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MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION. FINAL TECHNICAL REPORT

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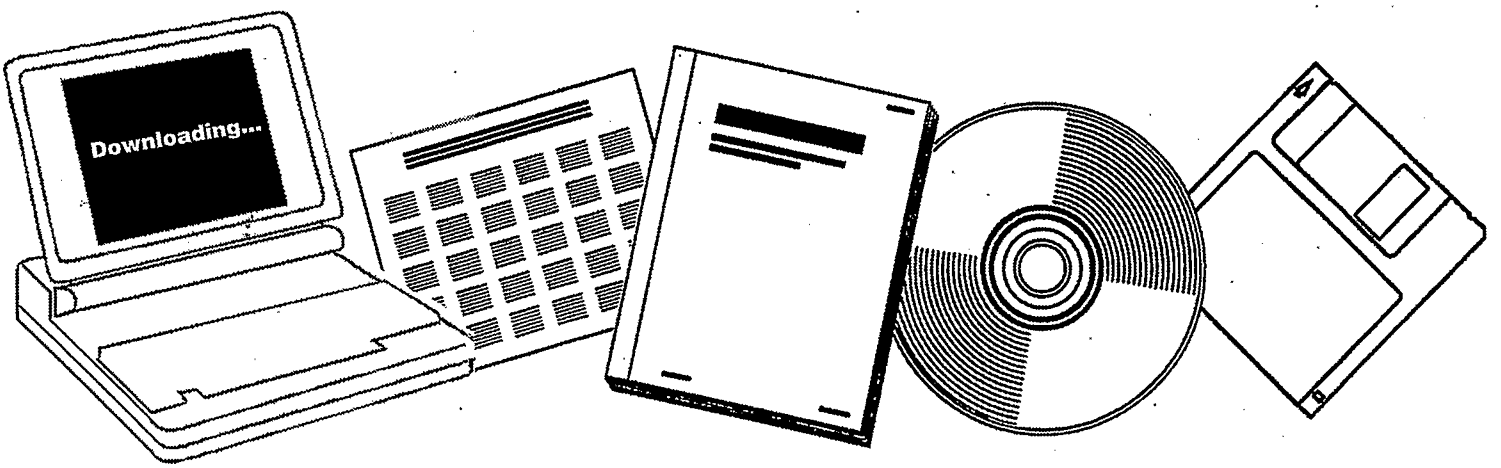

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Final Technical Report

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"Mechanistic Studies of Carbon Monoxide Reduction"

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by

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II. Introduction

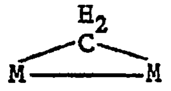
The eventual shortage of crude oil necessitates the development of alternative sources of fuels and organic feedstocks for the chemical industry. The use of synthesis gas, a mixture of CO and H_2, is one promising route since it can be used to produce a wide range of organic chemicals and fuels and it can be obtained from coal via steam gasification and perhaps eventually from other carbon sources as well. In order for synthesis gas reactions to proceed at useful rates, catalysts must be employed, and 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 burned as a fuel.

The major aim of nearly all synthesis gas research involves the development of more active and selective catalysts. One way to approach catalyst development is through mechanistic studies whereby an understanding of the mechanistic course of the reaction should allow the design of more efficient catalysts. It is the major aim of this research program to contribute to that mechanistic understanding. Two approaches will be employed in this research. First, certain aspects of the mechanism of the heterogeneous metal surface catalyzed reduction of CO will be probed using transition metal cluster complexes to model the chemistry of metal surfaces. Secondly, we will address various aspects of the mechanism of homogeneous CO reduction by focusing on a few key mechanistic steps, particularly halide-promoted reactions and the formation, stabilization, and reactivity of formyl, acyl, methylene, and ketene ligands. Some exploratory work is also proposed involving studies of the adsorbed state of simple unsaturated molecules on metal surfaces using solid-state ^{13}C NMR spectroscopy, as well as reactions which model non-synthesis gas chemistry of metal surfaces.

A. Heterogeneous Catalysis of CO Reduction.

The rationale of the metal cluster/surface analogy[1] that we employ is that by carefully studying the bonding and subsequent reactivity of substrates on clusters one should develop a better understanding of the bonding and reactivity of substrates on metal surfaces. Clusters are not perfect models of metal surfaces and their limitations have been discussed,[2] but they can provide a first approximation of the chemistry which occurs on metal particles. The advantage of clusters is that they are soluble, molecular compounds which can be examined by the battery of spectroscopic techniques used to characterize organometallic complexes. The way in which one generally proceeds in research of this type is to assume or propose what seems 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.

A number of different mechanisms have been suggested for the metal surface catalyzed reduction of CO,[3] but there is an increasing amount of evidence that surface methylene groups are key intermediates in the reaction.[3f,4] These would be expected to bridge between two metals as in I since model organometallic compounds have shown this coordination mode to be much more stable than a methylene ligand bound to a single metal.[5] These ligands are generally presumed to



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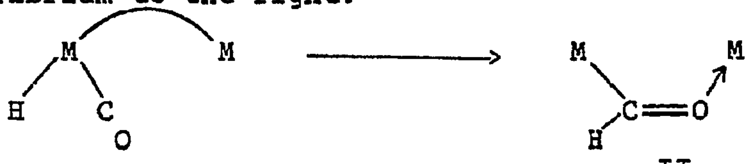
arise by a mechanism involving prior dissociation of CO upon adsorption followed by hydrogenation of the resultant surface carbon. However, there are still indications in the literature that CO dissociation does not occur over all metals and a case has been made for the formation of $\mu-CH_2$ groups via initial formation of surface formyl ligands.[6] In any event, given the probable importance of surface methylenes, it is necessary to fully define the chemistry of this interesting ligand. Such will be the focus of part of this proposed research using the methylene cluster $Os_3(CO)_{11}(\mu-CH_2)$ which has an unusually rich derivative chemistry.

An important reaction of $\mu-CH_2$ ligands that is relevant to synthesis gas chemistry but had little precedent in the organometallic literature until recently is insertion of CO into metal-($\mu-CH_2$) bonds to give ketene ligands. We recently documented this reaction for $Os_3(CO)_{11}(\mu-CH_2)$, a cluster which reacts with CO to give the ketene substituted cluster $Os_3(CO)_{12}(\mu-CH_2CO)$.[7] The latter was fully characterized by an x-ray structural analysis.[7] Nearly simultaneously Lin, et.al.[8] reported a similar transformation for $Ru_2Cp_2(CO)_4(\mu-CH_2)$. Several heterogeneous catalysis studies have indicated that CO insertion into surface-bound methylenes to give surface ketene intermediates may be an important step in the production of C_2-oxygenated products such as CH_3CHO and CH_3CH_2OH and also the hydrocarbons - ethylene and ethane from synthesis gas.[9] Thus, the structural and spectroscopic features as well as the chemistry of cluster-bound ketene ligands need a thorough examination and this is a principle focus of much of the research proposed herein.

