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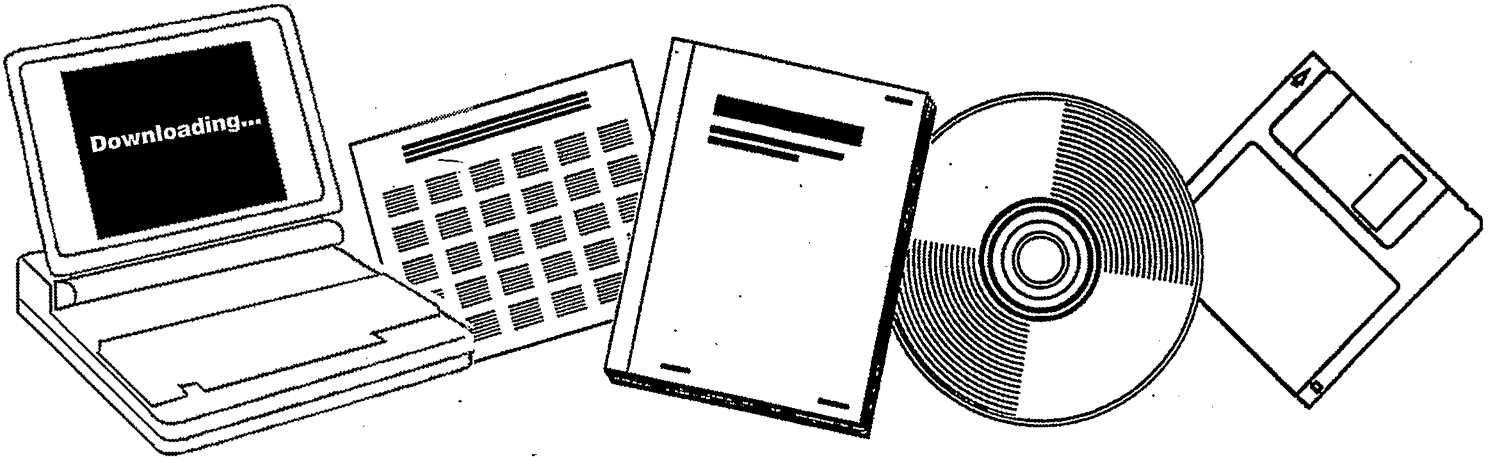
# MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION. PROGRESS REPORT, AUGUST 1, 1979-AUGUST 1, 1980

PENNSYLVANIA STATE UNIV., UNIVERSITY
PARK

29 JUL 1980



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# "Mechanistic Studies of Carbon Monoxide Reduction"

Progress Report

for Period August 1, 1979 - August 1, 1980

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Gregory L. Geoffroy
Associate Professor of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802
(814)865-1924
SSN: 400-64-5958

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  B. Preprint of Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L., "Synthesis and Structural Characterization of [PPN] $[ClRu_4(CO)_{13}]$: A Butterfly Cluster with a Bridging Chloride," Inorg. Chem., in press

## I. Abstract

Mechanistic schemes for the metal surface catalyzed reduction of carbon monoxide to methanol and hydrocarbons have been proposed and the feasibility of these mechanisms are being tested by preparing and studying the chemistry of metal clusters which resemble the proposed surface intermediates. In an effort to prepare clusters with bound formyl groups, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ have been treated with $Li[BH(O\text{-}\underline{i}\text{-}Pr)_3]$. Evidence for a formyl intermediate has been obtained with $Os_3(CO)_{12}$, and upon acidification of solutions containing this species, the new cluster $Os_3(CO)_{11}CH_2$ is isolated. The $CH_2$ group derives by the stepwise reduction of CO, and experiments directed toward delineating the mechanism of this transformation are described. Treatment of $Os_3(CO)_{11}CH_2$ with $H_2$ at 70-80°C yields $CH_4$, and thus the complete stoichiometric conversion of CO to $CH_4$ has been achieved on an $Os_3$ cluster. The new clusters [PPN][$HFeRu_3(CO)_{13}$] and [PPN][$HFe_2Ru_2(CO)_{13}$] ($PPN^+ = (Ph_3P)_2N^+$) have been prepared in an attempt to prepare analogs of $[HFe_4(CO)_{13}]^-$ which possesses an unusually bound and presumably activated CO. The crystal structures of each of these new clusters have revealed no unusual CO bonding modes and instead they adopt structures with pseudo-tetrahedral metal frameworks. Several reactions have been conducted directed toward the preparation of alkyl or acyl substituted clusters and these are described. The reaction of a series of mixed-metal clusters with CO have been studied. Each readily fragments under a CO atmosphere and for $H_2FeRu_3(CO)_{13}$ the rate and mechanism of this reaction have been determined.

