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# Synthesis and structures of new heteronuclear cluster complexes $[PPh_4][Fe_4Rh_3Se_2(CO)_{16}]$ and $[PPh_4]_2[Fe_3Rh_4Te_2(CO)_{15}]$

**D. A. Bashirov,[a] O. Fuhr,[b] and S. N. Konchenko[a]★**

[a]*A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
*3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.*
*Fax: +7 (383) 330 9489. E-mail: konch@che.nsk.su*
[b]*Institute of Nanotechnology, Research Center Karlsruhe,*
*Postfach 3640, D-76021 Karlsruhe, Germany.*
*Fax: +49 721 608 2086. E-mail: olaf.fuhr@gmx.de**

The reaction of the $K_2[Fe_3Q(CO)_9]$ clusters (Q = Se or Te) with $Rh_2(CO)_4Cl_2$ under mild conditions is accompanied by complicated fragmentation of cores of the starting clusters to form large heteronuclear cluster anions. The $[PPh_4][Fe_4Rh_3Se_2(CO)_{16}]$ and $[PPh_4]_2[Fe_3Rh_4Te_2(CO)_{15}]$ compounds were isolated by treatment of the reaction products with tetraphenylphosphonium bromide. The structures of the products were established by X-ray diffraction. In both compounds, the core of the heteronuclear cluster consists of two octahedra fused *via* a common $Rh_3$ face.

**Key words:** clusters, iron, rhodium, selenium, tellurium, X-ray diffraction study.

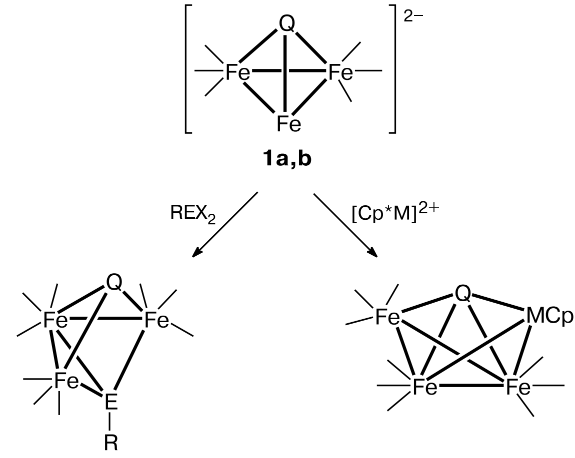
Heterometallic clusters containing main-group elements in the core have attracted interest because of their synthetic potential and the possibility of using these compounds for the design of highly organized nanoparticles.[1] Such clusters can serve as convenient building blocks in the assembly of large heteronuclear clusters.[2]

Earlier,[3,4] we have used the tetrahedral cluster anions $[Fe_3Q(CO)_9]^{2-}$ (Q = Se (**1a**) or Te (**1b**)) for the synthesis of larger heteronuclear chalcogenide clusters containing various combinations of both transition and main-group elements. For example, the addition of electrophilic species containing Group 15 elements to anions **1a,b** affords the square-pyramidal complexes $[Fe_3Q(ER)(CO)_9]$,[3] whereas the addition of the $[Cp^*Rh]^{2+}$ and $[Cp^*Ir]^{2+}$ species gives rise to the trigonal-bipyramidal clusters $[Fe_3MQ(CO)_9Cp^*]$ (see Ref. 4) (Scheme 1).

In these reactions, clusters **1a** and **1b** behave identically. The reaction products are similar to the products obtained in the reactions of their analogs, *viz.*, $[Fe_3O(CO)_9]^{2-}$ (see Ref. 5) and $[Fe_3S(CO)_9]^{2-}$.[6]

In the present study, we examined the reactions of clusters **1a** and **1b** with the dinuclear complex $Rh_2(CO)_4Cl_2$.

**Scheme 1**



E = As, Sb, Bi; X = Cl, Br, I; Q = Se (**1a**), Te (**1b**); M = Rh, Ir

## Results and Discussion

The reactions of $K_2[\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ with $[Rh_2(CO)_4Cl_2]$ in diethyl ether produced brown solutions and black amorphous precipitates insoluble in organic solvents. The precipitates were filtered off and discarded. The diethyl ether soluble products were isolated in the crystalline state as salts of the $[PPh_4]^+$ cation. The structures of the heteronuclear cluster compounds $[PPh_4][Fe_4Rh_3Se_2(CO)_{16}]$ ($[PPh_4][\mathbf{2}]$) and $[PPh_4]_2[Fe_3Rh_4Te_2(CO)_{15}]$ ($[PPh_4]_2[\mathbf{3}]$) (Scheme 2) were established by X-ray diffraction (Figs 1 and 2).

