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PREPARATION AND REACTIVITY OF RUTHENIUM CARBONYL ANIONS: IMPLICATIONS FOR CATALYSIS OF THE WATER-GAS SHIFT REACTION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
The Degree of Doctor of Philosophy in the Graduate School of The Ohio State University

By
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The Ohio State University
1983

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Advisor
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To my Mom and Dad
ACKNOWLEDGEMENTS

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Studies in Transition Metal Chemistry. Professors Daryl H. Busch, Daniel L. Leussing, Devon W. Meek, and Eugene P. Schram.
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INTRODUCTION

In the past twenty-five years, the field of transition metal cluster chemistry has expanded considerably. Early research in the 1960's was directed toward the preparation and characterization of these novel cluster compounds. These first attempts to prepare cluster compounds generally resulted in low yields and complex mixtures of products. During the 1970's, understanding of cluster bonding and reactivity increased rapidly, resulting in the development of rational, efficient synthetic methods. The current availability of metal cluster compounds in practical quantities has stimulated considerable interest in potential applications.

The most promising application of transition metal clusters has appeared to be in the area of catalysis [1-3]. In this regard, transition metal carbonyl clusters have received attention for a number of reasons. First, the presence of triangular arrays of metals is a structural feature of both metal clusters and metal surfaces. These triangular arrays of metal atoms exhibit multiple substrate binding capability, a property considered essential to many catalytic processes [4]. Additionally, coordinated ligands or substrates demonstrate great mobility between metal centers on both metal clusters and metal surfaces.
Thus, it was suggested that metal clusters may serve as models for reactions which occur at metal surfaces in heterogeneous catalysis [7-9]. In recent years, metal clusters have received attention as potential homogeneous catalysts in their own right [1, 10-13].

The primary concern of this investigation was to study the chemistry of ruthenium cluster anions relevant to the homogeneous catalysis of the water-gas shift reaction [14-20]. In the course of this work, it was necessary to synthesize and study the reactivity of a number of new ruthenium carbonyl anions. Also, work was initiated in a technique for the carbon-13 enrichment of transition metal carbonyl compounds. Thus, the introduction is presented in three parts: a discussion of the bonding and structure of transition metal clusters, a review of transition metal clusters in catalysis, and a survey on the available methods for carbon-13 enrichment of transition metal carbonyl compounds.

I. Structure and Bonding in Transition Metal Clusters

Transition metal clusters have been defined by Cotton [21] as "a finite group of metal atoms which are held together, to a significant extent, by bonds directly between the metal atoms." As the study of metal clusters progressed in the 1960's, it became apparent that the effective atomic number rule could not adequately describe the bonding in terms of two-center two-electron bonds between metal atoms [22]. For example, the octahedral structures of H₂Ru₆(CO)₁₈, Ru₆C(CO)₁₇, and Rh₆(CO)₁₆ were difficult to rationalize in terms of an inert gas configuration because they each contain two electrons too many to
allocate a bond pair to each octahedral edge [23,24]. In 1971, Williams [25] and Wade [26] independently applied the delocalized bonding theories developed for boron hydrides and carboranes to transition metal cluster compounds. This skeletal electron counting procedure has proved to be a successful method for predicting the geometries of small (3-6 metal atoms) cluster compounds [27-29]. A number of semiempirical LCAO-MO treatments have been applied to metal cluster [30,31]. Extended Hückel calculations have been employed to predict the shapes of large metal cluster compounds [32].

As stated above, the skeletal electron procedure has been accepted as the most reliable method of determining the geometric arrangement of metal atoms in small cluster compounds. In metal clusters, the metals are arranged in triangular arrays which, in turn, form 3-dimensional polyhedra. The shape of the polyhedron depends on the number of skeletal electrons in the cluster available for bonding. In a transition metal ion, there are nine valence orbitals, one ns, three np, and five (n-1)d. From these nine valence orbitals, six equivalent hybrid orbitals and three unhybridized orbitals (d<sub>xy</sub>, d<sub>xz</sub>, d<sub>yz</sub>) may be formed. In an M(CO)<sub>n</sub> fragment, the skeletal electron approach assigns six low-lying orbitals, primarily for metal-ligand bonding, and three higher energy orbitals for metal-metal bonding. The three higher lying orbitals of the fragment are allowed to mix and form skeletal molecular orbitals [25,26]. This distribution coincides for that obtained in an M(CO)<sub>3</sub> fragment, which can be deduced more quantitatively using the frontier orbital approach applied by Hoffman [33]. If each metal vertex contributes three atomic orbitals for skeletal bonding, (n+1) bonding
molecular orbitals will be generated for an N-vertex polyhedron. If an N-vertex cluster contains (N+1) skeletal bonding electron pairs, the metal atom vertices will occupy the corners of an n-vertex polyhedron. This corresponds to the closo arrangement. A cluster containing fewer vertices but the same number of electron pairs will adopt a geometry based on the closed n-vertex polyhedron, but with one or more vertices absent. A cluster containing more vertices but the same number of electron pairs will adopt a geometry where one or more of the faces of the closed n-vertex polyhedron is capped. Thus, the main structural arrangements are capped, closo, nido, arachno, and hypho, corresponding to N atoms bonded to one another by n, n+1, n+2, n+3, and n+4 skeletal electron pairs, respectively. These relationships for each structural type are summarized in Table 1 and known examples are given in Figure 1.

The skeletal electron counting scheme has been complemented by the frontier orbital, isolobal approach of Hoffman [33]. Elian and Hoffman carried out extended Hückel calculations on metal carbonyl fragments and assessed their bonding capabilities through a frontier orbital approach [34]. The orbital properties for a given M(CO)ₙ fragment are calculated such that the spatial orientation and energy of the frontier orbitals available for cluster bonding are known. This approach has been applied to the study of geometric and electronic structure of only a few metal cluster systems [35]. To date, no satisfactory method has been obtained to predict the spatial arrangements of the ligands in transition metal clusters. The carbon monoxide and hydride ligands in metal clusters are each capable of terminal, edge-bridging, and face-bridging bonding modes. In metal carbonyl clusters, terminally bound carbon monoxide
Table 1
Structural Types for Cluster with N Skeletal Metal Atoms

<table>
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<th>Skeletal Electron Pairs</th>
<th>Structural Type</th>
<th>Geometry</th>
<th>Examples</th>
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<tr>
<td>n+4</td>
<td>hypho</td>
<td>closed polyhedron-3 vertices</td>
<td>---</td>
</tr>
<tr>
<td>n+3</td>
<td>arachno</td>
<td>closed polyhedron-2 vertices</td>
<td>Os$<em>4$(CO)$</em>{12}$H$_3$I, [HFe$<em>4$(CO)$</em>{13}$]$^-$</td>
</tr>
<tr>
<td>n+2</td>
<td>nido</td>
<td>closed polyhedron-1 vertex</td>
<td>Fe$<em>5$(CO)$</em>{15}$C, [HRu$<em>6$(CO)$</em>{18}$]$^-$</td>
</tr>
<tr>
<td>n+1</td>
<td>closo</td>
<td>closed polyhedron</td>
<td>Rh$<em>6$(CO)$</em>{16}$, H$_2$Ru$<em>6$(CO)$</em>{18}$</td>
</tr>
<tr>
<td>n</td>
<td>capped</td>
<td>closed polyhedron</td>
<td>Os$<em>7$(CO)$</em>{21}$, [Rh$<em>7$(CO)$</em>{16}$]$^{3-}$</td>
</tr>
</tbody>
</table>
Figure 1. Examples of Metal Cluster Types

a. Rh$_6$(CO)$_{16}$; Closo.

b. Os$_4$(CO)$_{12}$H$_3$I; Arachno.

c. Os$_7$(CO)$_{21}$; Capped.

d. Fe(CO)$_{15}$; Nido.
ligands and edge-bridging hydride ligands are most common [7]. Both steric and electronic effects are believed to play an important role in the formation of carbonyl bridges [36,37]. The steric requirement of carbonyl ligands has been emphasized by Johnson in determining the geometric structure and fluxional behavior of metal carbonyl clusters [38]. Chini emphasized electronic factors in determining the number of carbonyl bridges present in a series of hexanuclear rhodium carbonyl anions [39].

II. Ruthenium Clusters in Homogeneous Catalysis

Transition metal clusters have recently received considerable attention in homogeneous catalytic research. The interest in potential cluster catalysts stems from several principle factors. First, there are a number of heterogeneously catalyzed reactions, such as alkane isomerization and $\text{N}_2$ hydrogenation, which are not catalyzed by soluble mononuclear catalysts [2]. It is generally thought that these processes may require multiple catalytic sites for substrate activation [7]. In principle, a metal cluster compound could provide several such reactive metal sites and function as a catalyst. Secondly, the mobility (flexionality) of ligands over the "surface" of a cluster and the migration of atoms and substrates on a metal surface are both low-energy, facile processes [5]. The catalytic combination of small molecules in reactions such as CO hydrogenation could be potentially be accomplished on the "surface" of a soluble polynuclear metal cluster. Polynuclear metal catalysts offer a third advantage over mononuclear complexes in that a combination of metals in a mixed-metal cluster may
be employed. From a catalysis viewpoint, mixed-metal cluster compounds should show unique reactivity features as a result of the different reactivity properties of the constituent metals [40]. Several mixed-metal cluster compounds have been reported to display synergistic catalytic behavior with respect to increased activity and selectivity [16, 41-44]. The importance of bimetallic heterogeneous catalysis in industrial processes is well known [45].

The reactions in which ruthenium cluster catalyst precursors have been employed are given in Table 2. Although a large number of catalytic systems have been reported, relatively little is known about the nature of the catalytic solutions. Discussed below are various classes of catalytic reactions which are initiated by ruthenium clusters, and in which something is known about the active solution.

**A. Carbon Monoxide Hydrogenation**

The Fischer-Tropsch synthesis (Equation 1) produces primarily hydrocarbons and alcohols from mixtures of CO and H₂, generally termed synthesis gas [46].

\[ n \text{CO} + 2n \text{H}_2 \rightarrow (\text{CH}_2)_n + n \text{H}_2\text{O} \]  

(1)

The direct conversion of H₂/CO mixtures to organic products is an important goal in catalytic research. Current commercial plants employ heterogeneous catalysts based on FeO [47]. Homogeneous catalysts for CO hydrogenation have been known since the early 1950's [48,49]. In the past 30 years, carbonyl complexes of virtually every transition metal
<table>
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<th>Reaction</th>
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<tr>
<td>Fischer-Tropsch</td>
<td>CO + H₂ → (CH₂)n + oxygenates</td>
<td>51-60</td>
</tr>
<tr>
<td>Hydroformylation of ethylene</td>
<td>( \text{HC} = \text{C} ) + CO + H₂ → ( \frac{1}{2} \text{C-C} + \text{H} )</td>
<td>15,65-71</td>
</tr>
<tr>
<td>of propylene</td>
<td></td>
<td></td>
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<tr>
<td>of pentene</td>
<td></td>
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<td>Isomerization</td>
<td></td>
<td>72-76</td>
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<tr>
<td>Hydrogenation</td>
<td>( \text{HC} = \text{C} ) + H₂ → ( \frac{1}{2} \text{C-C} )</td>
<td>65,76-83</td>
</tr>
<tr>
<td>Hydrosilylation</td>
<td>( \text{HC} = \text{C} ) + R₃SiH → ( \frac{1}{2} \text{C-C-SiR₃} )</td>
<td>65,84-86</td>
</tr>
<tr>
<td>Reduction of Nitro Group</td>
<td>R-NO₂ + H₂ → R-NH₂</td>
<td>91-95</td>
</tr>
<tr>
<td>Reduction of Ketones</td>
<td>R-C-R + H₂ → R-C-R</td>
<td>87-89</td>
</tr>
<tr>
<td>Reduction of Hetero-aromatic</td>
<td>( \text{N} ) + H₂ → ( \text{NH} )</td>
<td>83,90</td>
</tr>
<tr>
<td>Carbon Dioxide Activation</td>
<td>CO₂ + H₂ + CH₃OH → HCOOCH₃ + H₂O</td>
<td>96,97</td>
</tr>
<tr>
<td>Water-Gas Shift</td>
<td>CO + H₂O ↔ H₂ + CO₂</td>
<td>14-20,83</td>
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have been utilized as catalyst precursors for CO hydrogenation [50]. Of all the homogeneous systems studied to date, those initiated by ruthenium carbonyl complexes yield the highest conversion of synthesis gas to organic products [51-60].

The first report of homogeneous CO hydrogenation initiated by ruthenium carbonyl clusters appeared in 1977 [58]. The clusters Ru$_3$(CO)$_{12}$, H$_4$Ru$_4$(CO)$_{12}$, [H$_3$Ru$_4$(CO)$_{12}$]$^-$, and [Ru$_6$C(CO)$_{16}$]$^{2-}$ were all converted to a common species, Ru(CO)$_5$, under reaction conditions (Equation 2).

$$ \text{H}_2 + \text{CO} \xrightarrow{1300 \text{ atm. THF, 270°C}} \text{CH}_3\text{OH} + \text{HCOCH}_3 $$ (2)

The system produced methanol and methyl formate with a selectivity of > 99% to C$_1$ products. By adjusting the CO/H$_2$ ratio and adding phosphine promoter, a selectivity of > 95% methanol was achieved. This study clearly established that the active catalytic species was a soluble mononuclear ruthenium complex. In 1981, two studies involving a more detailed investigation of this system were reported by Dombek [56] and King [57]. Dombek found that the reaction was very sensitive to the solvent. When carboxylic acids were employed as solvents, a significant promoter effect on the formation of C$_2$ products, notably ethylene glycol, was observed (Equation 3). In carboxylic solvents, the rate of carbon monoxide hydrogenation at 340 atm CO/H$_2$ (270°C) was nearly equal to the rate in THF at 1300 atm CO/H$_2$ (270°C).

$$ \text{H}_2 + \text{CO} \xrightarrow{340 \text{ atm. RCH}_2\text{COOH, 270°C}} \text{CH}_3\text{OH} + (\text{CH}_2\text{OH})_2 $$ (3)
Based on detailed kinetic studies, the scheme in Figure 2 was proposed to account for the observed product distribution. This scheme also accounts for the observation that in the C₂ producing reaction (carboxylic acid), the kinetic dependences on CO and H₂ pressure and catalyst concentration are nearly identical to those in the C₁ forming reaction (no carboxylic acid present). Under the catalytic conditions employed (Equ. 3), conversion of Ru₃(CO)₁₂ to Ru(CO)₅ was extremely rapid as observed by high pressure infrared spectroscopy on the active catalysis solution [51,58]. The time dependence of concentrations for Ru(CO)₅ and products (CH₃OH) by all three groups working on this system clearly suggest that mononuclear ruthenium complexes are the active species. Thus, it seems apparent that although a large number of

\[
\frac{1}{3} \text{Ru}_3(\text{CO})_{12} \xrightleftharpoons{\text{CO}} \text{Ru}(\text{CO})_5 \xrightleftharpoons{\text{H}_2} \text{H}_2\text{Ru}(\text{CO})_4 \xrightleftharpoons{\text{CO}} \text{(CO)}_4\text{Ru-C=O} \xrightleftharpoons{\text{H}_2} \text{CO}
\]

\[
\begin{align*}
(CO)_3 & \xrightleftharpoons{\text{CO}} (CO)_4\text{Ru-CH}_2\text{OH} \\
(CO)_4\text{Ru-CH}_2\text{OH} & \xrightleftharpoons{\text{CO}} (CO)_4\text{Ru-C-CH}_2\text{OH} \\
(CO)_4\text{Ru-C-CH}_2\text{OH} & \xrightarrow{\text{CO}} \text{H}_2\text{OCH}_3
\end{align*}
\]

\[
\text{(CO)₄Ru-OCH₃} \xrightarrow{\text{CO}} \text{H-C-OCH}_3
\]

**Figure 2:** Proposed Scheme for the Production of Methanol and Ethylene Glycol [56]
ruthenium cluster catalyst precursors give active solutions, the active catalytic species are actually mononuclear [51,56,58].

