Russian Chemical Bulletin, International Edition, Vol. 52, No. 4, pp. 944—951, April, 2003

Heterometallic iron carbonyl chalcogenide clusters containing ruthenium, rhenium, manganese, and molybdenum

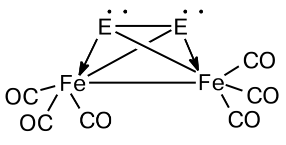
A. A. Pasynskii,[a]★ N. I. Semenova,[a] Yu. V. Torubaev,[a] P. V. Belousov,[a] A. R. Galustyan,[a] and K. A. Lyssenko[b]

[a]N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: aapas@rambler.ru
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 6471. E-mail: kostya@xrlab.ineos.ac.ru

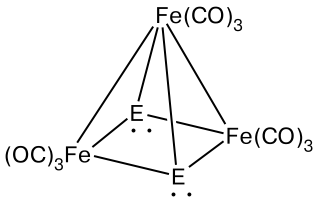
The reactions of $Fe_2Se_2(CO)_6$ (**1b**) with $Ru(CO)_4(C_2H_4)$, $Mn_2(CO)_{10}$, or Cp′$Re(CO)_2$THF gave the known cluster $Fe_2RuSe_2(CO)_9$ (**4b**) and new clusters $(CO)_6Fe_2Se_2Mn_2(CO)_8$ (**5**) and Cp′$Re(CO)_2Se_2Fe_2(CO)_6$ (**6**). By successive reactions of $Mo(CO)_5$THF with **1b** and $Fe_2Te_2(CO)_6$, the new heterometallic heterochalcogenide cluster $Fe_2(CO)_6(\mu_3\text{-}Se)_2Mo(CO)_2(\mu_3\text{-}Te)_2Fe_2(CO)_6$ (**8**) was synthesized. The structures of **4b**, **5**, and **6** were determined by X-ray diffraction analysis.

Key words: heterometallic clusters, metal carbonyls, cyclopentadienyl complexes, X-ray diffraction analysis, thermolysis.

Interest in heterometallic iron carbonyl chalcogenide clusters is largely stimulated by the important role of the MoFeS cofactor of nitrogenase responsible for fixing of molecular nitrogen.[1] Yet another promising route of using these clusters is the synthesis of complex inorganic chalcogenides.[2,3] These clusters can be prepared deliberately from the binuclear complexes $Fe_2E_2(CO)_6$ (E = S, Se, Te for **1a—c**, respectively) or trinuclear complexes $E_2Fe_3(CO)_9$ (**2a—c**, respectively) acting as ligands with respect to electron-deficient metal-containing fragments incorporating other transition elements, in particular, molybdenum.[4]



1a—c



2a—c

According to X-ray diffraction analysis[5—7] (Table 1), complexes **1a—c** contain short Fe—Fe and E—E bonds in a distorted Fe_2E_2 tetrahedron, three CO groups at each atom being directed away from the S_2 group.

Table 1. Selected bond lengths (*d*) and angles (ω) for complexes $Fe_2E_2(Co)_6$ (**1a—c**)

Parameter	E = S (**1a**) [5]	E = Se (**1b**) [6]	E = Te* (**1c**) [7]
Bond		*d*/Å	
E—E	2.007(5)	2.293(2)	2.700(4)
E—Fe	2.222—2.238(4)	2.354—2.378(2)	2.532—2.562(7)
Fe—Fe	2.552(2)	2.575(2)	2.647(8)
Angle		ω/deg	
E—Fe—E	53.5—53.6(1)	58.0—58.1(1)	64.1—64.0(2)
Fe—E—Fe	69.7—70.1(1)	66.3—66.8(1)	63.0—63.2(2)

* Two independent molecules.

The differences between the E—E and E—Fe bond lengths are determined by the difference between the covalent radii of the chalcogens, S, Se, and Te (1.03, 1.17, and 1.36 Å, respectively).[8] According to quantum-chemical calculations,[9] the frontier HOMO and LUMO for complex **1a** are the bonding and antibonding orbitals of the S—S bond. Therefore, the addition of electron-deficient metal-containing fragments to molecules **1a—c** starts with cleavage of the E—E bond;[10] in the case of addition of the $Fe(CO)_3$ group, this yields trinuclear dichalcogenide clusters $Fe_3E_2(CO)_9$ (**2a—c**). The three Fe atoms and the two chalcogen atoms in these species form a tetragonal pyramid with a planar Fe_2E_2 ring as the base; the Fe atoms in this ring are not linked directly to one another, neither are the chalcogen atoms[11,12] (Table 2).

The first step of formation of clusters **2a—c** is the addition of the $Fe(CO)_4$ fragment to molecules **1a—c** to give the clusters $(CO)_6Fe_2E_2Fe(CO)_4$, of which only the complex with E = Te (**3**) is relatively stable; it was charac-

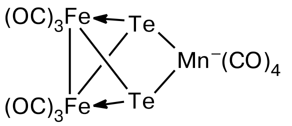
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 896—902, April, 2003.