B. Homogeneous Catalysis of CO Reduction.

A number of reports have illustrated the homogeneously catalyzed reduction of CO.[10] However, the rates of these reactions are generally quite low and high pressures are usually required, although product selectivities can be high. Nevertheless, if homogeneous catalysis of CO reduction by H_2 is ever to be important, much more active catalysts will have to be found. Most workers seem to agree that the rate-limiting step in the overall mechanism of homogeneous CO reduction is the initial formation of a metal formyl complex. The formyl ligand in such a complex may derive by hydride migration to a carbonyl ligand, but the carbonyl-hydride⇌formyl equilibrium is generally believed to lie far to the left; Halpern[11] has estimated that the conversion of $(CO)_5MnH$ to $(CO)_5Mn(CHO)$ is endothermic by ~15 kcal/mole. Alternatively, formation of the initial formyl intermediate could occur via hydride transfer from a second metal and thereby circumvent this unfavorable equilibrium. Such transfer could take place between two mononuclear complexes[12] or involve intermetallic transfer in a polynuclear complex. In any case, one of the more 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. One possible way to stabilize a formyl ligand is through binuclear coordination, eq. 1, whereby the extra bonding gained through coordination of the formyl oxygen could shift the carbonyl-hydride⇌formyl equilibrium to the right.



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II

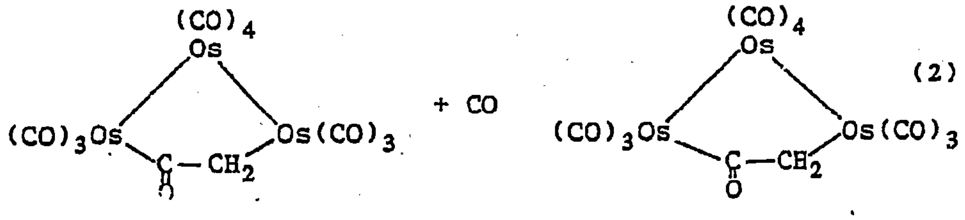
Although a number of μ_2-acyl complexes of type II are known,[13a] there is not a single example of a formyl complex of precisely this type, although a few binuclear formyls with other structures are reported.[13b,c] One of the objectives of the proposed research is to prepare such species. If this approach to CO reduction chemistry is to work, the formyl ligand in a complex such as II must be able to be transformed into other intermediates, and a portion of this research will focus on such derivative chemistry of polynuclear formyl and acyl ligands.

One of the more intriguing aspects of homogeneous catalysis of CO reduction is the promoting effect of halides and other anionic species on the reaction. Both Dombek[14a] and Knifton[14b] have found that the presence of halides increases the overall rate of the reaction and, significantly, shift the product distribution from C_1 to C_2 products, such as ethylene glycol. The C_2 products presumably form via a CO insertion process of some type and the tentative conclusion that can be drawn is that halides promote the insertion reactions. In our studies of methylene⇌ketene interconversions, we have found that halides greatly accelerate the rate of CO insertion into metal-methylene bonds, and one important objective of the proposed research is to try to define a mechanistic basis for this effect as well as to put it on a quantitative understanding.

III. Progress

A. Synthesis and Reactivity Studies of Ketene Clusters

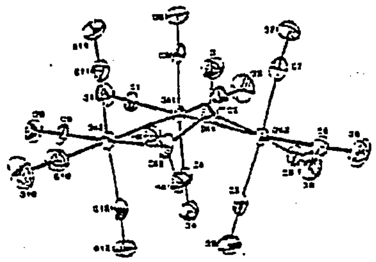
1. Insertion of CO into the Os-(μ-CH_2) bond of $Os_3(CO)_{11}(\mu$-$CH_2)$. As mentioned above, one reaction that had not been well documented until recently is insertion of CO into bridging-methylene-metal bonds to give coordinated ketene ligands.[7,8,15] We recently discovered such a CO insertion for $Os_3(CO)_{11}(\mu$-$CH_2)$[16], eq. 2.[7]



1 2

Since this is one of the first ketene-substituted clusters, we characterized the molecule by x-ray diffraction, Fig. 1.

Figure 1



The structure shows that the molecule is best described as a triosmacyclopentanone derivative since the ketene ligand has little resemblence to the structure and hybridization of free ketene. Nevertheless, since the coordinated ligand is a CH_2CO unit, we will call it a ketene for simplicity. Although this is the only crystallographically characterized ketene cluster, such a bonding mode also likely occurs in the spectroscopically characterized $Cp(CO)_2Ru(\mu$-$CH_2CO)RuCp(CO)_2$[8] and the transient species $Fe_2(CO)_8(\mu$-$CH_2CO)$.[15] The only other polynuclear ketene complexes are the Zr derivatives $Cp_2CH_3Zr\{\mu(O,C)$-$OCCH_2\}M(CH_3)L_2$ (M=Pt, Zr) recently reported by Grubbs and co-workers[17] which have a markedly different structure with the ketene oxygen coordinated to the much more oxophilic Zr center and which have an exocyclic methylene group.

There are several indications in the catalytic literature that surface ketene ligands play important roles in the metal-surface catalyzed reduction of CO.[9] For example, insertion of CO into surface-methylene bonds has been proposed to be a a key step in the production of both C_2-oxygenated products such as CH_3CHO and CH_3CH_2OH and also the hydrocarbons C_2H_4 and C_2H_6.[9] The CO insertion reaction which converts 1 into 2 effectively models this chemistry, especially since we demonstrated that CH_3CHO is produced upon hydrogenation of 2.[7] It was thus of importance to report spectroscopic data for the ketene moiety in well-characterized 2 for use by surface scientists in their search for this intermediate on metal surfaces. Thus, the complete infrared spectrum of 2 from 4000-400 cm^{-1} was recorded and interpreted with the ketene applicable portion summarized in Table I.