Two very active homogeneous ruthenium based systems for CO hydrogenation have recently been reported by Dombek [51,55] and Knifton [54,59]. These systems differ significantly from the one which was described above in that ruthenium cluster anions are the major components of the active catalysis solutions. Both systems are very similar in scope, producing C_2 products (ethylene glycol, ethanol, glycol esters) with a much greater CO/H_2 conversion than in previous homogeneous studies. The first system, described by Dombek, is based on ionic iodide promoters which enhance the overall activity of the system as well as the selectivity to two-carbon products. The second system, described by Knifton, is based on ruthenium "melt" catalysis, where the ruthenium source is dispersed in molten quaternary phosphonium or ammonium salts.

The important features of the iodide-promoted system are: (a) two ruthenium complexes, [HRu_3(CO)_{11}]^- and [Ru(CO)_3I_3]^-, are observed during catalysis by high-pressure infrared spectroscopy; (b) both complexes are necessary components for catalytic activity; (c) LiI, NaI, KI, CSI, and PPNI are all equally effective at promoting the reaction; (d) although polar solvents such as sulfanone, n-methylpyrrolidine, and 18-crown-6 are excellent solvents, hydroxyllic solvents such as n-butyl alcohol or water suppress the rate of CO hydrogenation dramatically; (e) the rate dependences for methanol and ethylene glycol formation are 0.6 power in iodide concentration, 3.8 order in CO/H_2 pressure, and 1.3 power in Ru concentration; (f) the conditions for catalysis are 425
\[
\text{H}_2 + \text{CO} \xrightarrow{\text{Ru}_3\text{(CO)}_{12}, \text{I}^-, \text{230}^\circ\text{C}} \text{CH}_3\text{OH} + \text{HOCH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{OH}
\] (4)

atm CO, 425 atm H\text{\textsubscript{2}}, 230°C, 0.08 M [Ru], and 0.24 M [I\text{\textsuperscript{-}}]. The observed catalytic components [HRu\textsubscript{3}(CO)\textsubscript{11}\text{\textsuperscript{-}}] and [Ru(CO)\textsubscript{3}I\textsubscript{3}\text{\textsuperscript{-}}] are formed according to the following reaction [55]. It has been proposed that under

\[
\frac{7}{3} \text{Ru}_3\text{(CO)}_{12} + 3\text{I}^- + \text{H}_2 \rightarrow [\text{HRu}_3\text{(CO)}_{11}]^- + [\text{Ru(CO)}_{3}\text{I}_3]^+ + 3\text{CO}
\] (5)

catalysis conditions, both [HRu\textsubscript{3}(CO)\textsubscript{11}\text{\textsuperscript{-}}] and [Ru(CO)\textsubscript{3}I\textsubscript{3}\text{\textsuperscript{-}}] are transformed into more reactive intermediates:

\[
[\text{HRu}_3\text{(CO)}_{11}]^- + 3\text{CO} \rightleftharpoons [\text{HRu(CO)}_4]^+ + 2\text{Ru(CO)}_5
\] (6)

\[
[\text{Ru(CO)}_3\text{I}_3]^+ + \text{CO} \rightleftharpoons \text{Ru(CO)}_4\text{I}_2 + \text{I}^-
\] (7)

Neither of these transformations has been observed directly, but are implied by the large pressure dependence of this system. However, it has been pointed out that the CO and H\text{\textsubscript{2}} pressure dependences can not be taken as indicating kinetic orders, since there is a substantial volume of activation effect [51]. The fragmentation of the [HRu\textsubscript{3}(CO)\textsubscript{11}\text{\textsuperscript{-}}] anion by CO (Equ. 6) has not been observed under even the most severe conditions of temperature and pressure [51,63]. However, the iron analog, [HFe\textsubscript{3}(CO)\textsubscript{11}\text{\textsuperscript{-}}], has been shown to fragment in a manner consistent with Equation 6 [61,62]. Thus, it has been suggested that CO reduction may occur through interaction of [HRu(CO)\textsubscript{4}\text{\textsuperscript{-}}] and Ru(CO)\textsubscript{4}I\textsubscript{2}, both of
which are present in steady-state concentrations. Indirect evidence for this proposal has been obtained through the demonstration that \([\text{HRu(CO)}_4]^-\) may reduce metal bound carbon monoxide to a metal formyl ligand [64]. Catalytic systems for homogeneous CO hydrogenation have been generally thought to proceed through formation of a metal formyl complex [50]. The following scheme (Figure 2) has been proposed for the iodide promoted carbon monoxide hydrogenation. Details of the stoichiometries given are described elsewhere [51].

\[
3[\text{HRu(CO)}_4]^- + 2\text{CpRe(CO)}_2(\text{NO})^+ \rightarrow \]
\[
[\text{HRu}_3(\text{CO})_4]^- + 2\text{CpRe(CO)(NO)(CHO)} + \text{CO}
\]

**Figure 3:** Proposed Mechanism for the Iodide-Promoted CO Hydrogenation System
There are a number of important conclusions that have been drawn from the examination of this system. First, it is clear that there are a number of ways in which ruthenium clusters may participate in catalysis. The direct participation of \([\text{HRu}_3(\text{CO})_{11}]^-\) in the reduction of coordinated carbon monoxide can not be ruled out on the basis of current experimental evidence. If the mononuclear anion \([\text{HRu}(\text{CO})_4]^-\) actually is the reductant in this system, the cluster anion \([\text{HRu}_3(\text{CO})_{11}]^-\) may be crucial to the catalytic process in two distinct ways. First, it has been suggested that the key to formyl ligand formation (through hydride transfer to an electrophillic carbonyl) may be the thermodynamic driving force of metal-metal bond formation which accompanies hydride transfer (Equation 8) \[51\]. Secondly, the separation of centers with very different oxidation states may be due to ability of \([\text{HRu}_3(\text{CO})_{11}]^-\) and \([\text{Ru}(\text{CO})_3\text{I}^-]\) to release highly reactive intermediates without undergoing oxidation-reduction coupling themselves. Although the exact role of ruthenium cluster anions in this system is unknown, it is certain that their chemistry is pertinent to the overall process.

The concept of "melt" or "molten salt" catalysis has been applied to the homogeneous hydrogenation of carbon monoxide by ruthenium catalysts \[53,54,59\]. The important features of this catalysis are: (a) a quaternary phosphonium or ammonium salt which, under catalysis conditions, provides a highly polar, fluid medium for solubilization of the catalyst; (b) the cluster anion \([\text{HRu}_3(\text{CO})_{11}]^-\) is the predominant species present after catalysis; (c) the major products are ethylene glycol, methanol, ethanol, and glycol esters; (d) there is a 1st order
dependence on the CO + H₂ (total pressure); (e) the rate of CO hydrogenation is highly dependent on the nature of the molten salt; (f) the conditions for catalysis are 215 atm CO, 215 atm H₂, 220°C, 15 g R₄PX, 4.0 mmole Ru.

Unlike the iodide-promoted system, little mechanistic information is available on the molten salt system. However, the basic experimental features of each system are similar and the cluster anion [HRu₃(CO)₁₁]⁻ is observed as the major component of both catalysis "solutions." The major difference between the two systems appears to be in the reaction medium employed. Although both systems employ a very polar reaction medium, the molten salt catalysis displays a significant counterion effect. While quaternary ammonium or phosphonium salts such as tetrabutylphosphonium bromide give similar results, quaternary arsonium or stibonium salts are inactive. The nature of the alkyl group in the tetraalkyl salt also plays an important role in catalytic activity and product distribution.

**B. Hydroformylation of Olefins**

The hydroformylation of olefins produces aldehydes and alcohols according to the following reaction:

\[
\begin{align*}
H₂C=CH₂ + CO + H₂ & \longrightarrow CH₃CH₂CHO \\
& \overset{H₂}{\longrightarrow} CH₃CH₂CH₂OH
\end{align*}
\]

If water is used in place of hydrogen, the reaction is called the Reppe modification.
Homogeneous ruthenium carbonyls have been employed widely as hydroformylation catalysts [15,65-71]. In most of these systems, reaction conditions are such that anionic cluster species would be expected to predominate. In two recent reports, the active catalysis solutions have been shown to contain the cluster anions [HRu$_3$(CO)$_{11}$]$^-$ and [H$_3$Ru$_4$(CO)$_{12}$]$^-$ as the major components [65-67]. The relative contribution of each cluster toward catalysis is unknown, although these two anions are known to interconvert readily under reaction conditions [20].

C. Isomerization of Alkenes

The isomerization of pentenes has been catalyzed by ruthenium carbonyl clusters in neutral solution [72-76]. Both thermal [72-75] and photochemical [76] conditions for olefin isomerization have been employed. Catalytic isomerization of 1-pentene to 2-cis and 2-trans-pentene with H$_4$Ru$_4$(CO)$_{12}$ as catalyst precursor has been studied mechanistically. All studies to date suggest that intact tetranuclear ruthenium clusters are responsible for catalysis. Similar mechanisms have been proposed for the thermal (70°C) and photochemical (25°C) initiated isomerizations. The active species is suggested to be mainly originated by loss of CO to give coordinatively unsaturated H$_4$Ru$_4$(CO)$_{11}$
[73,74]. It is thought that σ-alkyl intermediates are involved in the catalytic isomerization, but a contribution from π-allyl intermediates is also suggested.

D. Hydrogenation of Alkenes

The homogeneous hydrogenation of alkenes by ruthenium carbonyl clusters has been reported [65,76-83]. Mechanistic studies suggest that intact ruthenium clusters are responsible for hydrogenation, with both anion and neutral clusters capable of catalyzing the reaction [65,76,80,82]. However, hydrogenations catalyzed by ruthenium clusters have not been shown to offer a significant advantage over traditional hydrogenation catalysts.

E. Hydrosilylation of Alkenes

The hydrosilylation of alkenes has been catalyzed by ruthenium carbonyl clusters [84-86]. Little information regarding the nature of the active catalysis solution was reported.

\[
\text{CH}_2=\text{CH}_2 + \text{Et}_3\text{SiH} \xrightarrow{[\text{HRu}_3(\text{CO})_{11}]^-} \text{CH}_2=\text{CH}-\text{SiEt}_3 + \text{CH}_3-\text{CH}_2-\text{SiEt}_3 \quad [65]
\]

52% 22%

F. Reductions of Nitrocompounds, Ketones and Heteroatomics

The catalytic reduction of a number of different organic functional groups has been achieved utilizing either hydrogen or carbon monoxide and water (REPPE) as the reducing agent. Included in such reaction
schemes are ketone [87-89], nitrobenzene [91-95], and heteroatomic [83,90] reductions catalyzed by ruthenium carbonyl clusters.

\[
\text{Ru} = \frac{\text{H}_4\text{Ru}_4(\text{CO})_{12}}{100^\circ\text{C}} \rightarrow \text{OH} \quad [88]
\]

\[
\text{Ru} = \frac{\text{H}_4\text{Ru}_4(\text{CO})_{12}}{100^\circ\text{C}} \rightarrow \text{NH}_2 + \text{CO}_2 \quad [91]
\]

\[
\text{Ru} = \frac{\text{H}_4\text{Ru}_4(\text{CO})_{12}}{150^\circ\text{C}} \rightarrow \text{NH} \quad [83]
\]

G. Carbon Dioxide Activation

It has recently been reported that ruthenium cluster carbonyl compounds are effective catalyst precursors for the production of methyl formate from carbon dioxide [96,97].

\[
\text{CO}_2 + \text{H}_2 + \text{CH}_3\text{OH} \xrightarrow{250 \text{ psi}} \frac{[\text{H} \text{Ru}_3(\text{CO})_{11}]^-}{0} \text{HCOCH}_3 + \text{H}_2\text{O}
\]

The most effective catalyst precursor for methyl formate production is the $[\text{H} \text{Ru}_3(\text{CO})_{11}]^-$ anion under carbon monoxide pressure (250 psi). Over 100 turnovers (mol methyl formate/mol catalyst) were observed in a 24 hour period:
It is interesting to note that the most effective production of methyl formate does not require carbon dioxide. The mechanism of methyl formate production by [HRu3(CO)11]− in the presence of CO is consistent with chemistry observed in this research group [20].

H. Water-Gas Shift Reaction (WGSR)

The water-gas shift reaction has been extensively utilized industrially for the production of molecular hydrogen [98]. It is always used to adjust the CO to H2 ratio in syngas derived from coal gasification prior to Fisher-Tropsch processes. The WGSR is also of primary importance in the large scale production of hydrogen for ammonia synthesis and the treatment of combustion gasses in order to remove nitrogen and sulfur oxides [99,100]. Traditionally, the WGSR has employed heterogeneous Fe2O4 catalysts promoted by Cr2O3 which operate at 350°C [101]. Heterogeneous catalysts based on copper and zinc oxide as well as CoO and MoO3 combinations operate at lower temperatures (300°C<), but are more susceptible to sulfur poisoning [102]. There is interest in developing low temperature shift catalysts because the thermodynamically limiting conversion decreases as temperature increases. Based on the thermodynamics of the shift reaction, less
thermal input and greater efficiency would result if a catalyst could be found which was effective at lower temperatures (~100°C):

\[
\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)
\]

\[\Delta_{298}^0 = -6.82 \text{ Kcal}; \Delta H_{298}^0 = -9.84 \text{ Kcal}; \Delta S_{298}^0 = -10.1 \text{ cal/deg}\]

\[
\text{CO(g)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)
\]

\[\Delta_{298}^0 = -4.76 \text{ Kcal}; \Delta H_{298}^0 = +0.68 \text{ Kcal}; \Delta S_{298}^0 = -18.3 \text{ cal/deg}\]

It can be seen that when water is present in the condensed state the reaction is favored from a large positive entropy effect. Thus, \(K_p\) for the shift reaction is 1550 at 100°C and 9.5 at 300°C [103]. Although there has been interest in homogeneous WGS for over 50 years [104,105], the first definitive reports of a homogeneous shift catalyst did not appear until 1977 [14,15,106].

Since 1977 a great deal of effort has been directed at the homogeneous catalysis of the WGSR by the mononuclear metal carbonyls \(\text{Fe(CO)}_5\) and \(\text{M(CO)}_6\) (\(M = \text{Cr, Mo, W}\)) [109,112,113-121]. The following mechanistic schemes have emerged as a result of these studies.

