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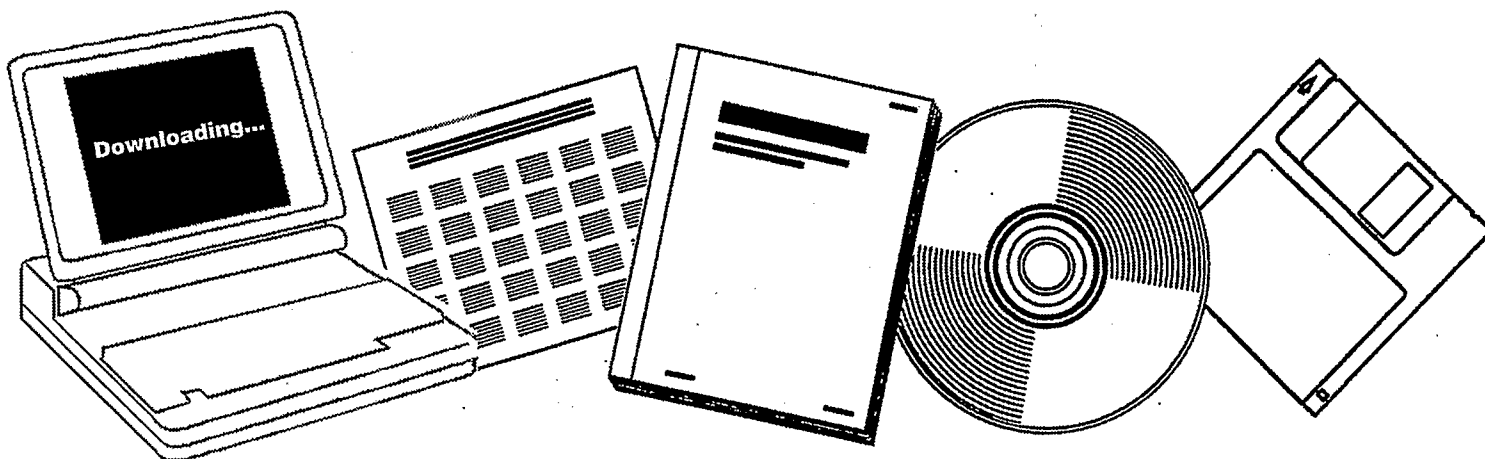
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MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION. PROGRESS REPORT

PENNSYLVANIA STATE UNIV., UNIVERSITY
PARK

1985



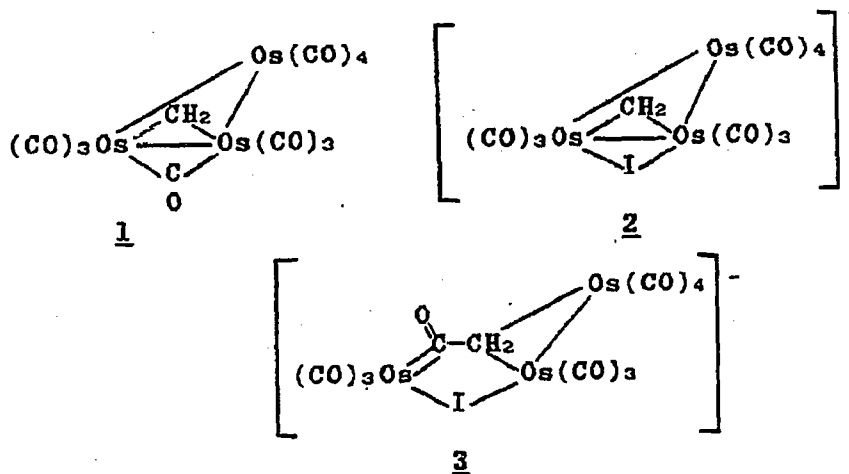
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Progress Report for
"Mechanistic Studies of Carbon Monoxide Reduction"