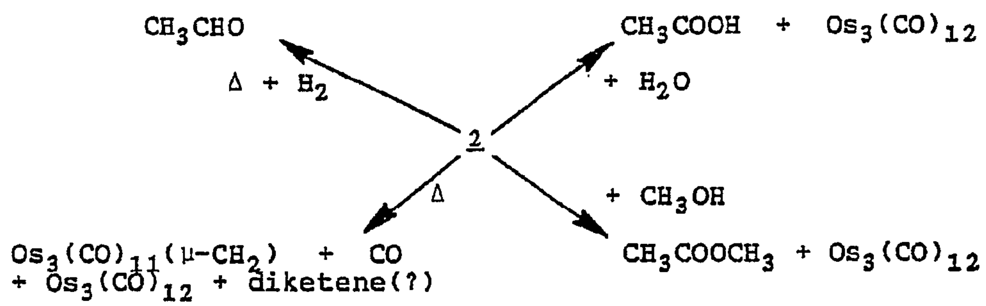
Table I. Vibrational Frequencies of the μ-CH_2CO ligand in 2.

Mode	ν, cm^{-1}	Mode	ν, cm^{-1}
Antisymmetric C-H stretch	2970vw	CH_2 wag	1143m
Symmetric C-H stretch	2942w	CH_2 twist	1081w
C-O stretch	1573s	CH_2 rock	997m
CH_2 deformation	1426w	Os-C stretch	666m

^{13}C NMR resonances of the ketene ligand of 2 are at δ219.4 (s,$CH_2\underline{C}O$) and δ32.8 (t, $\underline{C}H_2CO$, J=136 Hz.).

An important question concerns the reactivity of this coordinated ketene ligand. We have briefly explored this aspect of 2, although that is a subject that we wish to pursue in our future work. The reactions observed to date are summarized in Scheme I.

Scheme I.



Reaction of 2 with water and methanol gave quantitative formation of acetic acid and methylacetate, respectively, along with $Os_3(CO)_{12}$. Reduction of 2 with H_2 gave acetaldehyde in ~20% yield, thus effectively modeling the reduction of surface-bound ketenes. We suspect the low yield of CH_3CHO is due to reaction of 2 with traces of water present since the only other organic product detected was acetic acid. When 2 was heated under reduced pressure, CO evolved and the initial methylene-bridged cluster 1 was regenerated in about 10% yield. We do not presently know the fate of the remainder of the ketene complex except that $Os_3(CO)_{12}$ was formed in high yield and diketene was detected by GC/MS in the reaction mixture, observations which suggest the release of free ketene from 2, eq. 3.

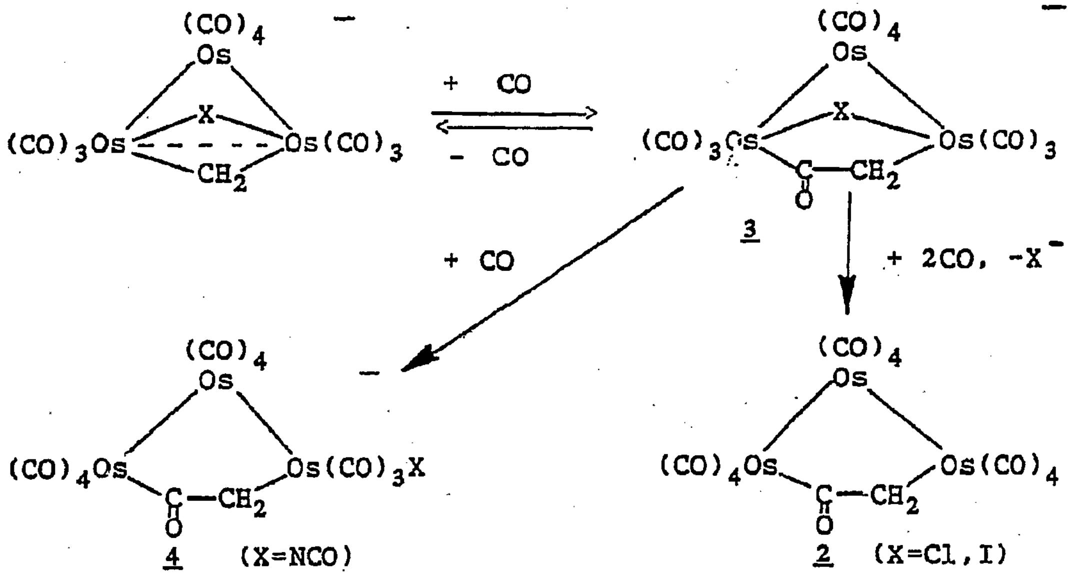
$$Os_3(CO)_{12}(\mu\text{-}CH_2CO) \xrightarrow{\Delta} Os_3(CO)_{12} + \text{"}CH_2CO\text{"} \ (?) \qquad (3)$$

In future work we plan to explore this reaction more fully to determine if free ketene is indeed released upon thermolysis of 2.

A second important question concerns the mechanism of formation of 2 from 1. A mechanism involving insertion of exogenous CO into an Os-methylene bond was eliminated by the observation that exposure of 1 to ^{13}CO did not lead to ^{13}CO incorporation into the ketene ligand but instead into the cluster carbonyls. Thus the ketene carbonyl must derive from one of the original cluster carbonyls. The experimental data could not distinguish between two other possibilities: (1) a pre-equilibrium involving prior insertion of a cluster carbonyl into the Os-CH_2 bond followed by the subsequent addition of two CO's or (2) coordination of an exogenous CO concomitant with Os-Os bond cleavage and then followed by CO insertion into the Os-CH_2 bond. In future studies, we plan to attempt to distinquish these mechanisms for 2 and for the other ketene complexes described below.

2. Insertion of CO into the Os-methylene Bonds of $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]$ (X=Cl, I, NCO). The new μ-CH_2 clusters $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]$ with X=Cl, I, and NCO were prepared as described below. All three of these compounds readily insert CO to give ketene derivatives although the reactions differ in detail, Scheme II.

Scheme II

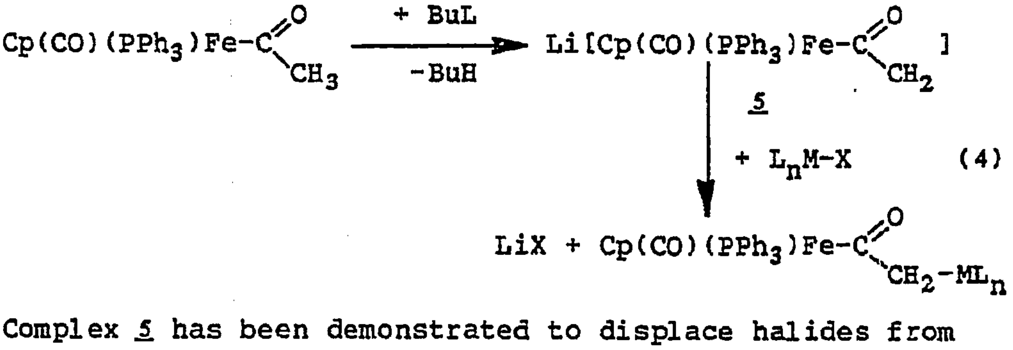


Presently, the reaction of $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}I)]$ with CO has been studied in most detail. Careful NMR and IR monitoring indicate that under 1 atm CO, this complex is in equilibrium with the ketene complex 3. ^{13}CO labelling studies have shown that the ketene carbonyl in 3 derives from one of the cluster carbonyls and not from the added CO.

