# Synthesis and Structure of a Trinuclear Rhenium Cluster Complex $[PEt_3H][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]$

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Reaction of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_6]Cl$ with triethylphosphine in benzene formed $[PEt_3H][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]$. The triangular cluster has eight metal cluster electrons and the cluster core resembles that of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4L_5]$ cluster complexes.

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In contrast to the remarkable progress of the chemistry of molybdenum and tungsten chalcogenide halide cluster compounds with the $M_3(\mu_3\text{-}E)(\mu\text{-}E)_3$ cores (M = Mo, W; E = S, Se),[1] similar chemistry of rhenium is still undeveloped.[2] Recent interest in the stepwise construction of larger cluster skeletons by condensation of building block clusters necessitates more new cluster units, especially triangular ones.[3,4] The only triangular rhenium cluster sulfides $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X_6]X$ (X = Cl, Br) which have the potentials of providing the cluster complexes to be used as building blocks have been reported by Timoshchenko.[5,6] We have reported the synthesis of triangular rhenium cluster complexes with $Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}X)$ (X = Cl or Br) cores starting from these compounds.[7] The present communication describes the synthesis of the first example of a triangular rhenium cluster complex having the $Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ core.

Reaction of $[Re_3S_7Cl_6]Cl$ with triethylphosphine in benzene at room temperature for 5 days gave a red solution. The solution was filtered and the volatile materials were evaporated. The residue was washed with diethyl ether and extracted with benzene. The benzene solution was left standing for a week and black crystals formed in 26% yield. The elemental analysis agreed with the formula $[PEt_3H][Re_3S_4Cl_6(PEt_3)_3].C_6H_6$. (**1**) UV-Vis ($CH_2Cl_2$, $\lambda$/nm): 390(sh), 440(sh), 540(sh), 1120. $^1H$ NMR ($CD_2Cl_2$, TMS $\delta$/ppm): 1.12 (27 H), 1.35 (9 H), 1.92 (1 H), 2.36 (24 H). $^{31}P$ NMR ($CD_2Cl_2$, 85% $H_3PO_4$ external standard $\delta$/ppm): 16.91, -35.33. $^{13}C$ NMR ($CD_2Cl_2$, TMS $\delta$/ppm): 18.23 (d), 10.90 (d), 10.14 (d), 7.33 (d). IR (KBr): 2398 $cm^{-1}$ ($\nu$(P-H)).

The structure of **1** was determined by the single crystal X-ray analysis.[8] The ORTEP drawing of the anionic cluster and the mean interatomic distances are shown in Figure 1. Three rhenium atoms form a triangular cluster core capped and bridged by sulfur atoms. Each rhenium is coordinated by a triethylphosphine and two chlorine ligands. All the triethylphosphine ligands are directed below the $Re_3$ plane capped by the $\mu_3$-S atom and the chlorine ligands above the plane. The coordination geometry around rhenium atoms is nearly octahedral if the Re-Re bonds are neglected. The Re-Re distances are 2.715 Å, 2.716 Å, and 2.725 Å and the Re-Re-Re angles range from 59.87° to 60.23° ; the trinuclear cluster core distorts slightly from a regular triangle. The triethylphosphonium cation (not shown) looks very distorted due to the disorder of phosphorus and carbon atoms as is often seen in the structures of the triethylphosphonim cation of other anionic complexes.[9-11] The infrared spectrum of **1** shows a weak P-H stretching vibration at 2398 $cm^{-1}$.[10] The doublet of triplet signal in the $^1H$ NMR spectrum is assigned to the methyl group in the ethyl groups of the phosphonium cation and the weak doublet of triplet at 1.92 ppm to the phosphonium hydrogen atom. The methylene proton signals of the coordinated triethylphosphine and the triethylphosphonium cation are overlapped in the multiplet at 2.36 ppm, whereas the methyl protons of the coordinated triethylphosphine appear at the field 0.23 ppm higher (1.12 ppm) than those of the triethylphosphonium cation (1.35 ppm). The $^{31}P$ NMR spectrum shows two phosphorus resonances assignable to the coordinated phosphorus at -35.33 ppm and to the phosphonium phosphorus at 16.91 ppm. The $^{13}C$ NMR spectrum shows the signals assignable to two sets of methyl and methylene carbons. The higher-field resonances (10.90 ppm ($CH_2$) and 7.33 ppm ($CH_3$)) are assigned to the phosphonium carbons.[12] The sharpness of the peaks in the NMR spectra suggests that **1** is a diamagnetic compound with even number (8 $e^-$) of metal cluster electrons. The Re-Re distances in **1** are slightly longer than those in the starting compound (2.701 Å),[6] reflecting the existence of two more electrons than necessary for three Re-Re bonds (6 $e^-$). The $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Cl)Cl_3(PEt_3)_3]$ (9 $e^-$; Re-Re 2.628 - 2.677 Å) and $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Br)Br_2(PEt_3)_4]$ (10 $e^-$; Re-Re 2.648 - 2.687 Å) which we