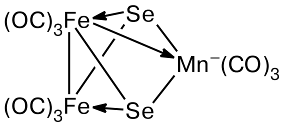
Table 2. Selected bond lengths (*d*) and angles (ω) for complexes $Fe_3E_2(CO)_9$ (**2a—c**)

Parameter	E = S (**2a**) [11]	E = Se (**2b**) [11]	E = Te (**2c**) [12]
Bond		*d*/Å	
Fe(1)—E	2.227, 2.240	2.351, 2.359	2.527, 2.528
Fe(2)—E	2.228, 2.243	2.354, 2.358	2.524, 2.532
Fe(3)—E	2.234, 2.251	2.354, 2.376	2.550, 2.531
E...E	2.893	3.10	3.380
Fe(1)...Fe(2)	3.372	3.520	3.774
Fe(2)—Fe(3)	2.590	2.645	2.740
Fe(1)—Fe(3)	2.595	2.657	2.754
Angle		ω/deg	
Fe—Fe—Fe	81.0	83.2	86.8

terized by X-ray diffraction analysis and was shown to contain only one Fe—Fe bond.[13]

The $[Mn(CO)_4]^-$ and $[Mn(CO)_3]^-$ anionic fragments are isoelectronic to $Fe(CO)_4$ and $Fe(CO)_3$, respectively; therefore, it is not surprising that a structure similar to that of compound **3** has been found for the anionic manganese-containing complex $[Fe_2(CO)_6Te_2Mn(CO)_4]^-$ (Fe—Fe 2.575 Å, Fe...Mn 3.942 Å, Te...Te 3.208 Å).[14]

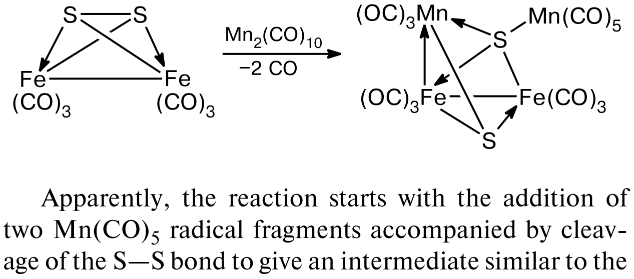




When the Te atoms are replaced by Se atoms, only the product of subsequent decarbonylation, the anionic cluster $[Fe_2(CO)_6Se_2Mn(CO)_3]^-$, can be isolated. In this compound, by analogy with **2b**, the Fe—Fe bond (2.619 Å) is retained and one additional Fe→Mn bond (2.711 Å) appears.[14]

A similar mode of Mn coordination exists in the tetranuclear neutral $Fe_2Mn_2S_2(CO)_{14}$ cluster, prepared by the reaction of **1a** with manganese carbonyl[15] (Scheme 1).

Scheme 1



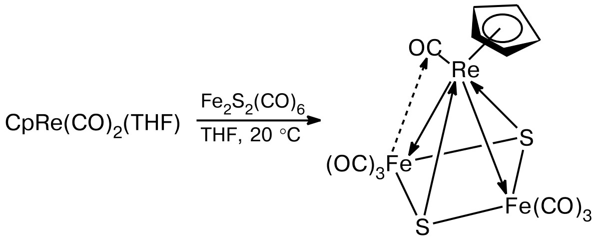
Apparently, the reaction starts with the addition of two $Mn(CO)_5$ radical fragments accompanied by cleavage of the S—S bond to give an intermediate similar to the known $[(CO)_5Re]_2Te_2Fe_2(CO)_6$ complex.[16] The subsequent elimination of two CO groups from one Mn atom gives rise to the S→Mn (2.265 Å) and Fe→Mn (2.714 Å) donor-acceptor bonds.[15]

Ruthenium-containing iron carbonyl chalcogenide clusters are formed in the reactions of the dichalcogenide and heterochalcogenide $E_2Fe_2(CO)_6$ complexes with $Ru(CO)_4(C_2H_4)$ in hexane. First, the reaction gives heterometallic trinuclear $Fe_2RuE_2(CO)_9$ complexes and subsequently, the tetranuclear $Fe_2Ru_2E_2(CO)_{11}$ complexes (E = E′ = Se,[17] Te[18] and E, E′ = Se, Te [19]).

The structures of trinuclear Fe_2Ru-clusters have not been reported previously. The only known cluster is $FeRu_2Se_2(CO)_9$, which contains a central Fe atom and no Ru—Ru bond. This cluster was prepared by the reaction of the diselenium ethene $(CO)_6Fe_2[Se_2(HC{=}CPh)]$ complex with $Ru_3(CO)_{12}$ in boiling benzene.[20]

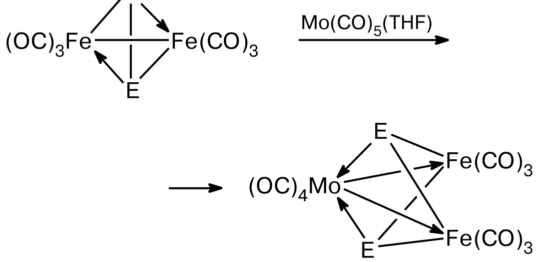
The reaction of compound **1a** with $CpRe(CO)_2THF$, prepared preliminarily by UV irradiation of $CpRe(CO)_3$, proceeds as elimination of the THF molecule and one CO group to furnish the $CpRe(\mu\text{-}CO)(\mu\text{-}S)_2Fe_2(CO)_6$ complex in which $S_2Fe_2(CO)_6$ is coordinated to the CpRe(CO) fragment; this involves cleavage of the Fe—Fe and S—S bonds with the formation of new Re—S (the average length is 2.344 Å) and Re→Fe bonds (the average length is 2.712 Å). In addition, an asymmetric carbonyl bridge is formed between the Re atom and one of the Fe atoms (Scheme 2).[21]

Scheme 2



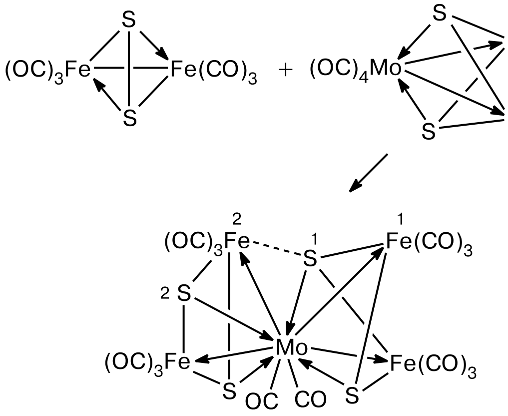
The structurally characterized heterometallic $Fe_2(CO)_6(\mu_3\text{-}E)_2Mo(CO)_4$ clusters (E = S,[22] Se[23,24]) are constructed in a similar way. The $Mo(CO)_4$ fragment is inserted into the Fe—Fe bond to give an E→Mo bond (2.441 and 2.437 Å for E = S; 2.544 Å for E = Se) and an Mo→Fe bond (2.767 and 2.750 Å for E = S; 2.793, 2.823 Å for E = Se) (Scheme 3).