## II. Research Goals

The overall goals of this research are to develop an understanding of the mechanisms by which metal surfaces catalyze the reduction of carbon monoxide and to design mixed-metal dimers which should function as homogeneous catalysts for CO reduction.

## III. Progress

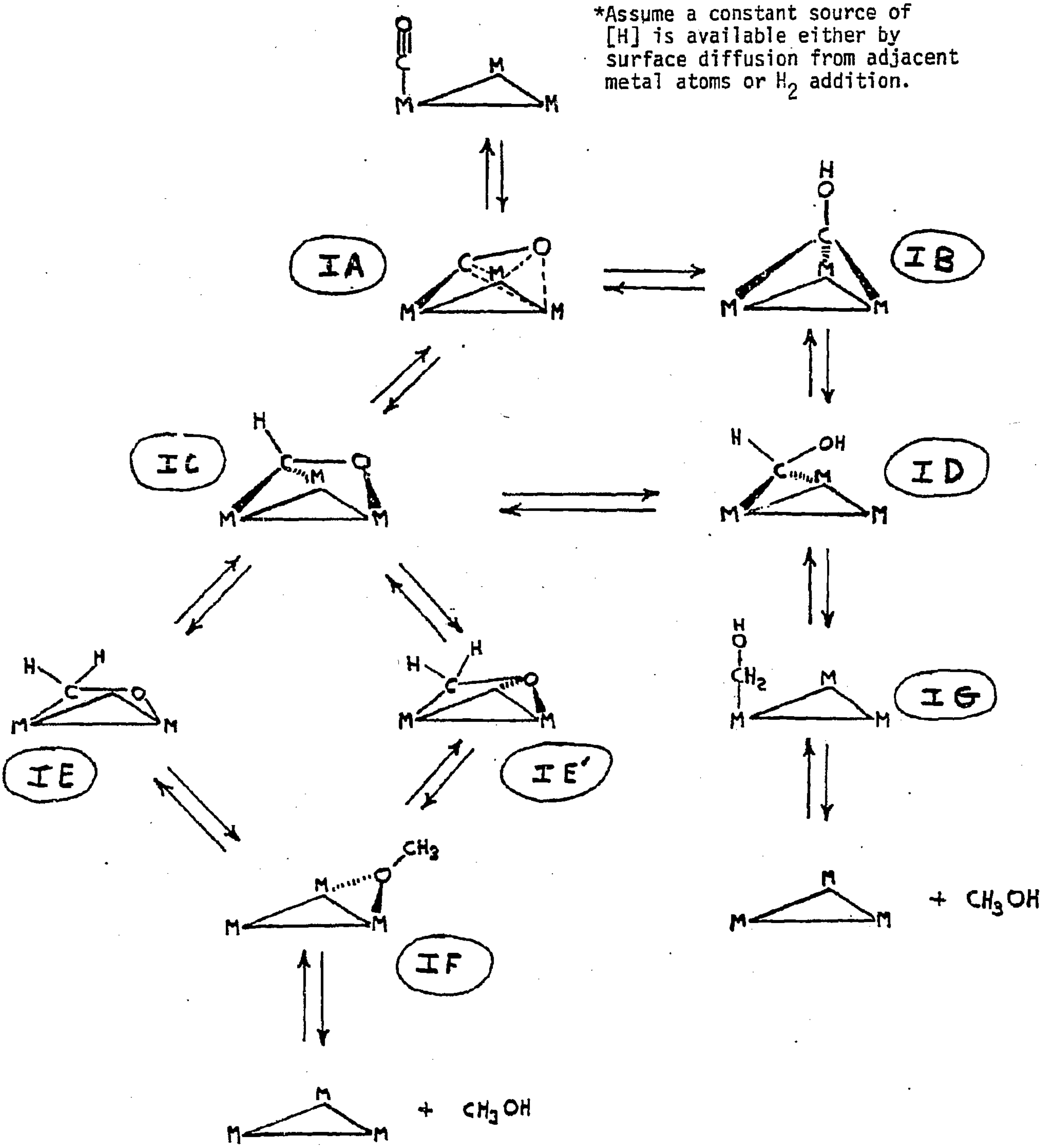
We initially proposed the mechanisms shown in Schemes I and II on the following pages for the metal surface catalyzed reduction of CO to methanol and to hydrocarbons and then set out to evaluate the feasibility of the individual steps in these proposed mechanisms by using metal clusters to model the various intermediates and individual reaction steps. The progress in these areas is summarized immediately below (A-D) and this is followed by a summary of our more recent studies directed toward homogeneous reduction of CO (E-F).