1. \(\text{Fe(CO)}_5 + \text{OH}^− \rightleftharpoons [\text{HFe(CO)}_4]^- + \text{CO}_2\)

2. \([\text{HFe(CO)}_4]^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{Fe(CO)}_4 + \text{OH}^−\)

3. \(\text{H}_2\text{Fe(CO)}_4 \rightleftharpoons \text{H}_2 + \text{Fe(CO)}_4\)

4. \(\text{Fe(CO)}_4 + \text{CO} \rightarrow \text{Fe(CO)}_5\)

**Catalysis** Temp. = 140°C

**Conditions:** Pressure = 40 atm. CO

[107] Solvents = 25% H₂O; 75% CH₃OH (200 ml)

KOH = 39 mmol

\(\text{Fe(CO)}_5 = 2.23 \text{ mmol}\)
The above mechanism, first proposed by Pettit [15], is believed to be operative in the homogeneous catalysis of the WGSR by Fe(CO)$_5$ [15, 107-112]. This cycle accounts for the kinetics under catalytic conditions [107]. The rate of H$_2$ production is first order in iron carbonyl catalyst, independent of CO pressure, and sensitive to pH. The overall activation energy is 22 Kcal/mol and the turnover frequency is ~2000 mol H$_2$ per mol of Fe(CO)$_5$ per day at 180°C. The first step, base attack at metal bound carbon monoxide, is rate-determining under catalytic conditions. This is based on studies of pH dependence on the rate of H$_2$ production [107]. It has been proposed [108] that this first step occurs through decarboxylation of [Fe(CO)$_4$CO$_2$]$^{2-}$ rather than [Fe(CO)$_4$COOH]$^-$. Protonation of [HFe(CO)$_4$]$^-$ would form H$_2$Fe(CO)$_4$ which is presumed to reductively eliminate H$_2$ and form the coordinatively unsaturated Fe(CO)$_4$. The intermediacy of H$_2$Fe(CO)$_4$ is based on the observation that both Reppe hydroformylation and water-gas shift reactions did not proceed at a pH greater than 10.7 when catalyzed by iron pentacarbonyl [15]. The trapping of Fe(CO)$_4$ by CO is crucial to the catalytic cycle. Although the H$_2$ production is independent of CO pressure, there is a minimum threshold of CO pressure necessary for catalysis to occur. Under this threshold pressure, carbon monoxide does not compete effectively with hydroxide ion for the Fe(CO)$_4$ fragment and the catalyst undergoes a series of electron transfer steps which render it inactive [122]. Above the threshold pressure (~10 atm. CO), the catalysis is zero-order in carbon monoxide. It is thought that only a slight improvement in catalytic activity could be achieved by optimizing
conditions in the iron pentacarbonyl system, primarily because steps 1
and 2 have opposite pH requirements [108].

The Group VI transition metal hexacarbonyls Cr(CO)\textsubscript{6}, Mo(CO)\textsubscript{6}, and
W(CO)\textsubscript{6} have been shown to be catalyst precursors for the WGS reaction under
basic conditions [109,112,113-121]. These catalysts have received
considerable attention because of their high sulfur tolerance. All
three hexacarbonyls display similar catalytic properties. The important
features of these three catalytic systems are: (1) the rate of H\textsubscript{2}
production is first order in metal hexacarbonyl, inversely proportional
to carbon monoxide pressure, and increasing with base concentration; (2)
at 200\textdegree C and 21 atm. CO pressure, turnover frequencies as high as 12,000
mol H\textsubscript{2}/mol hexacarbonyl-day are achieved; (3) the activation energy for
each system is about 33 Kcal/mol [118]. Two different mechanistic views
have emerged from these studies. One (Scheme A) is based on activation
of metal-bound carbon monoxide by hydroxide ion and the other (Scheme B)
proposed a mechanism involving formate decomposition. These two
mechanistic schemes are shown in Figure 4.

The major difference between these two mechanistic schemes is the
pathway for formation of [HM(CO)\textsubscript{5}]\textsuperscript{-}, the precursor to hydrogen
production. In Scheme A, Darenbourg and co-workers propose that metal-
bound carbon monoxide is activated by nucleophilic attack of hydroxide
ion, forming a metallocarboxylic acid intermediate which, in turn,
reacts with a second equivalent of base to form [HM(CO)\textsubscript{5}]\textsuperscript{-} [115]. King,
Slegelir, and co-workers propose dissociation (photochemical or thermal)
of carbon monoxide from the metal hexacarbonyl as a first step [118,
120]. Formate ion, generated from the reaction of carbon monoxide with
Scheme A [113-115,117,119]

Scheme B [116,118,120,121]

Figure 4. Proposed Mechanisms for Catalysis of the Water-Gas Shift Reaction by Group VI Metal Hexacarboxyls [113-121].

-24-
hydroxide, adds to the coordinatively unsaturated metal pentacarbonyl intermediate to form a metalloformate complex which decarboxylates to form \([HM(CO)\text{\textsubscript{5}}]\)\textsuperscript{−}. The steps following formation of \([HM(CO)\text{\textsubscript{5}}]\)\textsuperscript{−} are identical in the two mechanisms. It has been pointed out that since both cycles propose the formation of M(CO)\textsubscript{5} at some stage, that the relative contribution of each pathway might depend on how effectively M(CO)\textsubscript{5} is scavenged by HCO\textsubscript{2}\textsuperscript{−} or CO \[115]\). In this regard Scheme \textsuperscript{B} seems attractive since it more readily accounts for the observed inverse CO pressure dependence on hydrogen production.

Although catalysis of the WGSR by mononuclear metal carbonyl complexes is fairly well understood, studies on the metal cluster initiated WGS catalysis have not produced on understanding of the key mechanistic steps \[14-19\]. This situation exists because: (1) Many of the potential intermediates which may be involved have not been independently synthesized; (2) The reactivity of even well-characterized cluster compounds, identified in active WGS catalysis solutions, has not been studied. Thus, cycles involving cluster species have been necessarily limited to those based on an extrapolation of classical mononuclear reactivity patterns.

Ford and co-workers first reported the homogeneous catalysis of the WGSR with a metal carbonyl cluster as a catalyst precursor \[14\]. They observed that basic solutions of Ru\textsubscript{3}(CO)\textsubscript{12} catalyzed the shift reaction under mild conditions (100°C, 1 atm. CO pressure). It was found that under WGS conditions, each of the ruthenium cluster carbonyls Ru\textsubscript{3}(CO)\textsubscript{12}, H\textsubscript{2}Ru\textsubscript{4}(CO)\textsubscript{13}, and H\textsubscript{4}Ru\textsubscript{4}(CO)\textsubscript{12} produced a homogeneous solution exhibiting equivalent normalized catalytic activity and identical spectroscopic
properties. Additionally, the rate of H₂ productions was found to be first order with respect to both CO pressure and ruthenium concentration [17]. There has been some confusion concerning the mechanism by which this system is capable of catalyzing the WGSR. Initially a scheme based on tetraruthenium clusters (Figure 5) was proposed [18]. This scheme was based on ¹H NMR studies of active catalysis solutions which indicated that the known anion [H₃Ru₄(CO)₁₂]⁻ [123], was present as well as a second species, which was assumed to be [HRu₄(CO)₁₃]⁻. At the time of this proposal [18], the synthesis and characterization of [HRu₄(CO)₁₃]⁻ had not yet been reported by Shore and Nagel [124]. Additionally, the reactivity of [H₃Ru₄(CO)₁₂]⁻ toward H₂ or CO was unknown. It was subsequently determined [17, 24] that [HRu₃(CO)₁₁]⁻, not the presumed [HRu₄(CO)₁₃]⁻, was the second species present under catalysis conditions. This has led to the proposal of three additional cycles in which the active ruthenium species range from mononuclear to tetrarnuclear [17]. Little or no evidence supporting the proposed steps in any of these cycles has been reported.

![Figure 5. Proposed Mechanism for the Water-Gas Shift Reaction Catalyzed by Tetra-Ruthenium Clusters](image)

The key steps involved in the catalysis of the water-gas shift reaction by ruthenium clusters in basic solution are unknown. Given the
relative ease of interconversion between species of different nuclearity, it is clear that the reactivity of all species involved toward H₂, CO, CO₂, and H₂O must be examined if the feasibility of individual steps, and thus, an overall mechanism is to be advanced.

III. Carbon-13 Enrichment of Transition Metal Carbonyl Compounds

The utilization of the carbon-13 nuclide as a probe for the characterization and study of organometallic compounds is widespread [125-129]. In particular, the study of metal carbonyl complexes has benefitted significantly from the use of C₁₃ isotopically enriched compounds [126,129]. The carbon-13 nuclide has played an essential role in the determination of intermolecular CO exchange processes of transition metal cluster compounds [5,7]. The structure determination of mixed-metal cluster compounds, which generally possess lower symmetry, has hinged on the utilization of carbon-13 NMR spectroscopy [40].

Although a few transition metal carbonyl complexes exchange carbon monoxide ligands with gaseous C₁₃CO under mild conditions (Ni(CO)₄, Rh₄(CO)₁₂), most require elevated temperatures and prolonged reaction times. Table 3 gives reported C₁₃CO exchange rates for a number of transition metal carbonyl compounds [136,137]. As the data in Table 3 indicate, the rate of C₁₃CO exchange for many of the common starting materials of organometallic chemistry are quite slow. In practical terms, this means that preparation of carbon-13 labeled Ru₃(CO)₁₂ or
Table 3. Rates of $^{13}C\text{O}$ Exchange for Transition Metal Carbonyl Compounds

<table>
<thead>
<tr>
<th>Metal Carbonyl</th>
<th>Temp. (°C)</th>
<th>Rate of CO Exchange</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)$_5$</td>
<td>25°C</td>
<td>$T_{1/2} = 4$ yrs.</td>
<td>[130,131]</td>
</tr>
<tr>
<td></td>
<td>25°C</td>
<td>immeasurably slow</td>
<td>[132]</td>
</tr>
<tr>
<td>Ru$<em>3$(CO)$</em>{12}$</td>
<td>25°C</td>
<td>immeasurably slow</td>
<td>[133]</td>
</tr>
<tr>
<td>Os$<em>3$(CO)$</em>{12}$</td>
<td>25°C</td>
<td>immeasurably slow</td>
<td>[133]</td>
</tr>
<tr>
<td>Co(CO)$_6$</td>
<td>129.2°C</td>
<td>$K_1 = 9.85 \times 10^{-5}$ sec$^{-1}$</td>
<td>[134]</td>
</tr>
<tr>
<td></td>
<td>117°C</td>
<td>$K_2 = 2.0 \times 10^{-5}$ sec$^{-1}$</td>
<td>[135]</td>
</tr>
<tr>
<td>Mo(CO)$_6$</td>
<td>116°C</td>
<td>$K_1 = 7.5 \times 10^{-5}$ sec$^{-1}$</td>
<td>[138]</td>
</tr>
<tr>
<td></td>
<td>70°C</td>
<td>immeasurably slow</td>
<td>[129]</td>
</tr>
<tr>
<td>W(CO)$_6$</td>
<td>151.5°C</td>
<td>$K_1 = 7.8 \times 10^{-6}$ sec$^{-1}$</td>
<td>[134]</td>
</tr>
<tr>
<td>V(CO)$_6$</td>
<td>10°C</td>
<td>$T_{1/2} = 7$ hours</td>
<td>[139]</td>
</tr>
<tr>
<td>Mn$<em>2$(CO)$</em>{10}$</td>
<td>85°C</td>
<td>immeasurably slow</td>
<td>[129]</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>immeasurably slow</td>
<td>[140]</td>
</tr>
<tr>
<td>Re$<em>2$(CO)$</em>{10}$</td>
<td>50°C</td>
<td>immeasurably slow</td>
<td>[140]</td>
</tr>
<tr>
<td>Co$_2$(CO)$_8$</td>
<td>5°C</td>
<td>$3.5 \times 10^{-3}$ sec$^{-1}$</td>
<td>[139,141]</td>
</tr>
<tr>
<td></td>
<td>0°C</td>
<td>$3 \times 10^{-4}$ sec$^{-1}$</td>
<td>[143]</td>
</tr>
<tr>
<td>Co$<em>4$(CO)$</em>{12}$</td>
<td>24.6°C</td>
<td>$1.5 \times 10^{-5}$ sec$^{-1}$</td>
<td>[142]</td>
</tr>
<tr>
<td>Ir$<em>4$(CO)$</em>{12}$</td>
<td>80°C</td>
<td>immeasurably slow</td>
<td>[129]</td>
</tr>
<tr>
<td>Ni(CO)$_4$</td>
<td>0°C</td>
<td>rapid</td>
<td>[139]</td>
</tr>
</tbody>
</table>
Os$_3$(CO)$_{12}$, for example, may take 3 to 4 days at 70°C and 120°C, respectively. Thus, practical synthetic techniques for the preparation of metal carbonyl compounds enriched in $^{13}$CO are of great interest.

A number of methods for activating CO dissociation have been employed in order to prepare $^{13}$CO-enriched compounds. These methods include photochemical activation [144,145], heterogeneous surface catalysis with palladium on charcoal [146,147], and a labilizing ligand approach [129,148].

Of the three general approaches mentioned above, the utilization of a CO-labilizing ligand has been the most extensively applied technique [129,148]. The CO-labilizing ligand employed is (n-butyl)$_3$P=O. This technique requires the presence of at least one available coordination site for the (n-Bu)$_3$P=O. Thus, prior to $^{13}$CO exchange, it is necessary to synthesize derivatives of the parent carbonyl compound which contain a labile ligand such as pyridine (pyr) or piperidine (pip). Typical derivatives are py$_3$Mo(CO)$_3$, pyCr(CO)$_5$, (py)Fe(CO)$_4$, and pipW(CO)$_5$, which in the presence of an excess of (n-Bu)$_3$P=O and $^{13}$CO will react to give the respective parent carbonyl (Mo(CO)$_5$, Cr(CO)$_6$, Fe(CO)$_5$, W(CO)$_6$) in high yield and with a high level of $^{13}$CO content. The basic sequence of reactions is believed to be [148]:

\[
\begin{align*}
\text{L} \quad \text{PR}_3 \quad \text{PR}_3 \quad \text{13CO} \\
\text{[M]-CO} \quad \text{[M]-CO} \quad \text{[M]-CO} \\
\text{[-L]} \quad \text{[-CO]} \quad \text{[-CO]} \\
\text{[M]-CO} \quad \text{[M]-CO} \quad \text{[M]-CO} \\
\text{[M]-CO} \quad \text{[M]-CO} \quad \text{[M]-CO} \\
\text{[M]-CO} \quad \text{[M]-CO} \quad \text{[M]-CO} \\
\end{align*}
\]
Experimentally, a large excess of phosphine oxide ($R_3P=O\text{Metal}=30:1$) is required. Very high levels of $^{13}\text{CO}$ enrichment (>90%) have been obtained in this manner. There are a number of experimental difficulties which arise: (1) the labile ligand derivative must be prepared; (2) it is difficult to separate the metal carbonyl product from excess phosphine oxide and solvent. Nonetheless, this technique has been applied successfully to the preparation of $^{13}\text{CO}$ enriched samples of Fe(CO)$_5$, Cr(CO)$_6$, Mo(CO)$_6$, W(CO)$_6$, and Mn$_2$(CO)$_10$ [129, 148].

Photochemical activation of carbon monoxide has been employed to the $^{13}\text{CO}$ enrichment of metal carbonyls in a few specific cases [144, 145, 149]. It offers one distinct advantage over other methods in that stereospecific incorporation of $^{13}\text{CO}$ may often be achieved [144, 145]. However, it is not widely employed due to irreversible transformations which often occur with constant irradiation of the metal carbonyl (for example:

\[
\text{Fe(CO)}_5 \xrightarrow{\text{hr}} \text{Fe}_2(\text{CO})_9
\]

The surface catalyzed $^{13}\text{CO}$ enrichment of Fe(CO)$_5$ and Mo(CO)$_6$ has been achieved under mild conditions [146, 147]. The heterogeneous catalyst employed was a 10% dispersion of Pd on charcoal or alumina. Stirring a hydrocarbon solution of either Fe(CO)$_5$ or Mo(CO)$_6$ over the catalyst at 25°C under $^{13}\text{CO}$ gas led to rapid $^{13}\text{CO}$ enrichment of the respective metal carbonyls. Statistical $^{13}\text{CO}-^{12}\text{CO}$ exchange was complete in minutes for Fe(CO)$_5$ and in hours for Mo(CO)$_6$ at preparative scales (~4 mmol). Separation of metal carbonyl from catalyst was easily accomplished [146, 147]. Although this enrichment technique appears to be quite useful, it has not been extensively applied.
RESULTS AND DISCUSSION

I. The Water-Gas Shift Reaction Catalyzed by Ruthenium Carbonyl Clusters.

Although catalysis of the water-gas shift reaction [WGSR] has been studied in detail with the mononuclear catalyst precursors Fe(CO)₅, Cr(CO)₆, Mo(CO)₆, and W(CO)₆, information has been reported on the nature of catalytic WGS solutions initiated by transition metal clusters [14-20]. In 1977 it was reported that basic solutions employing ruthenium cluster carbonyl precursors were capable of catalyzing the WGSR [14]. Subsequently, two cluster anions, [HRu₃(CO)₁₁]⁻ and [H₃Ru₄(CO)₁₂]⁻ were identified in active WGS catalysis solutions [17]. The systematic synthesis and chemistry of ruthenium cluster anions has been of continuing interest in these laboratories [150-154]. It was thought that their role in the catalysis of WGSR could best be ascertained by studying their reactions with CO, H₂, H₂O, and other substrates. Thus a study of the chemistry of the cluster anions [HRu₃(CO)₁₁]⁻, [H₃Ru₄(CO)₁₂]⁻, [HRu₄(CO)₁₃]⁻ and
[H₂Ru₄(CO)₁₂]²⁻ with CO and H₂ was initiated and a number of reactions pertinent to WGS catalysis were found.

