

Synthesis and Reactivity Studies of Rhenium Carbido Carbonyl Cluster Compounds

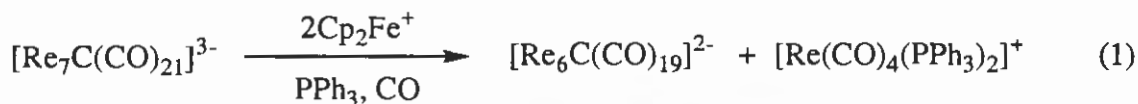
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Final Seminar

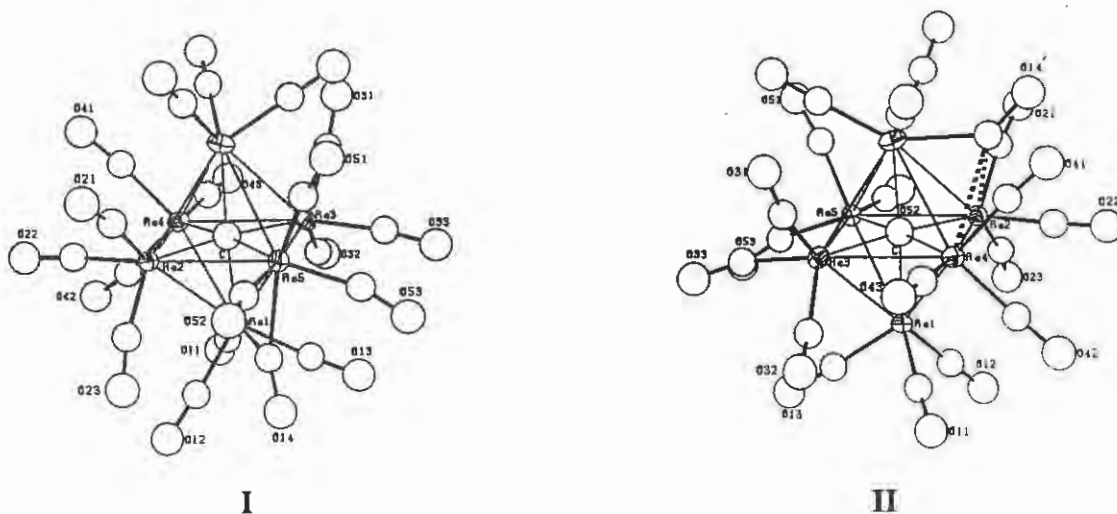
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The chemistry of transition-metal cluster compounds continues to receive attention [1]. The use of cluster compounds as models for heterogeneous catalysts remains an area of considerable interest. The relationship between ligands bonded to a cluster framework and organic fragments on metal surfaces has been recognized [2]. The incorporation of a ligand by a cluster compound and the reactions of that ligand are analogies for transformations of organic substrates by heterogeneous catalysts. Consequently, the systematic synthesis of cluster compounds and the exploration of their reactions are aspects of current research.

Our work began as an extension of our interest in the formation and interconversion of large rhenium carbonyl clusters [3]. The synthesis and characterization of new cluster compounds utilizing selective methods have been employed both to decrease and to increase nuclearity. The decapping reaction of $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ provided $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$ along with the mononuclear complex, $[\text{Re}(\text{CO})_4(\text{PPh}_3)_2]^+$ (eq 1).

