Chemistry 5325/5326
Inorganic Chemistry
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Predicting the Structures of Rhodium Carbonyl Clusters

The structures of neutral rhodium carbonyl clusters containing two, four, and six rhodium atoms have been known for some time.

The paper by Ingmar Swart, Frank M. F. de Groot, Bert M. Weckhuysen, David M. Rayner, Gerard Meijer, and André Fielicke *The Effect of Charge on CO Binding in Rhodium Carbonyls: From Bridging to Terminal CO*, J. Am. Chem. Soc. **2008**, *130*, 2126-2127 investigates the structures of the monocation rhodium carbonyl clusters via infrared multiphoton dissociation spectroscopy (IR-MPD), comparing experimental results to those predicted from computational modeling.

These are ideal problems to apply simple the tools of group theory to predict distinguishing features in the IR spectrum of each possible structure.

For this part of the project we will focus primarily on the υ_{CO} stretching frequencies. The stretching frequencies of terminally bound CO ligands (2060-2100 cm^{-1}) are typically well separated from those of bridging CO ligands (1750-1900 cm^{-1}), and so these vibrations could form separate basis sets for symmetry analysis.

Although static images from the paper are given below, PDB files each of these structures are also available for visualization with applications such as Jmol and VMD by clicking on the link next to the appropriate structure.

Goals of this project include the use of the tools of group theory and symmetry:

1. to predict how many υ_{CO} stretching frequencies one would see in the IR spectrum of each possible structure, and

2. to write a representation for the υ_{CO} stretching frequencies in each structure and determine how many peaks one would expect to see in the terminal and bridging CO regions of the IR spectrum.

The idea is to predict the structure of $[Rh_n(CO)_m]^+$ complexes based both on the experimental structures of neutral species and calculations performed on both neutral and analagous charged complexes.

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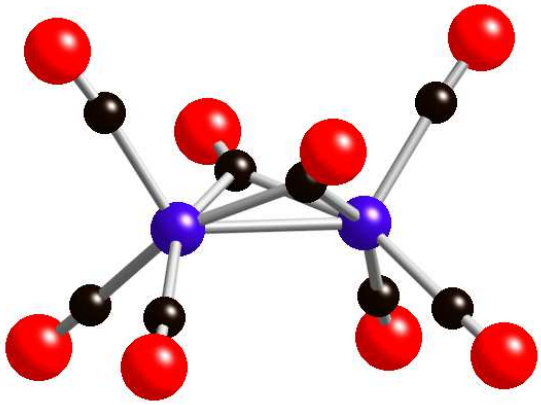
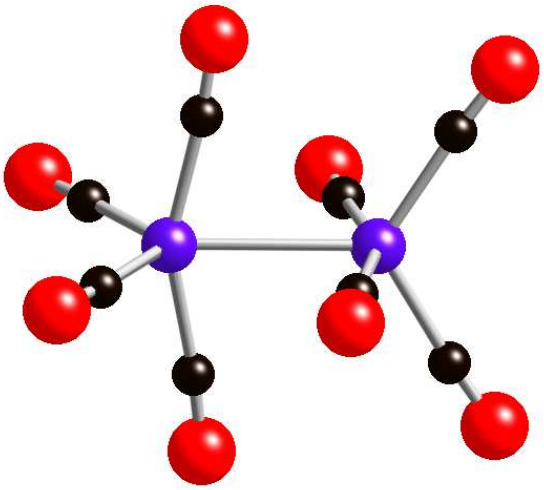
Calculated structures of $Rh_2(CO)_8$: the bridged structure is slightly lower in energy than the all-terminal structure, in agreement with experiment.

