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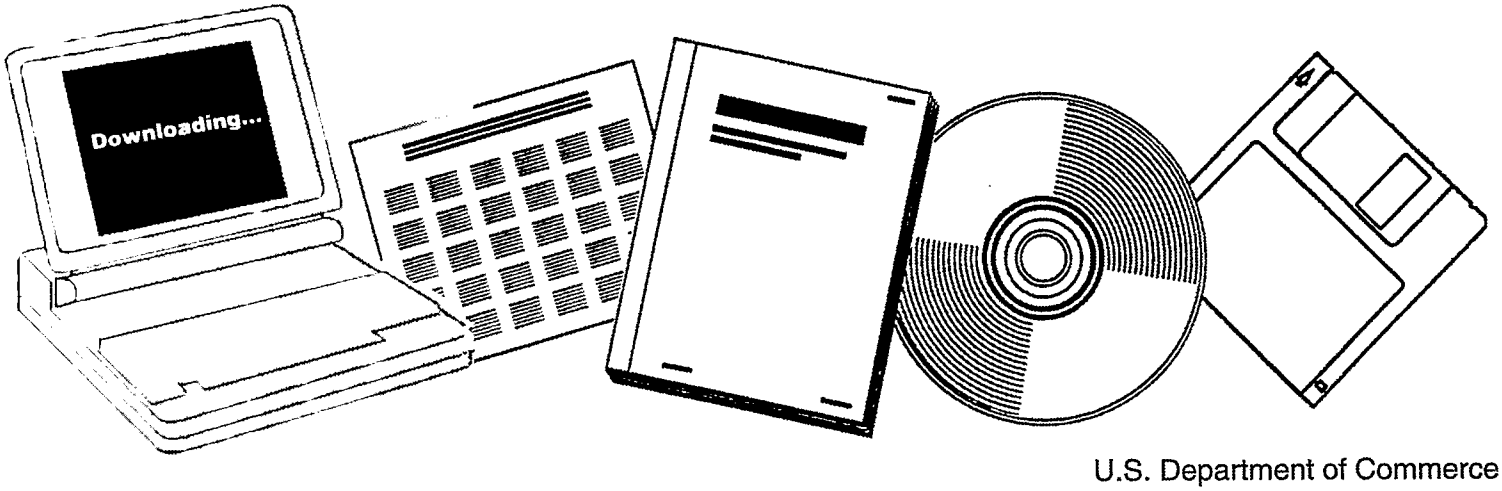
MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION. PROGRESS REPORT, AUGUST 1, 1980-AUGUST 1, 1981

PENNSYLVANIA STATE UNIV., UNIVERSITY PARK

20 JUL 1981



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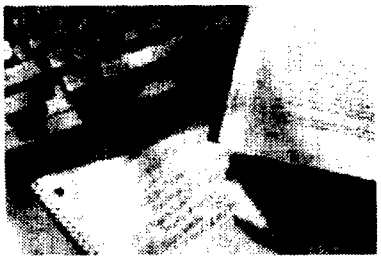

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I. Research Objectives

The long-range objective of this research program is to contribute to the understanding of the mechanisms by which carbon monoxide is reduced by hydrogen on the surface of metal particles and in homogeneous solutions.

II. Introduction and Rationale

The eventual shortage of crude oil has resulted in an increased interest in developing other sources of fuels and chemical feedstocks.[1] The use of a mixture of carbon monoxide and hydrogen, commonly called synthesis gas, has attracted much attention since in principle it can be used to produce a wide range of organic chemicals and may be obtained from coal via gasification with steam and perhaps eventually from other carbon sources. Every major chemical company today must surely have an aggressive research program underway in some aspect of synthesis gas chemistry, because of its inevitable importance in the future chemical industry.

In order for synthesis gas reactions to proceed at useful rates, catalysts must be employed. The key to any successful catalytic process utilizing synthesis gas is the selectivity toward products that the catalyst affords. The optimum process is one which uses synthesis gas to yield a single organic chemical. Processes which give several products with none in high yield are not economical because of high separation costs, unless the product mixture is to be used as a fuel, as with the current Fischer-Tropsch product mixture.[1-3] An illustration where poor selectivity has resulted in the lack of commercial exploitation is the catalyzed homologation of methanol to ethanol.[4] Since ethanol can be dehydrated to give ethylene, the premier chemical feedstock from which most industrial chemicals are eventually derived, ethanol production via the sequence of reactions 1 and 2 would provide an entry into present industrial processes directly from synthesis gas. However, the presently available catalysts for methanol homologation rarely give ethanol with greater than 50 to 60% selectivity.[4] This coupled with the relatively low reaction rates makes present processes economically unattractive.[4]

$$CO + 2H_2 \xrightarrow{ZnO/Cr_2O_3/CuO} CH_3OH \quad (1)$$

$$CH_3OH + CO + 2H_2 \longrightarrow CH_3CH_2OH + H_2O \quad (2)$$

Nearly all synthesis gas reactions are in need of better catalysts, particularly catalysts which give high selectivities toward the desired products. This constitutes the major aim of all synthesis gas research. There are two approaches to developing better catalysts. One is empirical and simply involves conducting a large number of experiments with different catalyst compositions and letting the results of those evaluation experiments guide one to the best catalyst system. The alternative method is through mechanistic studies whereby an understanding of the mechanistic course of a reaction should allow the design of more efficient catalysts for the reaction, especially by considering the critical steps in the reaction. Ideally, catalyst development should be a combination of both approaches in which available mechanistic information serves to guide the empirical studies.

Unfortunately the mechanisms of synthesis gas reactions are not at all well understood, with the possible exception of the hydroformylation reaction.[5] However, even here some uncertainty exists as to the intimate details of how aldehyde results from the precursor acyl complex.[6] There is clearly a need for good mechanistic studies directed toward developing an understanding of the details of the mechanisms of the various synthesis gas reactions with the expectation that such an understanding would lead to the development of better catalysts. In this proposed research we intend to conduct such mechanistic studies from two approaches. First we wish to probe the mechanism of the heterogeneous, metal particle catalyzed reduction of carbon monoxide (Fischer-Tropsch chemistry) by using transition metal cluster complexes to model the metal

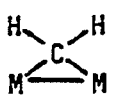
surfaces. We also propose to study the mechanism of synthesis gas chemistry carried out in homogeneous solution, focusing on a few key mechanistic steps. Some exploratory work is proposed concerning the methanol homologation reaction. The homogeneous and heterogeneous model studies necessarily overlap and it is likely that the mechanistic studies carried out with metal clusters will directly bear on certain mechanistic steps involved in the homogeneous reduction of CO. However, to facilitate discussion, the heterogeneous model studies have been separated from the homogeneous mechanistic studies in the more detailed introduction which follows in Sections IIIA-IIIC.

A. Metal Clusters as Models for the Metal Surface Catalyzed Reduction of Carbon Monoxide.

One approach which has been widely discussed for indirectly studying the chemistry of the metal surfaces of heterogeneous catalysts is to use polynuclear transition metal complexes, commonly called clusters, as models for those surfaces.[7-10] The rationale is that by carefully studying the bonding of substrates to clusters and their subsequent reactivity on clusters one should develop a better understanding of the bonding and reactivity of substrates adsorbed on metal surfaces. The principle advantage which clusters have is that they are molecular compounds capable of being studied by the full range of spectroscopic techniques available to the chemist. Their solubility, for example, means that high resolution NMR and IR spectra can be obtained, and the usual volatility of the carbonyl clusters allows characterization by mass spectrometry. Importantly, many cluster derivatives yield crystals suitable for x-ray diffraction studies and thus the intimate details of their structure and bonding can be determined. However, clusters are certainly not perfect models and some of their limitations have been mentioned elsewhere,[11] but to a first approximation they can provide insight into

the chemistry which occurs on metal particles. The way in which one generally proceeds in research of this type is to propose what seems to be a reasonable path for a given reaction and then test the likelihood of the proposed mechanism by examining the reactivity of appropriately selected or designed metal clusters which mimic the proposed reaction intermediates.