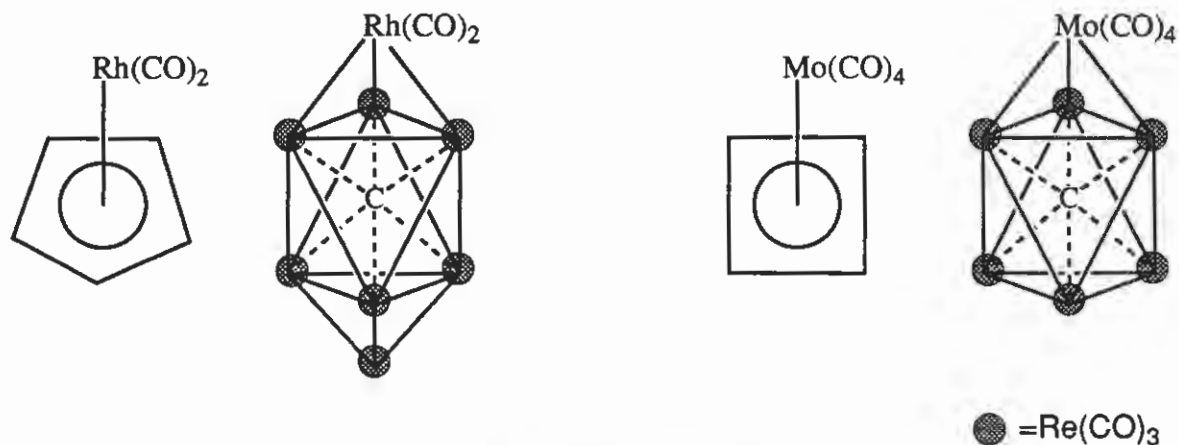


The structure of the cluster anion in $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{19}]$ shows eighteen terminal carbonyl ligands, three to each metal atom. Two unique positions exist for the nineteenth carbonyl ligand, one symmetrically edge-bridging (I) and the other nearly terminal but with weak bridging interactions to the other two rhenium atoms defining the triangular face (II). ^{13}C NMR studies on $[\text{Re}_6^{13}\text{C}(\text{CO})_{19}]^{2-}$ showed rapid scrambling of the carbonyls even at -85°C . Sunlamp irradiation of $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$ in the presence of H_2 gave $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$ [4].



In further exploration of the unique photoreactivity of $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$, we found that the reaction of $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$ with $\text{Mo}(\text{CO})_6$ and $\text{Ru}_3(\text{CO})_{12}$ under photolytic conditions provided the new mixed-metal clusters, $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ and $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]^{2-}$. These are the first large rhenium carbonyl cluster compounds that contain either

a group VI or a group VIII transition metal cap. The cluster anion in $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]$ is composed of a Re_6C octahedral core with a face capped by $\text{Mo}(\text{CO})_4$. The relationship between $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ and $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]^{2-}$ with $(\eta^4\text{-C}_4\text{R}_4)\text{Mo}(\text{CO})_4$ [5,6] and $(\eta^4\text{-C}_4\text{R}_4)\text{Ru}(\text{CO})_3$ [5], respectively, extends the isolobal analogy of η^4 -diene ligands to the triangular face of the unsaturated $[\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$. Previously, we have proposed the analogy between the cyclopentadienyl ligand and the $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ trianion based on the characterization of various $[\text{Re}_7\text{C}(\text{CO})_{21}\text{ML}_n]^{2-}$ compounds [7] (see below).

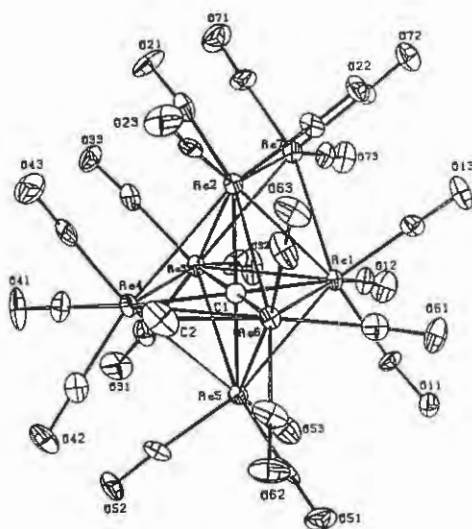


$[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ and $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]^{2-}$ provided the opportunity to compare the physical properties and reactivity of two closely related clusters. The variable temperature ^{13}C NMR spectrum of $[\text{PPN}]_2[\text{Re}_6^{13}\text{C}^{13}\text{CO}_{18}\text{Mo}^{13}\text{CO}_4]$ is consistent with the solid state structure at -40°C , but the carbonyl ligands undergo complete scrambling at ambient temperature. The ^{13}C NMR spectrum obtained for $[\text{PPN}]_2[\text{Re}_6^{13}\text{C}^{13}\text{CO}_{18}\text{Ru}^{13}\text{CO}_3]$ indicated an octahedral $\text{Re}_6\text{C}(\text{CO})_{18}$ core capped by a $\text{Ru}(\text{CO})_3$ fragment and showed no evidence for fluxional behavior at 20°C . An irreversible oxidation wave was observed for $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]$ while two quasi-reversible oxidation waves were observed for $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]$. A comparison of the absorption spectra of $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]$ and $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]$ showed that the comparable transitions for $[\text{PPN}]_2[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]$ are higher in energy. The molybdenum cap in $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ was cleaved to give $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$ upon heating or after treatment with acetonitrile. $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ reacted with H_2 under photolytic conditions to give $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$. Under thermal conditions, $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ reacted with H_2 to give a mixture of $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$ and $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$. The thermal reaction of H_2 (40 psig) with $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Mo}(\text{CO})_4]^{2-}$ gave exclusively $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$. The ruthenium cap in $[\text{Re}_6\text{C}(\text{CO})_{18}\text{Ru}(\text{CO})_3]^{2-}$ did not undergo a decapping reaction under similar conditions.