A. Hydride Donating Reactions of [HRu₃(CO)₁₁]⁻

The following results show that [HRu₃(CO)₁₁]⁻ can function as an apparent hydride donor in the presence of CO. A variety of hydride-acceptor reactions are described below. Under aprotic conditions, counterion effects are observed.

1. Reactions with CO

The salt K[HRu₃(CO)₁₁] is stable in aprotic media such as THF. When K[HRu₃(CO)₁₁] was exposed to CO (1 atm) at 25°C, Ru₃(CO)₁₂ precipitated from solution. Lowering the temperature of the system to -10°C maximized the yield of Ru₃(CO)₁₂. Carbon-13 and proton NMR spectra taken in the range -80°C to +25°C indicated that the only ruthenium containing species present were [HRu₃(CO)₁₁]⁻ and Ru₃(CO)₁₂. No proton signal attributable to the known [155] formyl [HRu₃(CO)₁₁CHO]⁻, a potential intermediate, was observed. Also, no signal due to a terminal metal hydride intermediate such as [HRu(CO)₄]⁻ (18.8 τ) was observed [156].

The following equilibrium (2a) is considered to be the most reasonable source of Ru₃(CO)₁₂, as evidenced by the following observations: (a) Removal of the CO atmosphere from the above system

$$K[HRu₃(CO)_{11}] + CO \iff Ru₃(CO)_{12} + KH \quad (2a)$$
cause a rapid back reaction to give [HRu$_3$(CO)$_{11}$]$^-$ and CO. (b) The reverse of Reaction (2a), Reaction (2b) occurred readily in THF at 25°C and accounts for observation (a). The back reaction was four times faster at 25°C than at -10°C, which is consistent with the observation that maximum Ru$_3$(CO)$_{12}$ production occurred at -10°C. (c) Reaction (2b)

\[ KH + Ru_3(CO)_{12} \rightarrow K[HRu_3(CO)_{11}] + CO \]  

was inhibited to less than 1% overall conversion to [HRu$_3$(CO)$_{11}$]$^-$ when CO at 1 atm. was above the solution. When excess $^{13}$CO (1 atm.) was employed, $^{13}$CO-$^{12}$CO equilibration occurred between carbon monoxide and Ru$_3$(CO)$_{12}$, even though the net formation of [HRu$_3$(CO)$_{11}$]$^-$ was less than 1%. Removal of the equilibrated $^{13}$CO-$^{12}$CO gas from the system resulted in Reaction (2b) taking place, going to completion. The gas evolved during the reaction was near quantitative (97%) and analyzed for $^{13}$CO-$^{12}$CO in the statistical ratio expected. When KH was absent from the system, no detectable $^{13}$CO-$^{12}$CO exchange occurred under identical conditions.

Attempts to separate KH from Ru$_3$(CO)$_{12}$ were unsuccessful, in part because removal of CO led to a rapid back reaction between KH and Ru$_3$(CO)$_{12}$. Attempts to identify KH by an X-ray powder pattern of the mixture were not definitive, most likely because KH is a poor X-ray scatterer compared to Ru$_3$(CO)$_{12}$ or K[HRu$_3$(CO)$_{11}$]. Attempts to identify the KH spectroscopically by solubilizing it with cryptate were unsuccessful because equilibrium (2a) was shifted rapidly to the left when the KH was solubilized. Thus, if Kryptofix222 or $B(CH_3)_3$ was added
to a 1:1 molar mixture of KH and Ru₃(CO)₁₂ under 1 atm CO K[Ru₃(CO)₁₁]
and CO were formed quantitatively in minutes at 25°C.

The salts M[Ru₃(CO)₁₁] where M = Li⁺, Na⁺, N(CH₃)₄⁺, and N(C₂H₅)₄⁺ are stable in THF and in CH₃CN. When CO (1 atm.) was placed over these solutions, a counterion effect was noted compared to K[Ru₃(CO)₁₁]. Formation of Ru₃(CO)₁₂ was significantly diminished in the case of the sodium salt, and did not appear to occur in the cases of the lithium or tetraalkylammonium salts. Results are given in Table 4. The tetraalkylammonium salts were insoluble in ether solvents, so that CH₃CN was employed. Acetonitrile solutions of [HRu₃(CO)₁₁]⁻ were made up such that if there were a 5% conversion to Ru₃(CO)₁₂, it would appear as a precipitate. This apparent counterion effect may be due to ion-pairing, a phenomenon which is suggested from the infrared spectra of the various salts.[157] The effect of ion-pairing on the hydride-donating reactions of mononuclear hydrido (phosphine) ruthenate complexes has been reported.[158]

Further evidence for a counterion effect was observed in the reactions of MH (M = K⁺, Na⁺, Li⁺) with Ru₃(CO)₁₂ under an excess of ¹³CO (1 atm). Results are given in Table 5. The rate of ¹³CO–¹²CO exchange followed the order K⁺ > Na⁺ > Li⁺ at 27°C. This order parallels the extent of reaction of M⁺[HRu₃(CO)₁₁] with CO (Table 4) where M⁺ = K⁺ > Na⁺ > Li⁺.

2. Hydride Transfer to B(OCH₃)₃ in the Presence of CO

Hydride transfer to boron was demonstrated in the reaction of K[Ru₃(CO)₁₁] with B(OCH₃)₃ under CO, according to reaction sequence
### Table 4.
Yield of $\text{Ru}_3(\text{CO})_{12}$ from the reaction of $\text{M}[\text{HRu}_3(\text{CO})_3]$ with CO (1 atm)

<table>
<thead>
<tr>
<th>M</th>
<th>Solvent</th>
<th>Temp.</th>
<th>Yield $\text{Ru}<em>3(\text{CO})</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}^+$</td>
<td>THF</td>
<td>$-10^\circ \text{C}$</td>
<td>10%</td>
</tr>
<tr>
<td>$\text{K}^+$</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>$25^\circ \text{C}$</td>
<td>8%</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>THF</td>
<td>$0^\circ \text{C}$</td>
<td>2%</td>
</tr>
<tr>
<td>$\text{Li}^+$</td>
<td>THF</td>
<td>$-10^\circ \text{C} + 25^\circ \text{C}$</td>
<td>0%</td>
</tr>
<tr>
<td>$\text{N(CH}_3\text{)}_4^+$</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>$-10^\circ \text{C} + 25^\circ \text{C}$</td>
<td>0%</td>
</tr>
<tr>
<td>$\text{N(C}_2\text{H}_5\text{)}_4^+$</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>$-10^\circ \text{C} + 25^\circ \text{C}$</td>
<td>0%</td>
</tr>
</tbody>
</table>

*aConditions: 0.3 M $\text{M}[\text{HRu}_3(\text{CO})_3]$; 1 atm. (5 mmole) of CO

### Table 5.
Rates of $^{13}\text{CO}$ Exchange Initiated by Metal Hydrides LiH, NaH and KH.

<table>
<thead>
<tr>
<th>MH\textsuperscript{a}</th>
<th>$\text{Ru}<em>3(\text{CO})</em>{12}$</th>
<th>$^{13}\text{CO}\textsuperscript{b}$</th>
<th>Temp.</th>
<th>Time</th>
<th>$^{13}\text{CO}$ observed</th>
<th>$^{13}\text{CO}$ stat. calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH</td>
<td>0.45</td>
<td>5.88</td>
<td>$27^\circ \text{C}$</td>
<td>1.5 hr</td>
<td>78%</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5 hr</td>
<td>70%</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.5 hr</td>
<td>53%</td>
<td>52%</td>
</tr>
<tr>
<td>NaH</td>
<td>0.45</td>
<td>5.74</td>
<td>$27^\circ \text{C}$</td>
<td>1.5 hr</td>
<td>88%</td>
<td>51%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5 hr</td>
<td>79%</td>
<td>51%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.5 hr</td>
<td>52%</td>
<td>51%</td>
</tr>
<tr>
<td>LiH</td>
<td>0.45</td>
<td>5.88</td>
<td>$27^\circ \text{C}$</td>
<td>1.5 hr</td>
<td>95%</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5 hr</td>
<td>91%</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.5 hr</td>
<td>70%</td>
<td>52%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}0.45 mmole metal hydride

\textsuperscript{b}$^{13}\text{CO}$ (99% $^{13}\text{C}$) at 1 atm. pressure
\[
\text{K[Ru}_3\text{(CO)}_{11}] + \text{CO} + \text{B(OMe)}_3 \xrightarrow{\text{THF} \text{ at } 20^\circ\text{C}} \text{Ru}_3\text{(CO)}_{12} + \text{KB(OMe)}_3 \quad \text{(3a)}
\]

(3a-b). This reaction sequence was complete after 48 hrs under CO (1 atm) at 20°C. The disproportionation of the [HB(OMe)]⁻ ion in ether solvents is well known [159] and we found that when KH reacted with B(OMe)₃, the intermediate K[HB(OMe)]⁻ disproportionated according to reaction (3b). The infrared spectrum in the B-H stretching region of the product from sequence (3a-b) was identical to the infrared spectrum of the product from the reaction of KH with B(OMe)₃, shown in Figure 6. Figure 6 gives infrared spectra derived from (a) commercial KBH₄; (b) the reaction of KH with B(OMe)₃ in THF at 20°C; (c) the reaction of K[Ru₃(CO)] with B(OMe)₃ under 1 atm. CO in THF. When CO was absent from the system, there was no apparent reaction between B(OMe)₃ and K[Ru₃(CO)]₁₁. The key to observing borohydride in this system is the limited solubility of KBH₄ and K(B(OMe)₄) in THF, which drives the reaction to the right. When Na[Ru₃(CO)]₁₁ was employed under identical conditions, no apparent reaction occurred because of the favorable solubility of NaBH₄ in THF which, in turn, favors the back reaction of NaBH₄ with Ru₃(CO)₁₂.

Reaction sequence (3a-b) best demonstrates the apparent hydridic character of [HRu₃(CO)]⁻ under CO pressure because the hydride ion is trapped as a hydridic salt, KBH₄.
Figure 6. Infrared spectra of KBH$_4$ derived from:
(a) commercial KBH$_4$; (b) Reaction of KH with B(OMe)$_3$
in THF; (c) Reaction between [HRu$_3$(CO)$_{11}$]$_-$ and
B(OMe)$_3$ in THF under CO (1 atm).
3. Hydride Transfer to [Ph₃C]

The cluster anion [HRu₃(CO)₁₁]⁻ was reacted with the known hydride-abstraction agent [Ph₃C][BF₄] under CO pressure and in the absence of CO. The following reaction was complete within 30 min. at 25°C, with 1 atm. of CO over a THF solution 0.3 M in K[HRu₃(CO)₁₁] and [Ph₃C][BF₄]:

\[ K[HRu₃(CO)₁₁] + [Ph₃C][BF₄] + CO \rightarrow KBF₄ + Ru₃(CO)₁₂ + Ph₃CH \quad (4) \]

No other products were detected. In the absence of CO, evidence of a reaction is apparent only after several days. Given the stability of the trityl radical, reaction (4) was studied by ESR spectrometry. Reaction (4) was carried out at 25°C, and in a separate experiment at -78°C, and ESR spectra (-196°C) of the reaction products were recorded as a function of time. In both experiments the reactions were performed in an ESR tube adapted such that CO gas could be delivered or removed rapidly. At both 25°C and -78°C, a radical signal (g = 2.03) attributed to Ph₃C⁺ was observed (Figure 7). The intensity of this signal was independent of CO pressure over the reaction solution at 25°C or -78°C. When reaction (4) was performed at 25°C under 1 atm. CO, the radical signal persisted even after the K[HRu₃(CO)₁₁] had been quantitatively consumed.

The behavior described above is consistent with two independent pathways: a CO-dependent hydride donation from [HRu₃(CO)₁₁]⁻ to [Ph₃C] and a slow radical mechanism in which an electron is transferred from [HRu₃(CO)₁₁]⁻ to [Ph₃C], forming the observed Ph₃C⁺. The radical pathway is not believed to be an important one in Reaction (4) for the
Figure 7. ESR Spectrum of the Reaction Between \([\text{HRu}_3(\text{CO})_{11}]\) and \([\text{Ph}_3\text{C}^+]\) under CO Pressure
following reasons. First, the cluster radical $[\text{HRu}_3(\text{CO})_{11}]$ was prepared and found to be extremely unstable. Under 1 atm. CO or in the absence of CO, $[\text{HRu}_3(\text{CO})_{11}]$ decomposed rapidly at temperatures above $-20^\circ\text{C}$, yielding insoluble materials which were not characterizable. The ESR signal of $[\text{HRu}_3(\text{CO})_{11}]$ was not observed in any of ESR experiments described above. Secondly, the rate of reaction (4) showed a marked CO-dependence while the concentration of $\text{Ph}_3\text{C}^\text{•}$ was independent of CO pressure. Thirdly, the rate of formation of $\text{Ru}_3(\text{CO})_{12}$ in the absence of CO was exceedingly slow. Thus, it is thought that $[\text{HRu}_3(\text{CO})_{11}]$ and $\text{Ph}_3\text{C}^\text{•}$ are formed only very slowly during the course of reaction (4). These experiments do not rule out a radical mechanism, but do suggest that, in the presence of CO, $[\text{HRu}_3(\text{CO})_{11}]^-$ transfers a hydride ion to $[\text{Ph}_3\text{C}]^\text{+}$.