Scheme 3



In the $Fe_2(CO)_6(\mu_3\text{-}S)_2Mo(CO)_4$ sulfide cluster, photochemical replacement of two more CO groups at the Mo atom by a second $Fe_2(CO)_6(\mu_3\text{-}S)_2$ binuclear complex can take place. This yields the pentanuclear $Fe_2(CO)_6(\mu_3\text{-}S)_2Mo(CO)_2(\mu_3\text{-}S)_2Fe_2(CO)_6$ cluster (Mo—Fe 2.749—2.961 Å; Fe—S 2.440 Å; Fe—S 2.280 Å)[25] (Scheme 4).

Scheme 4



Similar $Fe_4(CO)_{12}Mo(CO)_2(\mu_3\text{-}S)_2(\mu_3\text{-}Te)_2$ clusters in which different chalcogen atoms occur at each Fe_2Mo triangle have been obtained[26] by the reaction of heterochalcogenide $Fe_2STe(CO)_6$ clusters with $Fe_2(CO)_6Mo(CO)_4(\mu_3\text{-}S)(\mu_3\text{-}Te)$.

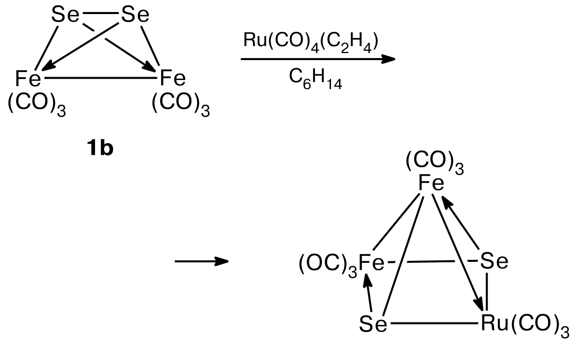
In this study, in order to elucidate the influence of the nature of the chalcogen on the geometry and properties of the complexes, we prepared clusters based on the diselenide iron carbonyl complex $Fe_2Se_2(CO)_6$ (**1b**), to which electron-deficient Ru, Mn, Re, and Mo complexes were added, and compared the structures of these clusters with known sulfide analogs.

Results and Discussion

The syntheses of the ruthenium-containing sulfide and selenide $Fe_2RuE_2(CO)_9$ clusters (E = S (**4a**), Se (**4b**)) has been reported previously;[17] however, the structure of only sulfide **4a** with retained Fe—Fe bond and a new Fe—Ru bond was briefly described.[27] The structure of the selenide cluster was unknown.

We prepared cluster **4b** as dark-red crystals by the reaction of the binuclear selenium cluster $Fe_2Se_2(CO)_6$ with the $Ru(CO)_4(C_2H_4)$ complex, synthesized preliminarily by UV irradiation of $Ru_3(CO)_{12}$ in the presence of ethylene (Scheme 5).

Scheme 5



According to X-ray diffraction data (Fig. 1, Tables 3 and 4) the geometry of the Fe—Fe—Ru metallic core resembles the geometry of the iron chalcogenide complexes $Fe_3E_2(CO)_9$ (**2**) and the iron diruthenium diselenide cluster $FeRu_2Se_2(CO)_9$,[17] *i.e.*, $Fe_2Se_2(CO)_6$ is coordinated with retention of the Fe—Fe bond (2.672(2) Å) and with formation of one new Fe—Ru bond (2.720(2) Å) and two Se—Ru bonds (2.422(1) and 2.435(2) Å), which make up for the four-electron deficiency at the Ru atom. Thus, the replacement of S atoms by Se atoms in diiron ruthenium clusters does not change significantly the geometry of the metal core.

We studied the photochemical reaction of **1b** with $Mn_2(CO)_{10}$, because sulfide complex **1a** is known[15] to be converted under these conditions into the $(CO)_6Fe_2S_2[Mn(CO)_3][Mn(CO)_5]$ cluster with retention of the Fe—Fe bond and formation of a new Mn—Fe bond. One could suggest that the greater radius of the Se atoms compared to sulfur would result in a new type of coordination to give an $Mn(CO)_4$ group instead of $Mn(CO)_3$ (Scheme 6).

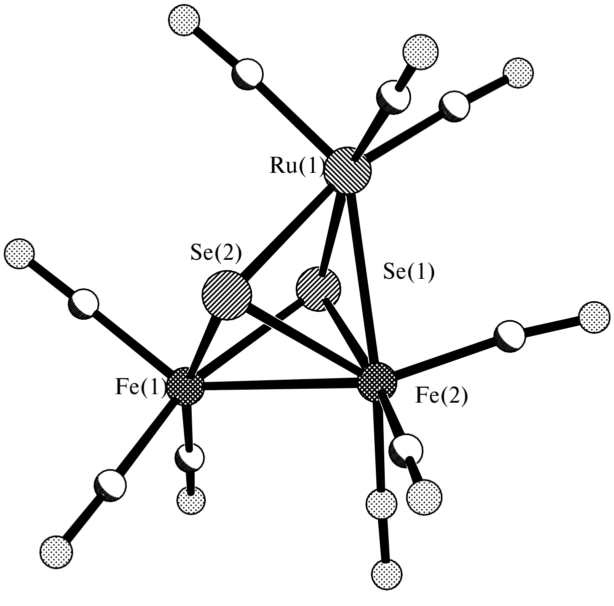


Fig. 1. Molecular structure of complex **4b**.