### A. Reduction of CO on an $Os_3$ Cluster Face

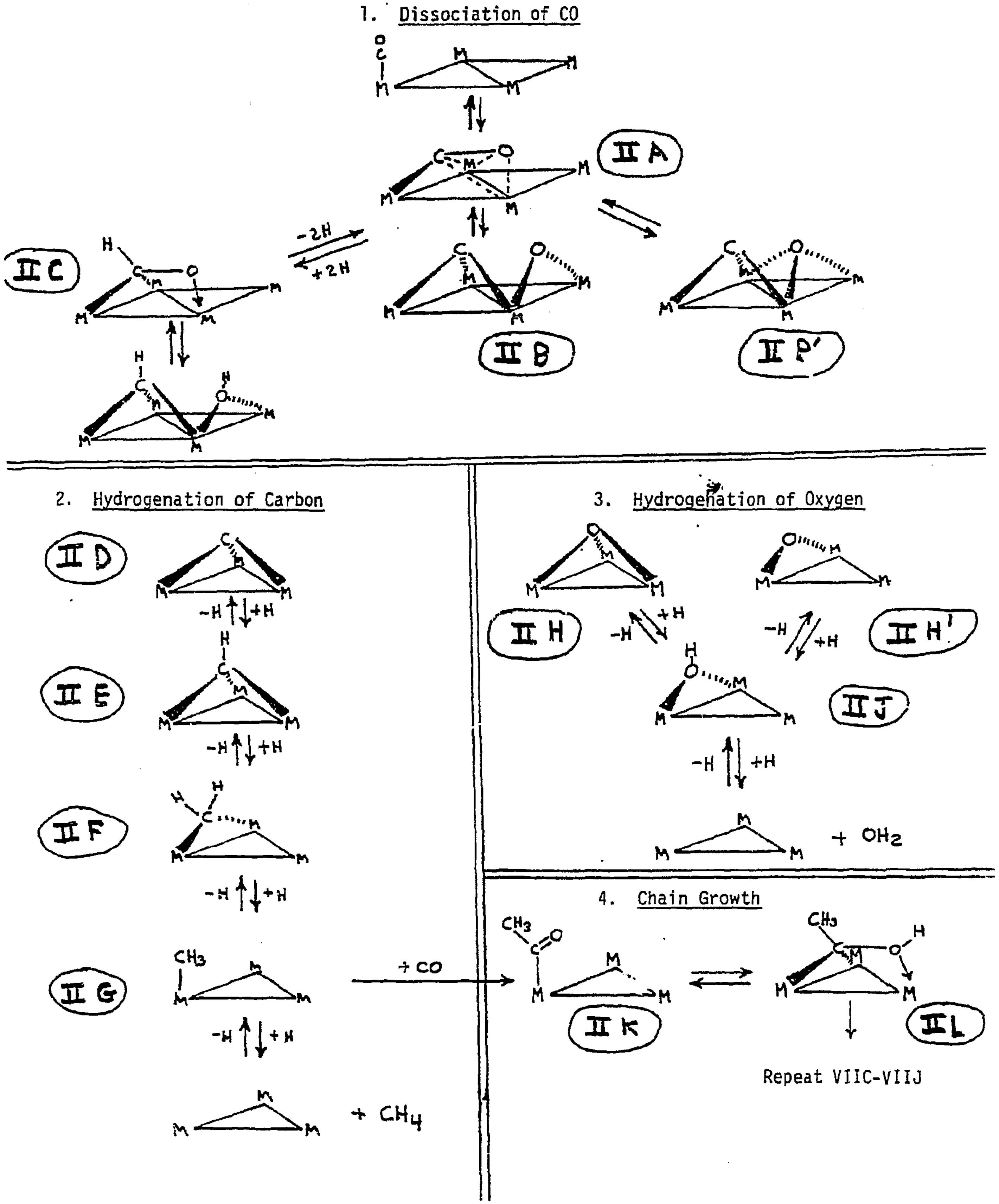
Key intermediates in both Schemes I and II are IC and IIC which are surface bound formyl species. Many mechanisms have invoked formyl species bound to a single metal atom as a key intermediate in Fischer-Tropsch chemistry.[1-4] Our suggestion has been that even in the currently popular CO-dissociation mechanisms,[6-9] a formyl species is still a key intermediate which assists the dissociation of CO according to Scheme II. Furthermore, studies have demonstrated that formyl species are key intermediates in the stepwise reduction of CO by soluble organometallic complexes.[10-12] We thus set out to prepare and ideally, isolate clusters containing formyl ligands.