4. Reaction with $\text{CH}_3\text{I}$

Reaction (5) went to completion in 36 hrs at 25$^\circ\text{C}$ in the presence of CO (1 atm). Proton NMR spectra of the reaction solution indicated

$$K[\text{HRu}_3(\text{CO})_{11}] + \text{CO} + \text{CH}_3\text{I} \rightarrow \text{CH}_4 + \text{Ru}_3(\text{CO})_{12} + K\text{I}$$

(5)

that only $K[\text{HRu}_3(\text{CO})_{11}]$ and $\text{CH}_3\text{I}$ were present. In the absence of CO, the production of $\text{CH}_4$ was insignificant, but a number of cluster species had formed. Clearly, reaction (5) can not proceed through a radical mechanism. However, it is not possible to rule out the formation of a Ru (alkyl) (hydride) intermediate, which could undergo CO-induced methane reductive elimination [160].
5. **Reaction with H$_2$O in the Presence of CO**

The reaction of [HRu$_3$(CO)$_{11}$]$^-$ with H$_2$O in the presence of CO was of interest due to its relationship to catalysis of the water-gas shift reaction. The K$^+$, Na$^+$ and Li$^+$ salts of [HRu$_3$(CO)$_{11}$]$^-$ (0.01 M) all reacted at similar rates (Reaction 6), while the N(CH$_3$)$_3^+$ and N(C$_2$H$_5$)$_4^+$ salts reacted only very slowly, possibly due to their limited solubilities in H$_2$O.

$$\text{[HRu$_3$(CO)$_{11}$]$^-$ + CO + H$_2$O} \xrightarrow{\text{H$_2$O} \text{ at 25°C}} \text{H}_2 + \text{Ru}_3$(CO)$_{12}$ + OH$^-$ (6)$$

The solvent water minimized the known back reaction of OH$^-$ with Ru$_3$(CO)$_{12}$ [161]. When the reaction was carried out at 60°C, Ru$_3$(CO)$_{12}$ was formed quantitatively over a period of 8 hours. The reaction was 80% complete after 48 hrs at 25°C. In the absence of CO, only a trace of H$_2$ and no Ru$_3$(CO)$_{12}$ was formed at 25°C and 60°C in the reaction periods cited above. These results are summarized in Table 6. The fact that Ru$_3$(CO)$_{12}$ was not formed in the absence of CO suggested that [HRu$_3$(CO)$_{11}$]$^-$ was not significantly protonated by H$_2$O. This is consistent with the fact that [HRu$_3$(CO)$_{11}$]$^-$ is a very weak base [17]. Protonation of [HRu$_3$(CO)$_{11}$]$^-$ has been shown to proceed through the unstable intermediate H$_2$Ru$_3$(CO)$_{11}$ [162], which decomposes giving H$_2$ and CO in a 1:1 ratio and Ru$_3$(CO)$_{12}$ in 90% conversion [153]. Thus, Reaction (6) reflects the apparent hydric character of [HRu$_3$(CO)$_{11}$]$^-$ in the presence of CO. A deuterium labeling experiment (Reaction 7) was performed analogous to Reaction (6) but employing K[DRu$_3$(CO)$_{11}$] instead of K[HRu$_3$(CO)$_{11}$]. The non-condensible gas products were measured as a
Table 6. Reactions of K[HRu$_3$(CO)$_{11}$] and K[DRu$_3$(CO)$_{11}$] with H$_2$O

A. In the Presence of CO (1 atm)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conc.</th>
<th>Temp.</th>
<th>Time</th>
<th>% Yield Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[HRu$<em>3$(CO)$</em>{11}$]</td>
<td>0.13M</td>
<td>25°C</td>
<td>48 hrs</td>
<td>80%</td>
</tr>
<tr>
<td>K[HRu$<em>3$(CO)$</em>{11}$]</td>
<td>0.13M</td>
<td>60°C</td>
<td>8 hrs</td>
<td>100%</td>
</tr>
<tr>
<td>K[DRu$<em>3$(CO)$</em>{11}$]</td>
<td>0.15M</td>
<td>50°C</td>
<td>32 hrs</td>
<td>60% (97(±3)% HD)</td>
</tr>
</tbody>
</table>

B. In the Absence of CO

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conc.</th>
<th>Temp.</th>
<th>Time</th>
<th>Moles Gas/Moles Cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[HRu$<em>3$(CO)$</em>{11}$]</td>
<td>0.13M</td>
<td>25°C</td>
<td>48 hrs</td>
<td>0.080 (95% CO, 5% O$_2$, a trace H$_2$)</td>
</tr>
<tr>
<td>K[HRu$<em>3$(CO)$</em>{11}$]</td>
<td>0.13M</td>
<td>60°C</td>
<td>8 hrs</td>
<td>2.5 (94% CO, 3% O$_2$, a 3% H$_2$)</td>
</tr>
<tr>
<td>K[DRu$<em>3$(CO)$</em>{11}$]</td>
<td>0.15M</td>
<td>50°C</td>
<td>32 hrs</td>
<td>0.068 (98% CO, 2% O$_2$, a 0.1% HD, H$_2$)</td>
</tr>
</tbody>
</table>

*The O$_2$ product was not due to reaction vessel leakage.*
Figure 8. Proposed Mechanism for Catalysis of the Water-Gas Shift Reaction by Ruthenium Carbonyls in Basic Solution
function of time (Table 6) by mass spectrometry. These spectra indicated that essentially pure HD (97%, ± 3%; no H₂ or D₂ detected)

\[ \text{K[DRu₃(CO)₁₁]} + \text{H₂O} + \text{CO} \xrightarrow{\text{H₂O}} \text{HD} + \text{Ru₃(CO)₁₂} + \text{KOH} \ (7) \]

was given off up until the time the reaction was 90% complete. Note the difference in the rate of reaction of K[HRu₃(CO)₁₁] and K[DRu₃(CO)₁₁], the latter being much slower. Very near the completion of Reaction (7) H₂ was observed along with HD (Table 6). This was probably due to the back reaction of KOH with Ru₃(CO)₁₂ to form K[HRu₃(CO)₁₁] which would then react with the H₂O to form the observed H₂. Such a competing process would become noticeable only very near the completion of Reaction (7). The results of Reaction (7) are consistent with deuterium derived from the cluster having negative character and reacting with protons in water.

B. Catalysis of Water-Gas Shift Reaction by the [HRu₃(CO)₁₁]⁻-Ru₃(CO)₁₂ System

In view of the above observations a cycle is proposed (Figure 8) for catalysis of the water-gas shift reaction that differs from previously proposed cycles [14] involving [HRu₃(CO)₁₁]⁻ because it emphasizes hydridic properties of this ion in the presence of CO. This cycle accounts for the observed first order kinetic dependence of catalytic activity on [CO] concentration [14]. Reaction of hydroxide ion and Ru₃(CO)₁₂ to produce [HRu₃(CO)₁₁]⁻ and CO₂ has been shown to occur [161]. Two possibilities for CO participation in these reactions
are considered: (1) a concerted [112] process in which H⁻ is eliminated as CO is added to [H\text{Ru}_3(\text{CO})_{11}]⁻; (2) an associative mechanism. The latter case requires that an electron rich intermediate, [H\text{Ru}_3(\text{CO})_{12}]⁻, be formed. Such a complex could function as a hydride transfer agent containing hydridic terminal hydrogen bound to either a metal or to a carbon atom of a formyl group. The hydridic character of mono- and binuclear metal carbonyl formyl complexes has been reported [163,164]. Also, a cluster formyl complex has been suggested to act as a hydride transfer agent [165]. The formation of a formyl intermediate would require the migratory insertion of CO into a metal-hydrogen bond:

\[
\text{M-H + CO} \quad \rightleftharpoons \quad \text{M-C=O}
\]

Such a migration has only been observed in two instances [166,167] and does not appear to be a favorable process. Nevertheless, if such an intermediate were formed in the reaction of [H\text{Ru}_3(\text{CO})_{11}]⁻ with CO, the known formyl [(CO)\text{Ru}_3-\text{CHO}]⁻ would be formed [155]. This formyl has been shown to be extremely unstable, decomposing to [H\text{Ru}_3(\text{CO})_{11}]⁻ and CO at temperatures above -50°C. Thus, it would be unlikely that [(CO)\text{Ru}_3-\text{CHO}]⁻ could be observed in the reactions discussed above. A second intermediate which might be formed would contain hydridic hydrogen bound terminally to ruthenium. The donation of two electrons by the incoming CO ligand could induce the opening of the 3-center, 2-electron bridge bond to a 2-center, 2-electron terminally bound hydrogen bond (Figure 9).
The hydridic character of terminally bound hydrogen in ruthenium anions has recently been reported \([64,158]\).

Thus, the cycle in Figure 8 is believed to be consistent with the apparent hydridic character of \([\text{HRu}_3(\text{CO})_{11}]^-\) in the presence of CO. This cycle also accounts for the following observations, which show that the catalytic activity of this system is roughly proportional to the concentration of \([\text{HRu}_3(\text{CO})_{11}]^-\).

### C. Reactivity of Tetranuclear Ruthenium Clusters

Under water-gas shift conditions, a variety of ruthenium carbonyl cluster precursors are capable of giving a catalytically active system. It has previously been shown that catalytic systems initiated by \(\text{H}_2\text{Ru}_4(\text{CO})_{13}\), \(\text{H}_4\text{Ru}_4(\text{CO})_{12}\), or \(\text{Ru}_3(\text{CO})_{12}\) gave solutions which were spectroscopically indistinguishable after an initial "maturing" period.
of 24 hrs [14]. Two species of different nuclearity, \([H_3Ru_4(CO)_{12}]^-\) and 
\([HRu_3(CO)_{11}]^-\) were observed in the \(^1\)H NMR spectra of active catalytic 
solutions [14]. We observed \([H_3Ru_4(CO)_{12}]^-\) only if the system was not 
recharged with fresh CO regularly. This, combined with proposals of 
catalytic cycles based on tetranuclear clusters [14] suggested that 
examination of the reactivity of the tetranuclear anions \([H_3Ru_4(CO)_{12}]^-\),
\([H_2Ru_4(CO)_{12}]^{2-}\), and \([HRu_4(CO)_{13}]^-\) with CO and \(H_2\) was in order.

1. Reactions of \([H_3Ru_4(CO)_{12}]^-\)

Although inert to \(H_2\) at 1 atm, \([H_3Ru_4(CO)_{12}]^-\) reacted with CO (1
atm) according to reaction (8).

\[
[H_3Ru_4(CO)_{12}]^- + 3CO \xrightleftharpoons{\text{glyme}} \rightarrow 
[HRu_3(CO)_{11}]^- + 1/3Ru_3(CO)_{12} + H_2 \text{(soln)} \quad (8)
\]

When Reaction (8) was performed at 80°C, the equilibrium was driven to
the right and to completion by Ru_3(CO)_{12} subliming from the solution.
\([HRu_3(CO)_{11}]^-\) and Ru_3(CO)_{12} were isolated in a 3:1 mole ratio and one
mole of \(H_2\) was evolved per mole of \([H_3Ru_4(CO)_{12}]^-\) consumed. That
Reaction (8) is an equilibrium was established by the following
observations. If the reaction of \([H_3Ru_4(CO)_{12}]^-\) with CO was carried out
at lower temperatures (\(\leq 60°C\)), where Ru_3(CO)_{12} did not sublime,
complete consumption of \([H_3Ru_4(CO)_{12}]^-\) did not occur. Instead, a
mixture of \([H_3Ru_4(CO)_{12}]^-\), \([HRu_3(CO)_{11}]^-\), and Ru_3(CO)_{12} was observed.
If the gas above this mixture was removed and replaced by a pure \(H_2\)
atmosphere, quantitative regeneration of \([H_3Ru_4(CO)_{12}]^-\) occurred.
Subsequent experiments showed that the ratio of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) to \([\text{HRu}_3(\text{CO})_{11}]^-\) was dependent on the CO to H₂ ratio in the system. Under 1 atm H₂ pressure, a 3:1 molar ratio of \([\text{HRu}_3(\text{CO})_{11}]^-\) to \(\text{Ru}_3(\text{CO})_{12}\) reacted rapidly at 60°C to give \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) and CO in accord with the back reaction of Equation (8). In order to determine the equilibrium constant for Reaction (8), \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) was reacted with varying CO/H₂ ratios at 60°C and a total gas pressure of 1 atm. In a separate experiment, a 3:1 molar ratio of \([\text{HRu}_3(\text{CO})_{11}]^-\):\(\text{Ru}_3(\text{CO})_{12}\) was reacted with varying CO/H₂ ratios under identical conditions. The reactions were followed with time by \(^1\text{H}\) NMR spectroscopy and the equilibrium CO/H₂ ratio was determined by mass spectrometry. Under a given CO/H₂ ratio, a constant molar ratio of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) to \([\text{HRu}_3(\text{CO})_{11}]^-\) was observed, irrespective of whether the starting point was \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) or a 3:1 molar ratio of \([\text{HRu}_3(\text{CO})_{11}]^-\) to \(\text{Ru}_3(\text{CO})_{12}\). These results are summarized in Table 7.

The data in Table 7 indicate that small partial pressures of H₂ were capable of producing a significant concentration of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\). From the data in Table 7, an equilibrium constant of \(K_p = 0.02\) was calculated.

It was also of interest to determine the pathway by which \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) and \([\text{HRu}_3(\text{CO})_{11}]^-\) interconvert. The forward reaction of Equation (8), in which \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) reacts with CO, was examined by \(^1\text{H}\) NMR spectroscopy as a function of time at 60°C and 80°C in glyme. Although no intermediate was observed at 60°C, the cluster anion \([\text{HRu}_4(\text{CO})_{13}]^-\) was observed as an intermediate at 80°C, but its concentration never exceeded 14% of the total ruthenium species in
Table 7
Relative Concentrations of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_3(\text{CO})_{11}]^-$
Under Varying CO/H$_2$ Ratios

<table>
<thead>
<tr>
<th>CO/H$_2^a$</th>
<th>Temperature, °C</th>
<th>Solvent(s)$^b$</th>
<th>$[\text{H}_3\text{Ru}<em>4(\text{CO})</em>{12}]^-/[\text{HRu}<em>3(\text{CO})</em>{11}]^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60°C</td>
<td>THF, glyme, EE</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>60°C</td>
<td>glyme</td>
<td>6.3</td>
</tr>
<tr>
<td>11.5</td>
<td>60°C</td>
<td>glyme</td>
<td>3.3</td>
</tr>
<tr>
<td>25</td>
<td>60°C</td>
<td>THF, glyme, EE</td>
<td>2.3</td>
</tr>
</tbody>
</table>

$^a$Mass spectrometry; total gas pressure 1 atm.
$^b$EE = ethoxyethanol

Thus, it appears as if the initial step in the reaction of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ with CO involves H$_2$ elimination according to Reaction (9). The reverse of this reaction was observed to occur; it rapidly and goes to apparent completion at low H$_2$ partial pressure. That the concentration of $[\text{HRu}_4(\text{CO})_{13}]^-$ was low throughout the course of the reaction was due, in part, to the ease with which CO was found to react with $[\text{HRu}_4(\text{CO})_{13}]^-$ according to Reaction (10).

$$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^- + \text{CO} \rightleftharpoons [\text{HRu}_4(\text{CO})_{13}]^- + \text{H}_2$$

We found that at relatively low CO partial pressure (20 torr), Reaction (10) goes to apparent completion. The reaction can be reversed only if CO is continuously removed from the system. Thus, equilibrium (8) can
be represented as the sum of equilibria (9) and (10). Clearly, the presence of H₂ favors the formation of [H₃Ru₄(CO)₁₂]⁻ while the presence of CO favors the formation of [H₃Ru₃(CO)₁₁]⁻.

Although equilibrium (8) was determined in neutral solutions, the possibility that a similar relationship applies to basic WGS catalysis solutions was considered. It was first necessary to consider the stabilities of these clusters in basic solution. Both [H₃Ru₃(CO)₁₁]⁻ and [H₃Ru₄(CO)₁₂]⁻ are stable in basic aqueous solutions as evidenced by their preparation under such conditions [14,123]. The reaction of Ru₃(CO)₁₂ with aqueous base has been shown to give [H₃Ru₃(CO)₁₁]⁻ and CO₂ [161]. We found that [H₃Ru₄(CO)₁₃]⁻ is unstable with respect to aqueous solutions. It was rapidly converted to [H₃Ru₄(CO)₁₂]⁻ according to Reaction (11).

\[
[H₃Ru₄(CO)₁₃]⁻ + H₂O/OH⁻ \xrightarrow{20^°C} [H₃Ru₃(CO)₁₁]⁻ + CO₂
\]

\[\text{pH} = 7-13\]

\[\text{OH}^- \xrightarrow{H^+} [H₂Ru₄(CO)₁₂]²⁻\]

The observation of Reaction 11 indicated that [H₃Ru₄(CO)₁₃]⁻ would not survive in detectable concentration in active catalysis solutions. Consistent with this proposal is the fact that [H₃Ru₄(CO)₁₃]⁻ has not been detected in active catalytic solutions. Proton NMR studies on active WGS catalysis solutions indicated that the ratio of [H₃Ru₄(CO)₁₂]⁻ to [H₃Ru₃(CO)₁₁]⁻ was highly dependent on the CO to H₂ ratio in the system. Thus, the scheme in Figure 10 indicates the relationships between ruthenium clusters in active WGS catalysis solutions. Additionally, Figure 11 demonstrates why similar normalized
Figure 10. Relationships Between Ruthenium Cluster Anions in Active WGS Catalysis Solutions.
Figure 11. Formation of Ruthenium Cluster Anions in Active WGS Solutions
activities are obtained irrespective of whether the starting point is a
tetranuclear or trinuclear cluster.