It is known[7] that the reaction of $[Fe_3O(CO)_9]^{2-}$ with $Rh_2(CO)_4Cl_2$ leads not merely to the addition of the electrophilic $[Rh(CO)_2]^+$ species to the $[Fe_3O]$ fragment but

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* Institut für Nanotechnologie, Forschungszentrum Karlsruhe Postfach 3640, D-76021 Karlsruhe, Germany.

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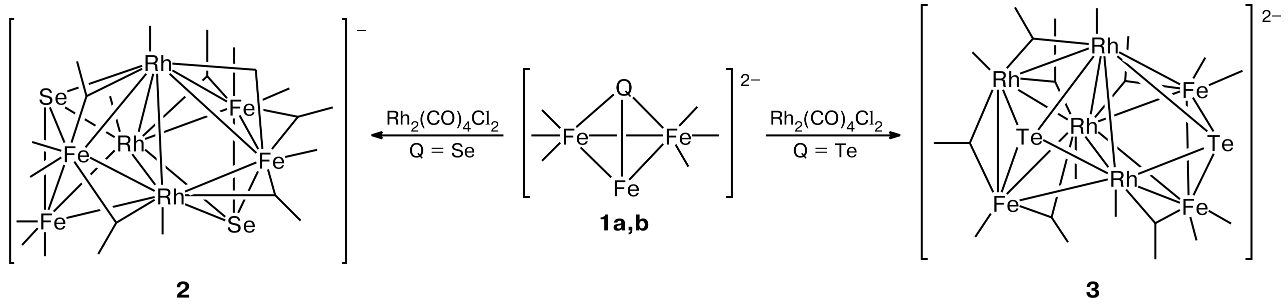
**Scheme 2**



Q = Se (**1a**), Te (**1b**)

to the formation of the larger $[Fe_3Rh_3O(CO)_{15}]^{2-}$ cluster containing the distorted octahedral core and the external $\mu_3$-O atom coordinated at the $Fe_3$ face. We found that the reactions of $K_2$[**1a**] and $K_2$[**1b**] with $Rh_2(CO)_4Cl_2$ produced radically different cores. The treatment of the reaction mixture with tetraphenylphosphonium bromide afforded the $[PPh_4]$[**2**] and $[PPh_4]_2$[**3**] compounds, whose cluster cores consist of two octahedra fused *via* a common $Rh_3$ face.

The bioctahedral core of cluster **2** contains two identical external triangular $Fe_2Se$ faces. As opposed to **2**, the external faces in anion **3** are different ($Fe_2Te$ and FeRhTe). Clusters **2** and **3** are isoelectronic because the additional electron of the Rh(4) atom and the additional negative charge in anion **3** are compensated by the absence of one CO ligand. Thus, there are 16 CO (ten terminal and six bridging) ligands in **2** and 15 CO (nine terminal and six bridging) ligands in **3**. The $[PPh_4]_2$[**3**] complex is the first structurally characterized compound containing simultaneously Fe, Rh, and Te (data on such complexes are lacking in the Cambridge Structural Database). We found only one complex with the Fe/Rh/Se combination. This is the $[Fe_3Rh(\mu_4\text{-}Se)(CO)_9Cp^*]$ cluster with the butterfly-like core.[4] The Rh—Se and Fe—Se distances in the latter complex, like those in complex **2**, have similar values, whereas the Rh—Fe bonds in **2** are somewhat longer. In anion **3**, the Rh—Te distances with the Rh atoms of the central triangle are in the range of 2.59—2.68 Å, which is typical of Rh—Te bonds. The Rh(4)—Te(1) bond in **3** is somewhat longer (2.74 Å). An interesting fact is that the structures of **2** and **3** differ in the mutual arrangement of the chalcogen atoms. In **3**, the Te atoms form an eclipsed conformation, whereas the external $Fe_2Se$ faces are twisted and the Se atoms are in skewed positions.