Scheme I. - Model for Methanol Synthesis

*Assume a constant source of [H] is available either by surface diffusion from adjacent metal atoms or $H_2$ addition.



Scheme II. Model for Hydrocarbon Synthesis



Our efforts to synthesize formyl substituted clusters have focused on the reactions of clusters with the strong hydride donor $[HB(O\text{-}\underline{i}\text{-}Pr)_3]^-$ which has been extensively used by Casey and coworkers[12-15] to synthesize monomeric formyl complexes. Although we have thus far been unsuccessful in *isolating* a formyl-substituted cluster, in at least one case we have spectroscopically observed such a species. Further, as discussed below, these reactions have led to the stepwise reduction of CO to $CH_4$ on a cluster face by a reaction scheme which we believe proceeds through a formyl intermediate.

We first examined the reaction of $Ru_3(CO)_{12}$ with $[HB(O\text{-}\underline{i}\text{-}Pr)_3]^-$ but even when conducted at -77°C, the only product formed was $[HRu_3(CO)_{11}]^-$, eq. 1.

$$Ru_3(CO)_{12} + [HB(O\text{-}\underline{i}\text{-}Pr)_3]^- \rightarrow [HRu_3(CO)_{11}]^- + CO + B(O\text{-}\underline{i}\text{-}Pr)_3 \qquad (1)$$

We believe that a formyl-$Ru_3$ cluster is initially formed but that it rapidly loses CO with hydride migration to Ru to give the observed $[HRu_3(CO)_{12}]^-$ product.

Since the decomposition of a $Ru_3$-formyl intermediate is likely enhanced by CO dissociation from the cluster, we turned to $Os_3(CO)_{12}$ for which the M-CO bonds are known to be stronger and more resistant to dissociation.[16] When a suspension of $Os_3(CO)_{12}$ in THF at -77°C is treated with $Li[HB(O\text{-}\underline{i}\text{-}Pr)_3]$, the $Os_3(CO)_{12}$ rapidly dissolves, indicating reaction, and a deep yellow solution results. Warm up to 25°C causes a change in color from yellow to orange and from these solutions $[HOs_3(CO)_{11}]^-$ can be isolated. A number of other, presently uncharacterized, cluster anions are also present. These observations indicate that an $Os_3$-formyl species is formed and has some stability at low temperature, but that it decomposes to

$$Os_3(CO)_{12} + [BH(O\text{-}\underline{i}\text{-}Pr)_3]^- \rightarrow \rightarrow \xrightarrow{H^+} Os_3(CO)_{11}CH_2 \qquad (2)$$

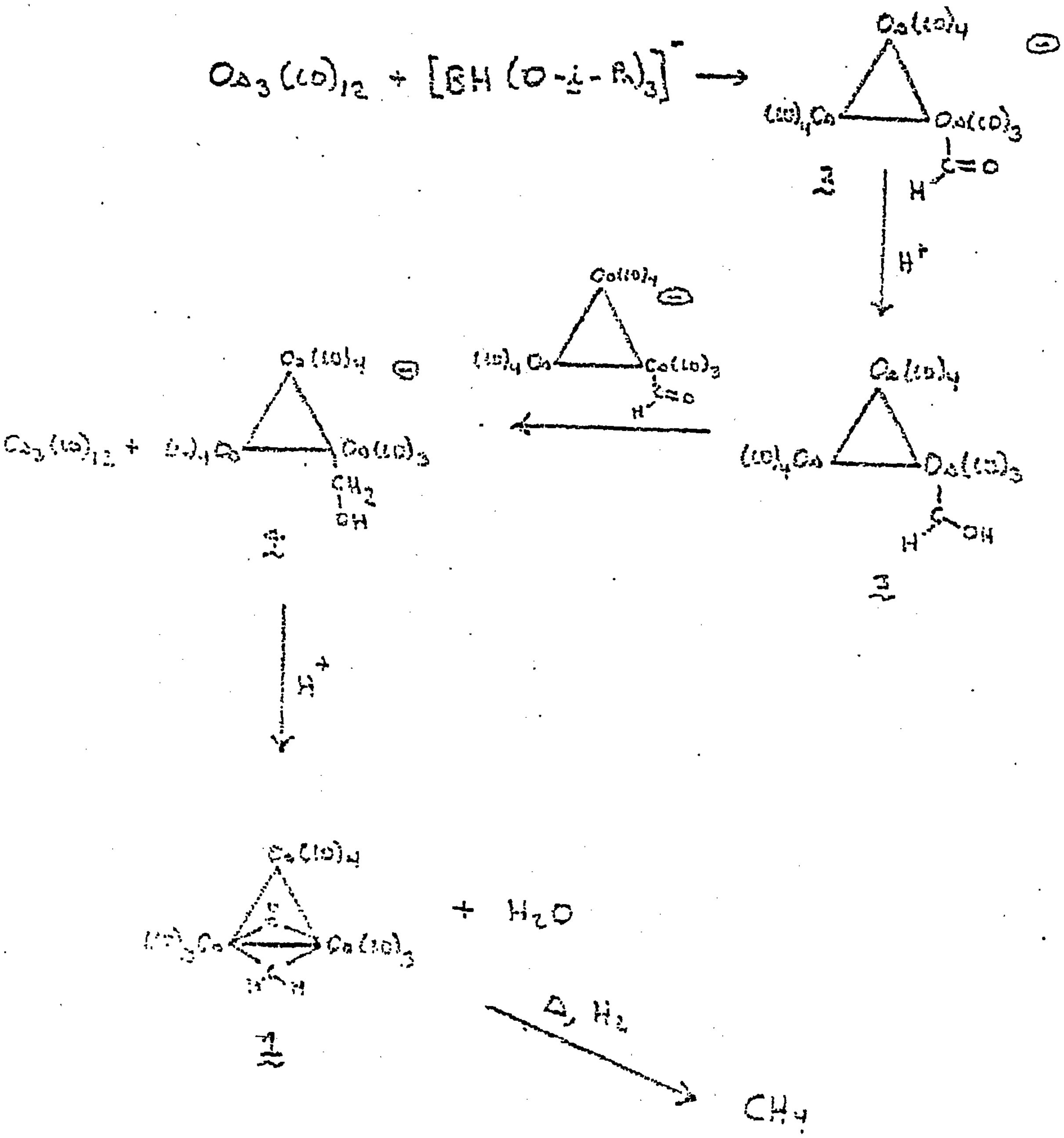
$$Os_3(CO)_{11}CH_2 + H_2 \xrightarrow{\Delta} Os_x \text{ clusters} + CH_4 \qquad (3)$$