D. Active Catalysis Solutions

Figure 10 suggests that if H₂ could be removed as it is formed in
the water-gas shift reaction, then the concentration and subsequent
contribution of [HRu₃(CO)₁₁]⁻ to catalysis could be maximized. This
point was tested by setting up a water-gas shift experiment (Figure 12)
in which H₂ was continuously removed from the apparatus by diffusion
through a palladium thimble while CO remained behind. As expected, only
[HRu₃(CO)₁₁]⁻ was observed in solution even though H₄Ru₄(CO)₁₂ was the
starting cluster. In this effectively H₂ free environment, the turnover
was approximately three times that observed in experiments in which the
H₂ was allowed to accumulate in the system. These results shows that
the activity increases as the concentration of trinuclear anion
[HRu₃(CO)₁₁]⁻ increases. The presence of H₂ shifts the equilibrium
towards [H₃Ru₄(CO)₁₂]⁻, but the presence of H₂ also inhibits the
reductive elimination step of Reaction 9. Data for the catalysis of the
water-gas shift reaction is summarized in Table 8.

The data in Table 8 indicate that the catalytic activity of this
system is roughly proportional to the concentration of [HRu₃(CO)₁₁]⁻ in
solution. These concentrations are based on ¹H NMR spectra of active
catalysis solutions following a 24-hr catalysis run. WGS catalytic
activity was evaluated using Li⁺, Na⁺, K⁺, N(Me)₄⁺, HN(Et)₃⁺
counterions. Based on the data in Table 8, there does not appear to be
a significant cation effect on the catalytic activity, although, the
Figure 12. Palladium Thimble Experiment for Continuous Removal of $H_2$ From Active Catalysis System
Table 8. Catalysis of the Water-Gas Shift Reaction

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Cluster</th>
<th>Conditions</th>
<th>Turnovers/24 hr</th>
<th>Mol % Composition (*H NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Day 1 2 3 4 5 6</td>
<td>[HRu$<em>2$(CO)$</em>{12}$]$^+$[HRu$<em>3$(CO)$</em>{12}$]^-</td>
</tr>
<tr>
<td>1</td>
<td>H$_4$Ru$<em>4$(CO)$</em>{12}$</td>
<td>H$_2$ Accumulates</td>
<td>3.1 2.2 2.0 2.0 2.0 2.0</td>
<td>~ 10% : 90%</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$Ru$<em>4$(CO)$</em>{12}$</td>
<td>Pd Thimble</td>
<td>3.4 2.7 2.6 2.8 2.8 2.8</td>
<td>~ 10% : 90%</td>
</tr>
<tr>
<td>3</td>
<td>Ru$<em>3$(CO)$</em>{12}$</td>
<td>H$_2$ Accumulates</td>
<td>3.0 2.2 1.9 2.3 2.1 2.1</td>
<td>~ 10% : 90%</td>
</tr>
<tr>
<td>4</td>
<td>Ru$<em>3$(CO)$</em>{12}$</td>
<td>Pd Thimble</td>
<td>3.8 2.8 2.8 2.9 1.2$^c$</td>
<td>~ 10% : 90%</td>
</tr>
<tr>
<td>5</td>
<td>Ru$<em>3$(CO)$</em>{12}$</td>
<td>H$_2$ Accumulates</td>
<td>-- 0.9 0.9 0.9</td>
<td>63% : 37% [14]</td>
</tr>
<tr>
<td>6</td>
<td>Ru$<em>3$(CO)$</em>{12}$(DPPE)$^e$</td>
<td>H$_2$ Accumulates</td>
<td>4.7 3.7 3.9 4.1 3.9 4.2</td>
<td>100% of K<a href="DPPE">HRu$<em>2$(CO)$</em>{12}$</a>**</td>
</tr>
<tr>
<td>7</td>
<td>Ru$<em>3$(CO)$</em>{12}$(DDPE)$^f$</td>
<td>H$_2$ Accumulates</td>
<td>--------</td>
<td>Non Catalytic--------</td>
</tr>
</tbody>
</table>

$^a$Conditions: 100°C; 0.9 atm CO; ethoxyethanol (3 mL); H$_2$O (0.36 mL); KOH (2.0 mmole); 0.04 mmole cluster.
$^b$Experiments 1-7 employed KOH ($K^+$ counterion). Effect of counterion in experiments 8-15.
$^c$Excess H$_2$ was added to the system prior to catalysis.
$^d$Pd was allowed to accumulate on day 4.
$^e$DPPE = $\phi_3$PCH$_2$CH$_2$P$_2$
$^f$DDPE = $\phi_3$PCH$_2$CH$_2$P$_2$
activity of N(CH₃)⁺ system is slightly reduced. There is, however, a
marked dependence of catalytic activity on phosphine substitution of the
cluster anions (Experiments 6 and 7). While catalysis initiated by
Ru₃(CO)₁₀(DPPE) produces an increase (30%) in activity relative to
Ru₃(CO)₁₂; Ru₃(CO)₈(DPPM)₂ produces an inactive system. The reasons for
this are discussed below.

E. Phosphine Substituted Clusters

In order to test the effect of phosphine substitution and possibly
develop a better WGS catalyst, the phosphine substituted clusters
Ru₃(CO)₁₀(DPPE) and Ru₃(CO)₈(DPPM)₂ were tested as catalyst precursors
for catalysis of water-gas shift reaction. Results are summarized in
Table 8. Although the Ru₃(CO)₁₀(DPPE) catalyst precursor is apparently
more active than Ru₃(CO)₁₂, the Ru₃(CO)₈(DPPM)₂ precursor was
catalytically inactive. This apparent contradiction may be explained by
examination of the model reactions described below.

In order to compare the reactivities of hydrido-cluster anions
formed upon reaction of OH⁻ with Ru₃(CO)₁₀(DPPE), Ru₃(CO)₈(DPPM)₂, and
Ru₃(CO)₁₂; the salts K[HRu₃(CO)₉(DPPE)] and K[HRu₃(CO)₇(DPPM)₂] were
prepared (see Results and Discussion, Section IV). Reaction of
K[HRu₃(CO)₉(DPPE)] and K[HRu₃(CO)₇(DPPM)₂] with H₂O under CO pressure
resulted in H₂ production at approximately a 7-fold rate increase as
compared with the parent [HRu₃(CO)₁₁]⁻.

\[
[HRu₃(CO)₉(DPPE)]⁻ + CO + H₂O \xrightleftharpoons{25°C \text{H}_2\text{O}} Ru₃(CO)₁₀(DPPE) + H₂ + OH⁻ \quad (12)
\]
[HRu₃(CO)₇(DPPM)₂]⁻ + CO + H₂O $\xrightarrow{25^\circ C}$ Ru₃(CO)₈(DPPM)₂ + H₂ + OH⁻ (13)

The rate increase observed with the phosphine substituted cluster anions is presumably due to increased electron density on the metal centers. If an expanded intermediate such as [HRu₃(CO)₁₀(DPPE)]⁻ were formed upon reaction with CO, it would be expected to be more hydridic than [HRu₃(CO)₁₂]⁻ since the phosphine ligands employed here are better σ-donors than CO. However, a second consequence of increased electron density on the metal is to increase backbonding to the remaining carbonyls, rendering them less susceptible to attack by nucleophiles (OH⁻) [114].

The reason that Ru₃(CO)₈(DPPM)₂ produces an inactive system is that the basic conditions employed in these catalytic studies are not sufficient to regenerate the metal hydride from Ru₃(CO)₈(DPPM)₂ and OH⁻. Even when K[HRu₃(CO)₇(DPPM)₂] was employed as a catalyst precursor, precipitation of Ru₃(CO)₈(DPPM)₂ occurred quantitatively in a few hours and the system was inactive. Although the initially prepared WGS solutions were sufficiently basic to generate K[HRu₃(CO)₇(DPPM)₂] from Ru₃(CO)₈(DPPM)₂, the basicity of catalysis solutions only two hours old was not sufficient to maintain the catalytic cycle. It is known [107] that basic catalysis solutions for the WGSR are buffered by formate and bicarbonate:
Thus a pH of 9.5 to 10.0 is achieved and maintained within hours of the onset of catalysis. Independently, it was shown that Reaction (14) did not occur to a significant extent at pH 10.

\[
\text{CO} + \text{OH}^- \rightarrow \text{HCO}_2^-
\]

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-
\]

In the case of Ru₃(CO)₈(DPPM)₂, the catalysis data in experiment 6 (Table 8) indicate that a modest (30%) increase in catalytic activity has been achieved relative to Ru₃(CO)₁₂. However, the rate increase is not as significant as would be expected based on the relative rates of model reactions (12) and (6). Reaction (12) is approximately 7 times more rapid than Reaction (6) at 25°C. It may be that in the active catalysis solution, the rate-determining step for the catalytic cycle has changed to base attack at carbon monoxide (Reaction 15), as in the case of Ru₃(CO)₈(DPPM)₂ (Reaction 14).

\[
\text{Ru}_3(\text{CO})_8(\text{DPPM})_2 + \text{OH}^- \rightarrow [\text{HRu}_3(\text{CO})_9(\text{DPPM})_2]^\text{−} + \text{CO}_2 \quad (14)
\]

A second possibility is that the relative rates of reactions (12) and (6) are not significantly different at 100°C. Whichever is the case, the results obtained with Ru₃(CO)₈(DPPM)₂ and Ru₃(CO)₁₀(DPPE) suggest
that only modest improvement in catalytic activity could be achieved through phosphine substitution.

F. Conclusion—Summary

The chemistry of ruthenium carbonyl anions was studied with respect to the catalysis of the water-gas shift reaction (WGSR: CO + H₂O → CO₂ + H₂). Sodium and potassium salts of [HRu₃(CO)₁₁]⁻ reacted with CO (1 atm.) to precipitate Ru₃(CO)₁₂ and probably metal hydride in THF. In the presence of CO, [HRu₃(CO)₁₁]⁻ functioned as an apparent hydride donor to B(OC₂H₅)₃ and H₂O. The effect of counterion (K⁺, Na⁺, Li⁺, N(CH₃)₄⁺, N(C₂H₅)₂⁺) on the hydride donating reactions of [HRu₃(CO)₁₁]⁻ was studied. For catalysis of the water-gas shift reaction, a catalytic cycle which involves [HRu₃(CO)₁₁]⁻ and Ru₃(CO)₁₂ and emphasizes the hydridic nature of [HRu₃(CO)₁₁]⁻ in the presence of CO is proposed as the major contributor to catalysis by ruthenium carbonyls in basic solution at low CO pressure (~1 atm). An equilibrium between tetranuclear and trinuclear clusters under CO/H₂ (1 atm.) gas was shown to exist in aprotic media: [H₃Ru₄(CO)₁₂]⁻ + 3 CO → [HRu₃(CO)₁₁]⁻ + 1/3 Ru₃(CO)₁₂ + H₂. In catalytic solutions, activity decreased when H₂ was allowed to accumulate in the system and the equilibrium shifted toward the formation of [H₃Ru₄(CO)₁₂]⁻. However, when H₂ was continuously removed from the system by diffusion through a Pd thimble while CO remained behind, the equilibrium shifted toward [HRu₃(CO)₁₁]⁻ and the activity increased in direct proportion to the increase in [HRu₃(CO)₁₁]⁻ concentration. Thus, [HRu₃(CO)₁₁]⁻ is a required component in the catalysis of the WGSR in basic solution. The effect of
counterion (K\textsuperscript{+}, Na\textsuperscript{+}, Li\textsuperscript{+}, N\textsubscript{(CH\textsubscript{3})\textsubscript{4}}, HHN\textsubscript{C\textsubscript{2}H\textsubscript{5}}\textsubscript{3}\textsuperscript{+}) and the effect of phosphine (DPPE = \textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P\textsubscript{2}; DPPM = \textsubscript{2}PCH\textsubscript{2}P\textsubscript{2}) substitution on [HRu\textsubscript{3}(CO)\textsubscript{11}]\textsuperscript{-} was examined. Although the counterion has little effect on catalysis, the degree of phosphine substitution had a pronounced effect on catalytic activity.
II. The Condensation of Mononuclear \([\text{HM(CO)}]^-\) to Trinuclear \([\text{HM}_{3}(\text{CO})_{11}]^-\) Metal Hydridocarbonyl Anions (\(M = \text{Fe, Ru, Os}\))

Under Protic and Water-Gas Shift Conditions

Minimal details have been reported concerning the abilities of mononuclear anions of the type \([\text{HM(CO)}]^-\) (\(M = \text{Fe, Ru, Os}\)) to form higher nuclearity cluster anions through self-condensation [168-170]. It is known, however, that these anions are stable in aprotic media and that \([\text{HRu(CO)}]^-\) is converted to \([\text{HRu}_3(\text{CO})_{11}]^-\) in CH\(_3\)OH at 60°C [170]. It is also known that the anion \([\text{HFe(CO)}]^-\) interconverts with \([\text{HFe}_3(\text{CO})_{11}]^-\) in aqueous amine solutions in the presence of CO [169].

The stoichiometries of these reaction systems have not been reported. In the present study, we have determined the relative tendencies of the title mononuclear anions to self-condense in protic media and under water-gas shift conditions. The stoichiometries of the condensation reactions have been determined. Since the possibility of mononuclear species existing in protic and in water-gas shift catalytic systems is a current consideration [52,69], it was of interest to determine the likelihood of their survival under such conditions. It was of special interest to determine whether \([\text{HRu(CO)}]^-\) could survive WGS conditions and what role it might play in the catalysis described in the previous section.
A. Ruthenium Anions.

In the presence of protic media, $\text{K}[\text{HRu(CO)}_4]$ was converted to $\text{K}[\text{HRu}_3(\text{CO})_1]_1$ [170]. Results are summarized in Table 9. A mixture of anhydrous HCl and $\text{K}[\text{HRu(CO)}_4]$ in THF in the molar ratio of 2:3 reacted within minutes according to Equation (1).

$$3\text{K}[\text{HRu(CO)}_4] + 2\text{HCl} \xrightarrow{25^\circ\text{C}} \text{K}[\text{HRu}_3(\text{CO})_1]_1 + 2\text{H}_2 + \text{CO} + 2\text{KCl} \quad (1)$$

Hydrogen and carbon monoxide were produced quantitatively in a 2:1 molar ratio and the reaction solution yielded spectroscopically pure $\text{K}[\text{HRu}_3(\text{CO})_1]_1$ which was isolated in 92% yield. Two protons were required for the quantitative conversion of $\text{K}[\text{HRu(CO)}_4]$ to $\text{K}[\text{HRu}_3(\text{CO})_1]_1$. When the molar ratio of reactants employed was less than 2HCl/3HRu(CO)_4, incomplete reaction was observed.

In $\text{H}_2\text{O}$, the condensation reaction proceeded to completion in 20 seconds according to Equation (2).

$$3\text{K}[\text{HRu(CO)}_4] + 2\text{H}_2\text{O} \rightarrow \text{K}[\text{HRu}_3(\text{CO})_1]_1 + \text{CO} + 2\text{H}_2 + 2\text{KOH} \quad (2)$$

The reaction was slightly retarded in basic $\text{KOH}$ (5.6 M) solution. In anhydrous methanol at $25^\circ\text{C}$, the reaction proceeded very slowly but in an alcohol:water (3:2) mixture it proceeded nearly as rapidly as in pure $\text{H}_2\text{O}$.