Table 3. Crystallographic data for complexes **4b**, **5**, and **6**

Parameter	**4b**	**5**	**6**
Molecular formula	$C_9Fe_2O_9RuSe_2$	$C_{14}Fe_2Mn_2O_{14}Se_2$	$C_{14}H_7Fe_2O_8ReSe_2$
M	622.78	771.64	759.02
Diffractometer	«Siemens P3/PC»	«Siemens P3/PC»	«Smart-1000CCD»
Temperature/K	293(2)	293(2)	293(2)
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	6.8634(14)	29.398(6)	9.074(3)
b/Å	9.3844(19)	10.888(2)	9.619(3)
c/Å	13.187(3)	15.475(3)	11.632(3)
α/deg	93.89(3)	90	112.169(6)
β/deg	94.47(3)	111.82(3)	92.263(6)
γ/deg	110.52(3)	90	102.609(6)
V/Å^3	788.9(3)	4598.2(16)	909.2(5)
Z	2	8	2
F(000)	580	2928	700
ρ_{calc}/g cm^{-3}	2.622	2.229	—
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
Absorption coefficient, μ/mm^{-1}	7.412	5.542	12.258
Absorption correction	Azimuthal ψ-scanning	Azimuthal ψ-scanning	Semiempirically (from the data on equivalent reflections)
Scan mode	θ/2θ	θ/2θ	ω (0.3°/10 s)
Range of angles/deg	2.33—52.1	2.01—45.10	1.91—58.18
Total number of reflections	3390	3015	12703
Number of independent reflections	3120 (R_{int} = 0.0265)	2950 (R_{int} = 0.0431)	4855 (R_{int} = 0.0437)
Number of independent reflections with $I > 2\sigma(I)$	2501	1225	3475
$R_1(I > 2\sigma(I))$	0.0645	0.0457	0.0526
wR_2 (over all reflections)	0.2085	0.0900	0.1266
GOF	1.070	0.675	1.156
(ρ_{max}/e·Å^{-3})/(ρ_{min}/e·Å^{-3})	2.514/–2.227	0.635/–0.570	4.563/–2.311

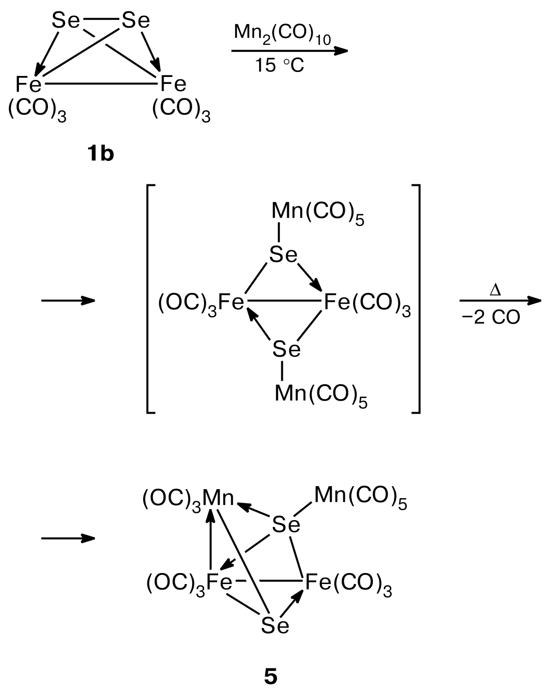
Table 4. Selected bond lengths (d) and angles (ω) for complexes **4b**, **5**, and **6**

Parameter	Value
4b	
Bond	d/Å
Ru(1)—Se(2)	2.4224(14)
Ru(1)—Se(1)	2.4347(16)
Ru(1)—Fe(1)	2.7203(19)
Fe(1)—Se(2)	2.3828(17)
Fe(1)—Se(1)	2.4035(16)
Fe(1)—Fe(2)	2.6718(18)
Fe(2)—Se(2)	2.3818(17)
Angle	ω/deg
Fe(2)—Fe(1)—Ru(1)	84.11(5)
Fe(2)—Se(1)—Fe(1)	67.83(5)
Fe(2)—Se(1)—Ru(1)	97.07(5)
Fe(1)—Se(1)—Ru(1)	68.42(5)
Fe(2)—Se(2)—Fe(1)	68.22(6)
Fe(2)—Se(2)—Ru(1)	97.50(5)
Fe(1)—Se(2)—Ru(1)	68.95(5)

Parameter	Value
5	
Bond	d/Å
Mn(1)—Se(2)	2.391(3)
Mn(1)—Fe(2)	2.709(3)
Fe(1)—Se(1)	2.373(3)
Fe(1)—Se(2)	2.397(3)
Fe(1)—Fe(2)	2.623(3)
Fe(2)—Se(2)	2.401(3)
Mn(2)—Se(1)	2.516(3)
Angle	ω/deg
Fe(1)—Fe(2)—Mn(1)	87.82(9)
Fe(1)—Se(1)—Fe(2)	67.04(8)
Fe(1)—Se(1)—Mn(1)	101.75(9)
Fe(2)—Se(1)—Mn(1)	69.21(8)
Fe(1)—Se(1)—Mn(2)	132.62(10)
Fe(2)—Se(1)—Mn(2)	124.71(10)
Mn(1)—Se(1)—Mn(2)	125.60(10)
Mn(1)—Se(2)—Fe(1)	101.15(9)
Mn(1)—Se(2)—Fe(2)	68.86(9)
Fe(1)—Se(2)—Fe(2)	66.28(8)