If $D_2$ is employed in these experiments, $CH_2D_2$ results.

While this work was in progress, a paper appeared by Pruett and coworkers[17] at Union Carbide which reported slightly different observations pertaining to similar chemistry. They were also studying the reaction of clusters with hydridic reducing agents but only with $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were they able to obtain evidence for a formyl species. With $Os_3(CO)_{12}$, they observed a weak band in the 1590-1610 $cm^{-1}$ region of the IR and a very weak $^1H$ NMR resonance at $\delta$ 14.9 ppm which may be attributed to a $Os_3$-formyl species, presumably $[Os_3(CO)_{11}(CHO)]^-$. Warm-up gave a mixture of $[HOs_3(CO)_{11}]^-$ and other unidentified anionic clusters. Treatment of the solution containing the initial formyl species with $CF_3COOH$ gave, in contrast to our results, small amounts of MeOH. They gave no mention of the $Os_3(CO)_{11}CH_2$ product.

This $Os_3(CO)_{12}$ based system appears ideally suited for a mechanistic study to ascertain how $CH_4$ and $CH_3OH$ are produced via reduction of CO on a cluster face. We have undertaken such a study and our various experimental results are most consistent with the reaction sequence shown in Scheme III. Many of the elementary steps in the proposed scheme take precedence from the reactions which monomeric formyl complexes undergo as demonstrated by Casey, Gladsyz, and others.[10-15] The key sequence is protonation of the initial formyl complex $[Os_3(CO)_{11}(CHO)]^-$, $\underline{2}$, to give the intermediate hydroxy-carbene $\underline{3}$ which can react with another molecule of $\underline{2}$ to produce the hydroxy-methyl complex $\underline{4}$. In the presence of $H_3PO_4$, $\underline{4}$ presumably loses $H_2O$ to generate $Os_3(CO)_{11}(CH_2)$, $\underline{1}$, which we isolate

Scheme III



Os3(CO)12 + [BH(O-i-Pr)3]⁻
Os(CO)4
(CO)4Os
Os(CO)3
H
C=O
H+
C
OH
CH2
OH
Os3(CO)12 +
+ H2O
Δ, H2
CH4

Under the different acidification conditions employed by Pruett and coworkers, 4 can apparently cleave to produce $CH_3OH$. Our various experiments which support the mechanism shown in Scheme III are briefly summarized below.

