic clusters. The rest clusters are formed with time in low quantities. Of course, the above stages are not separated and occur simultaneously, but in our opinion, compound V is the product of the reaction of cluster I properly, while the rest are the products of the reaction of cluster II formed in a solution. To verify this fact, compound II was reacted with [Rh(CO)<sub>2</sub>Cp\*] under similar condition. The resulting se of the reaction products was almost identical to that obtained in the reaction of I with  $[Rh(CO)_2Cp^*]$ . In this case, too, the predominant product was compound V, its yields in both cases being almost equal. The sole difference observed was that cluster VII was not detected in the reaction of  $[Rh(CO)_2Cp^*]$  with **II**. However, since it was formed in negligible amounts in the reaction with I, the above difference is not essential.

Thus, the above data indicate that the cluster complex  $[(\mu-H)_2Fe_5(\mu_3-Se)_2(CO)_{14}$  (I) can be used for synthesizing heterometallic clusters. At the same time the reactions studied show that it cannot be used as a single-piece "building block", and the obtained heterometallic products contain only the fragments of the staring cluster. The set of the reaction products do not almost differ from that formed with the use of the  $[(\mu-H)_2Fe_3(\mu_3-Se)(CO)_9(II)$  cluster, which is more studied.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 06-03-32946-a) and INTAS Young Scientists Fellowship (project no. 05-109-5302).

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