When X=NCO an additional CO is subsequently taken up to give complex 4 as the final stable product. Significantly, this latter ketene derivative does not further react, but instead it loses CO when placed under vacuum to quantitatively reform the initial $(\mu\text{-}CH_2)(\mu\text{-}NCO)$ complex. This is the first system which gives a clean and reversible μ-methylene=μ-ketene interconversion, and it appears ideally suited for the mechanistic studies which we plan to conduct. In contrast, when X=Cl or I, reaction with CO first gives 3 but this then adds 2 CO's to displace the halide and give the ketene cluster 2. Given the facility of these three insertion reactions, we anticipate the preparation of numerous other complexes containing ketene ligands on Os_3 frameworks, an area we plan to explore.

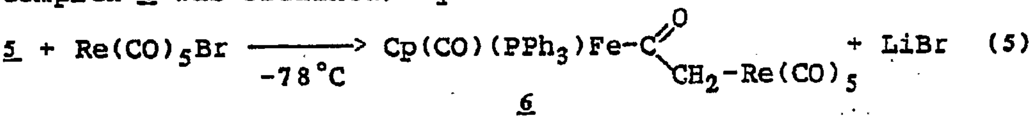
A particularly significant finding is that the above insertion reactions when X=Cl and I proceed with a rate limited only by the diffusion of CO into solution. In both cases, reaction with CO is complete in less than one minute, if the solution is rapidly stirred. These rates are $>10^2$ times greater than the rate of the reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with CO and illustrate the promoting effect of halides on such insertion reactions. Recall that both Dombek and Knifton[14] have demonstrated that halides promote the selectivity to C_2 products during homogeneous CO reduction catalysis, presumably via a CO insertion step. In our planned research, we intend to try to probe the basis for this important halide effect.

3. Reaction of $Re(CO)_5Br$ with $[Cp(CO)(PPh_3)FeC(O)CH_2]^-$. The recently reported iron-enolate complex $Li[Cp(CO)(PPh_3)FeC(O)CH_2]$[18] appears to be an ideal synthetic intermediate for the preparation of heterodinuclear ketene-bridged complexes via the general reaction sequence of eq. 4.



(4)

Complex 5 has been demonstrated to displace halides from various RX reagents to give C-alkylation products, and it seemed reasonable that analogous displacement of a metal halide would occur. Indeed, when Re(CO)$_5$Br was allowed to react with 5, generated *in situ*, the ketene-bridged Fe-Re complex 6 was obtained, eq.5.



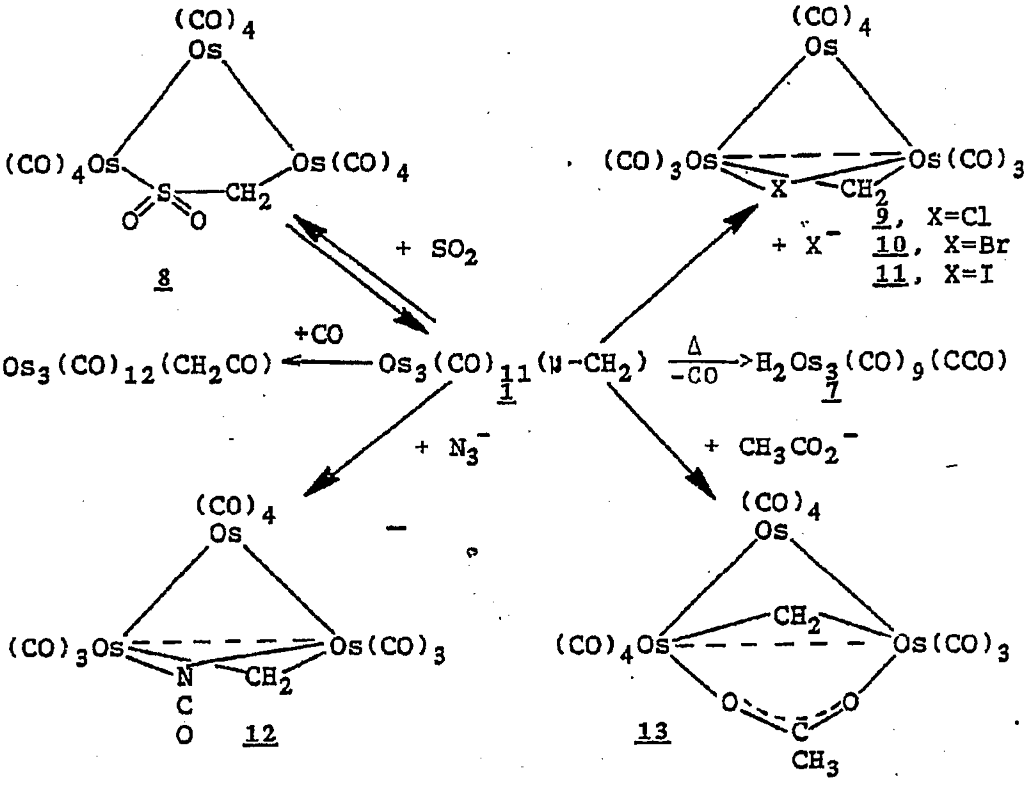
$$\underline{5} + Re(CO)_5Br \xrightarrow[-78°C]{} \underset{\underline{6}}{Cp(CO)(PPh_3)Fe-C(=O)CH_2-Re(CO)_5} + LiBr \qquad (5)$$

Complex 6 has proven too unstable to isolate in pure form but it has been characterized in solution [IR, νCO=1570 cm^{-1}; ^{1}H NMR, δ2.30 (s,$\underline{CH_2}$); ^{13}C NMR, δ221 (s,$\underline{C}$(O)CH$_2$), δ25.5 (t,C(O)$\underline{C}$H$_2$)]. This reaction approach should prove quite general and is one aspect of our planned research. Grubbs and coworkers[17] have recently used this strategy to prepare ketene-bridged ZrPt and Zr$_2$ complexes, but these have structures with the ketene ligand in a μ(C,O) bound form with the oxygen bound to Zr. It will be instructive to compare the factors which determine the preferred bonding mode of ketene ligands in binuclear and polynuclear complexes with different metal combinations.