Parameter	Value
6	
Bond	d/Å
Re(1)—Se(2)	2.5894(11)
Re(1)—Se(1)	2.5904(11)
Se(1)—Fe(1)	2.3784(18)
Se(1)—Fe(2)	2.3834(16)
Se(2)—Fe(1)	2.3772(18)
Se(2)—Fe(2)	2.3793(16)
Fe(1)—Fe(2)	2.5151(19)
Angle	ω/deg
Fe(1)—Se(1)—Fe(2)	63.76(5)
Fe(1)—Se(1)—Re(1)	99.65(5)
Fe(2)—Se(1)—Re(1)	96.71(5)
Fe(1)—Se(2)—Fe(2)	63.84(5)
Fe(1)—Se(2)—Re(1)	99.71(5)
Fe(2)—Se(2)—Re(1)	96.84(5)

Scheme 6



However, according to X-ray diffraction data (Fig. 2, see Tables 3 and 4), the Fe—Fe bond (2.623(3) Å) is retained in the obtained new cluster, $(CO)_6Fe_2Se_2Mn_2(CO)_8$ (**5**), as in the sulfide cluster, and $Mn(CO)_5$ is attached only through the Mn—Se bond (2.516(3) Å). The second $Mn(CO)_3$ fragment, which has lost CO groups, forms the additional donor-acceptor Se→Mn and Fe→Mn bonds (2.394(3) and 2.709(3) Å, respectively), which make up for the five-electron deficiency at the second Mn atom. Apparently, the reaction proceeds *via* the photochemical cleavage of the Mn—Mn bond and the addition of two $Mn(CO)_5$ radicals giving rise to an intermediate similar to the $[(CO)_5Re]_2Te_2Fe_2(CO)_6$ complex mentioned above.[16] However, the covalent radius of Se atoms, exceeding that of S atoms, is insufficient for preventing further decarbonylation. Note that this cluster is isoelectronic and isostructural to the $Fe_3(CO)_9S_2W(CO)_5$ cluster, synthesized previously[28] by addition of the $W(CO)_5$ fragment to the sulfide bridge in $Fe_3(CO)_9S_2$.

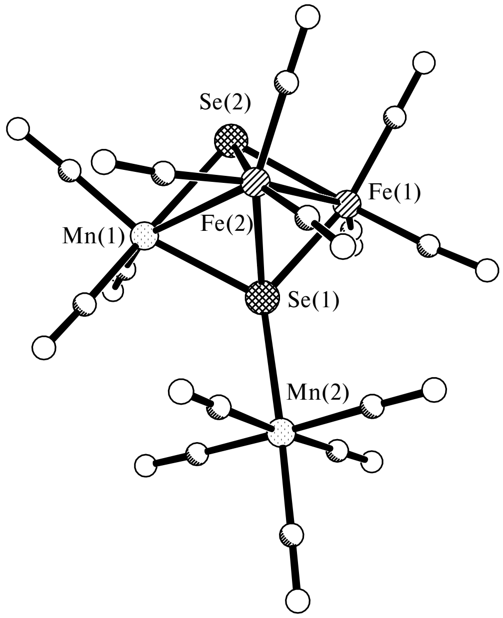
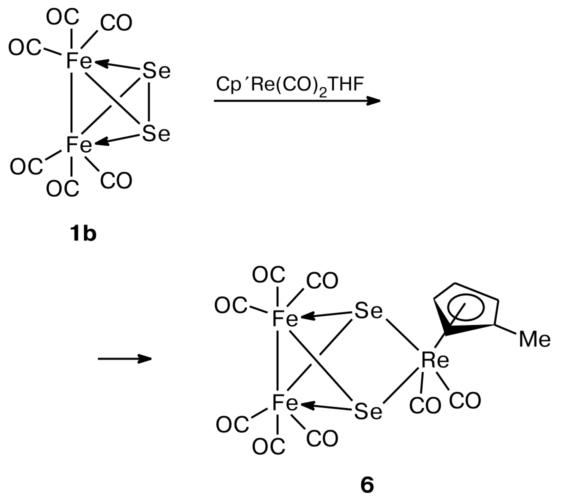


Fig. 2. Molecular structure of complex **5**.

The expected difference between selenium- and sulfur-bridged clusters shows itself in the reaction of cluster **1b** with the $Cp'Re(CO)_2THF$ complex ($Cp' = MeC_5H_4$), prepared previously by UV irradiation of $Cp'Re(CO)_3$ in THF. The reaction gave a new heterometallic cluster, $Cp'Re(CO)_2Se_2Fe_2(CO)_6$ (**6**), as black-brown crystals (Scheme 7).

Scheme 7



The X-ray diffraction data for this complex (Fig. 3, see Tables 3 and 4) indicate that the Re-containing fragment is linked to Fe only through two μ_3-Se bridges (Se—Re 2.589(1) and 2.590(1) Å), the Fe—Fe bond (2.515(2) Å) being retained and the Fe—Re bond being absent.

