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STUDIES RELEVANT TO THE CATALYTIC ACTIVATION OF CARBON MONOXIDE: THE WATER GAS SHIFT REACTION AND RELATED PROCESSES. TECHNICAL PROGRESS REPORT, DECEMBER 1, 1983-NOVEMBER 30, 1984

CALIFORNIA UNIV., SANTA BARBARA. DEPT. OF CHEMISTRY

1984
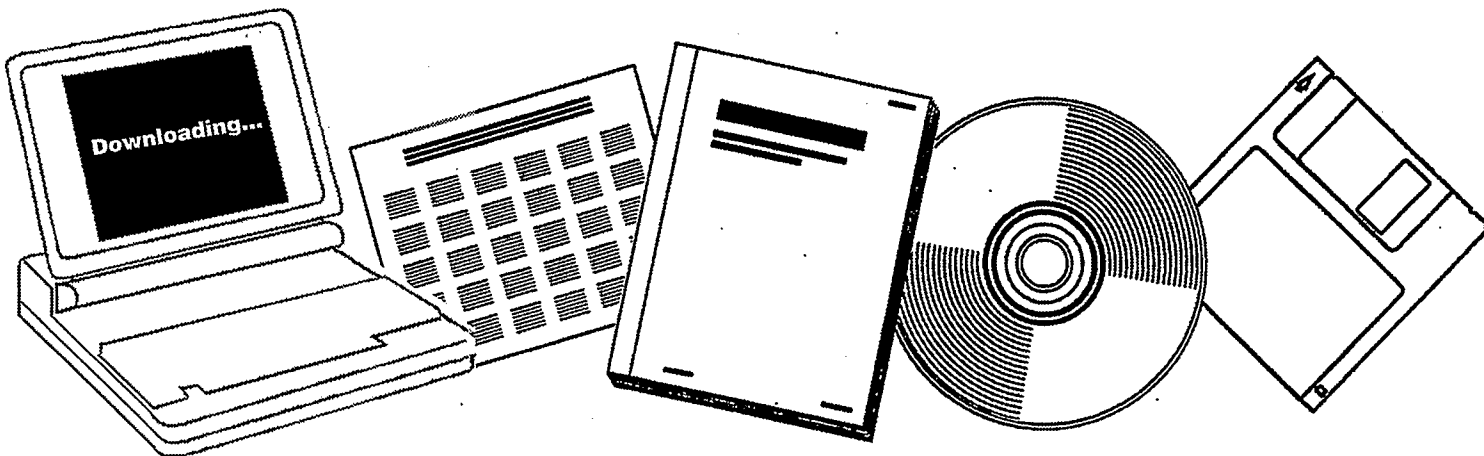
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Technical Progress Report

Department of Energy (Office of Basic Energy Sciences)

Contract No:	DE-AM03-76SF00034
Project Agreement No:	DE-AT03-76ER70262

Title: "Studies Related to the Homogeneous Catalysis
of the Water Gas Shift Reaction"

Period: December 1, 1983 - November 30, 1984

MASTER

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Attached to this cover page is a report and proposal submitted to the
Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic
Energy Sciences, Deparment of Energy (Dr. Robert S. Marianelli, Program
Manager) for continued support of the above ongoing research project. Dr.
Marianelli has indicated that the enclosed document is satisfactory to him as
the required annual Technical Progress Report and has suggested that I transmit
it to all other appropriate agencies as such.

DOE/ER/70262--T1

Sincerely,

DE85 000207

Peter C. Ford
Professor of Chemistry

copies to: ONR representative
Contracting Officer, DOE, Oakland, CA
⟶ Technical Information Center, DOE, Oak Ridge, TN

, ⁿ PROPOSAL TO: THE DEPARTMENT OF ENERGY
              OFFICE OF BASIC ENERGY SCIENCES

    (renewal of DOE-OBES #DE-AM03-76SF00034,PA-AT03-76ER70262)

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✓ "STUDIES RELEVANT TO THE CATALYTIC ACTIVATION OF CARBON
MONOXIDE: THE WATER GAS SHIFT REACTION AND RELATED PROCESSES"

I. ABSTRACT:
    Proposed are investigations related to the catalytic
activation of carbon monoxide. These studies will be
concerned with the design of catalysts for the water gas
shift reaction and related processes such as the
hydroformylation of olefins by homogeneous solution phase
systems as well as by selected metal catalysts
"heterogenized" by complexation to functionalized polymers.
Also under investigation will be quantitative mechanistic
aspects of reactions considered key to probable catalyst
cycles. These are principally concerned with the fundamental
chemistry of metal carbonyl and metal carbonyl hydride
complexes including acid/base properties, reductive
elimination, substitution and cluster fragmentation reactions
and the nucleophilic activation of metal coordinated
carbonyls toward reaction with water or dihydrogen. The goal
of these studies is to provide chemical guidelines for the
molecular design of new and more efficient catalysts for the
utilization of carbonaceous materials such as coal for the
production of fuels and other organic chemicals.

DISCLAIMER

II. PROPOSED RESEARCH:

A. INTRODUCTION:

This proposal represents a request, for continued support of research concerned with the fundamental chemistry related to the catalytic activation of carbon monoxide. The focal point of this research has been the homogeneous catalysis of the water gas shift reaction (eq 1, WGSR). In an evolutionary manner our interests have broadened to include other aspects of CO activation, although WGSR chemistry, the fundamental mechanistic aspects and the development of viable catalysts, remain a central part of these interests.

(1) $H_2O + CO \rightleftharpoons CO_2 + H_2$
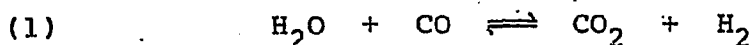
It would be difficult to exagerate the importance of the shift reaction to schemes for the conversion of hydrogen-poor carbonaceous materials, of which coal is the most prominant example, to hydrocarbon fuel and other hydrogen-rich organic chemicals. Since the report from these laboratories in 1977[1] describing the homogeneous catalysis of the WGSR by ruthenium carbonyls in alkaline aqueous alcohol solutions and independent reports of such catalysis from several other laboratories[2], there has been considerable research activity in this area[3]. There are several potential advantages of such homogeneous catalysis, for example, the insensitivity of several systems to high concentrations of sulfur impurities[4]. However, given the proven technology of heterogeneous catalysts for the shift reaction, it is likely that practical uses of homogeneous systems will require specialized applications, for example, in situ catalysis in conjunction with another catalytic function. Potentially greater benefits may ensue from catalysis applications in closely related processes such as

hydroformylation, hydrohydroxymethylation and hydrogenation of organic

substrates using carbon monoxide as the carbon source and reducing

agent and water as the hydrogen source(5). Furthermore, aspects of the

fundamental chemistry key to the shift reaction, e.g. the nucleophilic

activation of CO(6), are also important to understanding other

seemingly diverse examples of metal complex catalysis such as the

oxidation of CO in fuel cells(7), the photoreduction of CO_2 to CO(8),

the homologation of methanol(9), and the use of methoxide as a

cocatalyst (with metal carbonyls) in the reductive carbonylation of

nitroaromatics by synthesis gas(10).

Scheme I illustrates one proposed cycle for the WGSR as catalyzed

by metal carbonyls in alkaline solution(3a):

SCHEME I
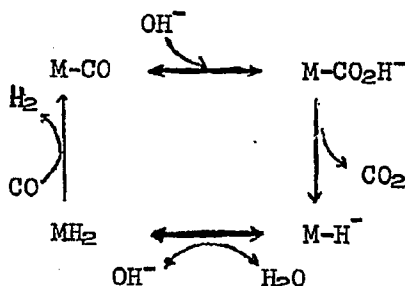
This cycle alone introduces a number of key species and chemical

transformations which must be characterized in order to understand

fully the catalysis mechanism(s). Such studies in this laboratory and

others indicate that catalysis by $Fe(CO)_5$ follows this scheme closely

with the formation of $HFe(CO)_4^-$ from $Fe(CO)_5$ being rate

limiting(11,12). However, we have shown that catalysis by $Ru_3(CO)_{12}$

follows a different pattern(13), since the MH^- species $HRu_3(CO)_{11}^-$ is

such a weak base that protonation to MH_2 is precluded in the alkaline

reaction medium.

Other potential catalytic WGSR cycles can be proposed such as
electrophilic activation of CO toward reaction with water by Lewis acid
coordination at the oxygen or by protonation of the metal(Scheme II,
3a).