B. Derivative Chemistry of $Os_3(CO)_{11}(\mu-CH_2)$.

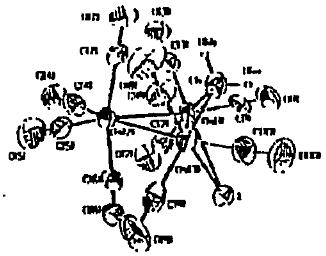
The methylene-bridged cluster $Os_3(CO)_{11}(\mu-CH_2)$ has a rich derivative chemistry as illustrated in Scheme III.

Scheme III



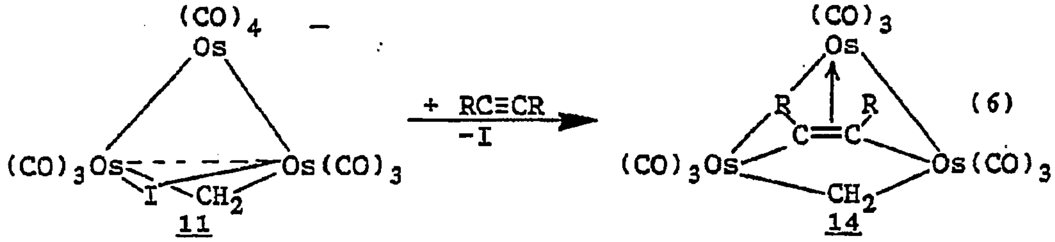
The synthesis of the ketenylidene complex 7 was described in ref 19 and the 1 to 2 conversion was mentioned above. The remainder of the complexes have been prepared in this work. Reaction of 1 with SO_2 gives an SO_2 adduct for which spectral data imply a sulfene[20] structure. Interestingly, this compound smoothly and quantitatively loses SO_2 when placed under vacuum to reform 1. Reaction of 1 with PPN salts of the halides gives the doubly-bridged products 9-13 with the halide derivatives 9 and 11 fully characterized by x-ray diffraction studies, *e.g.* Figure 2.

Figure 2



Reaction of 1 with $[PPN]N_3$ gives loss of N_2 and yields the isocyanate-bridged derivative 12. Spectroscopic data imply the structure of 12 to be analogous to those crystallographically determined for 9 and 11. Likewise, reaction of 1 with [PPN]acetate gives the acetate-bridged complex 13. It is apparent that 1 promises to have a rich derivative chemistry and should lead to many novel methylene-bridged clusters and probably to numerous derivatives in which the methylene ligand couples with the added molecules. This we intend to explore in our future work.

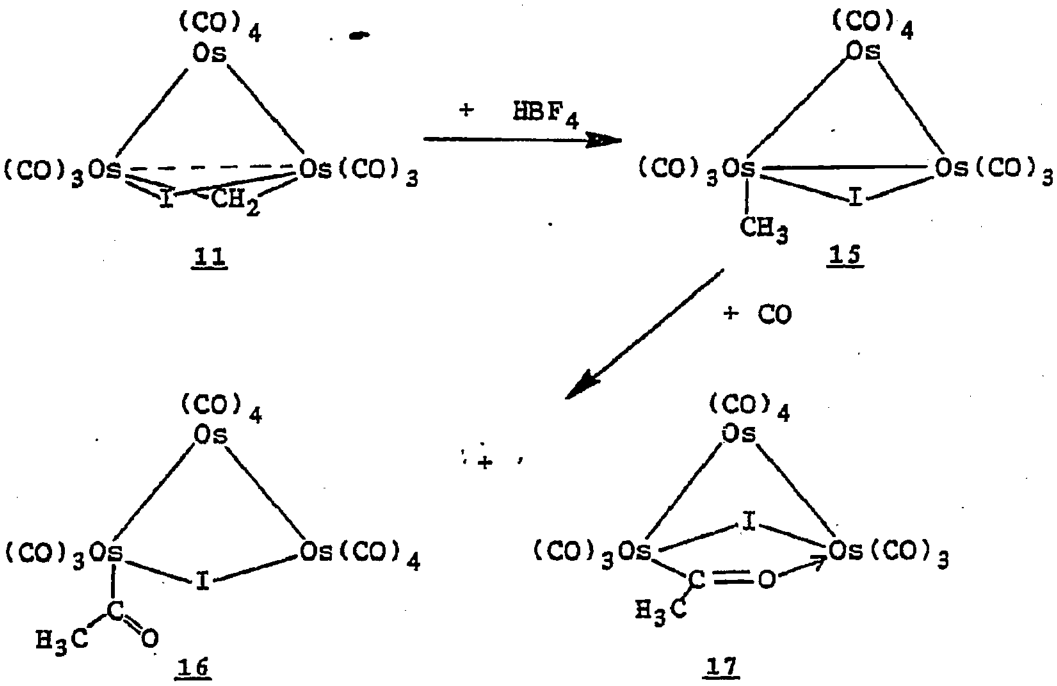
We have also examined the derivative chemistry of some of the complexes 8-13, and as noted above complexes 9-12 readily insert CO to give ketene derivatives. Since all of the halide-bridged complexes behave similarly, we have concentrated our efforts on the iodide complex 11. This complex reacts with activated alkynes to give displacement of I^- and form alkyne-(μ-CH_2) complexes, eq. 6.



The significance of this reaction is that the initial methylene-bridged complex *1 does not react with alkynes and thus the iodide ligand catalyzes this transformation*. Indeed, complex 1 and excess alkyne can be stirred for several days without detectable reaction but when a catalytic amount of iodide ion is added, transformation to the alkyne-bridged product 14 is complete within a few hours.

Protonation of 11 with HBF_4 initially gives a methyl derivative which has been isolated and characterized. This will then add and insert CC to give a mixture of terminal and bridging acetyl complexes, Scheme IV.

