Synthesis and structures of new heteronuclear cluster complexes

\([\text{PPh}_4][\text{Fe}_4\text{Rh}_3\text{Se}_2(\text{CO})_{16}]\) and \([\text{PPh}_4]_2[\text{Fe}_3\text{Rh}_4\text{Te}_2(\text{CO})_{15}]\)

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The reaction of the \(\text{K}_2[\text{Fe}_3Q(\text{CO})_9]\) clusters (\(Q = \text{Se} (1\text{a}) \) or \(\text{Te} (1\text{b})\)) with \(\text{Rh}_2(\text{CO})_4\text{Cl}_2\) under mild conditions is accompanied by complicated fragmentation of cores of the starting clusters to form large heteronuclear cluster anions. The \([\text{PPh}_4][\text{Fe}_4\text{Rh}_3\text{Se}_2(\text{CO})_{16}]\) and \([\text{PPh}_4]_2[\text{Fe}_3\text{Rh}_4\text{Te}_2(\text{CO})_{15}]\) 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 Rh3 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 \([\text{Fe}_3Q(\text{CO})_9]^{2-}\) (\(Q = \text{Se} (1\text{a}) \) or \(\text{Te} (1\text{b})\)) 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 \(1\text{a,b}\) affords the square-pyramidal complexes \([\text{Fe}_3Q(\text{ER})(\text{CO})_9])\),3 whereas the addition of the \([\text{Cp}^*\text{Rh}]^{2+}\) and \([\text{Cp}^*\text{Ir}]^{2+}\) species gives rise to the trigonal-bipyramidal clusters \([\text{Fe}_3MQ(\text{CO})_9\text{Cp}^*]\) (see Ref. 4) (Scheme 1).

In these reactions, clusters \(1\text{a}\) and \(1\text{b}\) behave identically. The reaction products are similar to the products obtained in the reactions of their analogs, viz., \([\text{Fe}_3\text{O}(\text{CO})_9])^{2-}\) (see Ref. 5) and \([\text{Fe}_3\text{S}(\text{CO})_9])^{2-}\).6

In the present study, we examined the reactions of clusters \(1\text{a}\) and \(1\text{b}\) with the dinuclear complex \(\text{Rh}_2(\text{CO})_4\text{Cl}_2\).

Results and Discussion

The reactions of \(\text{K}_2[1\text{a}]\) and \(\text{K}_2[1\text{b}]\) with \(\text{Rh}_2(\text{CO})_4\text{Cl}_2\) 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 \([\text{PPh}_4]^+\) cation. The structures of the heteronuclear cluster compounds \([\text{PPh}_4][\text{Fe}_4\text{Rh}_3\text{Se}_2(\text{CO})_{16}]\) \(([\text{PPh}_4]^+2\text{I})\) and \([\text{PPh}_4]_2[\text{Fe}_3\text{Rh}_4\text{Te}_2(\text{CO})_{15}]\) \(([\text{PPh}_4]^+3\text{I})\) (Scheme 2) were established by X-ray diffraction (Figs 1 and 2).

It is known7 that the reaction of \([\text{Fe}_3\text{O}(\text{CO})_9])^{2-}\) with \(\text{Rh}_2(\text{CO})_4\text{Cl}_2\) leads not merely to the addition of the electrophilic \([\text{Rh}(\text{CO})_3]^+\) species to the \([\text{Fe}_3\text{O}]\) fragment but...
to the formation of the larger \([\text{Fe}_3\text{Rh}_3\text{O(CO)}_{15}]^{2-}\) cluster containing the distorted octahedral core and the external \(\mu_3\text{-O}\) atom coordinated at the \(\text{Fe}_3\) face. We found that the reactions of \(\text{K}_2[1\text{a}]\) and \(\text{K}_2[1\text{b}]\) with \(\text{Rh}_2(\text{CO})_4\text{Cl}_2\) produced radically different cores. The treatment of the reaction mixture with tetraphenylphosphonium bromide afforded the \([\text{PPh}_4]_2[2]\) and \([\text{PPh}_4]_2[3]\) compounds, whose cluster cores consist of two octahedra fused via a common \(\text{Rh}_3\) face.

The bi-octahedral core of cluster 2 contains two identical external triangular \(\text{Fe}_2\text{Se}\) faces. As opposed to 2, the external faces in anion 3 are different (\(\text{Fe}_2\text{Te}\) and \(\text{FeRhTe}\)). Clusters 2 and 3 are isoelectronic because the additional electron of the \(\text{Rh}(4)\) 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 \([\text{PPh}_4]_2[3]\) complex is the first structurally characterized compound containing simultaneously \(\text{Fe}, \text{Rh,}\) and \(\text{Te}\) (data on such complexes are lacking in the Cambridge Structural Database). We found only one complex with the \(\text{Fe}/\text{Rh}/\text{Se}\) combination. This is the \([\text{Fe}_3\text{Rh}(\mu_4\text{-Se})(\text{CO})_6\text{Cp}^+]\) cluster with the butterfly-like core.\(^4\) The \(\text{Rh}—\text{Se}\) and \(\text{Fe}—\text{Se}\) distances in the latter complex, like those in complex 2, have similar values, whereas the \(\text{Rh}—\text{Fe}\) bonds in 2 are somewhat longer. In anion 3, the \(\text{Rh}—\text{Te}\) distances with the \(\text{Rh}\) atoms of the central triangle are in the range of 2.59—2.68 Å, which is typical of \(\text{Rh}—\text{Te}\) bonds. The \(\text{Rh}(4)—\text{Te}(1)\) 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 \(\text{Te}\) atoms form an eclipsed conformation, whereas the external \(\text{Fe}_2\text{Se}\) faces are twisted and the \(\text{Se}\) 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 \([\text{PPh}_4]_2[2]\) and \([\text{PPh}_4]_2[3]\) show one very broad band with a maximum at \(\sim 1960\) cm\(^{-1}\). To confirm the fact that the single-crystalline samples corre-