Scheme II

$$M-CO + H^+ \rightleftharpoons HM-CO^+$$

$$HM-CO^+ + H_2O \rightleftharpoons HM-CO_2H + H^+$$
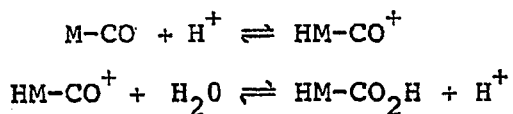
An example of the latter is the catalyst based on ruthenium carbonyl in
acidic diglyme solution(14). Our studies indicate that the principal
operating cycle involves solvento complexes of diruthenium carbonyl
hydride cations, i.e., that protonation of the metal core serves to
activate coordinated CO's toward reaction with H_2O.. Another
alternative would be for WGSR catalysis to proceed via formate
intermediates as suggested for several homogeneous catalysts(15) and
for heterogenous catalysis by mixed metal oxides(16):

Scheme III

$$CO + OH^- \longrightarrow HCO_2^-$$

$$HCO_2^- + H_2O \longrightarrow H_2 + OH^- + CO_2$$
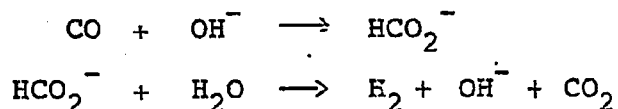
Our present investigations continue to address the fundamental
chemistry of such potential cycles as well as the use of the resulting
information as guidelines for the design of new optimized catalysts for
the shift reaction and other processes.

B. HOMOGENEOUS CATALYSTS FOR THE SHIFT REACTION AND OTHERS:

Our recent efforts in this area have been concerned with the characterization of demonstrated catalysts by in situ spectral techniques (^{13}CNMR, HNMR, IR, UV/VIS) and both batch and flow reactor kinetics (in collaboration with Prof R. G. Rinker of UCSB Chemical Engineering). These investigations focussed on ruthenium carbonyl in acidic diglyme(14) menztioned above and on iridium carbonyl in alkaline solutions(17), both previously reported(18) to be more active than the alkaline iron and ruthenium carbonyl catalysts. For the latter the spectral and kinetics results point to a mechanism analogous to Scheme I. In this case, M-CO = $HIr_4(CO)_{11}^-$ and the rate limiting step is the activation of CO (eq 2), subject to both specific and general base catalysis.

(2) $HIr_4(CO)_{11}^- + OH^- \longrightarrow H_2Ir_4(CO)_{10}^= + CO_2$.
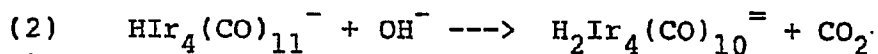
These solutions also decompose formate, thus Scheme II is a likely contributor to the WGSR activity. The quantitative reactions of the key iridium clusters $Ir_4(CO)_{12}$ and $HIr_4(CO)_{11}^-$ with formate are the subjects of continuing investigation in order to establish the importance of such a contribution. However, preliminary studies indicate that formate decomposition by $HIr_4(CO)_{11}^-$ is inhibited by CO, thus would be rather slow under WGSR conditons(17). We have noted that reaction with $Ir_4(CO)_{12}$ occurs quite facilely to give an unstable formate iridium complex and are investigating the kinetics of the formation and decomposition of this species(19).

In collaboration with W.C. Kaska we have initiated the synthesis and characterization of complexes of the naphthyridine derivative bpnp.

bpnp
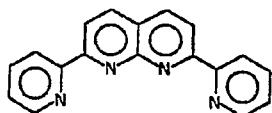
$$N - M -- M' - N$$
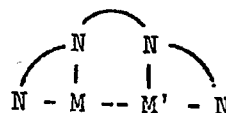
A

We have demonstrated that this crescent shaped ligand is capable of chelating two metal atoms in close proximity both for the case (dirhodium(II)) where the two atoms are linked by a metal-metal bond and the case (dicopper(II)) where the metals are bridged by ligands but not bonded to each other(20). The bpnp ligand also can chelate, using either two or three nitrogens, to a single metal center. Continuing synthetic studies in Kaska's group have been concerned with extending the scope of this ligand's complexes. Our interest has been possible utilization of such binuclear complexes in promoting the reactions of small molecules such as CO. Of particular interest would be complexes in which two different metal ions are held juxtaposed by the crescent shaped dinucleating ligand, e.g., A. In such a case one metal may serve to coordinate (and activate?) a reactant such as CO while the other might activate a second ligand such as H_2O (for the shift reaction) or dihydrogen (for CO reduction). Such bifunctional dimetallic activation has been proposed in the heterogeneous catalysis of methanol formation from synthesis gas(21). Preliminary attempts to prepare characterizable, robust complexes with $M' \neq M$ have not yet proved successful. However, several mononuclear heavy metal complexes of bpnp have now been prepared(22), and it should be possible to prepare heterobinuclear complexes in situ by allowing such complexes to react in solution with labile metal ions such as Cu(II), Zn(II) or Ni(II). We propose to examine the catalytic activity of such systems for the shift reaction and for reactions of synthesis gas.

The dirhodium bpnp derivatives did prove to be reasonably active,

stable catalyst precusors for the WGSR; however, control experiments utilizing Rh(III) salts and simpler nonchelating pyridines proved to have comparable or greater catalytic activity and are equally stable and reproducible(sigh!). These observations(23) and recent reports from other laboratories that rhodium porphyrin(24) and rhodium bipyridyl(25) complexes can catalyze the shift reaction point to the need for in depth analyses of the mechanisms of catalysis by rhodium complexes of nitrogen donor ligands. There have also been several preliminary reports of WGSR activity by rhodium carbonyl clusters cocatalyzed by amines as well as reports of the abilities of such solutions to catalyze the reduction of nitroaromatics and the hydroformylation and hydroxymethylation of olefins by H_2O/CO mixtures(2b,26), but there have been no detailed mechanistic investigations of these systems. Our principal focus will be on the characterization by in situ spectroscopy and batch and flow reactor kinetics of the catatysts based on $RhCl_3$ plus the simpler monodentate ligand derivatives such as 4-picoline. These pyridine ligands are readily available with a wide variety of substituents by which one can "tune" the electronic and steric properties both to optimize the catalytic activities and to probe the reaction mechanism. Present investigations are confined to the WGSR mechanism; however, these will be extended to the other CO catalysis properties of such solutions.

We also propose to extend these investigations of the rhodium amine systems by utilizing amines which are anchored to polymeric supports. One class of such polymer attached amines includes the polystyrene-divinylbenzene copolymer resins prepared by T.M. Suzuki (a former associate of this research group) which are functionalized by 2-pyridylmethylamine or N-[2-(2-pyridyl)ethyl]ethylenediamine(27). A third one of interest is the same polymer functionalized by

diethylenetriamine(28); however, catalysts based on this amine may be unstable owing to formamidation of the primary amine sites. Athough "heterogenizing" the rhodium catalyst in this manner may have few advantages for the WGSR where separation of the liquid phase catalyst and the gaseous reactants and products is relatively facile, much greater advantages can be envisioned for reactions such as hydroformylation where products would also be liquids, hence more difficult to separate in a flow reactor configuration. In addition, the anchoring of the catalyst may give different product selectivities than a strictly homogeneous system(29). If so, in situ spectroscopy and flow reactor kinetics will be studied. The goal of these investigations will be to establish whether such heterogenized catalysts are indeed active, whether they operate via mechanisms comparable to the homogeneous analogs and whether they offer any advantages of stability, activity or separability.

·C. MECHANISMS OF REACTIONS OF WGSR CYCLES AND RELATED PROCESSES:

The focus of mechanistic studies have largely been the individual reactions of the type indicated in Scheme I. These include the acid/base properties(30) and reductive elimination reactions(31) of metal carbonyl hydrides and their conjugate bases; the nucleophilic activation of coordinated CO by water, hydroxide and other bases(6,11,32); and the decarboxylation mechanisms of hydroxycarbonyl complexes(11,32,33). Also investigated have been the ligand substitutions of various key species in these cycles(31,34). Proposed studies fall into similar genre and are grouped somewhat arbitrarily into two categories: reactions of metal carbonyl hydrides and nucleophilic activation of coordinated carbon monoxide:

i) <u>REACTIONS OF METAL CARBONYL HYDRIDES</u>: Metal carbonyl hydrides have been implicated as intermediates in a number of catalytic applications, e.g., the shift reaction, hydroformylation, hydrogenations, Fischer-Tropsch chemistry, etc.. In such systems, the metal hydride complexes may act variously as dihydrogen(H_2), hydrogen atom (H·), hydride (H^-) or proton (H^+) sources. Previous studies in this laboratory(30) have been concerned with the quantitative equilibria and kinetics of the proton transfers to strong bases from the iron triad metal carbonyl hydrides:

(3) $\quad H_zM_x(CO)_y + B^- \quad \rightleftharpoons \quad H_{z-1}M_x(CO)_y^- + BH$
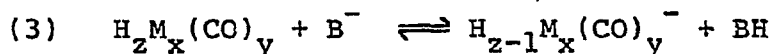
There is an obvious relationship of such equilibria to the WGSR cycle of Scheme I. Furthermore, given that the metal coordinated hydrogen is generally viewed as a hydride, proton transfer to or from the metal is formally the simplest oxidative addition/reductive elimination

reaction, and structural changes often accompanying such proton transfers are consistent with this view.