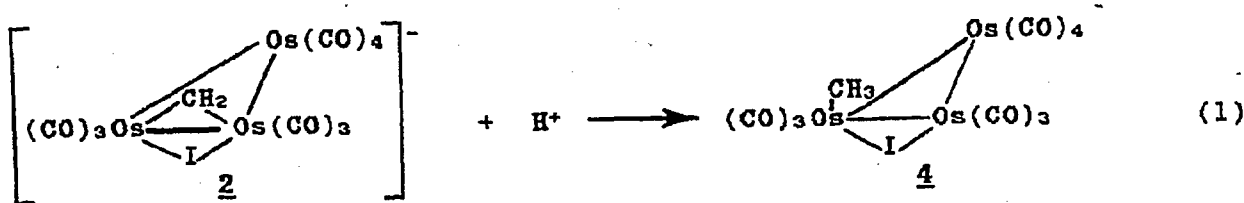
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by Gregory L. Geoffroy

I. Triosmium Clusters as Models for Carbon Monoxide Reduction. We have been studying the derivative chemistry of the methylene clusters 1 and 2 and the ketene cluster 3. The latter forms from 2 by CO insertion.

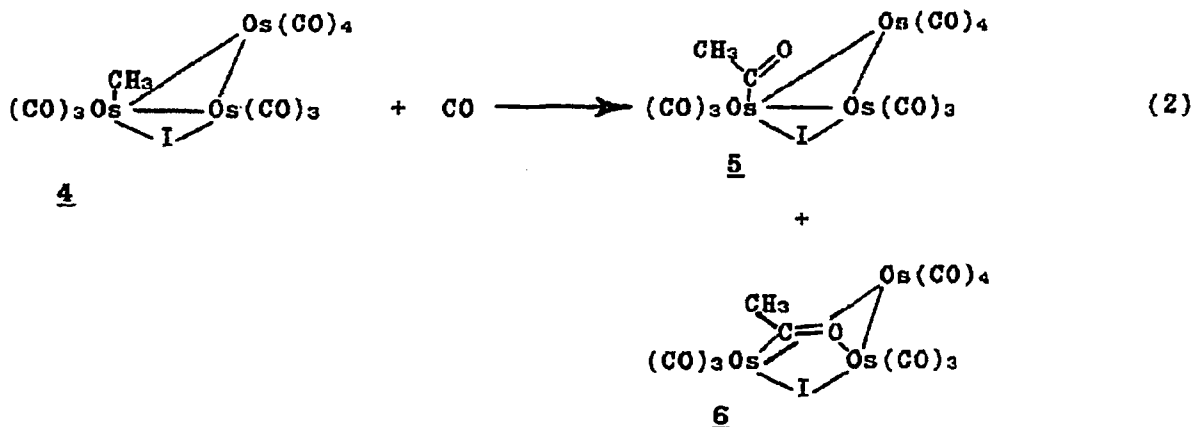


We have recently found that the $\mu\text{-CH}_2$ ligand of 2 can be protonated to give the new methyl cluster 4, eq. 1.



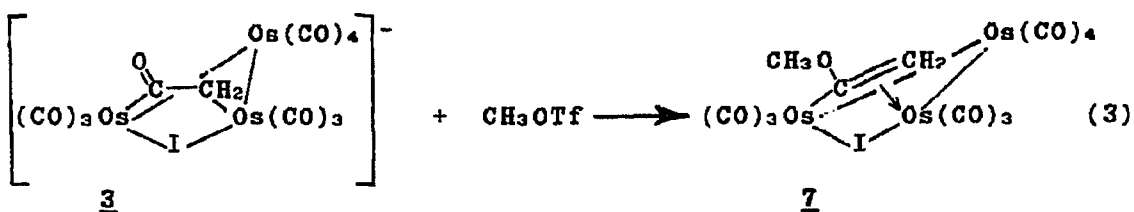
Methyl cluster 4 is a rare example of an alkyl substituted cluster. Not surprisingly, it readily transforms when placed under a CO atmosphere to

the terminal acetyl cluster 5 which then gives the bridging acetyl cluster 6, eq. 2.