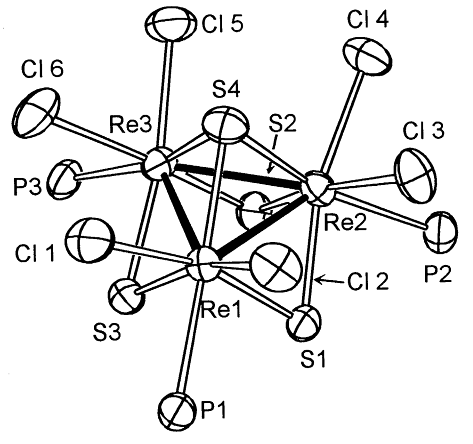

**Figure 1.** ORTEP drawing of the anionic cluster in $[PEt_3H][Re_3S_4Cl_6(PEt_3)_3]$. Ethyl groups are omitted for clarity. Mean interatomic distances are: Re-Re 2.719 Å; Re-Cl 2.423 Å; Re-$\mu_2$-S 2.290 Å; Re-$\mu_3$-S 2.333 Å; Re-P 2.562 Å.

have reported recently have shorter Re-Re distances but this may be due to their bi-capped triangular structures.[7] The comparison of the structure of **1** with that of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(MeOH)_2]$ (Mo-Mo 2.738(1) - 2.780(1) Å)[13] shows that the complex **1** has shorter M-M interatomic distances, which may be explained by the smaller Re radius (1.29 Å) as compared with that of Mo (1.31 Å).[14] The Re-S, Re-Cl, and Re-P distances are also shorter than the corresponding distances in the molybdenum analogue.

The formation of **1** is the result of the abstraction of one of the sulfur atoms in the $\mu$-$S_2$ ligands of the starting compound by triethylphosphine. Similar reaction pattern was originally applied to the preparation of the molybdenum cluster complexes.[13] The change of the $\mu$-$S_2$ into $\mu$-S ligand evacuates the coordination sites on the rhenium atoms which are taken by triethylphosphine ligands. Two Re(V) atoms in the starting compound $[Re_3S_7Cl_6]Cl$ are reduced to Re(IV) to change the metal cluster compound into an anionic complex with eight metal cluster electrons and a triethylphosphonium cation originated from triethylphosphine balances the charge. The number of terminal chlorine ligands remains six. In the previous communication, we have reported the formation of $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Cl)Cl_3(PEt_3)_3]$ in 26% yield from the similar reaction of $[Re_3S_7Cl_6]Cl$ with triethylphosphine.[7] The difference in the preparative procedure is the use of acetone instead of benzene for the crystallization. The preferential formation of one kind of crystals may well be due to the different solubilities of the cluster complexes in each solvent which contains both complexes.

The present cluster complex will be useful as the building blocks for the formation of larger rhenium clusters and mixed-metal clusters[15] which are similar to those obtained by the molybdenum analogues with the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster cores.[1,16]

## References and Notes

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8 Crystal data for $[PEt_3H][Re_3S_4Cl_6(PEt_3)_3].C_6H_6$: formula $C_{30}H_{67}Cl_6P_4Re_3S_4$, fw 1451.4, space group $P\bar{1}$, $a$ = 12.495(4) Å, $b$ = 16.787(4) Å, $c$ = 11.725(3) Å, $\alpha$ = 98.79(2) °, $\beta$ = 97.43(3)°, $\gamma$ = 81.72(3) °, $V$ = 2390(1) Å$^3$, $Z$ = 2, $D_{\text{calcd}}$ = 2.017 g cm$^{-3}$, $R$ = 0.046, $R_w$ = 0.038 for 10786 observed reflections ($|F_o| > 4\sigma(|F_o|)$; $6° < 2\theta < 60°$). The intensity data were collected by a Rigaku AFC-5R diffractometer with MoK$\alpha$ ($\lambda$ = 0.7107 Å) radiation at 291 K. The data were corrected for Lorentz-polarization and absorption (DIFABS).[17] The structure was solved by the teXsan package programs.[17] The positions of non-hydrogen atoms were located by the direct methods and on Fourier maps. The phosphorus atom of the phosphonium cation was found to be disordered in two sites. All the non-hydrogen atoms except for those of the phosphonium cation were refined anisotropically. Hydrogen atoms were not included in the refinements.

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