Our measurements led to the generalizations i) that replacement of CO by a weaker pi-acceptor such as a phosphite dramatically decreases acidity even for clusters where the site of substitution is remote from the hydride, ii) that bridging hydrides are more acidic than terminal ones and iii) that proton transfers to strong bases, with second order rate constants of 10 to 10^4 M^{-1} s^{-1}, are about six orders of magnitude slower than analogous reactions of oxygen or nitrogen protonic acids of comparable pKa's. Such rate differences can be attributed to electronic and structural rearrangement accompanying proton transfer from the metal complex and to the hydridic nature of the metal hydrogen which limits hydrogen-bonding to solvent, hence the role of solvent as a proton transfer mediator. Such generalizations, however, are based on a limited data set of quantitative investigations(30,35,36), and it is clear that careful pKa and kinetics measurements of other metal hydrides are needed to test these. For example, it is of interest to probe quantitatively the effect of changing the ligand L for two systematic series of complexes $H_zM_x(CO)_{y-1}L$, one mononuclear (x = 1), another polynuclear, given that variation of L may change chemical behavior of the complex from a proton donor to a hydride donor for a particular set of circumstances(38). We also propose to examine the pKa's and labilities of facial bridging hydrides (e.g., $H_4Re_4(CO)_{12}$ (37)) and of interstitial hydrides (e.g. $HRu_6(CO)_{18}^-$ or $HCo_6(CO)_{15}^-$ (39)).

Given the possible catalytic roles of metal carbonyls under acidic conditions(40), including the WGSR mechanism suggested in Scheme II, we also propose to explore (or, in some cases reexamine) the protonation

of simple neutral metal carbonyls by strong acids (eq 4). The $M(CO)_5$ (M =

(4) $M_x(CO)_y + H^+ \rightleftharpoons HM_x(CO)_y^+$.
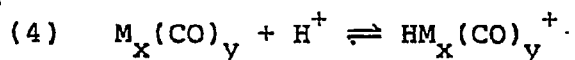
Fe or Ru) are both known to protonate at the metal center in strong
acid to give a hexacoordinate $HM(CO)_5^+$ species(41,42), formally in the
d^6 M(II) oxidation state. In contrast preliminary experiments in this
laboratory indicate that in very strong acid the Cr(0) complex $Cr(CO)_6$
protonates at an oxygen rather than a metal site(43). Although
protonation constants for some mixed ligand complexes have been
determined, there is very little quantitative information for the
analogous simple metal carbonyls. We propose to measure equilibrium
constants for the protonation of $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M =
Fe,Ru,Os) and perhaps one or more substituted series, e.g., $Ru(CO)_4L$ (L
= a series of stable ligands). Also of interest are cluster species
such as $Ru_3(CO)_{12}$ used as a precursor in WGSR catalysis in acidic
diglyme(14) and reported previously to undergo protonation in strong
acid(44). It should be possible to determine the pKa's of these
species spectrally by establishing the Ho value of the solution giving
50% protonation(45). In addition we will explore the possibility that
rates of proton exchange may be measureable by nmr techniques. pKa
measurements for such complexes of a series of different L's would
provide a quantitative chemical parameter for ligand effects which can
be compared to spectroscopic data such as the recently reported PES
measurements for the iron complexes $Fe(CO)_4L$ (46).

We also propose some exploratory reactivity studies of the
resulting cationic hydrides. For example, we have noted that
fragmentation of the trinuclear species $Ru_3(CO)_{12}$ under CO is
facilitated by strong acids(14, 47); however, no quantitative
information is available for such acid catalyzed cluster

fragmentations. Although for larger clusters the interaction with strong acids is accompanied by CO reduction to methane (along with oxidation of metal centers), this is not the case for simple neutral carbonyls of nuclearity one to three(40a). One possibility might be that the low nuclearity complexes cannot conveniently supply a sufficient number of electrons to reduce CO. In this context, it would be of interest to probe the electrochemical properties of simple protonated complexes by cyclic voltammetry and controlled potential electrolysis to determine whether ligand reduction is facilitated in strong acid and whether the electrochemical reactivities of a metal protonated species such as $HRu(CO)_5^+$ are significantly different than for species such as $Cr(CO)_6H^+$, which we believe may be protonated at the oxygen. Lastly, one can speculate on how substitution influences the site of protonation for mononuclear metal carbonyls such as $M(CO)_xL$. For example, would the ethylene complex $Ru(CO)_4(H_2C=CH_2)$ protonate at the ligand, or would protonation occur at the metal to give a hydride ethylene complex, possibly capable of reversible rearrangement to a cationic ethyl species? e.g,

(5) $Ru(CO)_4(H_2C=CH_2) + H^+ \rightleftharpoons HRu(CO)_4(H_2C=CH_2)^+$
$$+ CO \rightleftharpoons C_2H_5Ru(CO)_5^+ .$$
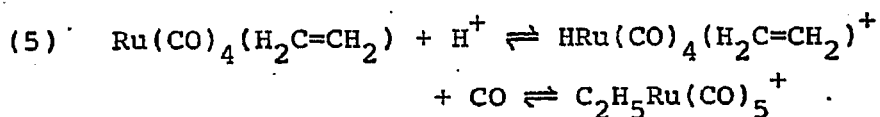
Another metal hydride reaction of fundamental importance to the WGSR is the reductive elimination of dihydrogen:

(6) $H_zM_x(CO)_y + L \rightleftharpoons H_2 + H_{z-2}M_x(CO)_yL$
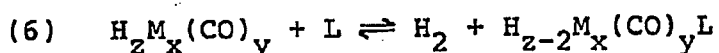
For example we have shown that the rate limiting step of the WGSR catalyzed by ruthenium clusters in alkaline solution is formation of $H_2(13)$. Given the conclusion that, under mild conditions, trinuclear complexes represent the principal active cycle for the catalysis (32,48), the key species would be the monohydride cluster $HRu_3(CO)_{11}^-$

(13,49). This ion will undergo facile H_2 elimination when dissolved in strongly acidic solutions giving $Ru_3(CO)_{12}$ quantitatively in the presence of CO(50). However, it is such a poor Bronsted base that, under the alkaline conditions of the catalysis, H_2 formation via sequential protonation, H_2 elimination and CO addition to the resulting unsaturated intermediate is precluded. Given that the WGSR rate is first order in P_{CO}(13) and Shore's observations that hydride loss is dependent on the presence of CO(48), it is clear that another pathway is key to H_2 production. We and Shore agree that this pathway probably involves CO addition to give a $HRu_3(CO)_{12}^-$ species, although the structure of that intermediate is as yet unknown. Three proposed candidates are (3a,48,51):

$$
\begin{array}{ccc}
\underset{\text{B}}{
\begin{array}{c}
\text{Ru(CO)}_4 \\
\text{H} \diagup \quad \diagdown \\
\text{(OC)}_3\text{Ru} \qquad \text{Ru(CO)}_4 \\
\diagdown \quad \diagup \\
\underset{O}{\overset{}{C}}
\end{array}^-
}
&
\underset{\text{C}}{
\begin{array}{c}
\text{Ru(CO)}_4 \\
\diagup \quad \diagdown \\
\text{(OC)}_4\text{Ru} \!-\!\!-\! \text{Ru(CO)}_3\text{(CHO)}
\end{array}^-
}
&
\underset{\text{D}}{
\begin{array}{c}
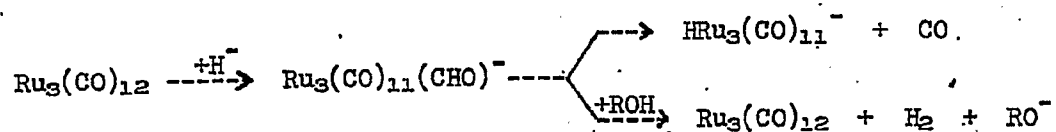\text{Ru(CO)}_4 \\
\diagup \quad \diagdown \\
\text{(OC)}_4\text{Ru} \qquad \text{Ru(CO)}_4 \\
\text{H}
\end{array}^-
}
\end{array}
$$
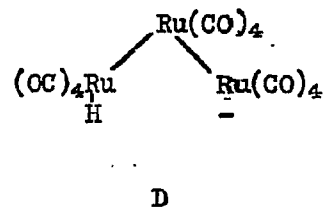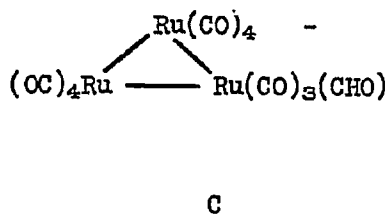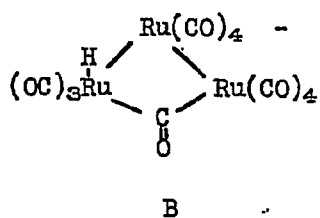
B and C might be expected to undergo facile H^- transfer to a hydride acceptor (e.g. water to give H_2) while D, having a terminal base site would protonate to give an open chain $H_2Ru_3(CO)_{12}$ species followed by rapid ring closure to $Ru_3(CO)_{12}$ plus H_2. Present data does not differentiate among the three proposals although Shore has made the interesting observation that formation of $Ru_3(CO)_{12}$ from $DRu_3(CO)_{11}^-$ plus H_2O gives HD(51). This suggests that the metal bound hydrogen remains ,unique and does not exchange with solvent protons throughout this process. Such an observation is perhaps more consistent with the intermediacy of B or C unless D, once formed, undergoes ring closure more rapidly than proton exchange. There is little established