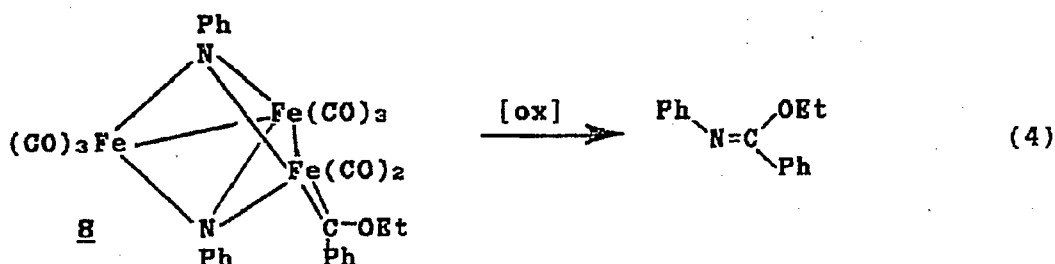
These reactions directly model one series of chain growth mechanisms during CO reduction on metal surfaces. A manuscript is in press in Organometallics describing these results.

We have also found that ketene complex 3 can be alkylated at the ketene oxygen to give the novel σ, π -vinyl complex 7, eq. 3.



The vinyl ligand in 7 undergoes a fluxional process in which the α carbon switches its coordination from one Os to an adjacent β Os. Preliminary structural results imply substantial oxycarbenoid character in this vinyl ligand. Protonation of the ketene oxygen of 3 also occurs, but the intermediate hydroxyvinyl complex rearranges to give the μ -acetyl complex 6. A manuscript describing these results is in preparation.

II. Coupling of Carbene and Nitrene Ligands on an Fe₃ Cluster. We have previously communicated the preparation of the carbene-nitrene cluster 8. This is the first cluster compound reported which contains both nitrene and carbene ligands. We have observed that these two organic fragments couple to give free imidate, again a reaction without precedent, eq. 4.

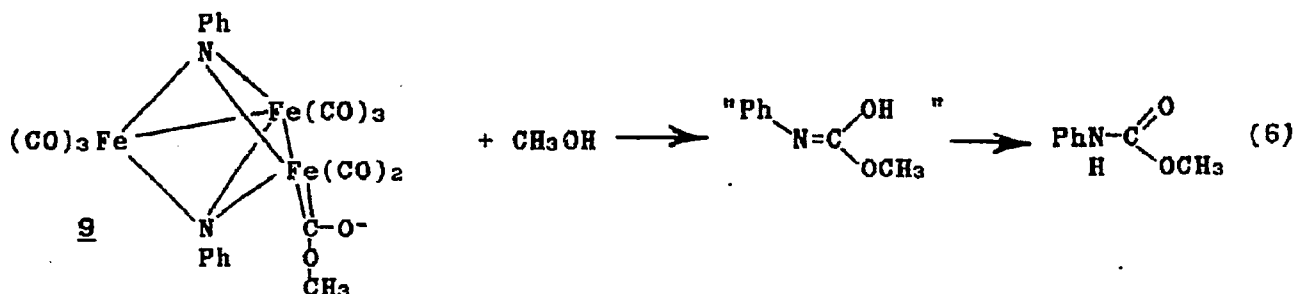


Because of the novelty of this reaction, and its apparent importance in a number of metal catalyzed nitrene reactions, we have studied the mechanism of this coupling in considerable detail. We find first that it is strictly intramolecular; both the nitrene and carbene ligands which form the imidate come from the same cluster molecule. We have also found that this reaction is induced by oxidation of the cluster. Addition of the one electron oxidant Cp₂Fe⁺ gives immediate reaction, whereas only a slow reaction occurs over weeks when the cluster is stirred under N₂. Electrochemical experiments are currently underway to define the oxidation properties of 8.

We believe that similar carbene-nitrene couplings may be important in a number of interesting carbonylation reactions which apparently involve nitrene intermediates. One such example is the carbonylation of nitroarenes in methanol solution to give carbamates, eq. 5.