Complex **6** is an analog of the hypothetical sulfide intermediate, $(CO)_6Fe_2S_2[CpRe(CO)_2]$, in which the decrease in the covalent radius of sulfur with respect to selenium should decrease the distance between the Re and Fe atoms, thus facilitating decarbonylation and giving rise to the known $(CO)_6Fe_2S_2[CpRe(\mu\text{-}CO)]$ cluster.[21]

It appeared of interest to carry out targeted synthesis of a heterometallic heterochalcogenide cluster by combining complexes **1b** and **1c** in the coordination sphere of the Mo atom. These clusters based on heterochalcogenide

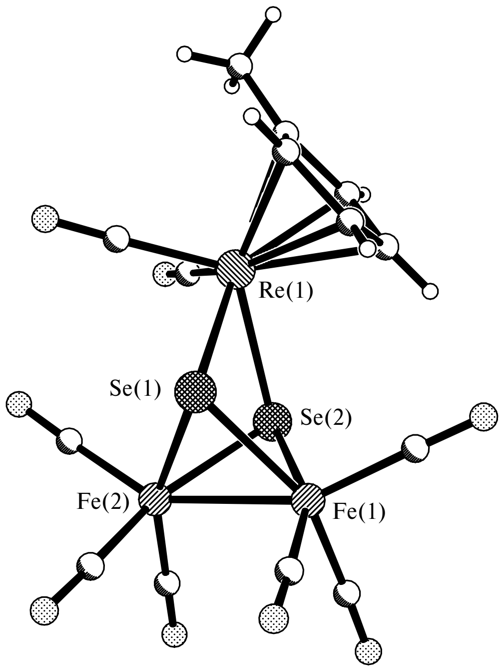
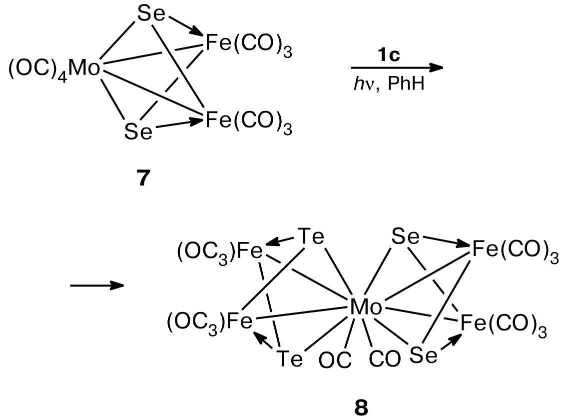


Fig. 3. Molecular structure of complex **6**.

binuclear Fe complexes such as $[Fe_2(CO)_6(\mu_3\text{-}Se)(\mu_3\text{-}Te)]$ are difficult to prepare, as it is difficult to separate them from homochalcogenide complexes.[29]

Therefore, we carried out the reaction between $Mo(CO)_5(THF)$ and cluster **1b**. The known[24] $Fe_2(CO)_6(\mu_3\text{-}Se)_2Mo(CO)_4$ cluster (**7**) thus formed was introduced in the photochemical reaction with **1c**. Finally, this yielded a new $Fe_2(CO)_6(\mu_3\text{-}Se)_2Mo(CO)_2(\mu_3\text{-}Te)_2Fe_2(CO)_6$ cluster (**8**) as black-brown crystals (Scheme 8). This product was characterized by elemental analysis, IR spectroscopy, and differential scanning calorimetry (DSC). An X-ray diffraction study was impossible because of crystal twinning. By analogy with the sulfide complex prepared previously,[25] cluster **8** probably contains a K-shaped metal core, Fe_2MoFe_2, with Se and, correspondingly, Te atoms located above and below the $MoFe_2$ triangles. The heterochalcogenide $[Fe_2(CO)_6(\mu_3\text{-}Se)(\mu_3\text{-}Te)]_2Mo(CO)_2$ cluster described previously[26] has a similar structure but with different chalcogen atoms at each $MoFe_2$ triangle.

Scheme 8



The thermal decomposition of clusters **4—8** is accompanied[30] by elimination of the CO and MeCp groups. One can follow some general features: first, incomplete elimination of the CO groups during thermolysis of the carbonyl chalcogenide clusters with M : E > 1, and second, the formation of metal chalcogenides containing no metal carbides or oxides in the presence of an MeCp ligand.

Thus, the replacement of the bridging S atoms in heterometallic clusters by Se atoms increases the metal—metal and metal—chalcogen distances, increases the stability of intermediate carbonyl-containing complexes, but does not influence the general pattern of the thermal decomposition of the clusters.

Experimental

All operations related to the synthesis and isolation of complexes were carried out under argon and in anhydrous solvents. The $Fe_2E_2(CO)_9$ (E = S, Se or Te),[31,32] $Fe_2(CO)_6(\mu_3\text{-}Se)_2Mo(CO)_4$,[23] $Cp'Re(CO)_3$,[33] and $Ru(CO)_4(C_2H_4)$ complexes[17] were synthesized by previously described procedures. Commercial decacarbonylmanganese (Aldrich) was recrystallized from pentane.

IR spectra were recorded on a Specord 75 IR spectrophotometer in KBr pellets. Elemental analysis of the complexes was carried out on a CHNS analyzer (Carlo Erba, Italy). Thermal decomposition of the complexes was studied by DSC on a Mettler TA-4000 thermal analyzer (Switzerland) in an atmosphere of dry argon.

X-ray diffraction study. The crystal structure data and X-ray experiment details for complexes **4b**, **5**, and **6** are presented in Table 3. All structures were solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation for F^2 (the H atoms were refined in the isotropic approximation) using the SHELXTL-97 program package. The positions of H atoms were calculated geometrically and refined using the "rider" model. Selected bond lengths and bond angles in the molecules of complexes are presented in Table 4.