Scheme IV

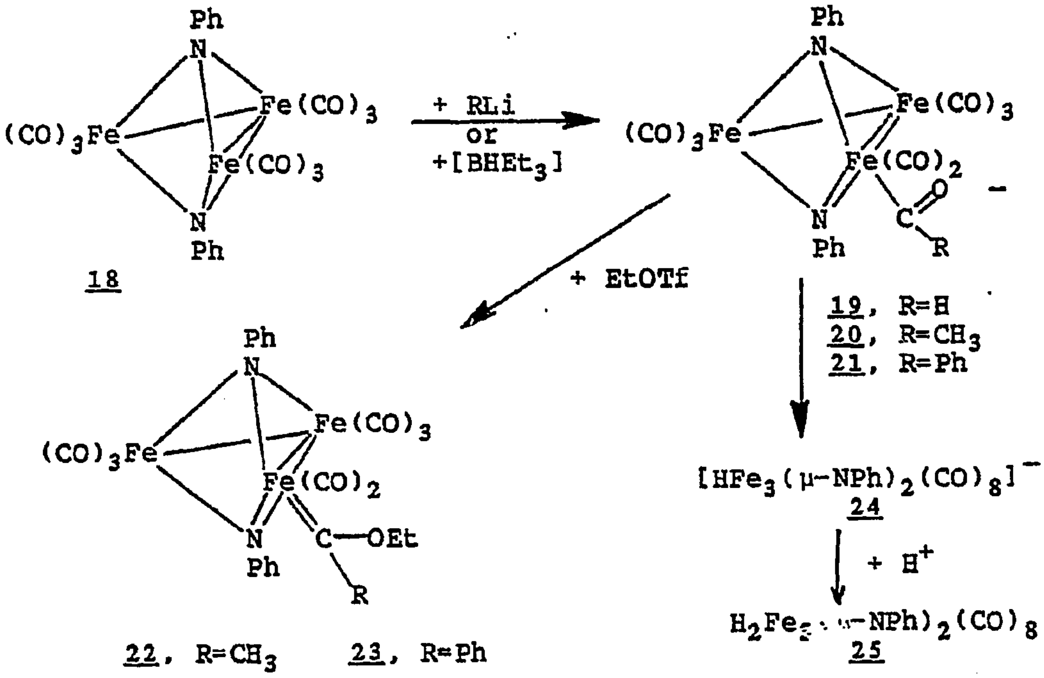


The insertion of CO into an isolable cluster alkyl to give a cluster acyl is not well-documented, although it is a well-studied reaction for mononuclear complexes. The terminal acetyl complex 16 loses CO upon heating to generate the bridging acetyl complex 17 in near quantitative yield.

C. Formyl, Acyl, Carbene, and Hydride Complexes Derived from the Nitrene-Bridged Cluster $Fe_3(\mu\text{-}NPh)_2(CO)_9$ -- Carbene-Nitrene Coupling.

In our earlier attempts to prepare formyl-substituted clusters, only $Os_3(CO)_{12}$ gave a formyl sufficiently stable to derivatize[16,21]. Other clusters such as $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ gave only hydride derivatives, presumably formed via rapid deinsertion reactions of unstable formyl intermediates. Clusters such as $Ru_3(CO)_{12}$ have two avenues to open coordination sites for this reaction to occur: dissociation of CO or metal-metal bond cleavage. We reasoned that we could suppress metal-metal bond dissociation by using clusters with strong bridging ligands and that CO dissociation could be retarded by limiting the number of CO ligands initially present, thereby increasing the metal-CO bond strength of those remaining. A cluster that appeared to meet these requirements was $Fe_3(\mu\text{-}NPh)_2(CO)_9$, 18.[22a] Indeed, this compound does lead to a relatively stable formyl derivative, 19, which lives for several hours at room temperature before it slowly deinserts to give the hydride cluster 24, Scheme V.

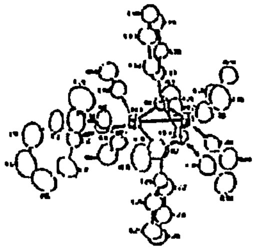
Scheme V



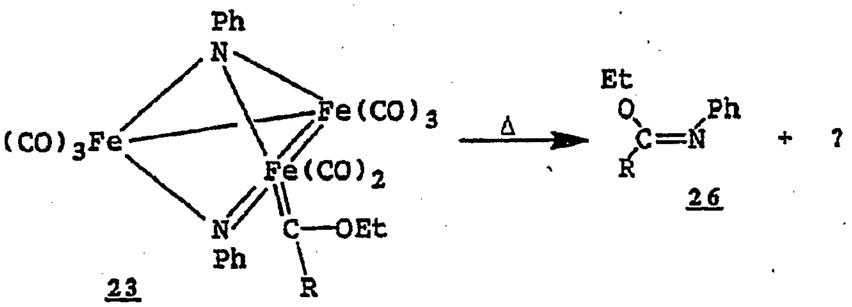
In an attempt to duplicate the formyl to methylene conversion established for $[Os_3(CO)_{11}(CHO)]^-$,[16] we protonated 19 but this gave only reformation of 18.

Reaction of 18 with RLi reagents leads quantitatively to acyl derivatives which are indefinitely stable at room temperature. Alkylation of these with ROTf gives neutral carbene derivatives of which 23 has been fully characterized by x-ray diffraction, Figure 3.

Figure 3



To my knowledge 22 and 23 are the first clusters that have both carbene and nitrene ligands attached to a metal framework and thus it is especially interesting to learn how these ligands can interact. In preliminary studies we have found that they couple to give an imine when 23 is exposed to air for prolonged periods or is heated under N_2 for several hours, eq. 7.

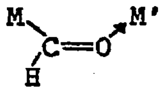


23 26 (7)

Such a transformation has never been previously reported. We do not yet know the organometallic product of eq. 7, but we expect that if a similar reaction is conducted under a CO atmosphere, the known compound $Fe_3(NPh)(CO)_{10}$[22b] should result. This and other aspects of the chemistry of this interesting chemical system will be explored in our planned research.

D. Binuclear Formyl and Acyl Complexes.

One of the original goals of this research was to prepare bridging formyl complexes of type I in order to evaluate their stability and subsequent transformations.



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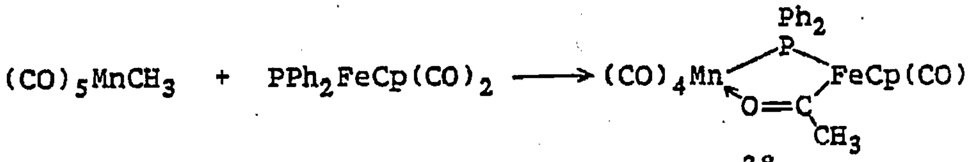
This we have not yet achieved although we have prepared several precursor complexes which could have led to such species and have also synthesized several binuclear bridging-acyl complexes of type I and have evaluated their chemistry.