Under water-gas shift conditions (Table 9) $\text{K}[\text{HRu(CO)}_4]$ did not survive in detectable concentration in the temperature range studied ($0$-$100^\circ\text{C}$). It was rapidly transformed into $\text{K}[\text{HRu}_3(\text{CO})_1]_1$. In the presence of the H2 that was formed in the reaction, this $\text{K}[\text{HRu}_3(\text{CO})_1]_1$ was slowly
Table 9
Conversion of $[\text{HM(CO)}_4^-]$ to $[\text{HM}_3(\text{CO})_{11}]^-$ in Protic Media

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Metal</th>
<th>$([\text{HM(CO)}_4^-])^a$</th>
<th>Temp.</th>
<th>Min.$^b$</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl/THF</td>
<td>Ru</td>
<td>0.08</td>
<td>25°C</td>
<td>1.0</td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.06</td>
<td>25°C</td>
<td>1800</td>
<td>$[\text{HFe}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>Ru</td>
<td>0.16</td>
<td>25°C</td>
<td>1200</td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td>CH$_3$OH/H$_2$O</td>
<td>Ru</td>
<td>0.13</td>
<td>25°C</td>
<td>0.3</td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Ru</td>
<td>0.10</td>
<td>0$^+5$°C</td>
<td>0.3</td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.15</td>
<td>25°C</td>
<td>600</td>
<td>$[\text{HFe}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td></td>
<td>Os</td>
<td>0.13</td>
<td>25°C</td>
<td>&gt;5000</td>
<td>$\text{H}_2\text{Os(CO)}_4^-$, $[\text{HOS}<em>3(\text{CO})</em>{11}]^-$, CO, H$_2$</td>
</tr>
<tr>
<td>H$_2$O/KOH</td>
<td>Ru</td>
<td>0.10</td>
<td>25°C</td>
<td>1.0</td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, $[\text{H}_2\text{Ru}<em>4(\text{CO})</em>{12}]^2^-$, CO, H$_2$</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, $[\text{HRu}<em>3(\text{CO})</em>{11}]^-$</td>
</tr>
<tr>
<td>Water-Gas</td>
<td>Ru$^d$</td>
<td>0.03</td>
<td>0$^+100$°C</td>
<td>2.0</td>
<td>$[\text{HRu}<em>3(\text{CO})</em>{11}]^-$, $^8$</td>
</tr>
<tr>
<td>Shift$^c$</td>
<td>Fe$^e$</td>
<td>0.03</td>
<td>0$^+100$°C</td>
<td>800</td>
<td>$\text{Fe}^{+2}$ species</td>
</tr>
<tr>
<td></td>
<td>Os$^f$</td>
<td>0.03</td>
<td>0$^+100$°C</td>
<td>1400</td>
<td>$[\text{HOS}<em>3(\text{CO})</em>{11}]^-$</td>
</tr>
</tbody>
</table>

$^a$ moles/liter.

$^b$ Time for complete consumption of $[\text{HM(CO)}_4^-]$ to occur.

$^c$ H$_2$O (0.35 mL); Ethoxyethanol (3.0 mL); KOH (2.0 mmole); CO (5.0 millimole) 1 atm.; 100°C.

$^d$ $[\text{HRu(CO)}_4^-]$ catalyst precursor.

$^e$ $\text{Fe}_3(\text{CO})_{12}$ catalyst precursor.

$^f$ $[\text{HOS(CO)}_4^-]$ catalyst precursor.

$^g$ If H$_2$ is removed continuously as it forms from the water-gas shift reaction.
converted to the tetranuclear anion $K_2[H_2Ru_4(CO)_{12}]$, as described in more detail in the preceding section:

$$[HRu_3(CO)_{11}]^- + \frac{1}{3}Ru_3(CO)_{12} + H_2 \rightleftharpoons [H_3Ru_4(CO)_{12}]^- + 3CO$$  \hspace{1cm} (3)

These results show that under a variety of conditions in protic media, $[HRu(CO)_4]^-\text{ is unstable with respect to forming } [HRu_3(CO)_{11}]^-$. Clearly, this makes difficult the observation of $[HRu(CO)_4]^-\text{ in aqueous catalytic systems. The only hope of observing it would be if a sufficiently high CO pressure could be achieved to force significant fragmentation of } [HRu_3(CO)_{11}]^-\text{. Two types of fragmentations can be envisioned. One would be the reverse of Reaction (2). This would require } H_2 \text{ as well as CO plus a base to absorb the protons formed. However, as pointed out above, } [HRu_3(CO)_{11}]^-\text{ forms tetranuclear clusters when } H_2 \text{ is present. Thus, in the presence of } H_2, \text{ a competing process could minimize the possibility of forming } [HRu(CO)_4]^-\text{. A second type of fragmentation which might occur in the presence of CO would produce } [HRu(CO)_4]^- \text{ and } Ru(CO)_5 \text{ as products [Reaction (4)].}

$$[HRu_3(CO)_{11}]^- + 3 \text{ CO} \rightleftharpoons [HRu(CO)_4^-] + 2 Ru(CO)_5$$  \hspace{1cm} (4)
This second type of fragmentation could occur in aprotic media and has been observed for the analogous iron system. However, attempts to fragment \([\text{HRu}_3(\text{CO})_{11}]^-\) in protic or aprotic media under high CO pressures (> 800 atm) have been unsuccessful [64]. Therefore, under the conditions employed in the low pressure catalysis of the water-gas shift reaction (100°C, 1 atm. CO), it is unlikely that \([\text{HRu}(\text{CO})_4]^-\) is an important intermediate [18-20].

Reaction (2) probably occurs through the following sequence of steps [170]:

\[
\text{[HRu(CO)_4]}^- + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{Ru(CO)_4} + \text{OH}^-} \text{H}_2\text{Ru(CO)_4} + \text{OH}^- \quad (5a)
\]

\[
2\text{H}_2\text{Ru(CO)_4} + \text{[HRu(CO)_4]}^- \xrightarrow{\text{[HRu_3(CO)_11]}^- + \text{CO} + 2\text{H}_2} \quad (5b)
\]

In the first step (5a) \([\text{HRu(CO)}_4]^-\) is protonated to give \(\text{H}_2\text{Ru(CO)}_4\). As the \(\text{H}_2\text{Ru(CO)}_4\) is formed, it undergoes rapid reaction (5b) with remaining \([\text{HRu(CO)}_4]^-\) to yield \([\text{HRu}_3(\text{CO})_{11}]^-\). Each step in the proposed sequence has been demonstrated. The protonation of \([\text{HRu(CO)}_4]^-\) to generate \(\text{H}_2\text{Ru(CO)}_4\) was demonstrated earlier [171]. We have shown the second step to be feasible by adding \(\text{H}_2\text{Ru(CO)}_4\) to \(\text{K}[\text{HRu(CO)}_4]\) in THF. This resulted in the rapid formation of \([\text{HRu}_3(\text{CO})_{11}]^-\) and CO and \(\text{H}_2\). The combination of steps (5a) and (5b) gives the stoichiometry observed in Equation (2).

A less likely pathway for the formation of \([\text{HRu}_3(\text{CO})_{11}]^-\) in Reaction (2) would involve formation of \(\text{H}_2\text{Ru(CO)}_4\) (5a), followed by thermal decomposition of \(\text{H}_2\text{Ru(CO)}_4\) to form \(\text{H}_2\text{Ru}_3(\text{CO})_{12}\) (Reaction 6).
3 H₂Ru(CO)₄ \xrightarrow{Δ} H₂Ru₃(CO)₁₂ + 2 H₂ \hspace{1cm} (6)

The H₂Ru₃(CO)₁₂ formed in this manner could be deprotonated by the hydroxide ion generated in (5a) to form [HRu₃(CO)₁₁]⁻ [Reaction (7a)].

H₂Ru₃(CO)₁₂ + OH⁻ \xrightarrow{} [HRu₃(CO)₁₁]⁻ + CO + H₂O \hspace{1cm} (7a)

The stoichiometry of Reaction (7a) is considered to be a reasonable one based on the stoichiometry of the following deprotonation reaction which has been observed [Reaction (7b)].

H₂Ru₃(CO)₁₂ + KH \xrightarrow{THF, 25°C} K[HRu₃(CO)₁₁]⁻ + CO + H₂ \hspace{1cm} (7b)

The major difference between these two reactions is that deprotonation of H₂Ru₃(CO)₁₂ by KH produces H₂ while deprotonation of H₂Ru₃(CO)₁₂ by OH⁻ produces H₂O. In either case the same intermediate, [HRu₃(CO)₁₁]⁻, is presumably formed, and decomposes to [HRu₃(CO)₁₁]⁻ and CO rapidly. No intermediate [HRu₃(CO)₁₁]⁻ was observed spectroscopically in either reaction. Although we find that H₂Ru(CO)₄ will form H₂Ru₃(CO)₁₂, according to Reaction (6), H₂Ru₃(CO)₁₂ is not deprotonated sufficiently rapidly by hydroxide ion (studied in the range of 0.07 - 5.6 M OH⁻) to contribute significantly to the formation of [HRu₃(CO)₁₁]⁻ in the condensation reactions considered above.
Reactions of $K[HFe(CO)_4]$ with anhydrous HCl in THF and H$_2$O (Equations 8 and 9) are analogous to the reactions of $K[HRu(CO)_4]$ (Equations 1 and 2). Results are summarized in Table 9.

3 $K[HFe(CO)_4] + 2 HCl \xrightarrow{\text{THF, 25°C}} K[HFe(CO)_{11}] + 2 H_2 + CO + 2 KCl$ \text{(8)}

3 $K[HFe(CO)_4] + 2 H_2O \xrightarrow{\text{25°C}} K[HFe(CO)_{11}] + 2 H_2 + CO + 2 KOH$ \text{(9)}

However, the rate of transformation of $K[HFe(CO)_4]$ to $K[HFe_3(CO)_{11}]$ is markedly slower than in the ruthenium system (Table 9). This is probably due to the fact that $K[HRu(CO)_4]$ is much more basic than $K[HFe(CO)_4]$ [170]. Furthermore, $K[HFe_3(CO)_{11}]$ is very susceptible to fragmentation under CO pressure compared to $K[HRu_3(CO)_{11}]$ [64]. We find that the presence of a large excess (12:1) of CO (1 atm.) in THF at 25°C, $K[HFe_3(CO)_{11}]$ (0.1M) is converted quantitatively to $K[HFe(CO)_4]$ and Fe(CO)$_5$ over a period of ten hours. This result shows that fragmentation of $K[HFe_3(CO)_{11}]$ will occur under much less severe conditions than previous studies would suggest [64,169].

Under water-gas shift conditions (Table 9) at 100°C and 1 atm CO pressure, $K[HFe_3(CO)_{11}]$ is completely converted to $K[HFe(CO)_4]$ (~ 6 hrs.) which, in accord with earlier observations [107] decomposes to insoluble, inactive Fe$^{II}$ species. Thus we find that after a period of one day, catalytic activity for the water-gas shift has ceased. Even under very mild conditions, the trinuclear iron system is converted to mononuclear species which, in turn, are not active at low CO
pressures. A previous report [18] for water-gas shift catalysis using Fe$_3$(CO)$_{12}$ as a catalyst precursor under relatively high CO pressure (75 atm) undoubtedly involved formation of the mononuclear anion [HFe(CO)$_4$]$^-$]. In this case, the system showed activity because of the high CO pressure. It has been shown [107] that [HFe(CO)$_4$]$^-$ is active at high CO pressures, but is converted to Fe II species at low CO pressure as indicated above (see Introduction)

C. Osmium Anions.-

The reaction of K[HOs(CO)$_4$] with H$_2$O (25°C) resulted in evolution of only 0.01 equivalent of non-condensable gas (Table 9), suggesting that conversion to higher nuclearity species had not occurred. This was confirmed by $^1$H NMR spectra which indicated that only H$_2$Os(CO)$_4$ (86%) and K[HOs(CO)$_4$] (14%) were in solution after 3 days at 25°C. Only after extended periods of time (~ 7 days) was [HOs$_3$(CO)$_{11}$]$^-$ present in detectable concentration (~ 10%). Under water-gas shift conditions (Table 9) employing Os$_3$(CO)$_{12}$ as a catalyst precursor, [HOs$_3$(CO)$_{11}$]$^-$ was the only species detectable by $^1$H NMR spectra.

When [HOs(CO)$_4$]$^-$ was employed as a water-gas shift catalyst precursor, the activity observed after 24 hrs, was 4 times greater than that observed when Os$_3$(CO)$_{12}$ was used as the catalyst precursor under identical conditions. In either case, however, the major species present after one day was the [HOs$_3$(CO)$_{11}$]$^-$ anion. Once formed under water-gas shift conditions, the [HOs$_3$(CO)$_{11}$]$^-$ is apparently stable. It has not been observed to fragment to [HOs(CO)$_4$]$^-$ under 1 atm CO pressure in THF or under water-gas shift conditions.
D. Summary—Conclusions

Stoichiometries and conditions for the condensation of \([\text{HM(CO)}_4]^–\) to \([\text{HM}_3(\text{CO})_{11}]^–\) for \(M = \text{Fe, Ru, Os}\) have been determined. Under protic and water-gas shift conditions, the \([\text{HRu(CO)}_4]^–\) anion is rapidly converted to the trinuclear cluster anion \([\text{HRu}_3(\text{CO})_1]^–\). In protic media the \([\text{HFe(CO)}_4]^–\) anion condenses to \([\text{HFe}_3(\text{CO})_{11}]^–\), but at a markedly slower rate. Under water-gas shift conditions, \([\text{HFe(CO)}_4]^–\) does not form \([\text{HFe}_3(\text{CO})_{11}]^–\). Instead, within a period of 24 hrs a catalytically inactive material is formed. In protic media \([\text{HOs(CO)}_4]^–\) slowly forms \([\text{HOs}_3(\text{CO})_{11}]^–\). The \([\text{HOs(CO)}_4]^–\) anion is more active than \([\text{HOs}_3(\text{CO})_{11}]^–\) for the catalysis of the water-gas shift reaction.

The reactivity of \([\text{HRu(CO)}_4]^–\) suggests that it would not be observed under WGS conditions. The stability of \([\text{HRu}_3(\text{CO})_{11}]^–\) with respect to formation of \([\text{HRu(CO)}_4]^–\) suggests that \([\text{HRu(CO)}_4]^–\) is probably not an important intermediate in catalysis of the WGSR by ruthenium clusters.
As discussed previously, we observed that the reaction of KH with triruthenium dodecacarbonyl occurred according to the following equilibrium [Reaction (1)].

\[ \text{KH + Ru}_3(\text{CO})_{12} \rightleftharpoons \text{K[Ru}_3(\text{CO})_{11}] + \text{CO} \]  

(1)

When a large excess of CO gas was present in the system, the forward reaction of Equation 1 was inhibited. When that gas was \(^{13}\text{CO}\), statistical exchange of \(^{13}\text{CO} - ^{12}\text{CO}\) occurred between gas and condensed phases but did not occur when KH was absent. These observations suggested the possibility that in the presence of a small amount of KH (\( \frac{\text{KH}}{\text{Metal carbonyl}} = 0.02 \) ) and molecular \(^{13}\text{CO}\), carbon-13 enrichment of metal carbonyls might be accomplished.

Since the utilization of the carbon-13 nuclide as a probe for the characterization and study of organometallic compounds is widespread, [125-129] a convenient general procedure for enriching metal carbonyls is desirable. In the present investigation we report the \(^{13}\text{CO}\) enrichment of a number of metal carbonyls using KH and \(\text{NaBH}_4\) as exchange initiators. Sodium borohydride also produces [HRu\(_3\)(CO)\(_{11}\)]\(^-\) in its reaction with \(\text{Ru}_3(\text{CO})_{12}\) [157]. This suggested that it might be useful
as an exchange initiator. The present procedures provide a general route which involves mild conditions and relatively rapid times for enrichment (Table 10).