The reaction of either $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$ or $[\text{HRe}_6\text{C}(\text{CO})_{18}]^{3-}$ with $(\text{AuPPh}_3)\text{Cl}$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{AuPPh}_3)_2]^{2-}$. The bicapped $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{AuPPh}_3)_2]^{2-}$ complex reacted with $(\text{AuPPh}_3)\text{NO}_3$ to give $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{AuPPh}_3)_4]$. The $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{AuPPh}_3)_2]^{2-}$ complex also reacted with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to give $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{AuPPh}_3)_2\text{Rh}(\text{CO})_2]^-$. Capping the " $[\text{Re}_6\text{C}(\text{CO})_{18}]^{4-}$ " core with precursors other than gold to give $[\text{Re}_6\text{C}(\text{CO})_{18}\text{ML}_n]^{3-}$ has been explored briefly.

The two electron oxidation of metal carbonyl cluster compounds followed by the addition of a two-electron donor ligand is a developing method to synthesize new cluster compounds. The term "redox activation" has been used to describe this process involving the treatment of anionic cluster compounds with oxidizing agents to facilitate reactivity [8].

Recently, the term "oxidative substitution" has been proposed to describe this process [9]. Treatment of $[\text{PPN}]_3[\text{Re}_7\text{C}(\text{CO})_{21}]$ with two equivalents of Cp_2Fe^+ in the presence of diazomethane gave $[\text{PPN}][\text{Re}_7\text{C}(\text{CO})_{21}(\text{CH}_2)]$. The structure of the cluster anion (III) shows the methylene ligand bridging a rhenium-rhenium edge. The rhenium-rhenium distance for the edge bridged by the methylene ligand was found to be shorter than the other rhenium-rhenium distances.



III

Treatment of $[\text{Re}_7\text{C}(\text{CO})_{21}(\text{CH}_2)]^-$ with acetonitrile gave $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{CH}_2)]^{2-}$. The decapped species was identified as $[\text{Re}(\text{CO})_3(\text{NCCH}_3)_3]^+$. The treatment of large carbonyl cluster compounds by acetonitrile has been reported to give smaller cluster compounds by removing one or more vertices from the parent cluster [10]. A comparison of the ^{13}C NMR spectra of $[\text{PPN}][\text{Re}_7^{13}\text{C}(^{13}\text{CO})_{21}(\text{CH}_2)]$ and $[\text{PPN}]_2[\text{Re}_6^{13}\text{C}(^{13}\text{CO})_{18}(\text{CH}_2)]$ showed hindered site exchange for carbonyl ligands associated with metal atoms bonded to the methylene carbon. The ^{13}C NMR spectra of $[\text{PPN}]_2[\text{Re}_6^{13}\text{C}(^{13}\text{CO})_{18}(\text{CH}_2)]$ also confirmed that the methylene ligand is edge-bridging.

Treatment of $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ with one equivalent of Cp_2Fe^+ gave the $[\text{Re}_7\text{C}(\text{CO})_{21}]^{2-}$ radical, which could be observed by infrared spectroscopy. Introduction of tributyltin hydride or a silane gave $[\text{HRe}_7\text{C}(\text{CO})_{21}]^{2-}$. The $[\text{Re}_7\text{C}(\text{CO})_{21}]^{2-}$ radical also reacted with solvents such as acetone or THF to give $[\text{HRe}_7\text{C}(\text{CO})_{21}]^{2-}$. The $[\text{Re}_7\text{C}(\text{CO})_{21}]^{2-}$ radical was observed not to react with toluene or triphenylmethane. The $[\text{Re}_7\text{C}(\text{CO})_{21}]^{2-}$ radical apparently disproportionated in the presence of carbon monoxide to form $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ and $[\text{Re}_7\text{C}(\text{CO})_{21}]^-$, followed by the reaction of $[\text{Re}_7\text{C}(\text{CO})_{21}]^-$ with carbon monoxide to give $[\text{Re}_7\text{C}(\text{CO})_{22}]^-$. The nature of the counter ion in the cluster compound and the Cp_2Fe^+ oxidant also played a role in the reactivity.

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