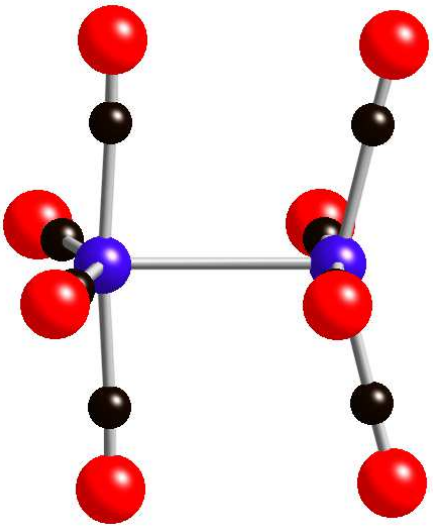


All Bridging COs

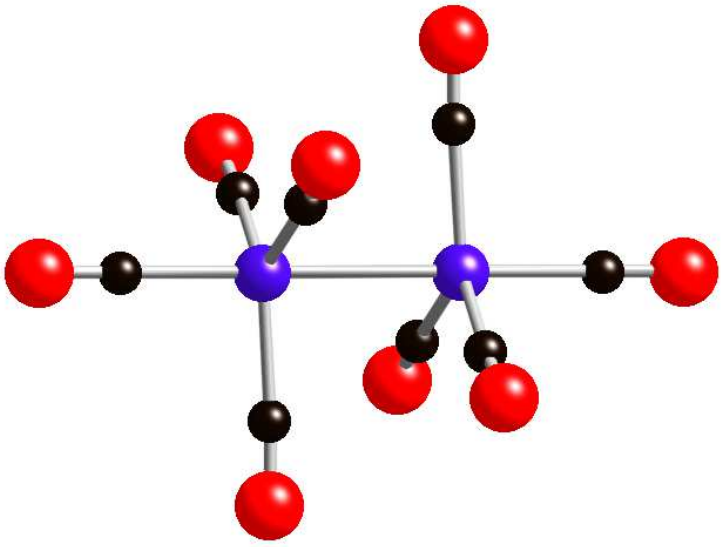


All Terminal COs

Calculated structures for $[Rh_2(CO)_8]^+$



Lowest Energy Structure



Another Possible Structure for $[Rh_2(CO)_8]^+$

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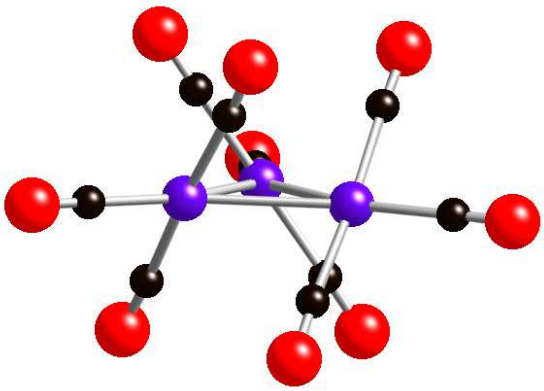
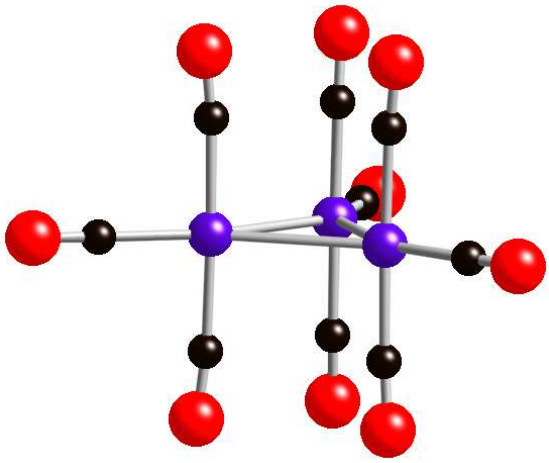
Calculated Structures for $[Rh_3(CO)_9]^+$

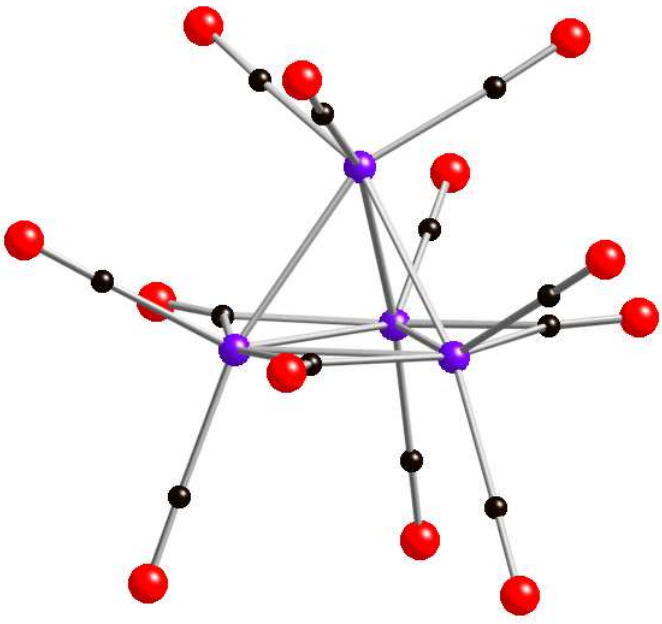


Lowest Energy Structure

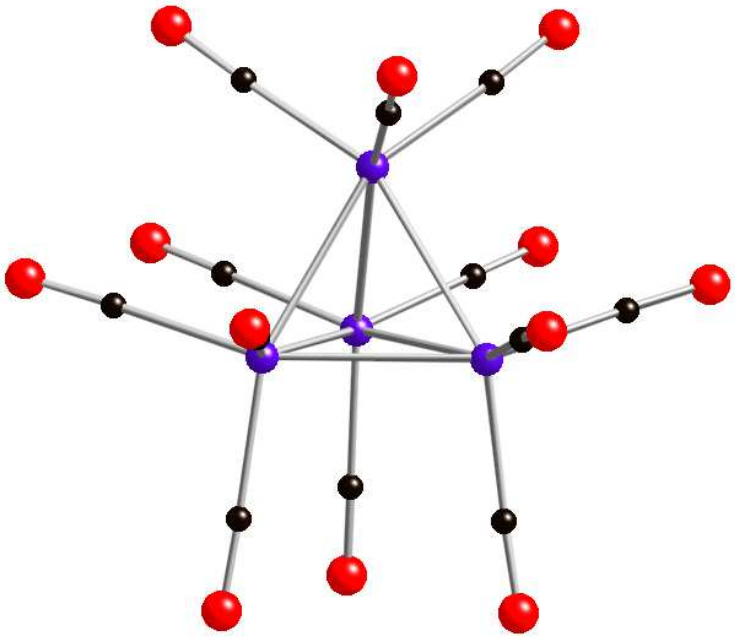


Another Possible Structure for $[Rh_3(CO)_9]^+$

Calculated structures of $Rh_4(CO)_{12}$, $[Rh_4(CO)_{12}]^+$: the neutral structure agrees with experiment.



Known Structure of Neutal Cluster



Proposed Monocationic Structure