Since we isolated only small amounts of crystalline phases, it was impossible to perform elemental analysis and record chalcogen and carbon NMR spectra. The IR spectra of both $[PPh_4]$[**2**] and $[PPh_4]_2$[**3**] show one very broad band with a maximum at ~1960 cm$^{-1}$. To confirm the fact that the single-crystalline samples corre-

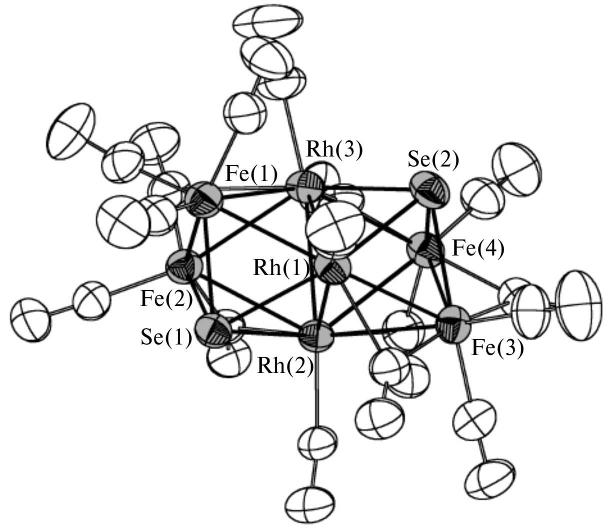


**Fig. 1.** Structure of cluster anion **2** in the crystal structure of $[PPh_4][Fe_4Rh_3Se_2(CO)_{16}]$.

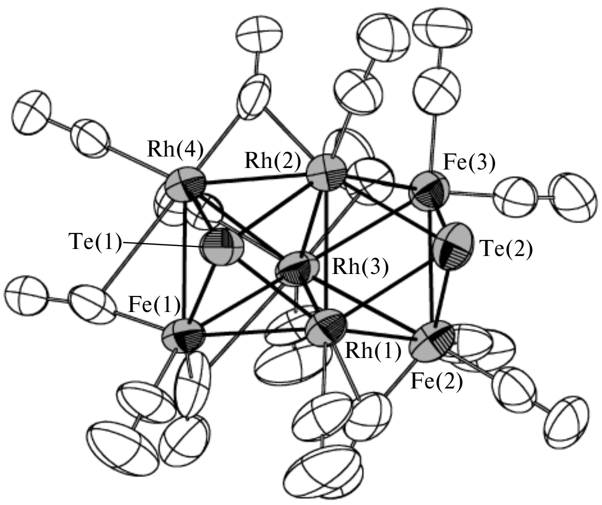


**Fig. 2.** Structure of cluster anion **3** in the crystal structure of $[PPh_4]_2[Fe_3Rh_4Te_2(CO)_{15}]$.

spond to the the weights of the respective compounds, we measured the mass spectra (ES) of [$PPh_4$][**2**] and [$PPh_4$]$_2$[**3**] solutions (samples of both crystalline phases were completely dissolved in $CH_2Cl_2$). The cationic region of the spectra has only peaks corresponding to the [$PPh_4$]$^+$ cations. The anionic region of the spectrum of [$PPh_4$][**2**] contains signals of anions **2** with a correct isotope distribution and signals of the [**2** – CO] fragment produced by the loss of one CO group. The anionic region of the spectrum of [$PPh_4$]$_2$[**3**] shows signals of **3** and [**3** – CO], but the main peaks correspond to the monoprotonated forms [$Fe_3Rh_4Te_2(CO)_{15}H$]$^-$ and [$Fe_3Rh_4Te_2(CO)_{14}H$]$^-$. This result can be attributed to the following two factors: either the starting crystalline sample contains a mixture of the protonated and deprotonated forms or protonation occurs during the mass spectroscopic measurements. The $^1$H NMR spectra of [$PPh_4$]$_2$[**3**] in THF-$d_8$ and $CD_2Cl_2$ show only signals for the protons of the Ph groups of the [$PPh_4$]$^+$ cation. Therefore, it can be concluded that protonation of **3** occurs in the course of the mass spectroscopic measurements, and the single-crystalline samples of [$PPh_4$][**2**] and [$PPh_4$]$_2$[**3**] correspond to the overall composition of the resulting products.