Bis(tricarbonyliron-μ_3-selenide)tricarbonylruthenium $(CO)_3Ru(\mu_3\text{-}Se)_2Fe_2(CO)_6$ (4b). A yellow-green solution of $Ru_3(CO)_{12}$ (0.07 g, 0.11 mmol) in 90 mL of petroleum ether in a Schlenk quartz vessel was irradiated with UV light (a DRT-2 lamp) for 15 min in a flow of ethylene. The resulting colorless solution of $Ru(CO)_4(C_2H_4)$ [17] was added to a black solution of $Fe_2Se_2(CO)_6$ (0.15 g, 0.34 mmol) in 10 mL of petroleum ether. The red solution thus formed was filtered, concentrated to 1/6 its initial volume, and kept in the cold for 2 days. The solution was again filtered to remove the brown precipitate formed, which was washed with 20 mL of petroleum ether. The combined solution was concentrated to 1/5 its initial volume and kept in the cold for 24 h. The black-red crystals thus formed were recrystallized from petroleum ether, separated from the solution, and dried. Yield 0.06 g (29%). Found (%): C, 17.36. $C_9Fe_2O_9RuSe_2$. Calculated (%): C, 18.39. TLC (Silufol, hexane): a red-orange spot with R_f 0.57. IR, ν/cm^{-1}: 535 m, 585 m, 600 m, 1951 m, 1985 s, 2012 s, 2030 s, 2058 s, 2085 s. The complex is soluble in saturated hydrocarbons, CH_2Cl_2, benzene, and THF.

Octacarbonylmanganesebis(tricarbonyliron-μ_3-selenide) $(CO)_8Mn_2(\mu_3\text{-}Se)_2Fe_2(CO)_6$ (5). An orange solution of $Fe_2Se_2(CO)_6$ (0.25 g, 0.6 mmol) in 15 mL of hexane was added to a yellow-green solution of $Mn_2(CO)_{10}$ (0.24 g, 0.6 mmol) in 10 mL of hexane. The mixture was irradiated with UV light (a DRT-2 lamp) for 80 min at 15 °C and then for 35 min at reflux. The resulting black-colored precipitate was collected on a filter, washed with 15 mL of hexane, dried, and extracted with 35 mL of CH_2Cl_2. The resulting brown-orange solution was concentrated to 1/3 its initial volume and diluted with 13 mL of hexane, and the mixture was kept for 24 h at −18 °C. The resulting black-brown crystals were separated from the solution, washed with 10 mL of hexane, and dried. Yield 0.11 g (27%). DSC analysis showed quantitative elimination of 12 CO groups: Found/Calculated (mass loss, %): 43.0/43.5; the final decomposition product was $Fe_2Mn_2Se_2(C)_2(O)_2$. TLC (Silufol, hexane—CH_2Cl_2, 1 : 1), a reddish-light-brown spot with R_f 0.68. IR, ν/cm^{-1}: 584 m, 608 m, 640 s, 1936 s, 1968 s, 2008 s, 2056 s, 2136 s. The complex is soluble in CH_2Cl_2 and benzene and insoluble in saturated hydrocarbons.

Methylcyclopentadienyldicarbonylrheniumbis(tricarbonyliron-μ_3-selenide) $(CH_3C_5H_4)(CO)_2Re(\mu_3\text{-}Se)_2Fe_2(CO)_6$ (6). A brown-yellow solution of Cp´Re(CO)$_2$THF prepared by irradiation of $(MeC_5H_4)Re(CO)_3$ (0.29 g, 0.83 mmol) with UV light (a DRT-2 lamp) in 30 mL of THF for 5.5 h was added to a yellow-orange solution of $Fe_2Se_2(CO)_6$ (0.18 g, 0.42 mmol) in 10 mL of THF. The mixture was stirred for 30 min until $Fe_2Se_2(CO)_6$ disappeared. The resulting greyish-brown solution was concentrated to dryness and the residue was washed with 30 mL of petroleum ether and extracted with ether (30 mL). The reddish-brown extract was concentrated to 1/5 its initial volume, 4 mL of petroleum ether was added, and the mixture was kept in the cold for 2 days. The precipitated dark-brown crystals were separated from the solution and recrystallized from an ether—petroleum ether mixture. Yield 0.1 g (33%). Found (%): C, 22.38; H, 0.24. $C_{14}H_7Fe_2O_8ReSe_2$. Calculated (%): C, 22.15; H, 0.93. IR, ν/cm^{-1}: 460 w, 500 w, 545 m, 555 m, 575 m, 615 m, 840 m, 1030 w, 1460 w, 1950 s, 1960 s, 1985 s, 2005 vs, 2020 vs, 2025 vs, 2050 s. DSC analysis showed quantitative elimination of the following fragments, Found/Calculated (% of mass loss): 8 CO, 29.2/29.5; MeC_5H_4, 11.0/10.4. The final decomposition product was $ReFe_2Se_2$. TLC (hexane—CH_2Cl_2, 4 : 3), a reddish-brown spot, R_f 0.58. The complex is soluble in ether, CH_2Cl_2, benzene, and THF.

Dicarbonylmolybdenumbis(tricarbonyliron-μ_3-selenide)bis(tricarbonyliron-μ_3-telluride) $Fe_2(CO)_6(\mu_3\text{-}Se)_2Mo(CO)_2(\mu_3\text{-}Te)_2Fe_2(CO)_6$ (8). A dark-orange solution of compound **1c** (0.25 g, 0.4 mmol) in 10 mL of benzene was added to a dark-crimson solution of $Fe_2Mo(CO)_{10}(\mu\text{-}Se)_2$ (0.2 g, 0.3 mmol) in 8 mL of benzene. The mixture was irradiated with UV light (a DRT-2 lamp) for 1 h at 15 °C and for 30 min at reflux. The resulting black-brown finely crystalline precipitate was collected on a filter, washed with 15 mL of hexane, and dried. The mother liquor was filtered and chromatographed on Al_2O_3 (a 4.5×8 cm column) using 15 mL of benzene for elution. The solution was concentrated to 1/3 the initial volume, diluted with 8 mL of hexane, and kept for 24 h at 0 °C. The finely crystalline precipitate was separated, washed with 10 mL of hexane, dried, and combined with the crystals precipitated during the reaction. Total yield 0.15 g (45%). Found (%): C, 15.73. $C_{14}O_{14}Fe_4MoSe_2Te_2$. Calculated (%): C, 14.95. TLC (Silufol, hexane—CH_2Cl_2, 1 : 1) a light-brown spot with R_f 0.7. IR, ν/cm^{-1}: 550 m, 570 m, 590 m, 1965 m, 1981 m, 2008 m, 2022 s, 2032 s, 2077 m. DSC analysis showed quantitative elimination of 10 CO groups: Found/Calculated (mass loss, %), 25.0/24.9. The final decomposition product was $Fe_4MoSe_2Te_2C_4O_4$.