precedence for any of these mechanisms, so we are attempting to elucidate the mechanism by a combination of reaction kinetics studies plus attempts to prepare proposed intermediates to investigate quantitatively their transformations. For example, it should be possible to prepare the formyl species C by the reaction of $Ru_3(CO)_{12}$ with a strong hydride donor at very low temperature. In the absence of a proton donor, C would be expected to lose CO to give $HRu_3(CO)_{11}^-$ and very likely is the intermediate in one synthesis of the latter ion(49). However, a key question is whether $Ru_3(CO)_{12}$ would be formed competitively in the presence of an added proton source.

$$Ru_3(CO)_{12} \xrightarrow{+H^-} Ru_3(CO)_{11}(CHO)^- \begin{cases} \xrightarrow{} HRu_3(CO)_{11}^- + CO \\ \xrightarrow{+ROH} Ru_3(CO)_{12} + H_2 + RO^- \end{cases}$$

We are aware of Shore's similar interest in the chemistry of $HRu_3(CO)_{11}^-$ but consider the H_2 elimination mechanism from such species of sufficient importance and the techniques from the different groups sufficiently complementary to warrant this attention.

We propose also to expand this investigation to the kinetics and mechanism details of H_2 formation from $HRu_3(CO)_{11}^-$ in acidic solution. In addition some other cluster hydride anions are of interest. Examples are the tetranuclear species $H_3Ru_4(CO)_{12}^-$, $HIr_4(CO)_{11}^-$ and $H_2Ir_4(CO)_{10}^=$ and the trinuclear species $HFe_3(CO)_{11}^-$ and $HOs_3(CO)_{11}^-$. The two iridium ions are of some interest in relation to the iridium carbonyl catalyzed shift reaction (above), while the two trinuclear clusters with Os forming stronger metal-metal bonds and Fe weaker ones than Ru (52), may provide some insight into the question of whether species such as B and D, the formation of which involves breaking a metal-metal bond, are viable intermediates in the H_2 formation.

The trinuclear ruthenium hydride system illustrates the complexity of the interrelated processes encountered when endeavoring to study a specific reaction. In the course of early investigations of H_2 formation from $HRu_3(CO)_{11}^-$ (31), we attempted to drive this reaction by using ligands such as trimethylphosphite rather than CO. The immediately obvious phenomenon was that the $HRu_3(CO)_{11}^-$ ion is exceedingly labile toward ligand substitution and undergoes rapid sequential replacement of three CO's in room temperature solutions.

(7) $3L + HRu_3(CO)_{11}^- === HRu_3(CO)_8L_3^-$
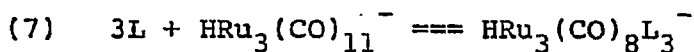
These reactions are orders of magnitude more rapid than analogous substitutions of the neutral carbonyl $Ru_3(CO)_{12}$ and of the neutral hydride species $HRu_3(CO)_{10}(\mu\text{-COCH}_3)$ (53). The high reactivity we observed has prompted Keister (53) to suggest a radical pathway for eq 7. However, our preliminary kinetics results indicate reproducible rates which are insensitive to addition of the radical scavenger 2,4,6-tri(t-Bu)phenol; thus we consider a radical chain process unlikely. We have also noted that $HRu_3(CO)_{11}^-$ reacts with ethylene to give substitution products which are yet to be characterized. Given the importance of ligand labilization to catalytic processes such as hydroformylation and hydrogenation of olefins, both which have been shown to be catalyzed by $HRu_3(CO)_{11}^-$ under mild conditions(both for H_2 plus CO(54) and for H_2O plus CO(5b)), we propose to investigate the detailed kinetics of the substitution reactions of this and related complexes.

Lastly, we also propose to study both the H_2 formation and ligand substitution reactions of the mononuclear species $H_2Ru(CO)_4$, $HRu(CO)_4^-$ and some substituted analogs. The interest in these species derives in

part from the potential role of mononuclear ruthenium complexes in several catalytic applications including WGSR under conditions different from those described for the ruthenium clusters(55) and for the reduction of CO to methanol and ethylene glycol (56). The dihydride is remarkably labile toward ligand substitution at very low temperatures (57), but the mechanism is not well established.

ii) NUCLEOPHILIC ACTIVATION OF COORDINATED CO: Our original interest in this topic stemmed from the proposal that reaction of OH^- with coordinated CO to give a hydroxycarbonyl adduct is a key step in Scheme I for WGSR catalysis.

(8) $\quad M\text{-}CO + OH^- \longrightarrow M\text{-}CO_2H^-$
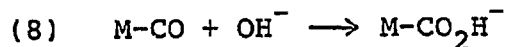
However, nucleophilic activation of CO has scope beyond the shift reaction given the employment of nucleophiles as copromoters in a variety of CO reactions catalyzed by metal carbonyls(5,10,58). Furthermore, numerous novel chemical species have been synthesized by the stoichiometric reaction of hydride, alkyl, amine and other nucleophilic donors with coordinated CO(59-62). Our focus in this area has been on the activation of CO by reactions of oxygen nucleophiles such as hydroxide or alkoxides to give (initially) hydroxycarbonyl ($M\text{-}CO_2H$) and alkoxycarbonyl ($M\text{-}CO_2R$) adducts. Notably, alkoxycarbonyl complexes are implicated in number of CO based organic reactions including the cobalt catalyzed carbalkoxylation of olefins(63), the reductive carbonylation of nitroarenes catalyzed by iron and ruthenium carbonyls(10) and the carbonylation of methanol with palladium(II) complexes(64). Hydroxycarbonyl complexes are most frequently mentioned as probable intermediates in the reaction of metal carbonyls with water or hydroxide to give either exchange of CO and solvent oxygen or

oxidation of CO to CO_2 with the resulting reduction of the metal or formation of metal hydrides (3b,65). However, they are also suggested as

(9) $M-CO_2H^- \longrightarrow M-H^- + CO_2$
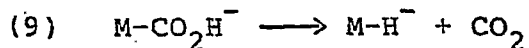
intermediates in the reduction of CO_2 by reduced metal species produced photolytically, i.e., as intermediates in a sequence of reactions leading to the photoreduction of carbon dioxide (8).

In this section we propose to continue our quantitative investigations of the formation equilibria and kinetics of hydroxycarbonyl and alkoxycarbonyl adducts and of the subsequent reactions of well characterized examples of these adducts.

Studies in this laboratory of methoxide and hydroxide reactions with the mono- and trinuclear carbonyls of the iron triad, $M(CO)_5$ and $M_3(CO)_{12}$ (M = Fe, Ru or Os) have led to these observations(6,11,32): The rate constants k_1 for formation of $M-CO_2R$ adducts are large for all the $M(CO)_5$ and $M_3(CO)_{12}$ complexes with values about 10^3 to 10^4 $M^{-1}s^{-1}$ and larger for $RO^- = CH_3O^-$ in methanol but somewhat smaller for OH^- in this solvent. Marked increases in these rates were noted as the solvent was made less polar and aprotic. Notably, the adduct formation K_{eq}'s were several orders of magnitude smaller for $Fe(CO)_5$ than for the other carbonyls, a feature which explains that the rate limiting step for WGSR catalysis by iron carbonyl is the formation of $HFe(CO)_4^-$ from $Fe(CO)_5$. Under our investigative conditions, the kinetics of the decarboxylation (eq 9) were mechanistically most consistent with β-elimination of CO_2 from the hydroxycarbonyl intermediates $M-CO_2H$ rather than prior deprotonation to give $M-CO_2^-$ followed by decarboxylation. For the iron complex $Fe(CO)_4CO_2H^-$, β-elimination is independent of P_{CO}; but $Ru_3(CO)_{11}(CO_2H)^-$ undergoes decarboxylation by both an P_{CO} independent step and a faster one with an inverse

dependence on P_{CO}, consistent with more facile transfer of hydrogen to the metal when a coordination site is open.