In the research proposed herein we are concerned with the metal surface catalyzed reduction of carbon monoxide by hydrogen. A number of different mechanisms have been suggested for the metal catalyzed reduction of CO, and these have been described in detail elsewhere.[12-18] There is an increasing amount of evidence that surface supported methylene groups, such as 1, are key intermediates in the reaction mechanism.[17,19,20]



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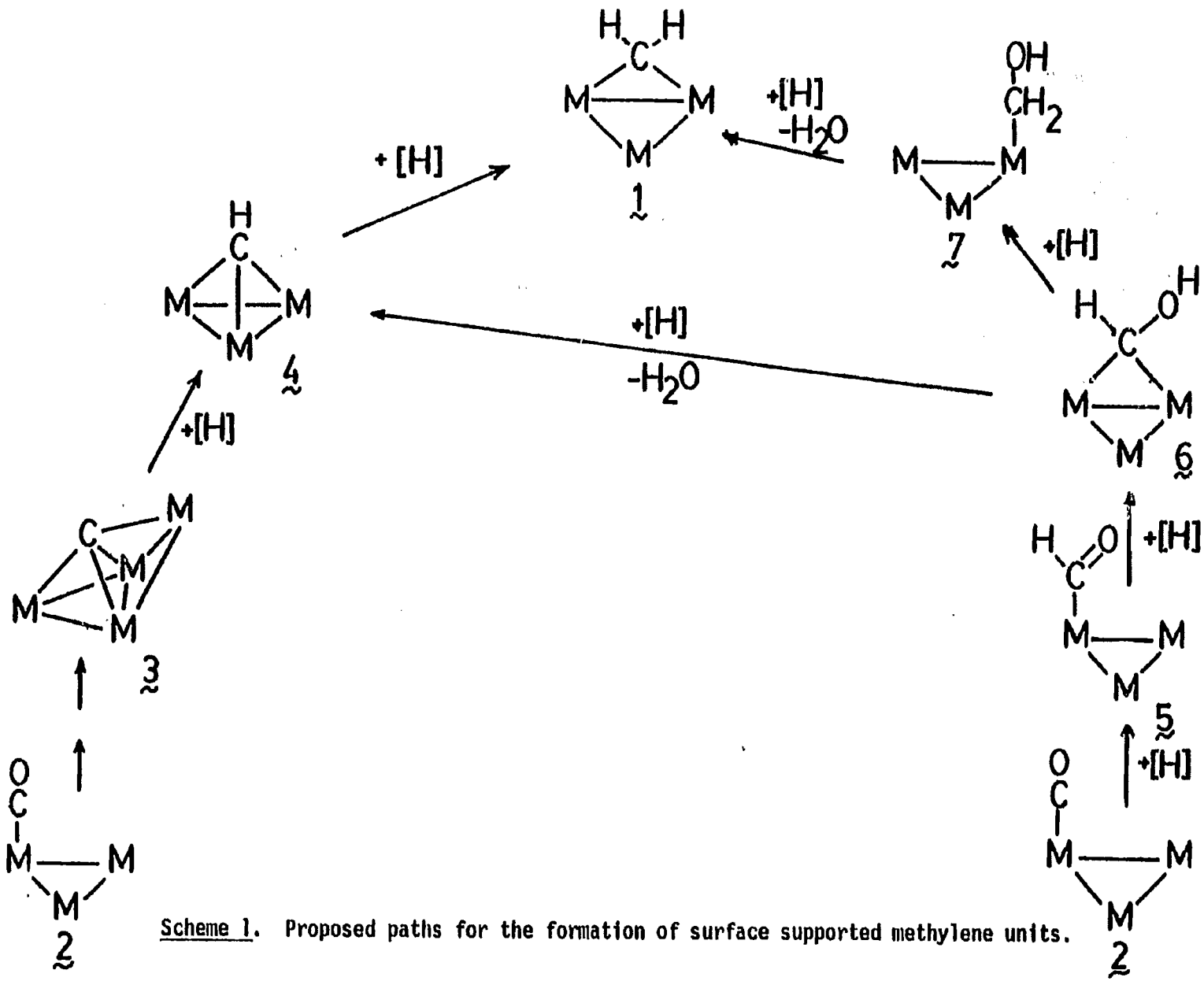
Pettit and Brady, for example, showed in a series of very creative experiments that the Fischer-Tropsch product distribution could be closely approximated by passing CH_2N_2, a known methylene precursor, and H_2 over typical Fischer-Tropsch catalysts.[17,19] Their conclusion was that CH_2N_2 decomposes on the catalyst surface to give surface-bound methylene units such as 1 and these polymerize and are hydrogenated to give the Fischer-Tropsch product distribution.[17] The methylene unit in 1 is drawn as bridging two metals since studies of discrete organometallic compounds have shown a strong preference for methylene groups to bridge two metals wherever possible.[21]

A central question concerns the mechanism by which methylene groups are produced on a metal surface during Fischer-Tropsch catalysis. There appear to be two principle schools of thought, and these independent mechanisms are summarized in Scheme 1. The mechanism on the left of Scheme 1, illustrated by the transformations 2 → 3 → 4 → 1, invokes initial dissociation of CO to produce surface bound carbon species which are then subsequently hydrogenated to the methylene stage. This is commonly called the CO-dissociation mechanism or the carbide mechanism, and is similar to that originally proposed by Fischer and Tropsch in the 1920's.[22,23] The mechanism on the right, commonly called the formyl mechanism, shown by the transformation 2 → 5 → 6 → 1 (via 4 or 7) invokes initial formation of a surface bound formyl group. It has the dissociation of the carbon-oxygen bond occurring at a much later stage in the reaction and assisted by hydrogen. This mechanism is somewhat similar to those proposed by Pichler and Schultz,[16] and by Olivé and Olivé,[19] except that the participation of several metals are illustrated in certain of the key intermediates in Scheme 1, e.g., 6, 4, and 1.

Both of the possible mechanisms shown in Scheme 1 for the formation of surface-bound methylene groups have been partially modeled by polynuclear complexes. All the steps involved in the carbide mechanism have been well modeled with metal clusters, except for the first and clearly the most important step involving initial dissociation of the CO bond. A few carbide clusters have been produced by thermal decomposition of metal carbonyl clusters,[24] but the steps involved in those transformations are complex and discrete intermediates have not been observed. For dissociation of the CO bond to occur, Muetterties[7] has suggested the necessity of simultaneous coordination to several atoms on a multi-metal site, as indicated below.

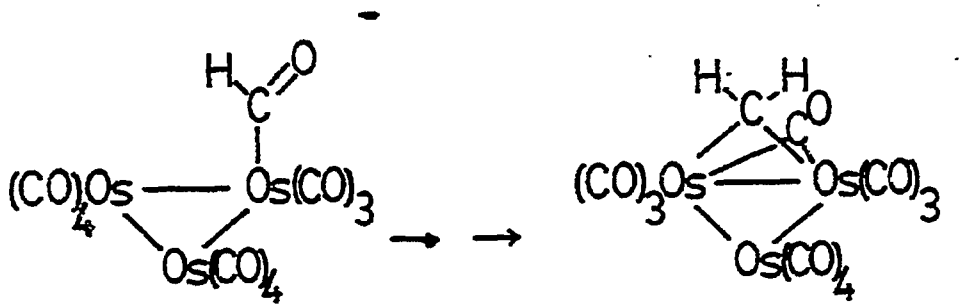


Scheme 1. Proposed paths for the formation of surface supported methylene units.

6-electron donor

Two polynuclear complexes have been reported which possess a CO ligand σ,π-coordinated to three or more metal atoms, $[HFe_4(CO)_{13}]^-$ [25] and $[(\eta\text{-}C_5H_5)_3\text{-}Nb_3(CO)_7]$[26], but neither of these have been observed to cleanly lead to CO dissociation. It still remains a challenge for the organometallic chemist to model this particularly important step of CO dissociation by unambiguously demonstrating its occurrence on discrete organometallic compounds. Reactions which model the other steps in the carbide mechanism have been summarized in a recent review by Muetterties and Stein,[27] and in several recent papers from the Muetterties group.[28-30]

Many of the elementary steps depicted in the formyl mechanism of Scheme 1 have been well modeled by transformations which occur on single metal atoms of monomeric organometallic complexes, largely through the pioneering efforts of Casey and Gladysz, and their coworkers.[31-34] We recently showed[35] that similar transformations occur on an Os_3 cluster face, and these experiments are discussed in more detail in the Progress section of this proposal. In that study we were able to convert an Os_3-formyl cluster, modeling 5 in Scheme 1, all the way to a methylene bridged cluster, modeling 1, eq. 3, and provided indirect evidence for the formation of intermediates similar to 6 and 7. The key step in the formyl mechanism is of course the first one,