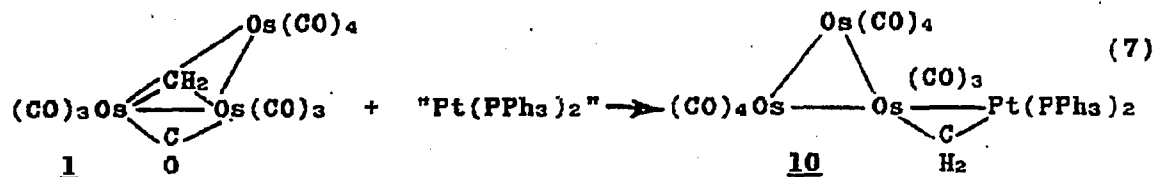
To test this hypothesis we have prepared the methoxy-carbonyl cluster 9 and have found that in methanol solution the acyl and nitrene ligands couple to give the corresponding carbamate during acidic workup, eq. 6.



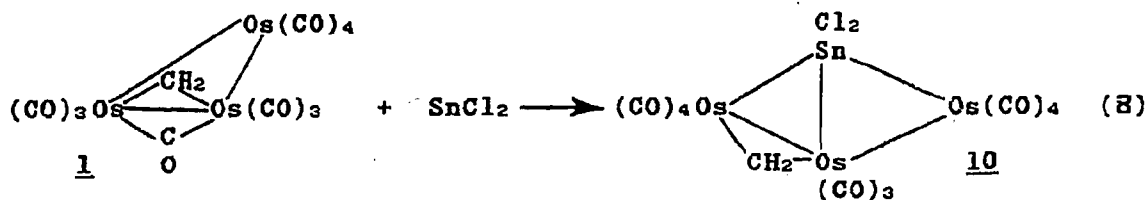
Mechanistic studies into this and related reactions are in progress. This work will be presented at a U.S.-W. German workshop on the Reactions of Polynuclear Organometallic Compounds to be held in Frankfurt in early September.

III. Halide Promoted Insertion Reactions. We have previously shown that halide ions, particularly iodide, promote the insertion of CO into the Os-CH₂ bond of 2 to give the ketene cluster 3. We believe this reaction may be general, and to test that hypothesis we have studied the carbonylation of (CO)₅Mn-CH₂Ph. This compound does not readily carbonylate at one atmosphere of CO pressure, but we have found that addition of catalytic amounts of iodide promotes this reaction to give the acyl compound (CO)₅Mn-C(O)CH₂Ph! This promotion may be of direct relevance to several reports of halide promotion during homogeneous catalysis of CO reduction, and we are in the process of determining the mechanism of this promotion and the extent of its generality.

IV. Insertion of Metals into Metal-Methylene Bonds. We have found that cluster 1 reacts with $(PPh_3)_2Pt(CH_2=CH_2)$ to give the unusual cluster 10, eq. 7.



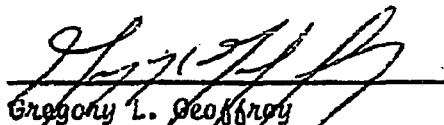
Cluster 10 has been characterized by an X-ray diffraction study and is a rare example of a tetrametallic methylene cluster and the only compound with such a structure. We have also found that reaction occurs when "Pt(PPh₃)₂" is added to solutions of $(CO)_6Fe_2(\mu-CH_2)$ and $Cp_2Co_2(\mu-CH_2)(CO)_2$. The products of these reactions are being characterized; preliminary results indicate that similar insertion reactions have occurred. We have also found that SnCl₂ reacts with 1 to give the unusual compound 11 which has been structurally characterized, eq. 8.



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9. Morrison, E. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. "Fifty Electron [Os₃(CO)₁₀(μ -CH₂)(μ -X)]⁻ Clusters Derived from Reaction of Os₃(CO)₁₁(μ -CH₂) with [(PPh₃)₂N]X Salts. Structural Characterization of the X = NCO and I Derivatives" Organometallics, in press.
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