Although decarboxylation of the iron and ruthenium hydroxycarbonyls described above followed kinetics consistent with simple unimolecular β-elimination of CO_2 from the $M-CO_2H$ species in the aqueous alcohol solutions used in these studies, there is ample precedent for the operation of an alternative mechanism proceeding via CO_2 loss from the conjugate base $M-CO_2^-$ (66). In addition, it was evident from the studies in this laboratory(11,32) that the solvent plays an important role in the reaction. The rate of hydride formation is much faster in protic solvents such as aqueous methanol than in mixtures predominantly of an aprotic solvent such as THF. In this context, we have embarked upon the synthesis and isolation of characterizable hydroxycarbonyl metal carbonyl derivatives $M_x(CO)_y(CO_2H)^-$. The goal is to measure the pKa's of such species and to

$$M_x(CO)_y CO_2H^- \xrightarrow{\text{pKa}} M_x(CO)_y CO_2^{=} + H^+$$
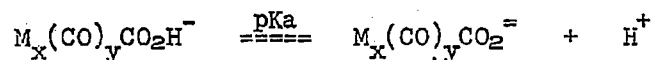
determine the rates of decarboxylation as a function of the metal center and of solution parameters including the nature of the counterions present, base concentration and solvent composition. Initial observations are rather qualitative; the tetra(n-butyl) ammonium salts of both $Fe(CO)_4(CO_2H)^-$ and $Ru_3(CO)_{11}(CO_2H)^-$ have been prepared as solids by low temperature reactions in aprotic solvents. The former is rather unstable and undergoes decomposition to cluster species in the solid; however, whether such decomposition is due to initial decarboxylation or to CO labilization (see below) is as yet unknown. The triruthenium analog is apparently more stable; solutions in dry THF are characterizable spectrally and can be shown to react with small ammounts of added acid or water to give $Ru_3(CO)_{12}$ or $HRu_3(CO)_{11}^-$, respectively. In solution $Ru_3(CO)_{11}(CO_2H)^-$ also

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demonstrates the high lability toward other ligands and toward reaction with H_2 shown previously for the methoxycarbonyl analog (34, see below). We will extend these studies to the other carbonyls of the iron triad and possibly to substitiuted derivatives of these and to other carbonyls demonstrated to be precursors of active WGSR catalysts. In addition it will be especially interesting to compare the behaviors of simple hydroxycarbonyl complexes in aprotic solvents to gas phase studies of such systems now in progress(67).

The Pco dependence of the decarboxylation kinetics of $Ru_3(CO)_{11}(CO_2H)^-$ as well as the tendency of the methoxycarbonyl analog to undergo CO loss and rearrangement to a bridging $n^2-CO_2CH_3$ group(50,59)) suggested to us the probability that the formation of such adducts leads to dramatically enhanced ligand substitution lability of the triruthenium clusters. Kinetics studies with the well characterized $Ru_3(CO)_{11}(CO_2CH_3)^-$ ion in solution have confirmed this proposal(eq 10)(34).

(10) $Ru_3(CO)_{11}(CO_2CH_3)^- + L \longrightarrow Ru_3(CO)_{10}L(CO_2CH_3)^- + CO$
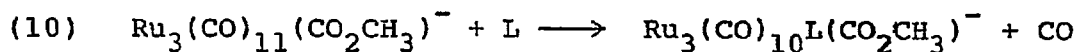
Thus, the role of methoxide and other strong nucleophiles used as cofactors in some catalytic applications of metal carbonyls may not only be to activate coordinated CO for further reactions but may also be to labilize ligands. This is likely to prove especially important for reactants which require coordination for activation. For example, we have shown that methanolic solutions of $Ru_3(CO)_{11}(CO_2CH_3)^-$ react readily at room temperature with H_2 to give $HRu_3(CO)_{11}^-$ plus methyl formate(eq 11)(31). In contrast $Ru_3(CO)_{12}$ does not react measurably with H_2 under comparable conditions. (Methyl formate may be of some interest as a precurser of acetic acid(68)).

(11) $Ru_3(CO)_{11}(CO_2CH_3)^- + H_2 \longrightarrow HRu_3(CO)_{11}^- + HCO_2CH_3$
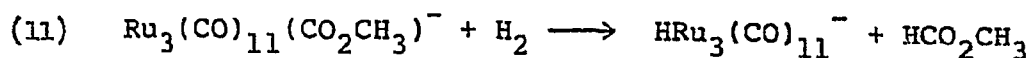
, · We are presently investigating the quantitative details·of both the substitution kinetics and the reaction with H_2 with the goal of evaluating the reaction mechanisms and propose to éxtend these studies to other mono- and polynuclear alkoxycarbonyl metal carbonyls in order to examine the effect of metal nuclearity and overall mechanistic generality. [Marko has recently described a similar, but slower, reaction of H_2 with $Co(CO)_4(CO_2Et)$; however, this alkoxycarbonyl species is not prepared directly from the alkoxide ion plus cobalt carbonyl(69).] There is certainly precedent for nucleophile induced (or catalyzed) ligand substitution reactions(70), but few quantitative studies with well defined adducts such as $Ru_3(CO)_{11}(CO_2CH_3)^-$. The reactivities of different alkoxylcarbonyl adducts $Ru_3(CO)_{11}(CO_2R)^-$ will be investigated in order to assess the electronic and steric effects of varying R. Lastly, qualitative observations of the iron analog $Fe_3(CO)_{11}(CO_2CH_3)^-$ indicate this species to undergo a different route,. namely cluster fragmentation to $Fe(CO)_4CO_2CH_3^-$ (32), .a possible

(12) $Fe_3(CO)_{11}(CO_2CH_3)^- + 3\ CO + 2\ CH_3O^- ---- 3\ Fe(CO)_4(CO_2CH_3)^-$.

explanation for the different product distributions observed when iron or ruthenium carbonyls are used with methoxide as a cocatalyst for the reductive carbonylations of nitroarenes (10). We propose to investigate this reaction in greater detail in order to evaluate the mechanistic relationship, if any, to the other alkoxide promoted reactions.

The various mechanistic investigations described above will be carried out using a full range of quantitative methods,e.g., H and C-13 NMR, GC-MS and optical and IR stopped-flow kinetics spectroscopy. The effects of variation of. a full range of reaction parameters (T, solvent, ligand substituents, the concentration and identity of counter

ion's in the case of ionic reactions, etc.) will be surveyed in a manner described in previous studies from this laboratory (6,11,32)

D. APPARATUS AND FACILITIES:

The Department of Chemistry, UCSB, has the full range of glass, machine and electronic shops and of instrumentation accessible for the successful prosecution of the proposed research. These include a Mass Spectrometer facility with AEI-MS60 GC-MS and ZAB-2F micromass high resolution mass spectrometers and a NMR facility with Nicolet 300 MHz multinuclear FT, a Varian XL-100 FT and several smaller NMR spectrometers. Both facilities are supervised by full-time professional, Ph.D level, staff spectroscopists. In addition, the University is in the process of establishing a major facility for X-ray structural characterization of materials to be supervised by a full time professional crystallographer and overseen by Prof. J.A.Ibers who will join the UCSB faculty this year. The Department also has several PDP and VAX computers with a number of terminals (including one in the PI's laboratory) for in house computation and for accessing the campus National AS/6 digital computer facility. Instruments dedicated to the present research of this group or accessible for major use (>50%) include a Durham stopped flow spectrophotometer, several high resolution, scanning UV-vis spectrophotometers equipped with constant temperature cell compartments and interfaced to a small computer, a Perkin-Elmer 683 IR spectrometer modified for stopped flow kinetics, a Hewlett-Packard 5830A integrating gas chromatograph for gas and liquid analysis, an IBM EC 225 Voltammetric Analyzer for electrochemical studies and a well equipped VAC glove box for handling air and moisture sensitive compounds.

E. REFERENCES AND NOTES:

1] R.M.Laine, R.G.Rinker, P.C.Ford; J. Amer. Chem. Soc., 99, 252 (1977)

2] a) C.H.Cheng, D.E.Hendricksen, R.Eisenberg; ibid, 99, 2791 (1977).
b) H.Kang, C.H.Mauldin, T.Cole, W.Slegeir, K.Cann, R.Pettit, ibid, 99,
8323 (1977). c) R.B.King, C.C.Frazier, R.M.Haines, A.D.King; ibid 100,
2959 (1978)

3] a) P.C.Ford, Accounts of Chem. Research, 14, 31 (1981). b) J.
Halpern, Comments on Inorg. Chem. 1, 1 (1981) c) R.Laine, "Aspects of
Homogeneous Catalysis", vol 5, R.Ugo editor, pp217-240, D.Reidel,
London, 1984.