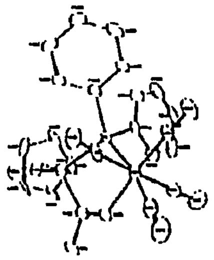
We found that the new bridging-acetyl complex 28, Figure 4, derives by the reaction shown in eq. 8.[23]



$$(CO)_5MnCH_3 \quad + \quad PPh_2FeCp(CO)_2 \longrightarrow (CO)_4Mn(\mu\text{-}PPh_2)(\mu\text{-}O{=}C(CH_3))FeCp(CO) \qquad (8)$$

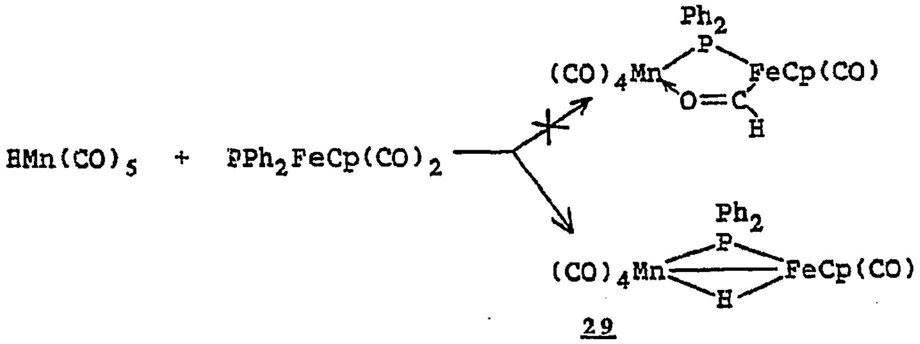
28

Figure 4



This reaction likely proceeds via initial methyl migration to CO on Mn followed by addition of $PPh_2FeCp(CO)_2$ to the opened coordination site and subsequent isomerization of the acetyl ligand from the Mn-carbon bound form to the observed Fe-carbon bound product. An important result from our studies of the chemistry of <u>28</u> was the finding that the acetyl ligand is firmly locked in place and it cannot be protonated nor alkylated, and neither tertiary phosphines, H_2, nor CO will displace the oxygen from the Mn center. This is obviously a very stable structural mode and strongly suggests that if similar bridging formyl complexes can be prepared, they also should be extremely stable. The problem with such stability is that the bridging acetyl ligand is quite unreactive and resists further transformations.

We reasoned that if <u>28</u> derives by the reaction given in eq. 8, then a formyl-bridged complex might result from an analogous reaction employing $HMn(CO)_5$ in place of $CH_3Mn(CO)_5$, eq. 9. However, such a product did not form,



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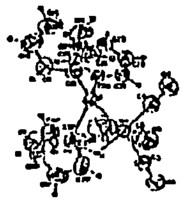
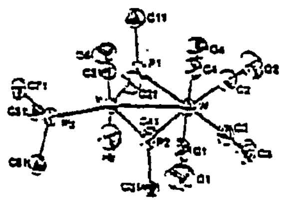
but rather the hydride-bridged product <u>29</u>, Figure 5, was obtained.[23]



<u>Figure 5</u>

Given the stability of the acetyl-bridged compound <u>28</u>, a formyl-bridged complex might result from CO insertion into <u>29</u>. However, no reaction occured when <u>29</u> was heated under CO and H_2 pressures.[23]

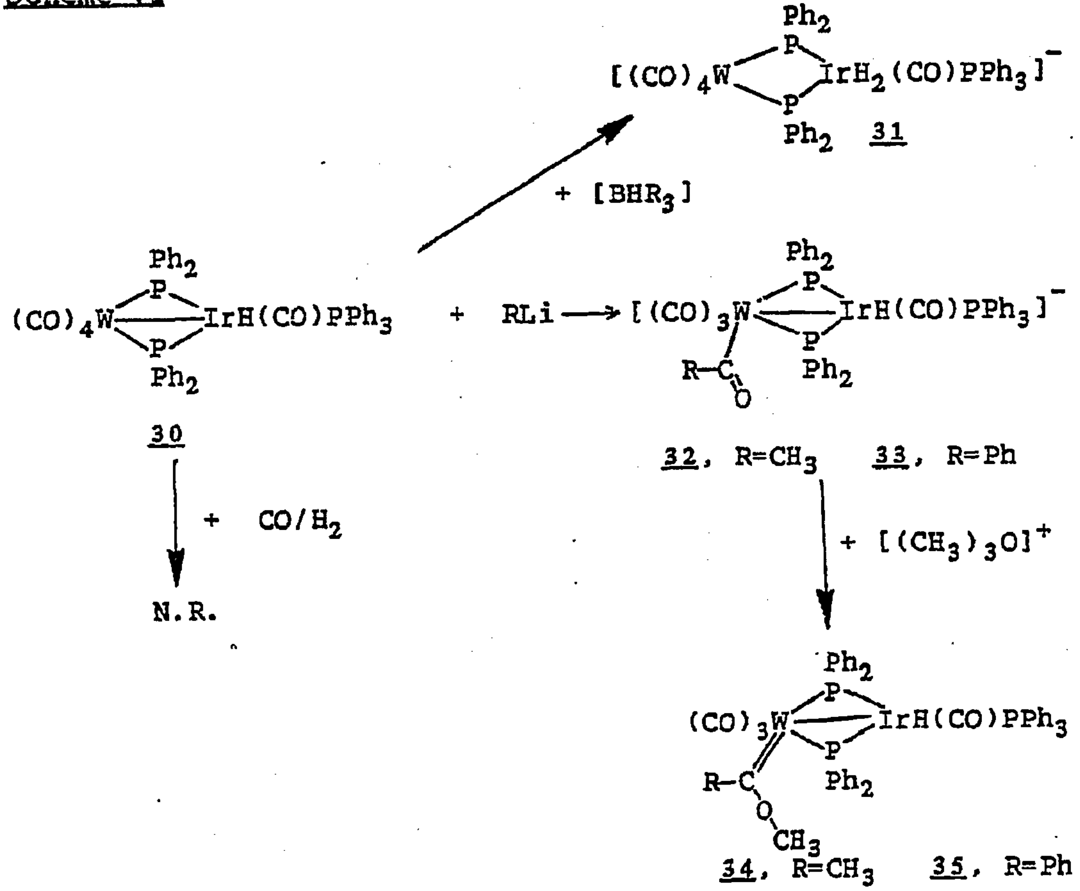
The binuclear WIr hydride complex <u>30</u> has also been prepared and structurally characterized, Figure 6.[24]



<u>Figure 6</u>

A stable bridging formyl species was a possible derivative of this species since it contained an early transition metal (W) which should be oxophilic enough to bind the formyl oxygen, and it also contained the necessary hydride to migrate to CO. However, no reaction occurred when this complex was heated under 1500 psi H_2 and H_2/CO pressures. Reaction of 30 with $Li[BHEt_3]$ also did not lead to a formyl complex but instead to the dihydride 31, Scheme VI.[24]

