

The Synthesis of $\text{Re}_2\text{Pt}(\text{CO})_{12}$ and its Use
as a Catalyst Precursor

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Final Seminar

December 1, 1983

In the past few years the use of transition metal carbonyl compounds as precursors to oxide- and polymer-supported catalysts has expanded tremendously [1]. The use of mixed-metal compounds for the preparation of bimetallic catalysts is of particular interest, since such compounds may allow the formation of catalytically active sites of well-defined composition. Several reviews on mixed-metal compounds have appeared recently [2].

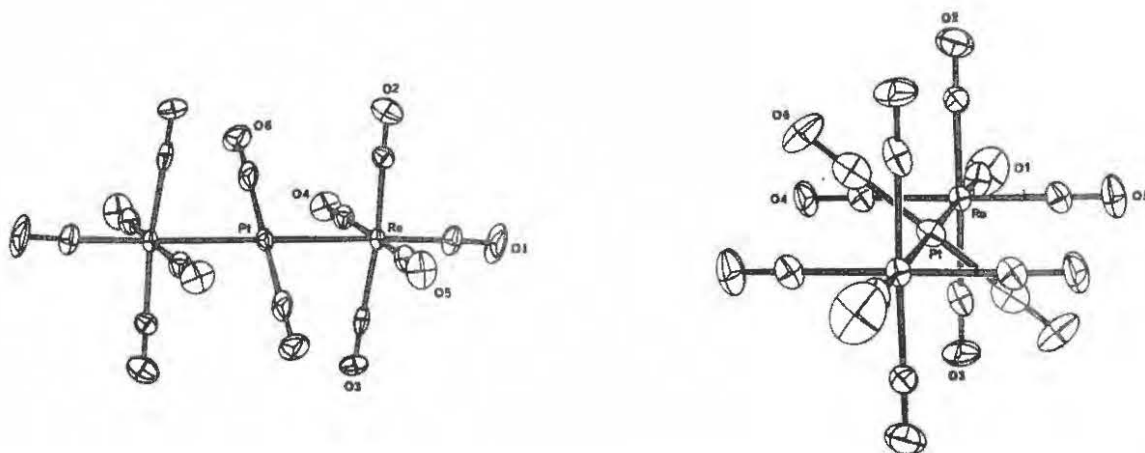
One of the most important commercial bimetallic catalysts is alumina-supported platinum-rhenium, which is used in the catalytic reforming of petroleum naphthas [3]. To date, however, only a few molecular bimetallic compounds of platinum and rhenium have been reported [4], and all of them contain phosphine ligands. This is an undesirable feature for a catalyst precursor, in that supported metal particles generated from such compounds may be poisoned by phosphorous. The preparation of platinum-rhenium bimetallic compounds that contain easily removable ligands is therefore a desirable goal.

Recently, the reaction of metal hydrides with metal alkyl compounds has been used to prepare mixed-metal species via "binuclear reductive elimination" [5]. This approach has been used to prepare the heterobimetallic compounds $\text{Re}_2\text{Pt}(\text{CO})_{12}$ and $\text{Mn}_2\text{Pt}(\text{CO})_{12}$ by the reaction of $\text{HM}(\text{CO})_5$ ($\text{M} = \text{Re}, \text{Mn}$) [6] with $\text{Me}_2\text{Pt}(\text{COD})$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) [7]. A single-crystal X-ray diffraction analysis of $\text{Re}_2\text{Pt}(\text{CO})_{12}$ shows that the molecule ideally possesses D_{2h} symmetry with octahedral coordination about each rhenium atom and square planar (trans) geometry about the platinum atom (see Figure).

The $\text{Re}_2\text{Pt}(\text{CO})_{12}$ cluster has been supported on activated alumina and decomposed by temperature programmed heating in flowing H_2 . Although some fragmentation of the cluster occurs during impregnation, the decomposition profile shows that methane formation occurs at a significantly lower temperature than for a rhenium-only catalyst prepared from $\text{Re}_2(\text{CO})_{10}$.

The reduced catalysts derived from $\text{Re}_2\text{Pt}(\text{CO})_{12}$ have been characterized by selective chemisorption measurements, temperature programmed decomposition of adsorbed CO, as well as by the following catalytic reactions: CO methanation, propylene metathesis, and ethane or n-butane hydrogenolysis. Catalysts prepared from conventional precursors [$(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2 + \text{NH}_4\text{ReO}_4$] show significant differences in catalytic behavior. For example, the cluster-derived catalysts exhibit higher activities (2-3x at 225°C) and higher apparent activation energies (~6 kcal/mole) for the hydrogenolysis reactions. This is of particular interest in view of the fact that Pt-Re/ Al_2O_3 catalysts prepared under conditions

expected to enhance bimetallic particle formation exhibited pronounced hydrogenolysis activity [8]. Enhanced activity has also been observed for Pt-Re/SiO₂ and bulk Pt-Re alloys [9]. Treatment of the reduced cluster-derived catalyst in air at elevated temperature followed by a second H₂ reduction, changes the catalyst in such a way that its catalytic properties are nearly identical to those of a conventionally-prepared catalyst. Taken altogether, these observations are consistent with the presence of bimetallic particles in the cluster-derived catalysts, while under oxidizing conditions, segregation of the individual metals presumably occurs.



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