4] A.D.King, R.B.King, D.B.Yang; J.C.S.Chem. Commun. 526 (1980)

5] a) N.von Kutepov, H.Kindler; Angew. Chem, 72, 802 (1960). b)
R.M.Laine; J. Amer. Chem. Soc., 100, 6451 (1978). c) R.H.Fish,
A.D.Thormodsen, G.A.Cremer; ibid, 104, 5234 (1982)

6] D.C.Gross, P.C.Ford, Inorg. Chem., 21, 1702 (1982)

7] C.Kubiak, J. Amer. Chem. Soc., 105, 7465 (1983)

8] J.M.Lehn, R.Ziessel, Proc. Nat'l Acad. Sci. 99, 701 (1982)

9] a) M.J.Chen, H.M.Feder, J.W.Rathke, J. Amer. Chem. Soc., 104, 7346
(1982). b) G. Braca et al, C1 Molecule Chem. 1, 9 (1984)

10] H.Alper, K.E.Hashem, ibid, 103, 6514 (1981)

11] R.Trautman, D.C.Gross, P.C.Ford; submitted for publication.

12] H. Mauermann, R. Pearson; J. Am. Chem. Soc. 104, 1444 (1982)

13] C.Ungermann, V.Landis, S.Moya, H.Cohen, H.Walker, R.G.Rinker,
P.C.Ford, J. Amer. Chem. Soc., 101, 5922 (1979)

14] P.Yarrow, H.Cohen, C.Ungermann, D.Vandenberg, R.G.Rinker, P.C.Ford,
J. Mol. Cat., 22, 239 (1983)

15] a) D. Darensbourg el al, J. Amer. Chem Soc. 103, 1297, 3223 (1981).
b) A.D.King, R.B.King, D.B.Yang, ibid, 103, 2699 (1981)

16] J.A.Cusumano, R.A.Dalla Betta, R.B.Levy, "Catalysis in Coal
Conversion", Academic Press, 1978

17] D.Vandenberg, T.M.Suzuki, P.C.Ford, J. Organomet. Chem., in press

18] P.C.Ford, R.G.Rinker, C.Ungermann, R.Laine, V.Landis, S.Moya, J.
Amer. Chem. Soc., 100, 14595 (1978)

19] D.Vandenberg, work in progress

20] a) W.R.Tikkanen, E.Binamira-Soriaga, W.C.Kaska, P.C.Ford, Inorg.

, Chem. 22, 1147 (1983); 23, 141 (1984). b) W.R.Tikkanen, W.C.Kaska, P.C.Ford, et al, Inorg. Chem. in press

21] W.Keim, Chpt 3 in "Catalysis in C1 Chemistry", W.Keim ed., D.Reidel Publishing Co, Dordrecht, Holland, 1983

22] E.Binamira-Soriaga, W.C.Kaska; work in progress

23] A.Pardey, work in progress

24] B.Wayland, B.A.Woods, R.Pierce; J. Amer. Chem. Soc., 104, 302 (1982)

25] a) P.A.Marnot, R.R.Ruppert, J.P.Sauvage; Nouv. J. Chim.; 5, 543, (1981). b) D.Mahajan, C.Creutz, N.Sutin, reported at the 185th ACS National Meeting, Seattle, March 1983, INORG 186

26] K.Keneda et al, J. Mol. Cat. 9, 227 (1980); 12, 385 (1981); Chem Let. 1763 (1981)

27] T.M.Suzuki et al, Bull. Chem. Soc. Jpn, 56, 463 (1983)

28] T.M.Suzuki, T.Yokoyama; Polyhedron, 2, 127 (1983)

29] a) R.Hemmerich, W.Keim, M.Roper; JCS Chem. Commun. 428 (1983); b) P. Garrou, D. Hunter et al Organomet. 3, 95(1984)

30] H.W.Walker, R.G.Pearson, P.C.Ford; J. Amer. Chem. Soc., 105, 1179 (1983)

31] D.Taube, work in progress

32] D.C.Gross, P.C.Ford, submitted for publication

33] Young Chung work in progress

34] M. Anstock, D.Taube, D.C.Gross, P.C.Ford, J.Amer.Chem.Soc, in press, June 1984

35 R.F. Jordan; J.R.Norton, ibid, 104, 1255 (1982)

36] a) D.F.Shriver, Acc.Chem.Res. 3, 231 (1970); b) R.A.Schumm, in "Transition Metal Hydrides" E.L.Muetterties, ed. Marcel Dekker, 1971, pp203-269

37] S.C.Kao, M.Y.Darensbourg; Organonmet.,3, 346 (1984)

38] R.D.Wilson, R.Bau, J.Amer.Chem.Soc., 98, 4689 (1976)

38] a) J.Lewis et al, JCS Chem.Commun., 295 (1980). b) R.Bau et al, Angew.Chem.I.E.; 18, 80 (1979)

40] a) D.F.Shriver, S.G.Shore et al, J.Amer.Chem.Soc., 105, 5630 (1983); b) B.D.Dombeck, ibid, 102, 6855 (1980); c) J.F.Knifton, ACS Symp Series, 152, 213 (1981); d) G.Braca et al, Ind.Eng.Chem.Prod.Res.Dev., 20, 115 (1981)

41] Z.Iqbal, T.C.Waddington; J.Chem.Soc. A; 2958 (1968)

42] P.Yarrow, P.C.Ford; J.Organomet.Chem. 214, 115 (1981)

43] A.Friedman, work in progress

44] J.Knight, M.J.Mays; J.Chem.Soc. A 711, (1970)

45] K.B.Wiberg, "Physical Organic Chemistry", J. Wiley, 1964, chpt 2-9

46] D.B.Beach, S.P.Smit, W.L.Jolly; Organomet. 3, 556 (1984)

47] M.F.Desrosiers, unpublished observations

48] J.C.Bricker, C.C.Nagel, S.G.Shore, J.Amer.Chem.Soc., 104, 1444
(1982)

49] B.F.G.Johnson, J.Lewis, P.R.Raithby, G.Suss-Fink, J.C.S.Dalton,
1356 (1979)

50] D.C.Gross, Ph.D. Dissertation, U.C.S.B., 1983

51] S.G.Shore, reported at the St. Louis National ACS Meeting, April
1984

52] C.E.Housecraft, K.Wade, B.C.Smith; J.C.S.Chem.Commun., 765 (1978)

53] J.Keister, SUNY Buffalo, private communication.

54] G.Suss-Fink, J.Reiner; J.Mol.Cat., 16, 231 (1982)

55] W.Slegier, R.Sapienza, B.Easterling. Ch. 21 in "Catalytic
Activation of Carbon Monoxide", ACS Symp. Series 152 (1981), P.C.Ford
ed.

56] B.D.Dombeck, A.M.Harrison; J.Amer.Chem.Soc., 105, 2485 (1983) and
references therein

57] R.G.Pearson, H.W.Walker, H.Mauermann, P.C.Ford; Inor.Chem., 20,
2741, (1981)

58] K.Doxse, R.H.Grubbs; J.Amer.Chem.Soc., 103, 7696 (1981)

59] H.Kaesz, Y.C.Lin, N.M.Boag, A.Mayer; Inorg.Chem. 21, 1706 (1982)

60] H.Motschi, R.J.Angelici; Organomet.,1, 343 (1982)

61] C.P.Casey, M.A.Andrews, R.E.Rinz; J.Amer.Chem.Soc., 101, 741 (1979)

62] W.Tam, W.Wong, J.A.Gladysz, ibid, 101, 1591 (1979)

63] D.Milstein, J.L.Huckaby, ibid, 104, 6150 (1982)

64] F.Rivetti, U.Romano; J.Organomet.Chem., 174, 221 (1979)

, 65] D.Darensbourg, Isreal.J.Chem. 15, 247 (1977)

66] J.E.Bercaw, L.V.Goh, J.Halpern; J.Amer.Chem.Soc., 94, 6534 (1972)

67] R.Squires, private communication

68] R.L.Pruett, R.T.Kacmarcik; Organomet. 1 1893(1982)

69] F.Ungvary, L.Marko; Organomet., 2, 1608 (1983)

70] T.Brown, P.A.Bellus, Inorg.Chem., 17, 3727 (1978)

III. PERSONNEL:

A. PRINCIPAL INVESTIGATOR:

Peter C. Ford was born in California in 1941. His undergraduate work at Caltech (B.S., 1962) was followed by graduate study on organic oxidation mechanisms at Yale University where he worked with Kenneth B. Wiberg and received his Ph.D in 1966. The following year was spent as a NSF Postdoctoral Fellow at Stanford University with Henry Taube. In 1967, he joined the Department of Chemistry, University of California, Santa Barabara, where he has held the rank of Professor since 1977. Awards include a Dreyfus Foundation Teacher-Scholar Grant (1971-75), a Fulbright Fellowship and Visiting Fellowship in the Research School of Chemistry, Australian National University (1974) and a Guest Professorship at the H.C.Orsted Institute of the University of Copenhagen (1981). Research interests are concerned with mechanistic Inorganic and Organometallic Chemistry. Current areas of emphasis are the reactions of coordinated ligands including homogeneous catalysis and the photochemistry and photophysics of transition metal compounds. Titles of recent publications are listed in Sec. G below.

