

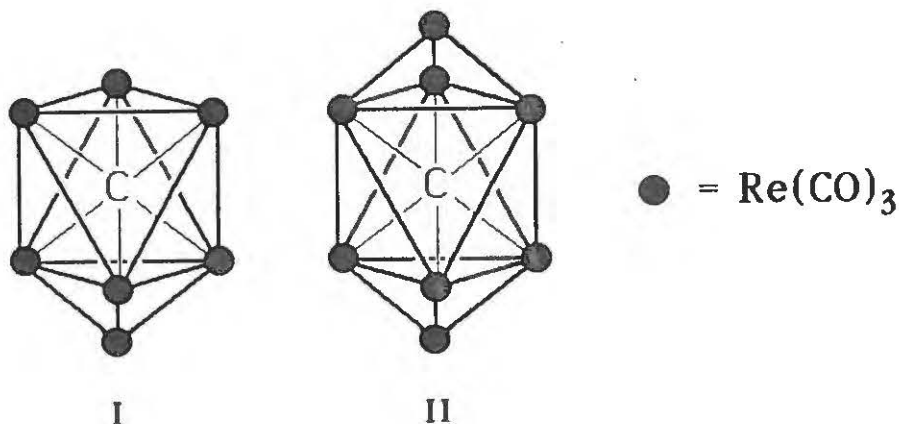
Synthesis, Structure, and Reactivity of
High-Nuclearity Carbido Clusters of Rhenium

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The largest known rhenium carbonyl clusters are $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ (I) and $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$ (II). These complexes were first prepared by Ciani and coworkers, who also showed their structures to consist of an octahedral $[\{\text{Re}(\text{CO})_3\}_6\text{C}]^{4-}$ core, with one or two additional $\text{Re}(\text{CO})_3^+$ caps [1,2].



Previous work in our group has resulted in the direct, high-yield synthesis of either $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ or $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$ by sodium reduction of $\text{Re}_2(\text{CO})_{10}$ at 200°C [3]. Furthermore, we have discovered that $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ reacts with $\text{Re}_2(\text{CO})_{10}$ to give $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$, a reaction which can be viewed formally as the capping of one face of $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ by a $\text{Re}(\text{CO})_3^+$ moiety.

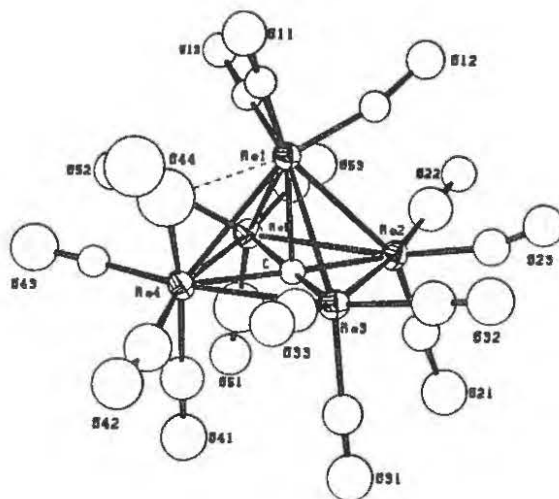
The cluster anion $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ also reacts with late transition metal-based electrophiles to yield the mixed-metal clusters $[\text{Re}_7\text{C}(\text{CO})_{21}\text{ML}_n]^{2-}$ and with H^+ to yield the hydrido species $[\text{HRe}_7\text{C}(\text{CO})_{21}]^{2-}$ [4,5]. These complexes have been fully characterized by IR, ^1H NMR, and fast-atom bombardment mass spectroscopies. ^1H and ^{13}C NMR, IR, and cyclic voltammetry studies on selected complexes indicate that the $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ cap is a poorer electron donor to the ML_n^+ moiety than the cyclopentadienide ligand in the analogous compounds ($\eta^5\text{-C}_5\text{H}_5$) ML_n . Variable-temperature ^{13}C NMR studies and X-ray diffraction experiments on several of the mixed-metal clusters demonstrate that each of these compounds adopts a trans-bicapped octahedral configuration of metal atoms, i.e., the ML_n fragment symmetrically caps the triangular face opposite the unique $\text{Re}(\text{CO})_3$ group. The compound $[\text{HRe}_7\text{C}(\text{CO})_{21}]^{2-}$ is a mixture of two isomers, which differ in the position of the hydride ligand on the metal framework.

A set of clusters $[\text{Re}_7\text{C}(\text{CO})_{21}\text{HgY}]^{2-}$ ($\text{Y} = \text{halide, pseudohalide, or hydrocarbyl}$) has also been prepared and characterized. Some of these compounds undergo ligand-exchange reactions of the type:



These reactions appear to be the first example of four-coordinate mercury ligand-redistribution reactions [6,7]. The position of the equilibrium depends on the electronic properties of Y and Z, with electron-withdrawing groups facilitating ligand redistribution.

The reaction of $\text{Re}_2(\text{CO})_{10}$ with a 1.2:1 mole ratio of sodium in triglyme at 200°C yields the new rhenium carbido clusters $[\text{HRe}_6\text{C}(\text{CO})_{18}]^{3-}$ and $[\text{HRe}_5\text{C}(\text{CO})_{16}]^{2-}$ (**III**). The former complex contains an octahedral arrangement of $\text{Re}(\text{CO})_3$ units; it reacts with transition metal electrophiles to give the mixed-metal clusters $[\text{HRe}_6\text{C}(\text{CO})_{18}\text{ML}_n]^{2-}$. The latter cluster consists of a square-based pyramid of rhenium atoms with a μ_5 -carbido atom 0.10 Å below the basal plane and a semibridging carbonyl. Potential-energy calculations suggest that the hydride bridges a basal-apical edge. This compound is the first example of such a M_5C complex outside of the iron triad elements.



III

References

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