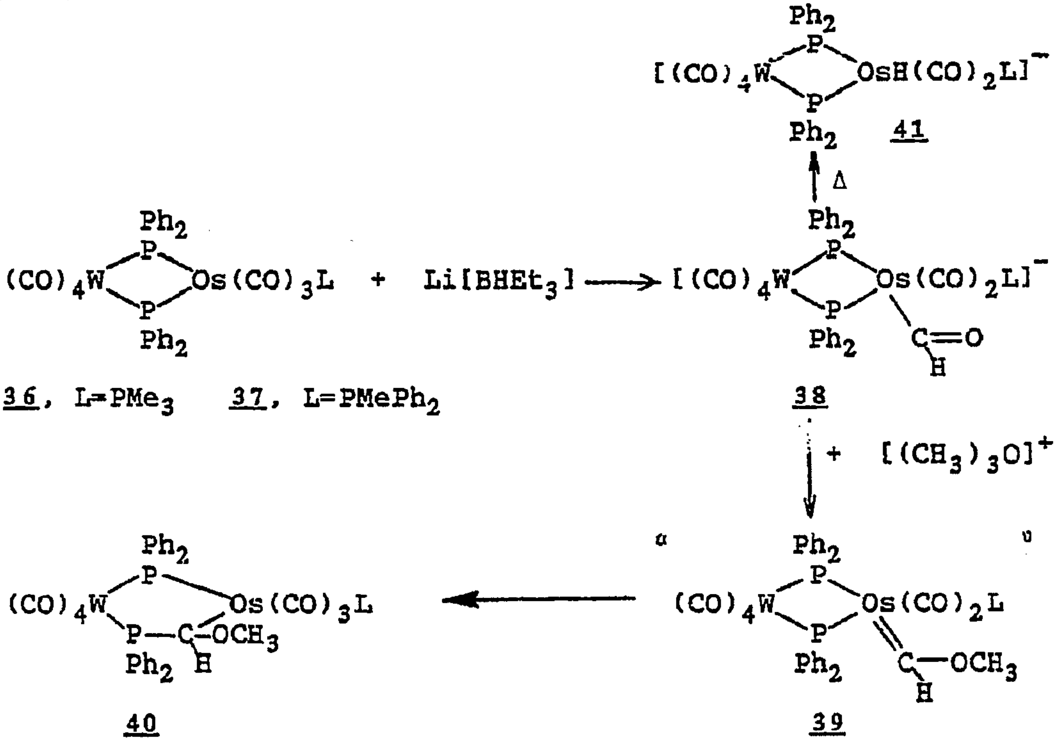
Scheme VI



However, reaction of 30 with RLi reagents gave the binuclear acyl-hydride complexes 32 and 33. Alkylation of the latter produced the binuclear carbene-hydride complexes 34 and 35. A surprising aspect of this chemistry is the stability of 32-35. Elimination of aldehyde from the acyl-hydride complexes 34 and 35 would seem a likely reaction, but this does not readily occur. Nor do the hydride ligands of 32 and 33 migrate to the carbene carbon to generate alkyl complexes. We assume that these two reactions would require prior migration of hydride to W, a coordinatively-saturated metal that does not have a low-energy path for opening a coordination site, and thus these reactions do not occur.

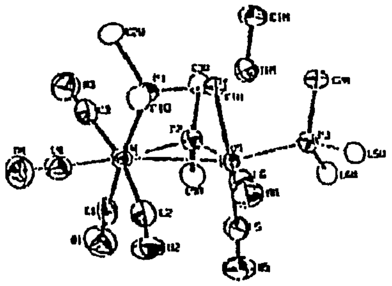
Although stable formyl complexes did not derive from the above series of compounds, they did form in a closely related set of WOs compounds. We prepared complexes 36 and 37 and these gave remarkably stable formyl complexes when treated with Li[$BHEt_3$], Scheme VII.[25]

Scheme VII



These formyl derivatives are stable at elevated temperatures. The PMe_3 derivative, for example, decomposes at 78 °C with $t_{1/2}$ = 4.3 hours by loss of CO to give the hydride complex 41. Interestingly, alkylation of the formyl complexes gives the derivatives 40, Figure 7, which form by coupling of carbene and phosphido ligands, presumably via the intermediate 39.

Figure 7



E. Low-Pressure Homogeneous Reduction of CO with H_2 Using a Mixed $Ru_3(CO)_{12}$/CuI Catalyst System.

Dombek[14a] has shown that $Ru_3(CO)_{12}$/I is an effective catalytic system for the homogeneous reduction of CO to give ethylene glycol in reasonably high selectivity. This reaction may proceed via transient formation of $[HRu(CO)_4]^-$ which was independently shown to be a good hydride donor for producing formyl ligands on other metal centers.[12a] We reasoned that if this species could be generated in solution in the presence of transition metals that weakly bind CO such that the CO ligand would have an unusually high νCO stretch and a high partial positive charge on carbon, hydride transfer from $[HRu(CO)_4]^-$ would be facilitated. Two such metals which fit this requirement are Pd^{2+} and Cu^+.[26] Thus the systems $Ru_3(CO)_{12}/PdI_2$ and $Ru_3(CO)_{12}/CuI$ were conceived as being possible active catalysts for homogeneous CO reduction. The first of these has not yet been studied, but in preliminary studies we have found that the Ru/Cu system is active for the quite low-pressure hydrogenation of CO, as illustrated in eq. 10.

$$CO/H_2\ (1:3)\ \xrightarrow[\substack{Ru_3(CO)_{12}/CuI \\ (1:9\ \text{molar ratio}), \\ \text{N-methylpyrrolidone}}]{185^{\circ}C,\ 1250\ \text{psi}}\ \underset{(84\%)}{MeOH} + \underset{(4\%)}{EtOH} + \underset{(2\%)}{{}^{n}PrOH} + \ldots \qquad (10)$$

(25% conversion to products in 24 hours)

Under these very low pressure conditions, the selectivity to MeOH was high with essentially no ethylene glycol produced. What is impressive is the relative activity. Although Dombek's study[14a] was conducted at higher temperatures and pressures, if one makes reasonable assumptions and extrapolates his data back to ours, the rate of CO hydrogenation to products in our system is at least 15 times greater than his. It should be pointed out that these are preliminary experiments on only three separate runs, and numerous control experiments must be conducted, as detailed in the proposed research section.

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