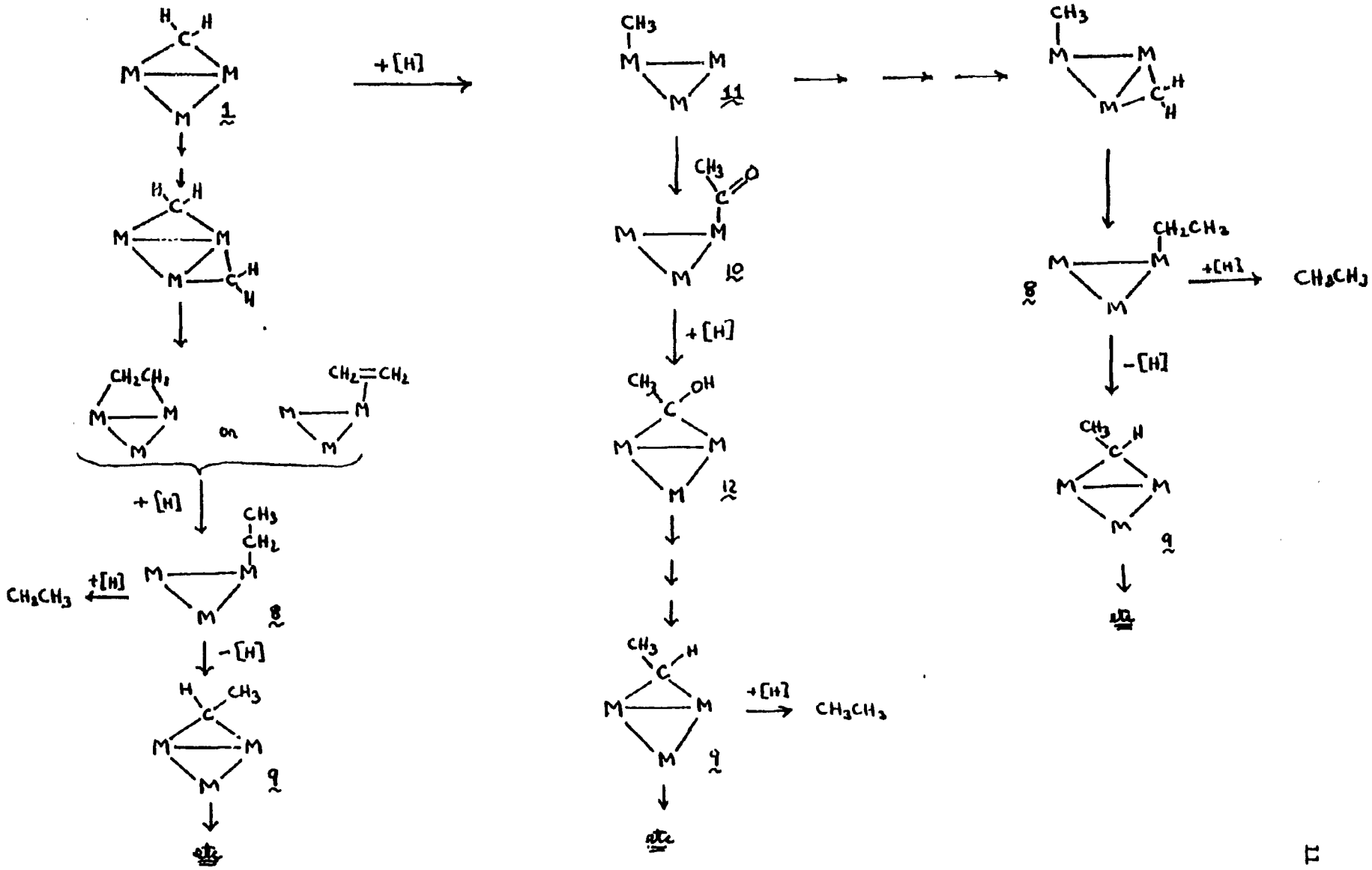


(3)

namely migration of hydrogen from the metal surface to a bound carbon monoxide to product the formyl. While formyl complexes can be indirectly prepared, usually via hydride reducing agents,[31-34] the direct migration of a hydride to a bound carbon monoxide has never been directly observed, although it has been inferred from the homogeneous catalysis studies discussed in the next section.

To summarize, the "clusters as models" approach has been partially successful in modeling both mechanisms of Scheme 1 for the formation of surface supported methylene groups. While neither mechanistic path has been completely modeled, the reactions which have been conducted do suggest that both mechanistic courses are reasonable. Whether this means that both mechanisms occur, but are catalyst and reaction condition dependent, or whether one is simply more energetically favorable than the other remains an open question.

Assuming that surface supported methylene units are indeed key intermediates in the metal surface catalyzed reduction of CO, an important question concerns the mechanism(s) of production of C_n hydrocarbons with $n \geq 2$ from these intermediates. Several mechanisms can be envisaged and these possibilities are outlined in Scheme 2. The mechanism on the left involves coupling of surface methylene units, the mechanism on the right involves insertion of a



Scheme 2. Proposed pathways for chain growth from methylene units during Fischer-Tropsch catalysis.

surface methyl group into a surface methylene, and the center mechanism invokes CO insertion into a surface metal-alkyl bond. There has been relatively little progress in modeling these various mechanisms since only recently have appropriate bridging methylene and alkylidene complexes been prepared and characterized which can be used in such studies. This is an area of current research interest and is actively being explored by various research groups, particularly those of Shapley,[36] Bergman,[37] Pettit,[38] and Herrmann.[21,39]

B. Homogeneous Reduction of Carbon Monoxide.

A number of recent reports have illustrated the reduction of carbon monoxide by hydrogen catalyzed by homogeneous molecular complexes. These include Muetterties, et al.[40] initial reports of alkane production by $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ catalyst precursors; Union Carbide's synthesis of methanol, ethylene glycol, and polyols using rhodium cluster catalysts[41]; Feder's report of methanol synthesis using $Co_2(CO)_8$[42]; Bradley's synthesis of methanol using $Ru(CO)_5$[43]; Dombek's version of this system using strong acid media and lower pressures for the synthesis of methanol and ethylene glycol[44]; and Wilkinson's very recent reports of the synthesis of methanol, ethylene glycol, and derived compounds using carbonyls of Fe, Ru, and Os.[45] The use of Mn, Fe, Ni, Pd, Os, Ir, and Pt complexes have also been described.[46] Although it is now clear that carbon monoxide can be reduced with the aid of homogeneous catalysts, the rates of the reactions are generally quite low and high pressures are usually required. Homogeneous systems do appear to offer promise for the selective production of oxygenated organics, but significant advances will have to be made before such processes will be economically feasible.

Fahey[46] recently reported a careful examination of the Rh and Co based systems for producing methanol, ethylene glycol, and their derivatives from synthesis gas, including the effect of a number of experimental variables. Fahey proposed mechanisms for the reactions which invoked free formaldehyde as the initial key intermediate, and he suggested that its rate of formation is the rate-limiting step for the entire process.[46] The basic features of these mechanisms are shown in Scheme 3 for cobalt carbonyl.

Part 1. Generation of Formaldehyde

$$HCo(CO)_4 \rightleftharpoons H\text{-}\overset{O}{\overset{\|}{C}}\text{-}Co(CO)_3 \overset{H_2}{\rightleftharpoons} H_2CO + HCo(CO)_3 \qquad (4)$$

Part 2. Hydrogenation of Formaldehyde

Route A.

$$H_2CO + HCo(CO)_3 \rightleftharpoons HOCH_2Co(CO)_3 \xrightarrow{H_2} HOCH_3 + HCo(CO)_3 \qquad (5)$$

$$\Updownarrow +CO$$

$$HOCH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Co(CO)_3 \xrightarrow{H_2} HOCH_2CHO + HCo(CO)_3 \qquad (6)$$

Route B.

$$H_2CO + HCo(CO)_3 \rightleftharpoons CH_3OCo(CO)_3 \xrightarrow{H_2} CH_3OH + HCo(CO)_3 \qquad (7)$$

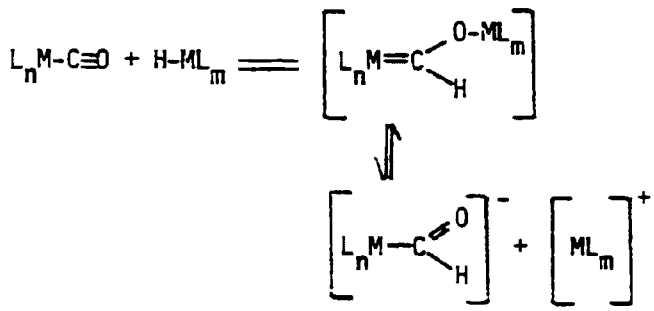
$$\Updownarrow +CO$$

$$CH_3\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Co(CO)_3 \xrightarrow{H_2} CH_3O\overset{O}{\overset{\|}{C}}H + HCo(CO)_3 \qquad (8)$$

Scheme 3. Proposed Mechanism for Homogeneous Reduction of CO by H_2 Using Cobalt Carbonyl.

