

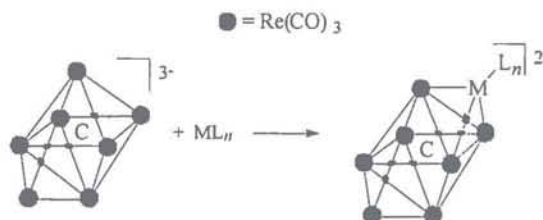
Rhenium Carbido Carbonyl Cluster Complexes With Group 12 Metal Centers

Chris A. Wright

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High nuclearity rhenium carbido carbonyl clusters, namely $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$, $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$, and $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$, have been known for less than 20 years.¹⁻³ High yield syntheses of these cluster compounds were reported in 1988.⁴ A companion report detailed systematic “capping” reactions at a triangular face of $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ with a variety of platinum based electrophiles (ML_n^+) to form mixed-metal octanuclear carbido clusters of the general formula $[\text{Re}_7\text{C}(\text{CO})_{21}\text{ML}_n]^{2-}$.⁵

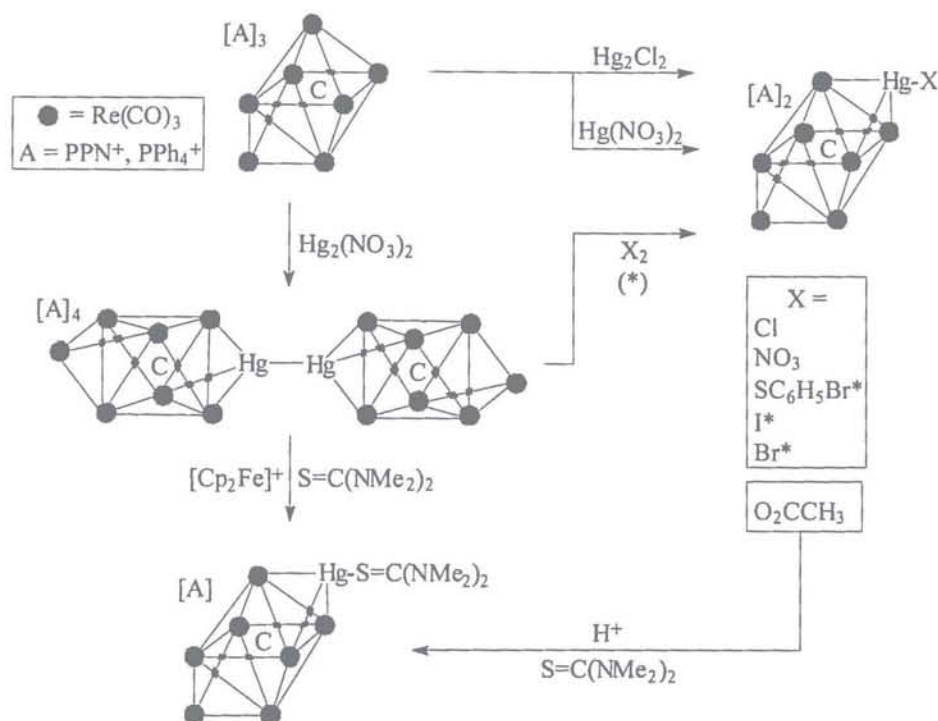


This capping procedure was extended to include various mercuric compounds, forming complexes of the formula $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgX}]^{2-}$, where $\text{X} = \text{Cl}, \text{Br}, \text{CN}, \text{Ph}, \text{Me}$, and $t\text{Bu}$.⁶ Recent work with mercuric complexes has focused on hydroxide, hydrosulfide, and thiolate derivatives,^{7,8} including an example where a carbidoheptarhenate cluster core is 1,4-bicapped by two mercury centers with acetate or thiolate ligands.⁹

Our objective has been to further investigate carbidorhenate complexes containing group 12 metal centers. This work has several possible applications. Some of these possibilities include linking cluster units to study supermolecular chemistry; exploring constrained geometry capping groups and their implications for model complexes; and development of the cluster unit as a labeling agent toward macromolecules.

During our investigations of carbidoheptarhenate mercury derivatives, a unique dimercury(I)-linked cluster complex, $[(\text{Re}_7\text{C}(\text{CO})_{21}\text{Hg})_2]^{4-}$, was discovered. This complex contains the first reported example of a $m_3, m_3\text{-Hg}_2^{2+}$ unit bound between transition metal centers. It is formed by reacting $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ with $\text{Hg}_2(\text{NO}_3)_2$. If Hg_2Cl_2 is used, $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgCl}]^{2-}$ is instead formed, while if $\text{Hg}(\text{NO}_3)_2$ is used, $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgNO}_3]^{2-}$ results. Subsequent investigation of the linked complex indicates that the dimercury(I) bond undergoes a variety of oxidative cleavage reactions with disulfides and halogens, and that it can be oxidized by the ferrocenium ion in the presence of 1,1,3,3-tetramethylthiourea to form $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgS}=\text{C}(\text{NMe}_2)_2]^-$. This complex contains the first example of a mercury center bound to a neutral ligand capping the carbidorhenate cluster framework. This complex can be made in higher yield by protonating $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgO}_2\text{CCH}_3]^{2-}$ in the presence of tetramethylthiourea. A summary of these reactions is presented in Scheme 1.

Scheme 1.



While investigating the mercury derivatives, we also became interested in studying capping chemistry of cadmium and zinc. Unlike mercury, few examples of m_3 -coordination to metal units exist for these elements. Also, it was of interest to see if pseudotetrahedral zinc geometry could be stabilized *via* a capping reaction, due to its widespread presence in zinc enzymes. We found that the cadmium and zinc chloride and nitrate capped cluster complexes can be synthesized similarly to the mercury complexes. Structural characterization of the ZnCl capped cluster confirms the pseudotetrahedral geometry. Studies of the Cd and Zn chloride complexes show that the metal capping moiety is stable in dichloromethane. However, unlike the mercury chloride cap, these caps dissociate from the rhenium cluster framework in acetone. The cadmium complex dissociates ~40%, while the zinc complex dissociates virtually completely. Despite this process, a cadmium arenethiolate capping complex was isolated in low yield, though a similar complex was not found for the zinc cluster. Conversion to a capping hydroxide derivative (known for Hg)⁷ was not successful for either complex. These complexes complete a set of group 12 capped clusters; however, their use for modeling chemistry at a zinc center is limited by the ease of dissociation found in coordinating environments.

The ability of mercury capped carbido-rhenate clusters to act as labeling agents toward biomolecules was also investigated. These clusters are electron dense, easily detected by IR spectroscopy (carbonyl region), and capable of reacting with sulfhydryl groups. We made a relevant derivative by reacting $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgOH}]^{2-}$ with cysteine, illustrating an ability to react with a biological sulfhydryl moiety. We also achieved limited water solubility by working with sodium salts of the cluster complexes. Preliminary reactions between $[\text{Na}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgCl}]$ and myoglobin modified to contain a sulfhydryl group indicate a possible coupling reaction; further studies are required. Collaborative work with the P.A.B. Harbury research group at Stanford U. has

indicated that $[\text{Na}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgCl}]$ can bind to cysteine sites in a protein environment; however, protein destabilization and insolubility at low pH are problematic. Future work will focus on modifying the carbidoheptarhenate cluster complex to introduce more hydrophilic ligands.

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