B. RESEARCH GROUP:

Members of the group presently involved in aspects of the DOE supported catalysis research include five Ph.D. candidates: Douglas Taube (B.S., CSU Hayward), David Vandenberg (B.S., CSU Hayward), Alvaro Pardey (B.S., Universidade Centrale, Venezuela; supported by a Venezuelan government Fellowship), Tyrina Chin (B.S., U.C.Berkeley) and Alan Friedman (B.S. San Diego State Univ.). In addition one postdoctoral fellow Dr. Young Chung (Ph.D. 1984, Brown University) is participating in this research. Over the past three years, three Ph.D. candidates, H. Walker (1981), W.Tikkanen (1982) and D. Gross (1983), have completed their theses on work based on the DOE supported research while the following postdoctoral fellows have also contributed: Dr. Ray Trautman, Dr. Paul Yarrow and Dr. Martin Anstock (NATO Fellow from the Univ. of Aachen, Germany). Titles of theses completed since 1981 and based on DOE-OBES sponsored research are listed in Sec. E below.

C.CURRENT RESEARCH SUPPORT:

[1] "Homogeneous Catalysis of the Water Gas Shift Reaction", a contract from the Department of Energy, Office of Basic Energy Sciences. $71,000 for the period 12/83--11/84

[2] "Photochemcal Reaction Mechanisms of Transition Metal Complexes", a grant from the National Science Foundation. $71,000 for the period 2/84--1/85

[3] "Activation Volumes for the Photosubstitution Reactions of Transition Metal Complexes", a grant from the National Science Foundation, (Division of International Programs, U.S.-Germany Cooperative Science Program). $13,160 for the period 8/83--7/86

D.PENDING PROPOSALS:

[1] The present proposal is a request for continued DOE-OBES support for research in homogeneous catalysis, i.e, a renewal of item 1 above

[2] A proposal will be submitted later this year for renewal of the NSF grant listed in item 2. There will be no significant overlap of the research supported by the two separate grants.

E. THESES based on research sponsored by the DOE contract since 1981

[1] Howard W. Walker, Ph.D. (1981)
    "Rates of Deprotonation and pKa Values of Some Transition Metal Carbonyl Hydrides in Methanol"

[2] Wayne R. Tikkanen, Ph.D. (1982)
    "Dinuclear Ligands Utilizing 1,8-Napthyridine as the Bridging Unit: Complexes with Copper and Rhodium"

[3] David C. Gross, Ph.D. (1983)
    "Reaction Kinetics of the Nucleophilic Activation of Coordinated Carbon Monoxide in Mono- and Trinuclear Complexes of Iron, Ruthenium and Osmium"

[4] In addition two Chemical Engineering M.S. theses based on collaborative kinetics studies of WGSR catalysts were completed. The names of the students were N.L.Agarawalla (M.S., 1982) and Holly R. Nony (M.S., 1983)

F. PRESENTATIONS at Regional, National and International Meetings

    Since 1981 fourteen presentations have been made at regional, national and international meetings by members of this research group describing the catalysis research sponsored by DOE. These include invited lectures in 1984 as part of the following meetings:

    [1] NSF/CONICIT US/Latin America Workshop on Catalysis, Caracus, Vz, March 1984

    [2] Symposium on "the Mechanisms of Synthesis Gas Catalysis and Related Reactions", Sponsored by the Division of Petroleum Chemistry at the American Chemical Society National Meeting, St. Louis, April, 1984.

    [3] In addition an invited lecture will be presented at the "Symposium on Metal Cluster Chemistry" sponsored by the 1984 International Chemical Congress of Pacific Basin Societies, Honolulu, December 1984.

G. PUBLICATIONS by the Principal Investigator since 1981:
     Those related to the DOE-OBES sponsored catalysis research are
marked by a #. Abstracts of DOE related research manuscripts "in press"
or "submitted" are included as an appendix to this proposal: *Removed*

71. M. Nishizawa and P. C. Ford*, "Long Wavelength Excitation of
    Hexacyano Cobaltate (III), Co(CN)$_6^{3-}$, in Aqueous Solution.
    Questions Regarding Intersystem Crossing Efficiencies,"
    Inorg. Chem. 20, 294 (1981).

72. M. Nishizawa and P. C. Ford,* "The Photochemistry of the
    Dinuclear Cobalt (III) Complexes Co(CN)$_5$(μ-CN)CO(NH$_3$)$_5$ and
    CO(CN)$_5$(μ-NC)CO(NH$_3$)$_5$. Intramolecular Energy Transfer Between
    Metal Centers, Inorg. Chem., 20, 2016 (1981).

73. M. A. Bergkamp, R. J. Watts* and P. C. Ford,* "Intramolecular
    Energy Transfer in a Rhodium Metalloorganic Bichromophore System:
    Photochemical and Photoluminescence Studies," Inorg. Chem., 20,
    1764 (1981).

≠74. P. C. Ford, "The Water Gas Shift Reaction: Homogeneous Catalysis
     by Ruthenium and Other Carbonyls," Accounts of Chemical Research,
     14, 31 (1981).

≠75. P. C. Ford,* P. Yarrow and H. Cohen, "The Water Gas Shift Reaction
     as Catalyzed by Ruthenium Carbonyl in Acidic Solution," ACS
     Symposium Series 152, 95 (1981).

76. M. A. Bergkamp, R. J. Watts* and P. C. Ford,* "Temperature
    Dependence of the Luminescence Lifetimes of Halopentaammine and
    Hexaammine Rhodium (III) Compounds in the Solid State," J. Phys.
    Chem. 85, 686 (1981).

≠77. P. I. W. Yarrow and P. C. Ford,* "The Nature of Mononuclear
     Ruthenium Carbonyl Complexes in Solution," J. Organomet Chem.
     214, 115 (1981).

≠78. Peter C. Ford, editor: "Catalytic Activation of Carbon Monoxide,"
     ACS Symposium Series Volume No. 152, American Chemical Society,
     Washington, D.C., 1981

≠79. H. W. Walker and P. C. Ford,* "Synthesis and Characterization
     of [PPN][HRu(CO)$_4$] and a Convenient Route to [PPN][HOs(CO)$_4$]"
     J. Organomet Chem. 214, C43 (1981).

≠80. R. G. Pearson,* H. W. Walker, H. Mauermann and P. C. Ford,
     "Hydrogen Migration Mechanism for Ligand Substitution
     Reactions in Metal Carbonyl Hydrides," Inorg. Chem. 20,
     2741 (1981).

81. Peter C. Ford,* "The Ligand Field Photosubstitution Reactions of
    d^5 Hexacoordinate Metal Complexes," Coord. Chem. Rev. 44, 61 (1982)

≠82. R. G. Pearson* and P. C. Ford,* "The Brønsted Acidity of Transition
     Metal Hydrides," Comments on Inorganic Chemistry, 1, 279 (1982).

≠83. H. W. Walker and P. C. Ford*, "Isotope Effects in the Infrared Spectra of the Metal Carbonyl Hydride/Deuteride Anions (H/D)M(CO)$_4^-$ (M=Fe, Ru or Os)" Inorg. Chem. 21, 2509 (1982)

84. D. Sexton, L. Skibsted, D. Magde and P. C. Ford*, "Ligand Effects on the Dynamics of Ligand Field Excited States: Photosubstitution Reactions of the Rhodium (III) Complexes cis- and trans-Rh(NH$_3$)$_4$Br$_2^+$ in 298 K Aqueous Solution," J. Phys. Chem. 86, 1738 (1982)

≠85. D.C. Gross and P.C. Ford, "Kinetics of Carbon Monoxide Activation: Reactions of Methoxide and Hydroxide with Ruthenium and Iron Carbonyls", Inorganic Chemistry, 1982, 21, 1702.

86. P.C. Ford, "Photosubstitution and Photoisomerization Reactions of Werner Complexes," Chapter 13.2 in Inorganic Reactions and Methods, J.J. Zuckerman, editor, Verlag Chemie, in press.

87. P.C. Ford, David Wink and J. DiBenedetto, "Mechanistic Aspects of the Photosubstitution and Photoisomerization Reactions of d^6 Metal Complexes," Progress in Inorganic Chemistry, 30, 213-271 (1983).