The initial formation of formaldehyde may occur by migration of hydride to a metal carbonyl to give a metal formyl intermediate which is then hydrogenated to give free formaldehyde, eq. 4 of Scheme 3. Although the initial migration of hydride to CO is a step which has never been directly observed for discrete organometallic complexes, it is not unreasonable in view of the facile migration of alkyl ligands to carbon monoxide to produce metal acyls. However, the equilibrium shown in eq. 9 is generally believed to lie far to the left; Halpern[47] has estimated that the conversion of $(CO)_5MnH$ to $(CO)_5Mn(CHO)$ is endothermic by roughly 20 kcal/mole. Alternatively, formation of the initial formyl intermediate could occur via hydride transfer from a second metal center, as in eq. 10, and thereby circumvent the unfavorable equilibrium of eq. 9. Such reaction could involve intermolecular hydride transfer between two mononuclear complexes, or intramolecular transfer in a dinuclear complex. Such reaction is similar to that which has been extensively studied by Bercaw and coworkers[48] using $(Me_5C_5)_2ZrH_2$. <u>One of the most important challenges facing organometallic chemists in regards to homogeneous CO reduction is in devising methods for promoting the formation of formyl ligands from metal hydrides and metal carbonyls.</u>

$$HM(CO)_x + CO \rightleftharpoons H-\overset{O}{\overset{\|}{C}}-M(CO)_x \qquad (9)$$



(10)

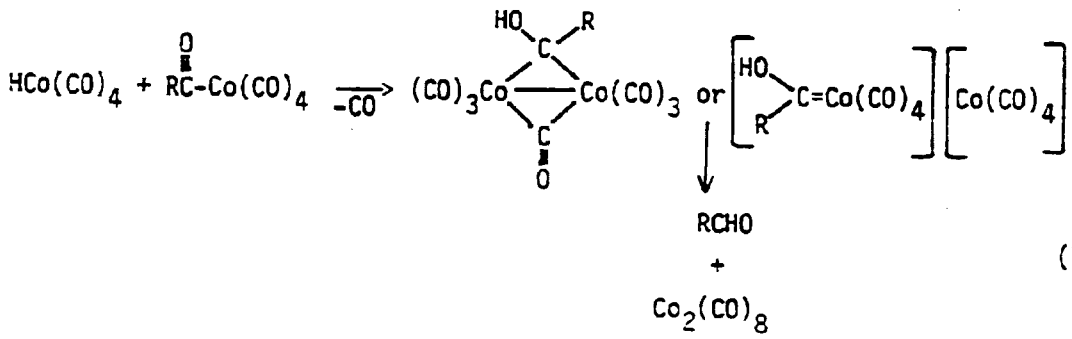
An alternative to Fahey's direct hydrogenation of the intermediate formyl, eq. 4, is to invoke hydrogenation instead by $HCo(CO)_4$, eq. 11.

$$\overset{O}{\overset{\|}{HC}}\text{-}Co(CO)_3 + HCo(CO)_4 \longrightarrow H_2CO + Co_2(CO)_7 \qquad (11)$$

In the related hydroformylation reaction, Norton[6] has suggested that aldehyde is produced by the interaction of $HCo(CO)_4$ with $R\overset{O}{\overset{\|}{C}}Co(CO)_3$, eq. 12.

$$\overset{O}{\overset{\|}{RC}}\text{-}Co(CO)_3 + HCo(CO)_4 \longrightarrow \overset{O}{\overset{\|}{RC}}\text{-}\underset{\underset{Co(CO)_4}{|}}{\overset{H}{\overset{|}{Co}}}(CO)_3 \longrightarrow \underset{\underset{Co_2(CO)_7}{+}}{RCHO} \qquad (12)$$

Bergman and Jones[49] have provided experimental evidence for this proposal using Mo compounds to model the Co reactions. Although such hydrogenation by $HCo(CO)_4$ has been suggested to proceed through the type of intermediate shown in eq. 12, it could also proceed by hydrogen transfer to the acyl oxygen to give a hydroxy carbene, eq. 13, a type of intermediate which is known to be unstable and which apparently can decompose to aldehyde.[50,51]



(13)

While such a mechanism does not appear to have been seriously considered for the production of aldehydes from acyls and metal hydrides, it does not appear unreasonable. $HCo(CO)_4$ is a strong acid and should easily transfer a proton to the acyl oxygen, the most electronegative center in $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$. Such a mechanism would seem to be more likely in polar media, where homogeneous reduction of CO works best, and under high pressures of CO, where the coordinatively-unsaturated intermediate $H\overset{O}{\overset{\|}{C}}-Co(CO)_3$, required in eq. 4, would be expected to have a very low concentration. Note that the reaction in eq. 13 does not require the presence of a coordinatively-unsaturated metal center. Little consideration has apparently been given to the mechanistic path indicated in eq. 13.

Reduction of the formaldehyde intermediate to products was rationalized by Fahey[46] to occur via either or both of the two paths shown in Part B of Scheme 3. These two paths differ only in the mode of metal-hydride addition to the formaldehyde intermediate. In path A hydrogen addition occurs at the oxygen to give a carbon-bound hydroxymethyl intermediate, eq. 14, and in path B,

$$H_2CO + HCo(CO)_3 \longrightarrow HOCH_2Co(CO)_3 \qquad (14)$$

hydrogen addition occurs at the carbon to give an oxygen-bound methoxy derivative, eq. 15.

$$H_2CO + HCo(CO)_3 \longrightarrow CH_3OCo(CO)_3 \qquad (15)$$

Hydrogenation or CO insertion into these intermediates would lead to CH_3OH, glycolaldehyde, and methylformate. A similar scheme was proposed for the interaction of glycolaldehyde with $HCo(CO)_3$ to account for other C_2 and C_3 products. These steps are obviously critical for controlling the selectivity toward certain products. For example, if one wishes to minimize the formation of methyl formate and instead enhance the formation of ethylene glycol, one would need a catalyst which preferentially hydrogenates formaldehyde by path A. Unfortunately, very little is understood about the factors which affect the stereospecificity of metal hydride addition to aldehydes and this is an area in which meaningful research is needed.

C. Homologation of Methanol with CO/H_2 to Produce C_2 Chemicals

The homologation of methanol to C_2 chemicals has been recently reviewed by Slocum[4] and will be only briefly summarized here. The reaction is catalyzed by $Co_2(CO)_8$ in polar media and is promoted by iodide and ruthenium salts. Although there has been a great deal of industrial interest in the methanol homologation reaction, very little academic attention has been given to study of the details of the reaction. Consequently very little mechanistic detail has been published and the overall reaction mechanism is not well understood.

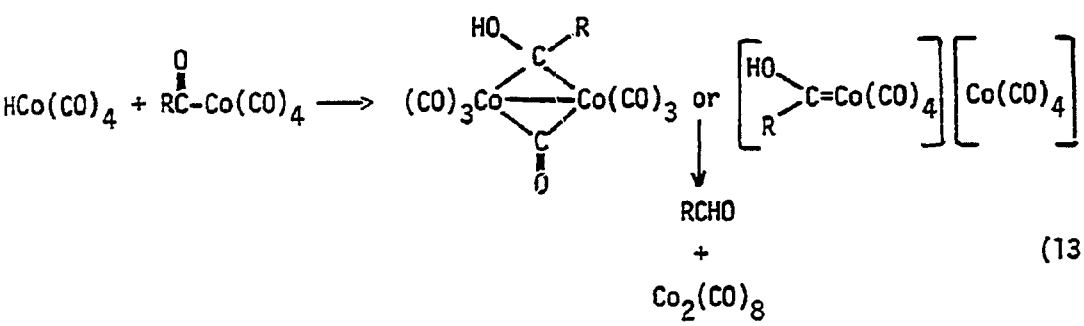
The key intermediate in the reaction is almost surely $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$, formed by addition of either CH_3OH or CH_3I to $[Co(CO)_4]^-$. As noted earlier, poor selectivity to specific products has been partly responsible for limiting commercial utilization of the homologation of methanol to produce C_2 chemicals, other than acetic acid and acetic anhydride. The selectivity of the reactions would appear to be determined by the pathways by which the $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$ intermediate decays to products. For example, addition of H_2O to $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$ would lead to acetic acid, eq. 16, and addition of methanol would give methylacetate,

$$CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4 + H_2O \rightarrow CH_3COOH + HCo(CO)_4 \qquad (16)$$

eq. 17.