## Experimental

All operations associated with the synthesis, isolation of the reaction products, and spectroscopic measurements were carried out under argon with the use of the standard Schlenk techniques. All solvents were purified by distillation under argon with the corresponding drying agents immediately before use.[8] The starting compounds were prepared according to known procedures (see Ref. 9 for [$Rh_2(CO)_4Cl_2$] and Ref. 3b for $K_2[Fe_3(\mu_3\text{-}Q)(CO)_9]$ (**1a,b**)). The electrospray mass spectra of solutions of the clusters in $CH_2Cl_2$ were measured on a Bruker Daltonics APEX ion cyclotron resonance mass spectrometer equipped with a superconducting magnet (7T) and an infinite cylindrical cell. The $^1$H NMR spectra were recorded on a Bruker AC 250 instrument (250.133 MHz) for solutions of [$PPh_4$][**2**] and [$PPh_4$]$_2$[**3**] in THF-$d_8$ and $CD_2Cl_2$. The $^1$H NMR spectra show signals only for the protons of the [$PPh_4$] cation.

**Synthesis of tetraphenylphosphonium decacarbonylhexa(μ-carbonyl)di(μ$_3$-selenido)trirhodiumtetraferrate, [$PPh_4$][$Fe_4Rh_3Se_2(CO)_{16}$] ([$PPh_4$][2]).** Diethyl ether (20 mL) was condensed *in vacuo* into a flask, which contained a mixture of the solid compounds [$Rh_2(CO)_4Cl_2$] (0.041 g, 0.11 mmol) and $K_2$[**1a**] (0.061 g, 0.11 mmol) and was cooled with liquid nitrogen. After removal of the cooling bath, the reaction mixture was gradually heated to room temperature with constant stirring. Then the reaction mixture was stirred for 24 h, the mixture gradually turning dark-brown. The solution was filtered off from the black precipitate, which was insoluble in organic solvents. The filtrate was concentrated to dryness *in vacuo*. The solid residue was washed with toluene (10 mL) and dissolved in ethanol (10 mL). The solution was filtered off and [$PPh_4$]Br (0.09 g, 0.215 mmol) was added. The resulting mixture was stirred for 24 h and filtered off. The filtrate was concentrated to dryness *in vacuo* without heating. The residue was dissolved in $CH_2Cl_2$ (2 mL), after which a hexane layer (4 mL) was carefully deposited onto the solution. After complete mixing of the solvent layers (several days), black crystals of [$PPh_4$][**2**] were obtained in a yield of 0.020 g (26%). Electrospray mass spectrum, *m/z* (*I* (%)): 1138 (100) [**2**], 1110 (62) [**2** – CO].

**Synthesis of bis-tetraphenylphosphonium nonacarbonylhexa(μ-carbonyl)di(μ$_3$-tellurido)tetrarhodiumtriferrate, [$PPh_4$]$_2$[$Fe_3Rh_4Te_2(CO)_{15}$] ([$PPh_4$]$_2$[3]).** Diethyl ether (20 mL) was condensed *in vacuo* into a flask, which contained a mixture of the solid compounds [$Rh_2(CO)_4Cl_2$] (0.041 g, 0.11 mmol) and $K_2$[**1b**] (0.066 g, 0.11 mmol) and was cooled with liquid nitrogen. After removal of the cooling bath, the reaction mixture was gradually heated to room temperature with constant stirring, and then the mixture was stirred for 72 h. Further treatment of the reaction mixture, which was carried out as described above, afforded black crystals of [$PPh_4$]$_2$[**3**] in a yield of 0.026 g (24%). Electrospray mass spectrum, *m/z* (*I* (%)): 1256 (34) [(**3** + H$^+$)], 1228 (100) [(**3** + H$^+$ – CO)], 628 (2) [**3**], 614 (6) [(**3** – CO)].

**X-ray diffraction study.** The structures of [$PPh_4$][**2**] and [$PPh_4$]$_2$[**3**] were established by X-ray diffraction. Black single crystals were taken from the crystalline substance prepared as described above. Crystallographic data and details of X-ray diffraction study are given in Table 1. The structures were solved by