88. W. Weber, R. Van Eldik, H. Kelm, J. DiBenedetto, Y. Ducommen, H. Offen and P. C. Ford, "Pressure Effects on the Photochemical and Photophysical Properties of the Rhodium (III) Complexes RhA$_5$X^{2+} (X = Cl$^-$ or Br, A = NH$_3$ or ND$_3$) in Aqueous Solution," Inorg. Chem., 22, 623 (1983).

89. L.H. Skibsted, W. Weber, R. Van Eldik, H. Kelm* and P.C. Ford*, "Pressure Effects on Photoisomerization/Photosubstitution Reactions of the Rhodium (III) Complexes cis- and trans Rh(NH$_3$)$_4$Xy^{n+} (X = Cl or Br, Y = X of H$_2$O)," Inorg. Chem., 22, 541 (1983).

90. M.F. Desrosiers and P.C. Ford*, "Photochemical Fragmentation of the Cluster Ru$_3$(CO)$_{12}$: Evidence Against Homolytic Bond Cleavage, Organometallics, 1, 1715 (1982).

≠91. H.W. Walker, R.G. Pearson* and P.C. Ford*, "Brönsted Activities or Carbonyl Hydride Complexes of Iron, Ruthenium and Osmium: pKa Values of Deprotonation Rates in Methanol Solution," J. Amer. Chem. Soc., 105, 1179 (1983).

92. D.A. Sexton, P.C. Ford* and D. Magde*, "Dual Emissions in the Solution Phase Photoluminescence of Rhodium (III) Complexes: Ligand Field Fluorescence from a Heavy Metal Complex?" J. Phys. Chem., 87, 197 (1983).

≠93. W.R. Tikkanen, E. Binamira-Soriaga, W.C. Kaska* and P.C. Ford*, "Crescent Shaped Dinuclear Complexes: A Rhodium Complex of the New Tetradentate Ligand 2.7-bis(2'-pyridyl)-1,8-napthyridine (bpnp), [Rh$_2$(bpnp)(u- CH$_3$CO$_2$)3]-(PF$_6$)', Inorg. Chem., 21. 1147 (1983).

≠94. P. Yarrow, H. Cohen, C. Ungermann, D. Vandenberg, R.G. Rinker and P.C. Ford*, "Homogeneous Catalysis of the Water Gas Shift Reaction by Ruthenium Carbonyl Complexes: Studies in Acidic Solution," J. Molecular Catalysis, 22, 239-256 (1983).

95. L.H. Skibsted and P.C. Ford, "Photoreactions of Rhodium (III) Complexes: The Cyanoamines Rh(NH$_3$)$_5$CN^{2+} and trans- Rh(NH$_3$)$_4$(H$_2$O)CN^{2+}," Inorg. Chem., 22, 2749 (1983).

96. Peter C. Ford "Case Study I: The Photosubstitution Reactions of Rhodium (III) Ammine Complexes" J. Chemical Education, 60, 829 (1983).

97. W.R. Tikkanen, E. Binamira-Soriaga, W.C. Kaska* and P.C. Ford*, "Preparation and Spectral and Electrochemical characterization of Dirhodium (II) Complexes with Bridging 1,8-Naphthyridne Ligands: 2,7-Bis(2-pyridyl)-1,8-naphthyridine, 5,6-Dihydro(2,3,8,9b) dipyrido-1,10-phenanthroline, 2,2-pyridyl)-1,8-Naphthyridine and 1,8-Naphthyridine. X-ray Structure of Tris(μ-acetate)-2,7 -bis(2-pyridyl)-1,8-naphthyridinedirhodium (II) Hexafluorophosphate," Inorg. Chem., 23, 141-6 (1984).

98. D.A. Sexton, J.C. Curtis, H. Cohen and P.C. Ford*, "The Outer Sphere Charge Transfer Photochemistry of Ruthenium (III) Complexes: Flash Photolysis of $Ru(NH_3)_5py^{3+}$, Halide Ion Pairs, Inorg. Chem., 23, 49-52 (1984).

99. M. Nishizawa, T.M. Suzuki, S. Sprouse, R.J. Watts* and P.D. Ford*, "Ligand Steric Effects on Photophysical and Photochemical Properties of Transition Metal Complexes. 3,3'-Dimethylbipyridine Complexes of Rhodium (III)", Inorg. Chem., in press.

100. M.E. Frink, D. Magde, D. Sexton and P.C. Ford*, "Reaction Dynamics and Hydroxide Ion Quenching of Rhodium (III) Ligand Field Excited States: Photo Reactions of $Rh(NH_3)_5I^{2+}$", Inorg. Chem., 23, 1238 (1984).

≠ 101. W. R. Tikkanen, C. Kruger, K. Bomben, W. L. Jolly, W. C. Kaska* and P. C. Ford*, "Synthesis, Characterization and X-Ray Molecular Structures of Mono- and Dinuclear Copper Complexes with 2,7-bis(2-pyridyl)-1,8-Naphthyridine," Inorg. Chem., in press.

102. W. Weber, J. DiBenedetto, H. Offen, R. van Eldik* and P. C. Ford*, "Pressure Effects on the Photochemical and Photophysical Properties of the Rhodium(III) Ion, $Rh(NH_3)_5Cl^{2+}$ in Nonaqueous Solvents," Inorg. Chem., in press.

≠ 103. A. T. Baker*, W. R. Tikkanen, W. C. Kaska and P. C. Ford*, "Observation of both Bridging and Chelating Modes of a 2-(2'-pyridyl)-1,8-napthyridine Ligand (pynp) in a Single Dirhodium (II) Complex: the X-ray Structure of $[Rh_2(pynp)_3Cl_2]- [PF_6]_2-CH_3CN$," Inorg. Chem., in press.

≠ 104. P. C. Ford, "Mechanistic Studies Related to the Activation of Carbon Monoxide via the Water Gas Shift Reaction," Preprints of the Division of Petroleum Chemistry, ACS, 29, pp567-576 (1984).

105. M. F. Finlayson, P. C. Ford and R. J. Watts, "Excited States and Transients Formed in Laser Flash Photolysis of Ir(III) Complexes of 2,2'-Bipyridine," submitted.

≠ 106. M. Anstock, D. Taube, D. Gross and P. C. Ford*, "Reactivities of Activated Carbonyl Clusters. Ligand Substitution Kinetics of the Methoxycarbonyl Adduct, $Ru_3(CO)_{11}(CO_2CH_3)^-$," J. Amer. Chem. Soc., in press.

107. D. A. Sexton, L. H. Skibsted, D. Magde and P. C. Ford*, "Ligand Effects on the Excited State Dynamics of Rhodium (III) Complexes. Photoluminescence Properties of the Tetraammine Complexes $Rh(NH_3)_4XY^{n+}$ and their Relationship to Photoreactivity," submitted.

108. M. E. Frink, P. C. Ford* and L. H. Skibsted*, "Low Temperature Luminescence properties of Mono- and Dinuclear Tetraammine Complexes of Rhodium (III) and Iridium (III)," Acta Chem. Scand. Ser A, in press.

≠ 109. D. M. Vandenberg, T. M. Suzuki and P. C. Ford*, "Homogeneous Catalysis of the Water Gas Shift Reaction by Iridium Carbonyl in Alkaline Solution," *J. Organometallic Chem.*, in press.

110. John DiBenedetto, R. J. Watts and P. C. Ford*, "Pressure Tuning of Excited State Equilibria as Probed by Photoemission Properties of Iridium Complexes," submitted.

≠ 111. R. J. Trautman, D. C. Gross and P. C. Ford*, "Nucleophilic Activation of Coordinated Carbon Monoxide II. Reaction of the Mononuclear Complexes $M(CO)_5$ (M = Fe, Ru, or Os) with Hydroxide and Methoxide," submitted.

≠ 112. D. C. Gross and P. C. Ford*, "Nucleophilic Activation of Coordinated Carbon Monoxide III. Hydroxide and Methoxide Reactions with the Trinuclear Clusters $M_3(CO)_{12}$ (M = Fe, Ru, or Os). Implications with Regard to Catalysis of the Water Gas Shift Reaction," submitted.

113. M. E. Frink and P. C. Ford*, "Deuterium Isotope Effects in the Ligand Field Excited State Kinetics of Hexamminerhodium (III)," submitted.

114. M. F. Desrosiers, D. Wink and P. C. Ford*, "Photoreactions of the Trinuclear Cluster $Ru_3(CO)_{12}$. Evidence for Intermediates in Competing Fragmentation and Ligand Substitution Pathways," in preparation.

≠ 115. D. Taube and P. C. Ford*, "Kinetics of the Activation of Dihydrogen by the Methoxycarbonyl Adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$," in preparation.