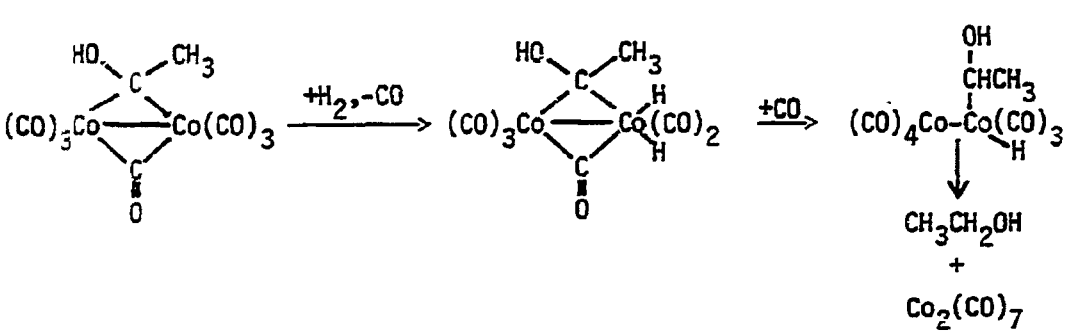
$$CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4 + HOCH_3 \rightarrow CH_3COOCH_3 + HCo(CO)_4 \qquad (17)$$

Acetaldehyde could result from hydrogenation of the acyl intermediate by either H_2 or $HCo(CO)_4$, perhaps proceeding through a hydroxycarbene intermediate as suggested in eq. 13.



(13)

The latter appears especially likely in the polar media in which methanol homologation is usually conducted where $HCo(CO)_4$ behaves as a strong acid and is largely dissociated. Interestingly, the hydroxycarbene intermediate of eq. 13 could either decompose directly to acetaldehyde, which could then be hydrogenated to ethanol by the cobalt catalyst, or could react with H_2 to produce ethanol directly, eq. 18.



(18)

Such reactions are unknown for hydroxycarbenes, although other carbene complexes have been shown to react with H_2 to give hydrogenation of the carbene with addition of the two hydrogens to the carbene carbon.[50,52]

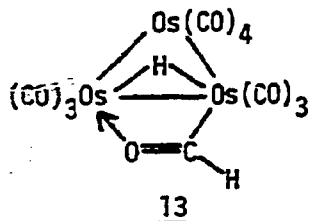
In summary, very little is understood about the mechanism of the homologation of CH_3OH catalyzed by cobalt carbonyl, and this system is ripe for mechanistic study. A particular area where further research is needed is to determine how the acyl-cobalt intermediate reacts with the various reagents present in the catalyst system and what factors influence the rates of these various reactions because of their apparent ability to govern the selectivity of the catalyst system.

III. Progress

The Office of Basic Energy Sciences, Department of Energy, has supported research within this group on various studies of the mechanism of CO reduction for the last 2.5 years. Nearly all attention has focused on the use of metal clusters to model the reduction of CO on metal surfaces and that is where the most progress has been made, as noted below. Recently we have turned our attention to various aspects of the reduction of CO under homogeneous conditions but most of these studies are still in the preliminary stages. Some of these studies necessarily overlap, and what we have learned from our stepwise reduction of CO to CH_4 on the Os_3 cluster face may well be applicable to both homogeneous and heterogeneous catalysis of CO reduction.

A. Preparation and Reactivity Studies of Cluster Formyl Complexes. Stepwise Reduction of CO to CH_4 on a Triosmium Cluster Face and Related Studies.

The salient features of this study were recently reported in a JACS communication[35] and consequently are only briefly summarized here. We initially set out in this study to prepare a series of formyl substituted clusters as models for intermediate 5 of Scheme 1. It was our objective to determine the bonding modes of formyl groups to clusters and the types of reactions that formyl substituted clusters undergo. We were curious, for example, as to whether it would be possible to prepare a stabilized formyl bound in an η^2-fashion, 13, analogous to one of the ways in which acyls have been shown to bond to Os_3 clusters.[53]



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What we found in the course of these studies was that none of the cluster formyls examined were particularly stable. The methodology used was that which has been developed by Casey, Gladysz, and their coworkers[31-34] employing borohydride reducing agents to produce the formyls. We first noted that treatment of $Ru_3(CO)_{12}$ with $[BH(O\text{-}\underline{i}\text{-}Pr)_3]^-$ gave rapid formation of $[HRu_3(CO)_{11}]^-$, even at -77°C, eq. 19, and we were able to obtain no evidence

$$[BH(O\text{-}\underline{i}\text{-}Pr)_3]^- + Ru_3(CO)_{12} \longrightarrow [HRu_3(CO)_{11}]^- + CO + B(OR)_3 \qquad (19)$$

for a formyl intermediate. However, when $Os_3(CO)_{12}$ was allowed to react with either $[BHEt_3]^-$ or $[BH(O\text{-}\underline{i}\text{-}Pr)_3]^-$, at 0°C, a formyl substituted cluster was formed and was spectroscopically characterized.[35] However, upon warmup to 25°C this species decomposes within a 2-3 hour period, and, following metathesis with $[(Ph_3P)_2N]Cl$, $[(Ph_3P)_2N][HOs_3(CO)_{11}]$ can be isolated in 92% yield, eq. 20.

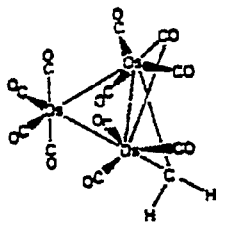
$$\begin{array}{l} Os_3(CO)_{12} + [BH(O\text{-}\underline{i}\text{-}Pr)_3]^- \xrightarrow{0°C} [Os_3(CO)_{11}(CHO)]^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow 25°C \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad [HOs_3(CO)_{11}]^- + CO \end{array} \qquad (20)$$

While this work was in progress similar results were published by workers at Union Carbide who spectroscopically characterized the $[Os_3(CO)_{11}(CHO)]^-$ formyl cluster and noted its instability. In a more recent report, these workers took advantage of the H/D kinetic isotope effect and prepared and spectroscopically characterized $[Ru_3(CO)_{11}(CDO)]^-$.[55]

In an attempt to isolate a stable neutral product from the $[Os_3(CO)_{11}(CHO)]^-$ reaction, we added 20% H_3PO_4 to the solution when the IR spectrum indicated that $[Os_3(CO)_{11}(CHO)]^-$ was at its maximum concentration. The solution immediately turned dark red and workup gave the new cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$ in 20-30% yield, eq. 21. This cluster was spectroscopically

$$[Os_3(CO)_{11}(CHO)]^- + H^+ \rightarrow\rightarrow\rightarrow Os_3(CO)_{11}(\mu\text{-}CH_2) \qquad (21)$$

characterized and the structure 14 indicated.[35]



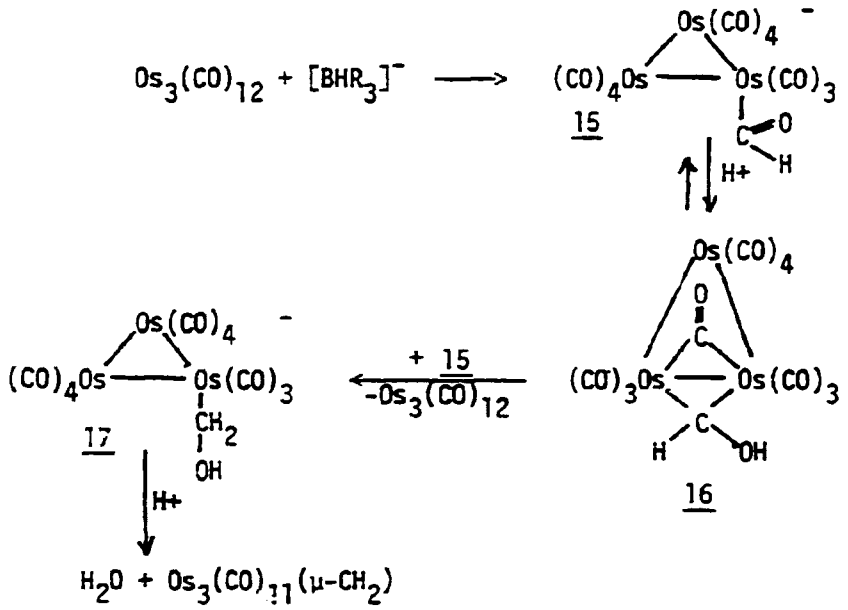
14

Crystals of the compound were sent to Prof. Melvyn Churchill at SUNY, Buffalo, for structural analysis but proved to have a disorder problem too severe to allow a full structure determination. While this work was in progress we learned that Shapley and coworkers had also prepared $Os_3(CO)_{11}(\mu\text{-}CH_2)$, but by a completely different route involving the reaction of CH_2N_2 with $Os_3(CO)_{11}(CH_3CN)$. Through their reaction approach, they were able to prepare a trimethylsilyl derivative, $Os_3(CO)_{11}(\mu\text{-}CHSiMe_3)$ for which an x-ray crystallographic study has confirmed the structure analogous to 14.[56,57]

We further observed that when $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was heated to 70-80°C under an H_2 atmosphere, CH_4 was evolved in ~20% yield, eq. 22.

$$Os_3(CO)_{11}(\mu\text{-}CH_2) + H_2 \xrightarrow{\Delta} CH_4 + Os_3(CO)_{12} + H_2Os_3(CO)_9(CCO) + \text{other products} \quad (22)$$

Similarly, heating under D_2 gave CH_2D_2. Taken together these above experiments demonstrate the reduction of CO to CH_4 on a triosmium cluster face. The mechanism of such conversion is of obvious relevance both for its implications in the modeling of the metal surface catalyzed CO reduction and for potential homogeneous catalysis of the reaction. A series of mechanistic experiments were conducted and are described in the published report (ref. 35). They imply the mechanism shown in Scheme 4.