**Table 1.** Crystallographic data for the [$PPh_4$][**2**] and [$PPh_4$]$_2$[**3**] compounds

| Parameter | [$PPh_4$][**2**]* | [$PPh_4$]$_2$[**3**]* |
|---|---|---|
| Molecular weight | 1477.58 | 1933.28 |
| Crystal system | Triclinic | Triclinic |
| $a$/Å | 11.245(2) | 13.023(3) |
| $b$/Å | 13.961(3) | 13.868(3) |
| $c$/Å | 16.048(3) | 19.818(4) |
| α/deg | 101.81(3) | 91.45(3) |
| β/deg | 92.72(3) | 106.50(3) |
| γ/deg | 111.05(3) | 110.25(3) |
| $V$/Å$^{-3}$ | 2281.2(8) | 3189.1(11) |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $Z$ | 2 | 2 |
| $\rho_x$/g cm$^{-3}$ | 2.151 | 2.013 |
| Diffractometer | STOE IPDS II | |
| Radiation | Mo-Kα (λ = 0.71073 Å) | |
| $T$/K | 203(2) | 200(2) |
| μ/mm$^{-1}$ | 3.994 | 2.685 |
| Number of reflections measured/independent | 22792/ 11624 | 22921/ 11694 |
| $R$ factors | | |
| based on reflections with $I > 2\sigma(I)$ | | |
| $R_1$ | 0.0719 | 0.0559 |
| $wR_2$ | 0.2057 | 0.1471 |
| based on all reflections | | |
| $R_1$ | 0.0813 | 0.0743 |
| $wR_2$ | 0.2152 | 0.1578 |

* The molecular formulas of the compounds [$PPh_4$][**2**] and [$PPh_4$]$_2$[**3**] are [$C_{40}H_{20}Fe_4O_{16}PRh_3Se_2$] and [$C_{63}H_{40}Fe_3O_{15}P_2Rh_4Te_2$], respectively.

**Table 2.** Selected bond lengths (*d*) in cluster anions **2** and **3**

| Bond | *d*/Å | |
|---|---|---|
| | **2** (Q = Se) | **3** (Q = Te) |
| Rh(1)—Q(1) | 2.4944(15) | 2.5900(15) |
| Rh(1)—Q(2) | 2.4655(11) | 2.6779(13) |
| Rh(2)—Q(1) | 2.5277(11) | 2.6691(11) |
| Rh(3)—Q(2) | 2.5156(15) | — |
| Rh(2)—Q(2) | — | 2.6246(16) |
| Rh(4)—Q(1) | — | 2.7381(14) |
| Q(1)—Fe(1) | 2.3703(13) | 2.5492(19) |
| Q(1)—Fe(2) | 2.3917(13) | — |
| Q(2)—Fe(3) | 2.4482(14) | 2.5549(17) |
| Q(2)—Fe(2) | — | 2.549(2) |
| Q(2)—Fe(4) | 2.4321(13) | — |
| Rh(1)—Fe(1) | 2.6071(14) | 2.647(2) |
| Rh(1)—Fe(3) | 2.6403(15) | — |
| Rh(1)—Fe(2) | — | 2.6204(19) |
| Rh(2)—Fe(4) | 2.6568(13) | — |
| Rh(2)—Fe(2) | 2.6818(13) | — |
| Rh(2)—Fe(3) | 2.7549(17) | 2.6968(18) |
| Rh(3)—Fe(2) | 2.6198(16) | 2.781(2) |
| Rh(3)—Fe(1) | 2.7054(14) | 2.8640(17) |
| Rh(3)—Fe(3) | — | 2.7211(18) |
| Rh(3)—Fe(4) | 2.6291(14) | — |
| Rh(4)—Fe(1) | — | 2.7375(15) |
| Rh(1)—Rh(2) | 2.6718(9) | 2.7710(12) |
| Rh(1)—Rh(3) | 2.7224(10) | 2.6925(14) |
| Rh(2)—Rh(3) | 2.6795(10) | 2.7846(14) |
| Rh(2)—Rh(4) | — | 2.7122(18) |
| Rh(3)—Rh(4) | — | 2.7221(16) |
| Fe(1)—Fe(2) | 2.6823(16) | — |
| Fe(2)—Fe(3) | — | — |
| Fe(3)—Fe(4) | 2.5927(15) | 2.7034(19) |

direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms using the SHELXTL program package (version 5.04). The positions of the hydrogen atoms were calculated geometrically and refined using a riding model. Selected bond lengths are given in Table 2. The coordinates of the nonhydrogen atoms were deposited with the Cambridge Structural Database (CCDC 272836 for [$PPh_4$][**2**] and CCDC 272837 for [$PPh_4$]$_2$[**3**]) and can be obtained from the authors.

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