1. An appreciable yield of $Os_3(CO)_{11}CH_2$ is obtained only when acid is added when the 1570 $cm^{-1}$ band of 2 is at its maximum intensity. Acidification before this band grows in or after it decays gives none of the desired $Os_3(CO)_{11}CH_2$, thus indicating that acid must react with $[Os_3(CO)_{11}(CHO)]^-$ to give the observed $Os_3(CO)_{11}CH_2$ product.
2. Only $Os_3(CO)_{11}CH_2$ is formed when acidification is carried out with $D^+$. When $[BD(Et)_3]^-$ is used in the initial reaction and acidification is carried out with $H^+$, only $Os_3(CO)_{11}CD_2$ results. These experiments indicate that both hydrogens in the $Os_3(CO)_{11}CH_2$ product come from the initially produced formyl species, and thus necessitate hydride transfer from the second molecule of $[Os_3(CO)_{11}(CHO)]^-$.

We are continuing to investigate the mechanism(s) of these unique transformations including the final reaction of $Os_3(CO)_{11}CH_2$ with $H_2$ to produce $CH_4$, and aim to have the various experiments completed and a manuscript submitted by October, 1980.

### B. Reaction of $Ir_4(CO)_{12}$ with $[BH(O\text{-}i\text{-}Pr)_3]^-$

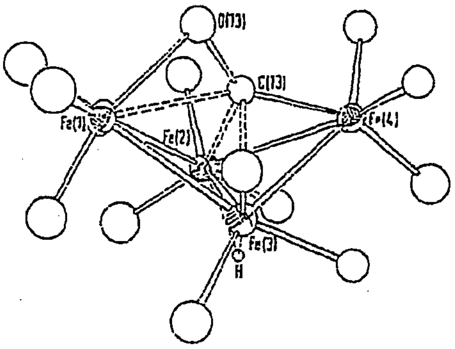
We have briefly examined the reaction of $Ir_4(CO)_{12}$ with $[BH(O\text{-}\underline{i}\text{-}Pr)_3]^-$. Upon combination of these reagents at -78°C or 0°C, a rapid yellow to orange color change ensues and a new band at 1600 $cm^{-1}$ appears in the IR spectrum. This is in the same position as the band attributed to $[Ir_4(CO)_{11}(CHO)]^-$ prepared by a similar procedure by Pruett and coworkers.[17]

Acidification of this solution gives a new hexane soluble cluster ($Ir_4(CO)_{12}$ is insoluble in hexane) which shows a mass spectrum which is consistent with the formation of $Ir_4(CO)_{11}CHOH$. This species is analogous to compound 3 in Scheme III. We thus may have isolated a second intermediate in the overall transformation of CO into $CH_4$ and $CH_3OH$. Further characterization of this compound and a study of its reactivity is in progress.

A very interesting aspect of this complex, if indeed $Ir_4(CO)_{11}(CHOH)$ proves to be the correct formulation, in that it is an analog of the type of complex proposed to exist in Union Carbide's $Rh_x$ cluster catalyzed production of ethylene glycol from $CO/H_2$. Further hydrogenation to yield $Ir_4(CO)_{11}(CH_2OH)$ followed by condensation of two such species would yield $HOCH_2CH_2OH$. Obviously, we are very interested in the chemistry which this compound will show and plan to explore it in detail in the coming months.

## C. Structures of Tetranuclear Fe-Ru Clusters as Models for CO Activation

The cluster $[HFe_4(CO)_{13}]^-$ has been shown to adopt the butterfly structure sketched in 5 with a folded-over, multiply-bonded and presumably activated CO.[18]



5

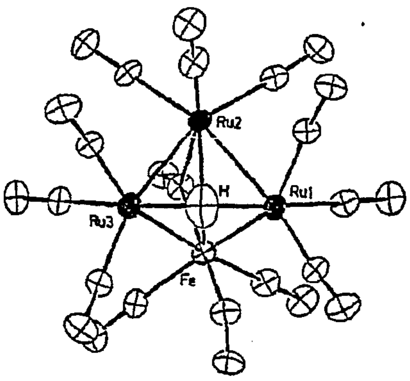
Significantly, Shriver and coworkers[19] have recently shown that treatment of this particular anion with strong acid leads to CO reduction and the production of $CH_4$. In order to assess the factors which influence the formation of a cluster with such an activated CO, and ideally to prepare analogs more suitable for a mechanistic study of the CO reduction step, we set out to prepare the mixed-metal derivatives, $[HFe_xRu_{4-x}(CO)_{13}]^-$ ($x = 3, 2, 1$).

Two of these have been prepared via the reactions shown in eqs. 4-5.