Scheme 4. Proposed Mechanism for Formation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ upon protonation of $[Os_3(CO)_{11}(CHO)]^-$.

Protonation of the formyl cluster is believed to initially give a hydroxy-carbene intermediate, drawn as 16 in Scheme 4. Although we have not been

able to conclusively prove the existence of this intermediate, its formation is implied by the mechanistic experiments.[35] Furthermore, it is known that protonation of acyl complexes gives hydroxycarbenes,[50] and studies of monomeric formyl complexes by Casey, Gladsyz, and their coworkers have implied that protonation of formyl complexes occurs at the formyl oxygen to give monomeric hydroxycarbene intermediates.[31-34] The monomeric experiments indicate that hydroxycarbenes are strong acids, and thus 16 is likely in equilibrium with 15. Reaction of 16 with an equivalent of 15 would give the hydroxymethyl cluster 17 which upon further protonation and loss of H_2O would yield $Os_3(CO)_{11}(\mu\text{-}CH_2)$. All the steps described in Scheme 4 are analogous to steps which have been well demonstrated for monomeric complexes. Further support for the proposed mechanism comes from our attempt to isolate a methoxycarbene cluster by reacting $[Os_3(CO)_{11}(CHO)]^-$ with $[(CH_3)_3O]BF_4$. None of the desired $Os_3(CO)_{11}$-(μ-CH(OMe)) cluster was produced but instead $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was formed in a yield comparable to that achieved with H_3PO_4 protonation. As with H_3PO_4, the function of the $[(CH_3)_3O]^+$ reagent is to remove the formyl oxygen as CH_3OCH_3, and both hydrogens on the methylene carbon come from the initial formyl complex $[Os_3(CO)_{11}(CHO)]^-$. As described in ref. 35, this conclusion was also indicated by a series of H/D labeling experiments.

We also attempted to prepare a series of PR_3 substituted $Os_3(CO)_{11}$-(μ-CH_2) clusters in anticipation that they might give crystals suitable for an x-ray diffraction study. Two routes were examined. First, the series of $Os_3(CO)_{12-x}(PMe_2Ph)_x$ (x = 1,2,3) and $Os_3(CO)_{12-x}\{P(OPh)_3\}_x$ (x = 1,2) clusters were prepared and allowed to react with $[BH(O\text{-}i\text{-}Pr)_3]^-$. However, only with $Os_3(CO)_{11}(PMe_2Ph)$ and $Os_3(CO)_{11}\{P(OPh)_3\}$ were the corresponding formyl complexes $[Os_3(CO)_{10}(PR_3)(CHO)]^-$, produced. No reaction occurred with the di- and

trisubstituted clusters. Protonation of these substituted formyl clusters gave the reactions indicated in eqs. 23 and 24.

$$[Os_3(CO)_{10}(PMe_2Ph)(CHO)]^- + H_3PO_4(aq) \rightarrow Os_3(CO)_{11}(PMe_2Ph) \quad (23)$$

$$[Os_3(CO)_{10}\{P(OPh)_3\}(CHO)]^- + H_3PO_4(aq) \rightarrow Os_3(CO)_9\{P(OPh)_3\}(\mu\text{-}CH_2) \quad (24)$$

We do not understand why reaction 23 failed but no trace of any methylene cluster was obtained. The product of reaction 24 is that desired but unfortunately it did not yield crystals suitable for an x-ray diffraction study.

We also attempted to prepare PMe_2Ph substituted clusters by reacting $Os_3(CO)_{11}CH_2$ with PMe_2Ph. Addition of these two reagents at 23°C in hexane gave immediate formation of $Os_3(CO)_{10}(PMe_2Ph)_2$ as the major product, with a trace of $Os_3(CO)_{11}(PMe_2Ph)$. No $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was recovered nor was any $Os_3(CO)_{11-x}(PMe_2Ph)_x(\mu\text{-}CH_2)$ product observed. We have not yet ascertained the fate of the methylene group.

Because of the success with $Os_3(CO)_{12}$, most of our attention has been given to this system. However, we also briefly examined the reaction of $[BH(O\text{-}\underline{i}\text{-}Pr)_3]^-$ with $Ir_4(CO)_{12}$. A rapid color change from yellow to orange occurs upon mixing these reagents at -78°C or 0°C and a new band at 1600 cm^{-1} appears in the IR spectrum. This band suggests the formation of $[Ir_4(CO)_{11}(CHO)]^-$, a conclusion also drawn by the Union Carbide group who carried out a similar reaction and further characterized the $[Ir_4(CO)_{11}(CHO)]^-$ product by ^1H NMR (δ 14.2 s).[54] Solutions of $[Ir_4(CO)_{11}(CHO)]^-$ were acidified in an effort to obtain $Ir_4(CO)_{11}(\mu\text{-}CH_2)$, analogous to $Os_3(CO)_{11}(\mu\text{-}CH_2)$ but the only product isolated from this reaction was $Ir_4(CO)_{12}$ in near quantitative yield.

Several significant conclusions can be drawn from this study. First, the transformation of $[Os_3(CO)_{11}(CHO)]^-$ into the methylene-bridged cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$ demonstrates the feasibility of the transformations 5→→1 shown on the right of Scheme 1 for the metal surface catalyzed reduction of CO by H_2. While these experiments in no way argue that such a mechanism does indeed occur on a metal surface, especially since H_2 in the surface reaction has been replaced by the H^-/H^+ couple in our study, they do demonstrate that such a mechanistic path is feasible.

Secondly, these results also suggest that it should be possible to produce hydrocarbons from CO with the aid of homogeneous catalysts through a sequence of reactions analogous to those of Scheme 4, again allowing the replacement of the H^-/H^+ couple by H_2. It has been suggested that homogeneous catalysis can only produce oxygenated products and that the formation of hydrocarbons in a homogeneous experiment can be taken as indication of catalysis by adventitious metal particles.[43] However, I submit that our results indicate that this is not necessarily so and that if the intermediate methylene unit can be stabilized by bridging two metal centers, as in $Os_3(CO)_{11}(\mu\text{-}CH_2)$, hydrocarbons could be produced in a homogeneous experiment. In this regard, Muetterties and coworkers[40a] have reported that solutions of $Os_3(CO)_{12}$ slowly catalyze CO reduction to give CH_4, although with an extremely low turnover number, and it may well be that a mechanism similar to that of Scheme 4 obtains. The course of homogeneous catalysis would seem to depend on whether the presumed hydroxymethyl intermediate, 17 in Scheme 4 and eq. 5 of Scheme 3, reacts by protonation of the carbon to give CH_3OH or at the oxygen to give H_2O and an intermediate methylene complex.

This study also reveals several important but unanswered questions which we wish to investigate in our future research. I summarize those questions here but leave the details to the proposed research section of this proposal.

1. We would like to determine why our results differ from those reported by the Union Carbide group[54] concerning protonation of $[Os_3(CO)_{11}(CHO)]^-$. These workers reported that protonation of $[Os_3(CO)_{11}(CHO)]^-$ gave a small amount of CH_3OH but did not report any $Os_3(CO)_{11}(\mu\text{-}CH_2)$ produced. This probably reflects different reaction conditions but it is important to determine exactly how the reaction variables effect the outcome of such reactions.

2. A key intermediate in the mechanism for formation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$, Scheme 4, is the hydroxycarbene species $Os_3(CO)_{11}(\mu\text{-}CHOH)$. We would like to try to spectroscopically detect this intermediate and study its subsequent chemistry. Hydroxycarbenes may be important intermediates in the homogeneous catalyzed reduction of CO, and we intend to study the properties of this class of complexes and to prepare and study examples of di- and polynuclear complexes with bridging hydroxycarbene ligands in our future research.