The authors are grateful to Zh. V. Dobrokhotova for investigation of the thermal decomposition of complexes.

This work was financially supported by the Russian Foundation for Basic Research (Projects No. 02-03-06170, No. 02-03-06171, No. MP-99-2, and N. 03-03-32730).

References

1. J. Kim and D. C. Rees, *Science*, 1992, **257**, 1677.
2. M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **23**, 83.
3. S. V. Larionov and S. M. Zemskova, *Ros. Khim. Zhurn.*, 1996, **40**, 171 [*Mendeleev Chem. J.*, 1996, **40** (Engl. Transl.)].
4. P. Mathur, *Adv. Organomet. Chem.*, 1997, **41**, 243.
5. C. H. Wei, and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1.
6. C. F. Campana, F. Y. Lo, and L. F. Dahl, *Inorg. Chem.*, 1979, **18**, 3060.
7. R. E. Bachmann and K. H. Whitmare, *J. Organomet. Chem.*, 1994, **479**, 31.
8. S. S. Batsanov, *Zh. Neorgan. Khim.*, 1991, **36**, 3015 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
9. B. K. Teo, M. B. Hall, D. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, 1975, **14**, 3103.
10. T. P. Weatherill, T. B. Rauchfuss, and R. A. Scott, *Inorg. Chem.*, 1986, **25**, 1466.
11. R. Seidel, B. Schnautz, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1710.
12. H. Schumann, M. Magerstadt, and J. Pickardt, *J. Organomet. Chem.*, 1982, **240**, 407.
13. D. A. Lesch and T. B. Rauchfuss, *Organometallics*, 1982, **1**, 499.
14. M. Shieh, T.-F. Tang, Sh.-M. Peng, and G.-H. Lee, *Inorg. Chem.*, 1995, **34**, 2797.
15. D. Seyferth, R. S. Henderson, J. P. Fackler, Jr., and A. M. Mazany, *J. Organomet. Chem.*, 1981, **213**, 21.
16. S. Huffer, K. Polborn, and W. Beck, *Organometallics*, 1995, **14**, 953.
17. P. Mathur, Md. M. Hossain, and R. S. Rashid, *J. Organomet. Chem.*, 1993, **460**, 83.
18. P. Mathur, I. J. Mavunkal, V. Rugmini, and M. F. Mahon, *Inorg. Chem.*, 1990, **29**, 4838.
19. D. Chakraborty, Md. M. Hossain, R. K. Kumar, and P. Mathur, *J. Organomet. Chem.*, 1991, **410**, 143.

20. P. Mathur, S. Ghosh, Md. M. Hossain, and C. V. V. Satyanarayana, *J. Organomet. Chem.*, 1997, **538**, 57.
21. A. A. Pasynskii, B. I. Kolobkov, S. E. Nefedov, I. L. Eremenko, E. S. Koltun, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1993, **454**, 229.
22. S. E. Nefedov, B. I. Kolobkov, A. A. Pasynskii, I. L. Eremenko, I. D. Sadekov, A. I. Yanovskii, and Yu. T. Struchkov, *Zh. Neorgan. Khim.*, 1992, **37**, 335 [*Russ. J. Inorg. Chem.*, 1992, **37** (Engl. Transl.)].
23. P. Mathur, D. Chakraborty, Md. M. Hossain, and R. S. Rashid, *Inorg. Chem.*, 1992, **431**, 1106.
24. P. Mathur, P. Sekar, C. V. V. Satyanarayana, and M. F. Mahon, *J. Chem. Soc., Dalton Trans.*, 1996, 2173.
25. A. A. Pasynskii, I. L. Eremenko, S. E. Nefedov, B. I. Kolobkov, A. D. Shaposhnikova, R. A. Stadnichenko, M. V. Drab, Yu. T. Struchkov, and A. I. Yanovsky, *Nouv. J. Chim.*, 1994, **18**, 69.
26. P. Mathur, P. Sekar, A. L. Rheingold, and L. M. Liable-Sands, *J. Chem. Soc., Dalton Trans.*, 1997, 2949.
27. R. S. Rashid, Ph. D. Thesis, Indian Institute of Technology, Bombay, 1991.
28. A. A. Pasynskii, B. I. Kolobkov, I. L. Eremenko, S. E. Nefedov, S. B. Katser, and M. A. Porai-Koshits, *Zh. Neorgan. Khim.*, 1992, **37**, 563 [*Russ. J. Inorg. Chem.*, 1992, **37** (Engl. Transl.)].
29. P. Mathur, D. Chakraborty, and Md. M. Hossain, *J. Organomet. Chem.*, 1991, **401**, 167.
30. A. A. Pasynskii, Zh. V. Dobrokhotova, N. I. Semenova, Yu. V. Torubaev, and V. M. Novotortsev, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 103 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 109].
31. W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, 1958, **296**, 91.
32. P. Mathur, Md. M. Hossain, S. N. Datta, R.-K. Kondru, and M. M. Bhadbhad, *Organometallics*, 1994, **13**, 2532.
33. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and L. I. Baryshnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 193 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1963, **12** (Engl. Transl.)].

Received November 1, 2002
in revised form January 23, 2003