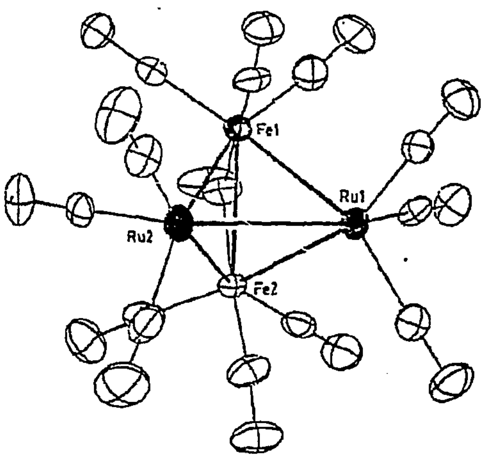
$$Ru_3(CO)_{12} + [HFe(CO)_4]^- \rightarrow [HFeRu_3(CO)_{13}]^- \quad (\underline{6}) \qquad (4)$$

$$Ru_2Fe(CO)_{12} + [HFe(CO)_4]^- \rightarrow [HFe_2Ru_2(CO)_{13}]^- \quad (\underline{7}) \qquad (5)$$

The remaining member of the series, $[HFe_3Ru(CO)_{13}]^-$, has not yet been synthesized. We have determined the crystal structure of 6 by neutron diffraction with R. Bau and T. Koetzl[20] and 7 by x-ray diffraction in our laboratories, but, unfortunately, neither of these clusters adopt an open butterfly structure analogous to 5 but instead they have the closed pseudo-tetrahedral frameworks as shown in the ORTEP drawings below.



$[HFeRu_3(CO)_{13}]^-$



$[HFe_2Ru_2(CO)_{13}]^-$

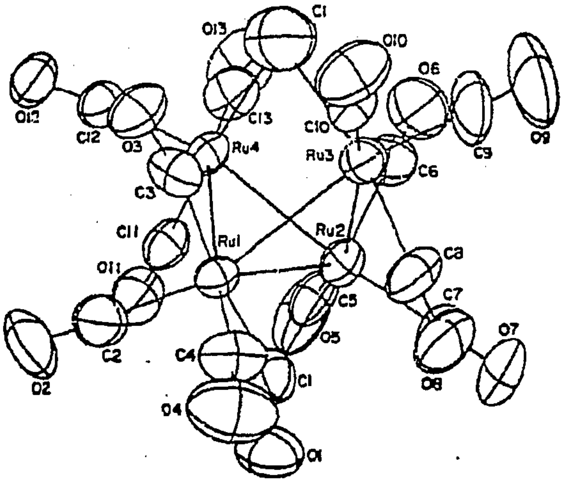
The $^1$H NMR spectrum of $[HFeRu_3(CO)_{13}]^-$ does suggest the presence of isomers in solution but the only one presently characterized is 6.

## D. Reactions Directed Toward the Preparation of Acyl-Substituted Clusters

Acyl and alkyl substituted clusters are direct models for intermediates IIk and IIg, respectively, of Scheme II. Furthermore, an acyl cluster can be viewed as an analog of a formyl cluster and thus is an indirect model for IC and IIC. In our initial experiments, we allowed MeLi to react with $Ru_3(CO)_{12}$ in the presence of [PPN]Cl, but the product actually isolated was not an acyl cluster but instead $[PPN][ClRu_4(CO)_{13}]$, eq. 6.

$$[PPN]Cl + Ru_3(CO)_{12} + LiMe \xrightarrow{\Delta} [PPN][ClRu_4(CO)_{13}] \qquad (6)$$

The structure of this product was determined by x-ray diffraction and is shown in 8.[21]



8

In subsequent experiments we showed that the $[ClRu_4(CO)_{13}]^-$ anion derives by simply heating $Ru_3(CO)_{12}$ in the presence of a $Cl^-$ source. This work is described in a paper now in press in Inorg. Chem.[21]

When the reaction shown in eq. 6 is conducted without [PPN]Cl or another $Cl^-$ source present a material is isolated in 20-30% yield for which chemical analysis suggests the formulation $[PPN][Ru_3(CO)_{11}(-\underset{\underset{O}{\|}}{C}CH_3)]$. Although this product may be the desired acyl substituted cluster, it still needs to be completely characterized, ideally by a single-crystal x-ray diffraction study. We are currently carrying out such characterization studies and are beginning to explore its reactivity.

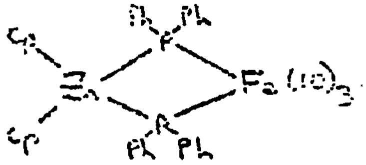
### E. Synthesis and Characterization of Dimeric Metal Complexes for Catalysis of CO Reduction

It has been our intent in this phase of our research to design and direct the synthesis of homogeneous catalysts which should be able to reduce carbon monoxide. Under the premise that two or more metals are necessary to effect such reduction by polarizing CO or by stabilizing the initially formed formyl intermediate, our attention has been focussed on transition metal dimers and especially dimers possessing one early and one late transition metal.