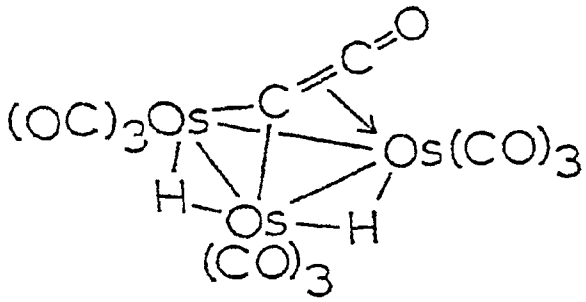
B. <u>Conversion of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ into $H_2Os_3(CO)_9(CCO)$ - A Model for Chain Growth on a Metal Surface?</u>

We observed that when benzene solutions of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ were heated to 70-80°C under N_2, a new cluster with the formulation $H_2Os_3(CO)_9(CCO)$ formed and was isolated in ~80% yield,[35,56] eq. 23. This product shows only a sharp

$$Os_3(CO)_{11}(\mu\text{-}CH_2) \xrightarrow{\Delta} CO + H_2Os_3(CO)_9(CCO) \qquad (23)$$

singlet at δ -20.1 in its ^1H NMR spectrum, indicative of one or more equivalent hydrides but not hydrogen bound to carbon. Simultaneously with our work,

Professor John Shapley and his group at Illinois prepared the same compound by thermolysis of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Their ^{13}C NMR and reactivity studies and our ^1H NMR studies led us to jointly deduce the ketenylidene formulation and propose the structure 18 for the thermolysis product. Structure 18 is analogous to that established for $H_2Os_3(CO)_9(CCH_2)$,[58] 19.



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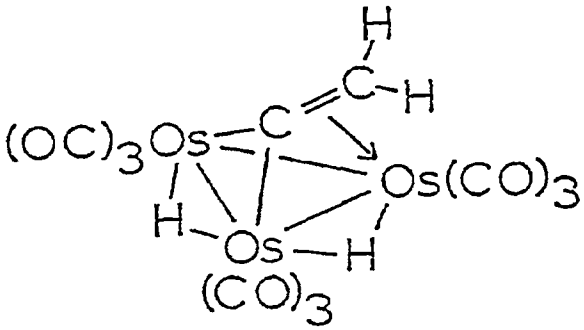
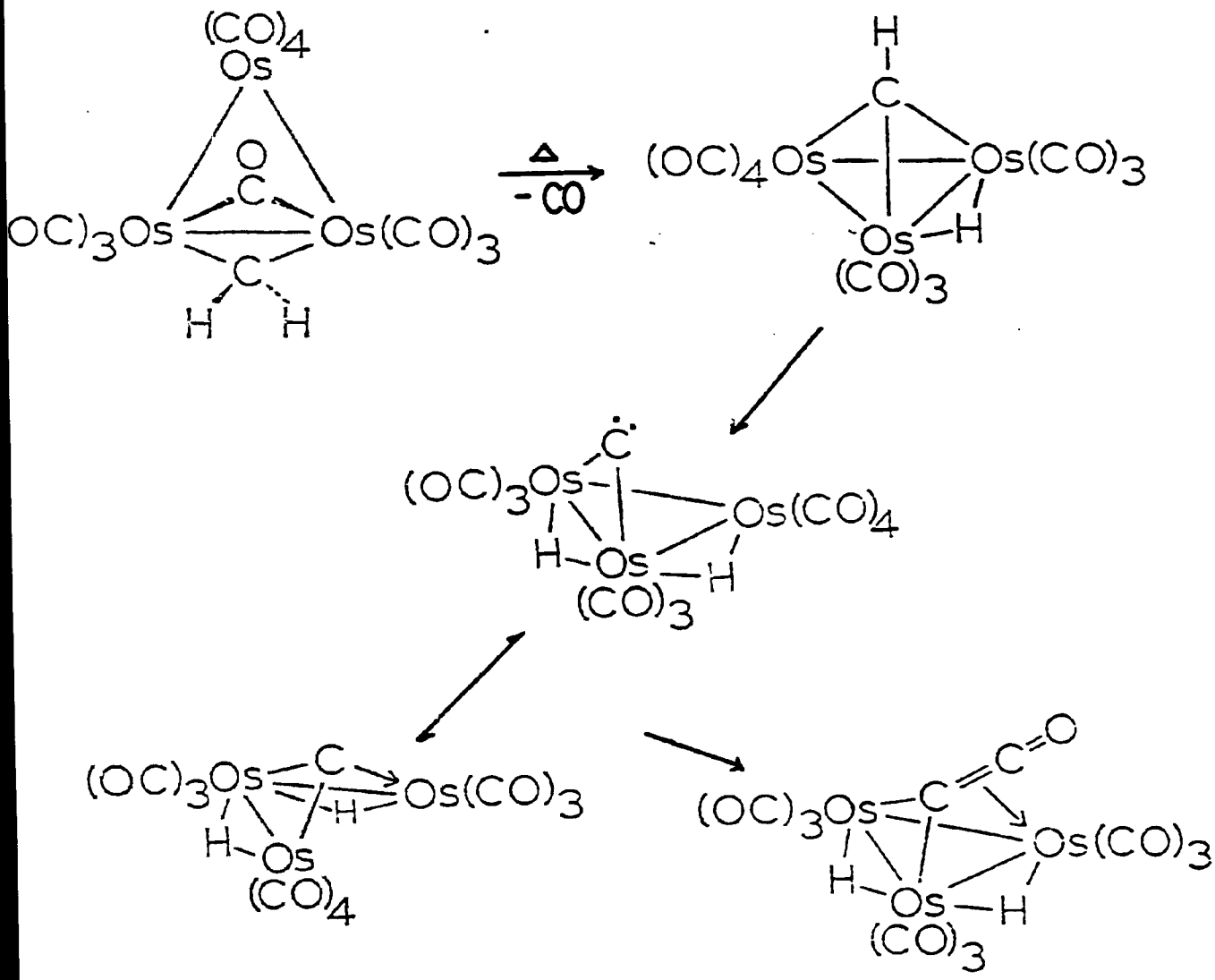


19

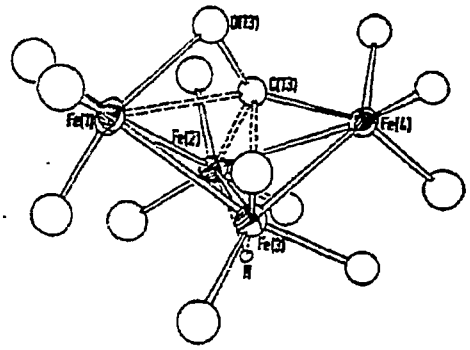
The synthesis and characterization of this compound are described in a manuscript submitted jointly by the Shapley group and by us to Organometallics and is included as Appendix A. The mechanism by which $Os_3(CO)_{11}(\mu\text{-}CH_2)$ is converted into $H_2Os_3(CO)_9(CCO)$ is not yet clear. One likely possibility involves the sequence of reactions shown in Scheme 5. This mechanism has as a key feature formation of a tricoordinate surface carbon to which CO migrates and is not unlike that which has been proposed by Bradley, et al.[59] to account for the formation of $[Fe_4(CO)_{12}(\mu_4\text{-}C\text{-}CO_2Me)]^-$ from reduction of $[Fe_6C(CO)_{16}]^{2-}$ in methanol. A mechanism of this type could mimic the formation of C_2 products from CO reduction on a metal surface where carbon monoxide might be expected to adsorb onto surface supported carbon atoms.



Scheme 5. Proposed Mechanism for Formation of $H_2Os_3(CO)_9(CCO)$ from $Os_3(CO)_{11}(\mu\text{-}CH_2)$.

C. <u>Structures of Tetranuclear Fe-Ru Clusters as Models for CO Activation</u>

The cluster $[HFe_4(CO)_{13}]^-$ has been shown to adopt the butterfly structure sketched below with a folded-over, multiply-bonded and presumably activated CO.[25]



Significantly, Shriver and Whitmore[60] have recently shown that treatment of this particular anion with strong acid leads to CO reduction and the low-yield 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 = 1-3) which we anticipated might also possess a multiply-bonded CO.