Following the precedent set by Bercaw's[22] stoichiometric reduction of CO using $(C_5Me_5)_2Zr$ derivatives, we initially set out to prepare mixed-metal dimers containing Zr. Although a variety of reactions have been conducted and a large number of product mixtures have been obtained, only a few compounds have thus far been characterized because of separation and purification difficulties. The reaction which has been the most successful is that leading to the preparation of the Zr-Fe dimer shown in eqs. 7 and 8.

$$Fe(CO)_3(PPh_2H)_2 + 2n\text{-}BuLi \rightarrow 2\ BuH + Li_2[Fe(CO)_3(PPh_2)_2] \qquad (7)$$

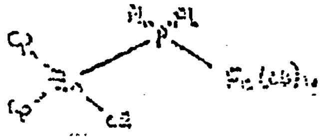
$Li_2[Fe(CO)_3(PPh_2)_2] + (C_5H_5)_2ZrCl_2 \rightarrow 2\ LiCl +$



This compound has been characterized spectroscopically and its chemistry is presently being examined. Initial results indicate that it will not assist CO reduction, presumably because of the presence of the two bridging $\mu$-$PPh_2$ groups which prevent the desired interaction of Zr with the CO.

In other attempts to prepare Zr-Fe dimers with only one bridging group, we have carried out the reactions shown in eqs. 9 and 10. The products shown are those expected and although materials have been obtained from these reactions, their full characterization is still in progress.

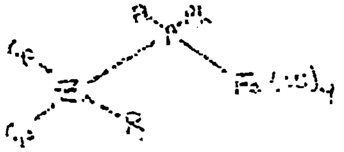
$Cp_2ZrCl(R) + HPPh_2Fe(CO)_4 \xrightarrow{\Delta}$ [illegible] +



(9)

R = hexyl

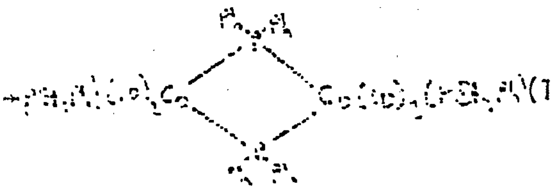
$Cp_2ZrCl(R) + [PPh_2Fe(CO)_4]^- \xrightarrow{\Delta} Cl^- +$



(10)

In another set of experiments we have prepared the $Co_2$ dimer 9 shown in eq. 11.

$[Co(CO)_3(\mu\text{-}PPh_2)]_x + PEt_2Ph \rightarrow$



(11)

Treatment of 9 with $[BH(O\text{-}\underline{i}\text{-}Pr)_3]^-$ produces what appears to be a dimeric formyl species at -78°C. This species is reactive and decomposes upon warm-up to give a product mixture which is presently being characterized.

### F. Reaction of Tetranuclear Mixed-Metal Clusters with CO

We have examined the reactions of a number of mixed-metal clusters with CO and found that they all readily fragment under rather mild conditions. Full details of this work are described in the manuscript which is in press (September, 1980) in Inorganic Chemistry and ~~is enclosed as Appendix I~~.[23] The most important conclusions drawn from this study are:

1. Realization that metal clusters with nuclearity greater than 3 are generally inherently unstable under CO atmospheres and readily fragment to produce lower-nuclearity products. Thus, unless such clusters are tied together with bridging ligands, they will probably be unsuitable for directly catalyzing reduction of CO. They may, however, fragment to yield catalytic pieces.
2. Determination of the mechanism by which these fragmentation reactions occur. This was accomplished by the series of kinetic experiments outlined in Appendix 1 which also gives the derived mechanism.

(In Inorganic Chemistry ✓
Sept 1980)

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## V. Publications Which Have Acknowledged DOE Support

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2. Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L., "Synthesis and Structural Characterization of $[PPN][ClRu_4(CO)_{13}]$: A Butterfly Cluster with a Bridging Chloride," Inorg. Chem., in press (October, 1980).
3. Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Gladfelter, W. L.; Rosen, R.; Geoffroy, G. L.; Bruck, M. A.; Bau, R., "X-ray and Neutron Diffraction Studies on the Structure of $[((C_6H_5)_3P)_2N]$ $[HFeRu_3(CO)_{13}]$," Inorg. Chem., to be submitted.
4. Steinmetz, G.; Geoffroy, G. L., "Synthesis and Structural Characterization of $[PPN][HFe_2Ru_2(CO)_{13}]$," Inorg. Chem., manuscript in preparation.

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21. Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L.; Inorg. Chem., in press.

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