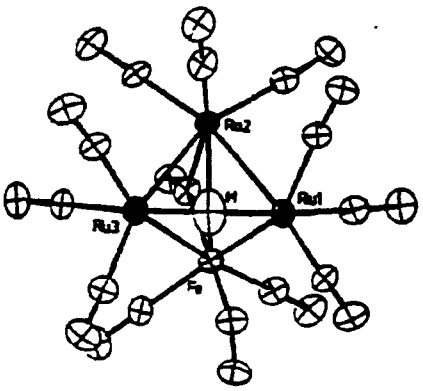
Two of the clusters in this series were prepared via the reactions shown in eq. 24-25 and their crystal structures determined in a collaborative study

$$Ru_3(CO)_{12} + [HFe(CO)_4]^- \rightarrow [HFeRu_3(CO)_{13}]^- \qquad (24)$$

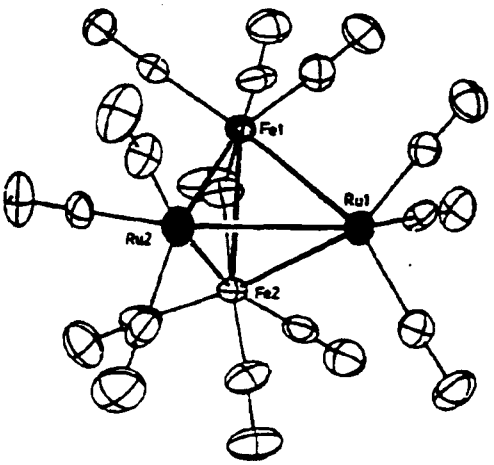
$$RuFe_2(CO)_{12} + [HFe(CO)_4]^- \rightarrow [HFe_2Ru_2(CO)_{13}]^- \qquad (25)$$

with R. Bau (USC) and T. Koetzle (Brookhaven). The results of this study are described in a manuscript in press in Inorg. Chem.[61] The crystal structure of $[(Ph_3P)_2N][HFeRu_3(CO)_{13}]$ was determined by an x-ray diffraction study at USC and by a neutron diffraction study at Brookhaven and the structure of $[(Ph_3P)_2N][HFe_2Ru_2(CO)_{13}]$ by an x-ray diffraction study in our laboratory. Unfortunately, neither of these clusters was found to adopt an open butterfly structure analogous to $[HFe_4(CO)_{13}]^-$ but instead they have the closed pseudo-tetrahedral frameworks as shown in ORTEP drawings on the next page.

Our rationalization for the differences in the $[HFe_4(CO)_{13}]^-$ and Fe/Ru structures is that the Fe_4 tetrahedron is simply not large enough to accommodate 13 CO's and a hydride, in contrast to the $FeRu_3$ and Fe_2Ru_2 clusters which, as we have shown, clearly are large enough. It is interesting to speculate on where the cross-over point between the "closed" and "open" structures might be. The only member of the series whose structure is not known is



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



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

$[HFe_3Ru(CO)_{13}]^-$, Scheme 6, but so far this anion and its neutral protonated analog have defied all isolation attempts.

$[HRu_4(CO)_{13}]^-$	$[HFeRu_3(CO)_{13}]^-$	$[HFe_2Ru_2(CO)_{13}]^-$	$[HFe_3Ru(CO)_{13}]$	$[HFe_4(CO)_{13}]^-$
presumably closed [in analogy to $H_2Ru_4(CO)_{13}$]	closed	closed	?	open

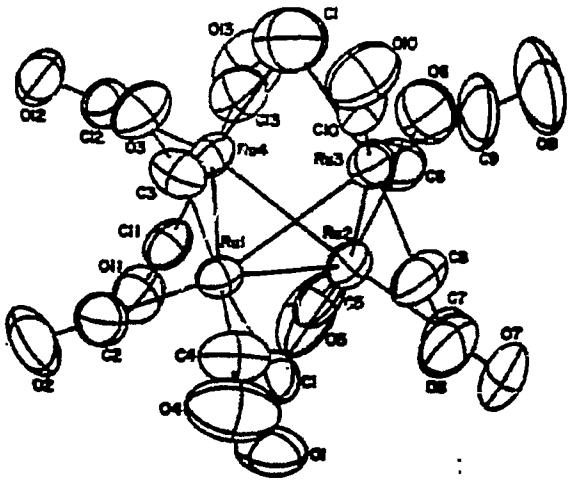
Scheme 6

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

Acyl and alkyl substituted clusters are direct models for proposed intermediates in the chain growth sequence of Scheme 2 for CO reduction on a metal surface. Furthermore, an acyl cluster can be viewed as an analog of a formyl cluster and thus is an indirect model for 5 of Scheme 1. We thus set out to prepare new examples of acyl and alkyl substituted clusters, both of which are rare at present. In our initial experiments, we allowed MeLi to react with $Ru_3(CO)_{12}$ in the presence of [PPN]Cl (PPN = $(Ph_3P)_2N^+$), but the product actually isolated was not an acyl cluster but instead $[PPN][ClRu_4(CO)_{13}]$, eq. 26. The structure of this product was determined in our

$$[PPN]Cl + Ru_3(CO)_{12} + MeLi \xrightarrow{\Delta} [PPN][ClRu_4(CO)_{13}] \qquad (26)$$

laboratories by x-ray diffraction and is shown below.[62]



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, although MeLi does speed up the reaction, apparently through reductive fragmentation of $Ru_3(CO)_{12}$. No reaction was observed when $Os_3(CO)_{12}$ was heated with $[(Ph_3P)_2N]Cl$. These various results have been published and are described in detail in Inorg. Chem., 1980, 19, 2987.

The reaction of $Os_3(CO)_{12}$ with MeLi has also been recently studied. Treatment of $Os_3(CO)_{12}$ in THF at 0°C with MeLi resulted in an orange, air-sensitive solution. Acidification of the solution gave largely $Os_3(CO)_{12}$ and an orange solid in ∿2% yield, tentatively identified as $HOs_3(CO)_{11}CH_3$ solely on the basis of its mass spectrum (m/e = 896 (parent) + fragment ions corresponding to the loss of 11 CO's; IR(CH_2Cl_2) = 2075 s, 2060 m, 2020 s, 2000 cm^{-1}). We are in the process of carrying out this reaction on a larger scale to obtain enough material for NMR characterization, but the very low yield of the reaction is not encouraging. We also intend to try to isolate the initial product of the reaction with MeLi without adding acid. The IR spectrum of this solution is complex, although we see no bands in the 1500-1700 cm^{-1} region which might indicate an acyl complex.

E. Fragmentation of Tetranuclear Mixed-Metal Clusters by Reactions with CO

Because of the potential role of metal cluster complexes as catalysts for CO reduction,[7,40] we undertook a basic mechanistic study to determine how clusters react with CO. We thus examined the reactions of a series of mixed-metal clusters which we had prepared in our laboratory with carbon monoxide and found that all underwent fragmentation to produce lower nuclearity products. This work is described in detail in Inorg. Chem., 1980, 19, 2574. Some examples of the reactions observed are given in eqs. 27-29.

$$H_2FeRu_3(CO)_{13} + CO \xrightarrow[\text{1 atm}]{\text{50°C, 42h}} Ru_3(CO)_{12} + Fe(CO)_5 + H_2 \quad (27)$$

10% conv.

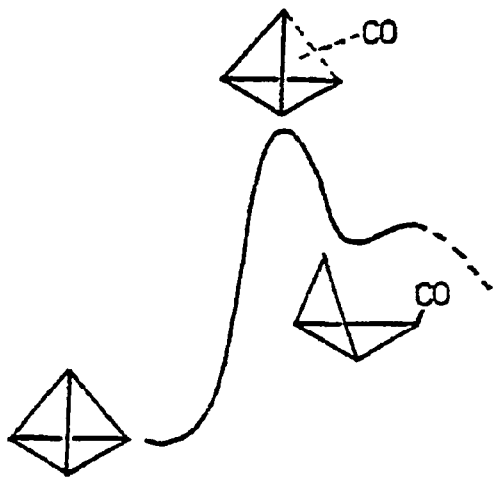
$$H_2Ru_4(CO)_{13} + CO \xrightarrow[\text{1 atm}]{\text{25°C, 1h}} Ru_3(CO)_{12} + Ru(CO)_5 + H_2 \quad (28)$$

30% conv.

$$[CoRu_3(CO)_{13}]^- + CO \xrightarrow[\text{1 atm}]{\text{25°C, 96h}} Ru_3(CO)_{12} + [Co(CO)_4]^- \quad (29)$$

100% conv.

We especially wanted to understand the mechanisms of these reactions and so we carried out a series of kinetic experiments to determine the mechanism by which $H_2FeRu_3(CO)_{14}$ and $H_2Ru_4(CO)_{13}$ react with CO, details of which are given in the published report.[63] The kinetic data indicated an associative mechanism and an activation profile similar to that depicted below.



The most important aspect of this study was the demonstration that none of the clusters examined was stable under 1 atm CO pressure and all underwent fragmentation, although at greatly different rates.

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V. Publications Which Have Acknowledged DOE Support

1. Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L., "Reaction of Tetranuclear Mixed-Metal Clusters with Carbon Monoxide," Inorg. Chem., 1980, 19, 2574.

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., 1980, 19, 2987.

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12. List of publications

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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., 1980, 19, 2987.

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