A. Ru₃(CO)₁₂, Os₃(CO)₁₂, Fe₃(CO)₁₂⁻⁻

Reaction of KH with trinuclear dodecacarbonyls of the iron triad occurred according to equation (2) (M = Fe, Ru, Os).

\[ \text{KH} + M_3(CO)_{12} \rightarrow \text{K}[H_3(CO)_{11}] + CO \] (2)

Relative rates of reaction at 25°C were: Fe₃(CO)₁₂/Ru₃(CO)₁₂/Os₃(CO)₁₂ = 24/15/1. Quantities of KH as small as 2 mole percent were capable of initiating $^{13}\text{CO}$ enrichment in Ru₃(CO)₁₂ and Os₃(CO)₁₂. The $^{13}\text{CO}-^{12}\text{CO}$ exchange probably occurred through the anions [HRu₃(CO)₁₁]⁻ and [HOs₃(CO)₁₁]⁻ [formed via Reaction (2)] which: (1) exchange with free $^{13}\text{CO}$ rapidly and; (2) are in equilibrium with Ru₃(CO)₁₂ and Os₃(CO)₁₂ respectively. In the absence of KH, no exchange occurred.

When KH was used to initiate $^{13}\text{CO}-^{12}\text{CO}$ exchange in Ru₃(CO)₁₂ (Experiment 1, Table 10) near statistical exchange (Found: 54% $^{13}\text{CO}$; Statistical: 59% $^{13}\text{CO}$) occurred within 48 hrs at 25°C, in accord with Equilibrium 1. However when NaBH₄ was used as an exchange initiator (Experiment 2) after 60 hrs at 25°C only 16% enrichment had occurred. Statistical exchange would have produced 52% enrichment. The slowness of the exchange process when NaBH₄ was used compared to KH may be due to the following equilibrium, which could have a larger equilibrium constant than Equilibrium 1.
Table 10. Carbon-13 Enrichment of Metal Carbonyls Employing KH and NaBH₄ as Exchange Initiators.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Metal Carbonyl</th>
<th>Mole % of Initiator</th>
<th>(^{13}\text{CO}/^{12}\text{CO})</th>
<th>(^{13}\text{CO}) in Metal Carbonyl</th>
<th>Stat.</th>
<th>Expected Temp</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru₃(CO)₁₂</td>
<td>2.0 --</td>
<td>19.7</td>
<td>54%</td>
<td>59%</td>
<td>25°C</td>
<td>46hr</td>
</tr>
<tr>
<td>2</td>
<td>Ru₃(CO)₁₂</td>
<td>-- 2.0</td>
<td>14.4</td>
<td>16%</td>
<td>52%</td>
<td>25°C</td>
<td>60hr</td>
</tr>
<tr>
<td>3</td>
<td>Os₃(CO)₁₂</td>
<td>100 --</td>
<td>34.2</td>
<td>1.1%</td>
<td>70%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
<tr>
<td>4</td>
<td>Os₃(CO)₁₂</td>
<td>2.0 --</td>
<td>54.9</td>
<td>46%</td>
<td>78%</td>
<td>58°C</td>
<td>48hr</td>
</tr>
<tr>
<td>5</td>
<td>Os₃(CO)₁₂</td>
<td>-- 2.0</td>
<td>23.5</td>
<td>60%</td>
<td>66%</td>
<td>25°C</td>
<td>24hr</td>
</tr>
<tr>
<td>6</td>
<td>Fe₃(CO)₁₂</td>
<td>2.0 --</td>
<td>30.6</td>
<td>66%</td>
<td>69%</td>
<td>25°C</td>
<td>21hr</td>
</tr>
<tr>
<td>7</td>
<td>Fe(CO)₅ ᵉ</td>
<td>2.0 --</td>
<td>15.6</td>
<td>75%</td>
<td>75%</td>
<td>25°C</td>
<td>24hr</td>
</tr>
<tr>
<td>8</td>
<td>Fe(CO)₅ ᵉ</td>
<td>-- 2.0</td>
<td>14.2</td>
<td>69%</td>
<td>70%</td>
<td>25°C</td>
<td>24hr</td>
</tr>
<tr>
<td>9</td>
<td>Mn₂(CO)₁₀</td>
<td>2.0 --</td>
<td>18.3</td>
<td>64%</td>
<td>64%</td>
<td>25°C</td>
<td>24hr</td>
</tr>
<tr>
<td>10</td>
<td>Mn₂(CO)₁₀</td>
<td>-- 2.0</td>
<td>22.3</td>
<td>61%</td>
<td>69%</td>
<td>25°C</td>
<td>24hr</td>
</tr>
<tr>
<td>11</td>
<td>Mn₂(CO)₁₀</td>
<td>-- --</td>
<td>14.3</td>
<td>54%</td>
<td>58%</td>
<td>28°C</td>
<td>24hr</td>
</tr>
<tr>
<td>12</td>
<td>Re₂(CO)₁₀</td>
<td>2.0 --</td>
<td>20.6</td>
<td>1.1%</td>
<td>66%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
<tr>
<td>13</td>
<td>Re₃(CO)₁₀</td>
<td>-- 2.0</td>
<td>16.7</td>
<td>1.1%</td>
<td>62%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
<tr>
<td>14</td>
<td>Cr(CO)₆ ⟹</td>
<td>-- 3.0</td>
<td>9.35</td>
<td>52%</td>
<td>59%</td>
<td>28°C</td>
<td>24hr</td>
</tr>
<tr>
<td>15</td>
<td>Cr(CO)₆ ⟹</td>
<td>3.0 --</td>
<td>10.2</td>
<td>24%</td>
<td>62%</td>
<td>60°C</td>
<td>24hr</td>
</tr>
<tr>
<td>16</td>
<td>Cr(CO)₆ ⟹</td>
<td>2.0 --</td>
<td>10.0</td>
<td>1.1%</td>
<td>61%</td>
<td>25°C</td>
<td>24hr</td>
</tr>
<tr>
<td>17</td>
<td>Mo(CO)₆ ⟹</td>
<td>-- 2.0</td>
<td>6.55</td>
<td>38%</td>
<td>52%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
<tr>
<td>18</td>
<td>Mo(CO)₆ ⟹</td>
<td>2.0 --</td>
<td>7.27</td>
<td>26%</td>
<td>55%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
<tr>
<td>19</td>
<td>W(CO)₆ ⟹</td>
<td>-- 2.0</td>
<td>7.53</td>
<td>33%</td>
<td>56%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
<tr>
<td>20</td>
<td>W(CO)₆ ⟹</td>
<td>2.0 --</td>
<td>7.36</td>
<td>1.1%</td>
<td>53%</td>
<td>25°C</td>
<td>48hr</td>
</tr>
</tbody>
</table>
NaBH₄ + Ru₃(CO)₁₂ \rightleftharpoons Na[HRu₃(CO)₁₁] + CO + THF BH₃  (3)

The anions Na[HRu₃(CO)₁₁] and K[HRu₃(CO)₁₁] exchange carbon monoxide with free $^{13}$CO at almost identical rates. However, as discussed earlier, a counterion effect is noted when KH, NaH, and LiH are employed as exchange initiators (Table 5). The rate of $^{13}$CO-$^{12}$CO exchange as a function of counterion follows the same order as the extent of reaction of M[HRu₃(CO)₁₁] with CO (Table 4): K > Na > Li. Since KH, NaH and LiH react with Ru₃(CO)₁₂ at similar rates, Equilibrium (1) may be more favorable than Equilibrium (3) with respect to $^{13}$CO-$^{12}$CO exchange.

Figure 13 shows the infrared spectrum of a Ru₃(CO)₁₂ sample which was enriched to level of 28% $^{13}$CO using LiH as an exchange initiator.

In the case of Os₃(CO)₁₂, ready $^{12}$CO enrichment as was observed for Ru₃(CO)₁₂, could not be achieved at 25°C (Experiment 3), even when KH and Os(CO)₁₂ were in approximately a 1:1 ratio. At 60°C, however, significant although not statistical exchange was observed at 48 hrs (Experiment 4). Furthermore, the use of NaBH₄ as an initiator (Experiment 5) resulted in near statistical exchange occurring at 25°C (24 hrs). Experiments 3, 4, and 5 suggest that formation of [HOs₃(CO)₁₁⁻] is critical to achieving $^{13}$CO enrichment in Os₃(CO)₁₂.

The reaction of KH and Os₃(CO)₁₂ is ~ 15 times slower than the reaction of KH with Ru₃(CO)₁₂ at 25°C. Thus, the lack of $^{13}$CO incorporation in Experiment 3 is probably due to the slowness of this reaction. At 58°C, the reaction of KH and Os₃(CO)₁₂ is much faster and $^{13}$CO enrichment occurs. Experiment 5 indicates that exchange will occur at 25°C if [HOs₃(CO)₁₁⁻] is present, since the reaction of NaBH₄ with Os₃(CO)₁₂ is
Figure 13. $\text{Ru}_3(\text{CO})_{12}$ Enriched in $^{13}\text{C}O$ to a Level of 28% by LiH Initiator, CH$_2$Cl$_2$ Solution
Figure 14. $\text{Os}_3(\text{CO})_{12}$ Enriched in $^{13}\text{CO}$ to a Level of 46% of KH Initiator, $\text{CH}_2\text{Cl}_2$ Solution
known to be rapid at 25°C [157]. Figure 14 shows a sample of Os$_3$(CO)$_{12}$ enriched to a level of 46% $^{13}$CO using KH as an initiator.

Under the conditions used to enrich Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$; Fe$_3$(CO)$_{12}$ is transformed to Fe(CO)$_5$. Statistically enriched Fe(CO)$_5$ was obtained in this way. (Experiment 6).

$$\text{Fe}_3(\text{CO})_{12} + 3 \text{ CO} \xrightarrow{\text{THF}} 3 \text{Fe(CO)}_5$$

**B. Fe(CO)$_5^-$**

In the absence of KH or NaBH$_4$, no measurable enrichment occurs. Previous reports [130,131] indicate that T$_{1/2}$ for complete exchange in this system is 4 years at 25°C. When a small amount of KH or NaBH$_4$ was added to the system Fe(CO)$_5$ was rapidly enriched with $^{13}$CO at 25°C (Experiments 7, 8). The mechanism by which KH is able to greatly accelerate $^{13}$CO exchange was studied and summarized in Figure 15.

$$\text{KH} + \text{Fe(CO)}_5 \xrightarrow{a} \text{K[(CO)$_4$-Fe-C-H$^-$]} \xrightarrow{b} \text{K[Fe$_2$(CO)$_8$] + Fe(CO)$_5$}$$

$$\text{K[HFe(CO)$_4$]} + \text{Fe(CO)$_5$} \xrightarrow{c} \text{K[Fe$_2$(CO)$_8$] + K[HFe$_3$(CO)$_{11}$]} + \text{CO} \xrightarrow{d}$$

**Figure 15.** Proposed Mechanism of $^{13}$CO Exchange in Fe(CO)$_5$

Initiated by KH (2 mole %)
Step (a) involves attack of hydride (KH) on Fe(CO)$_5$ to generate the known formyl [172], K[(CO)$_4$-Fe-C-H] which was identified by its $^1$H NMR and IR spectra. Step (a) demonstrates that a formyl may be formed via hydride attack in the absence of a Lewis Acid. This formyl reacts (b) with Fe(CO)$_5$ to produce K[HFe$_2$(CO)$_8$] (identified by $^1$H NMR, IR spectra) and CO rapidly. Reaction of K[HFe$_2$(CO)$_8$] with excess CO (1 atm.) has been shown [173] to occur rapidly and in accordance with forward reaction (c) to yield K[HFe(CO)$_4$]$^{20}$ and Fe(CO)$_5$. We find that K[HFe(CO)$_4$] exchanges its carbon monoxide with free $^{13}$CO very rapidly. This is in accord with previous studies which showed that Na[HFe(CO)$_4$] rapidly exchanged bound carbon monoxide with gaseous $^{13}$CO [174]. Interestingly, the salt PPN[HFe(CO)$_4$] does not exchange $^{13}$CO at a significant rate, emphasizing the effect of counterion on reactivity of metal carbonyl anions [174,175]. Reaction (d) between K[HFe(CO)$_4$] and Fe(CO)$_5$ produces K[HFe$_2$(CO)$_8$] and K[HFe$_3$(CO)$_{11}$] and CO gas. Thus, exchange between bound carbon monoxide and free $^{13}$CO may occur in K[HFe(CO)$_4$], which is in equilibrium with Fe(CO)$_5$. Presumably, the enrichment via NaBH$_4$ occurs similarly. Figure 16 shows an infrared spectrum of Fe(CO)$_5$ which has been enriched in $^{13}$CO to a level of 55%.

C. Mn$_2$(CO)$_{10}$; Re$_2$(CO)$_{10}$

The reaction of Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$ with KH has been previously studied [176]. Although KH and Mn$_2$(CO)$_{10}$ react rapidly in THF at 25°C (Equation 3), Re$_2$(CO)$_{10}$ and KH do not react appreciably under identical conditions. Thus, little enrichment of Re$_2$(CO)$_{10}$ is observed at 25°C using KH as an exchange initiator (Table 10, Experiment 12). At 25°C,
KH as an initiator is capable of yielding enriched \( \text{Mn}_2(\text{CO})_{10} \) (Table 10, Experiment 9). We also find that \( \text{K}[\text{Mn}(\text{CO})_5] \) exchanges \(^{13}\text{CO}\) rapidly at 28°C. Thus, enrichment of \( \text{Mn}_2(\text{CO})_{10} \) might occur through interaction of \( \text{K}[\text{Mn}(\text{CO})_5] \) with \( \text{Mn}_2(\text{CO})_{10} \). To test this idea, a small amount (2 mole %) of \( \text{K}[\text{Mn}(\text{CO})_5] \) was added to a THF solution of \( \text{Mn}_2(\text{CO})_{10} \) and \(^{13}\text{CO}\) was expanded above the solution. Carbon-13 enrichment occurred in \( \text{Mn}_2(\text{CO})_{10} \) as before (Experiment 11). The stoichiometric reaction between \( \text{K}[\text{Mn}(\text{CO})_5] \) (0.167 mmole) and \( \text{Mn}_2(\text{CO})_{10} \) (0.16 mmole) is slow, producing a red solution and slight CO gas evolution. No significant new product formation could be identified by infrared spectroscopy.

The reaction of \( \text{NaBH}_4 \) and \( \text{Mn}_2(\text{CO})_{10} \) and \( \text{Re}_2(\text{CO})_{10} \) has been previously reported [177,178]. Sodium borohydride was a suitable initiator for \(^{13}\text{CO}\) enrichment of \( \text{Mn}_2(\text{CO})_{10} \) (Experiment 10) but significant incorporation of \(^{13}\text{CO}\) did not occur in \( \text{Re}_2(\text{CO})_{10} \) under similar conditions (Experiment 13). Figures 17 and 18 show infrared spectra of \( \text{Mn}_2(\text{CO})_{10} \) which have been enriched in \(^{13}\text{CO}\) to levels of 48% and 61%, by KH and \( \text{NaBH}_4 \) initiator, respectively.

**D. \text{Cr(CO)}_6, \text{Mo(CO)}_6, \text{W(CO)}_6**

Employing \( \text{NaBH}_4 \) as an initiator, \( \text{Cr(CO)}_6, \text{Mo(CO)}_6, \) and \( \text{W(CO)}_6 \) were conveniently enriched in \(^{13}\text{CO}\). In all three cases, \( \text{NaBH}_4 \) proved to be a superior initiator to KH. This is probably because the Group VI hexacarbonyls react more rapidly with \( \text{NaBH}_4 \) than with KH in THF.
Figure 16. Fe(CO)$_5$ Enriched in $^{13}$CO to a Level of 55% by KH Initiator, Hexane Solution
Figure 17. Infrared Spectrum of Mn$_2$(CO)$_{10}$ Enriched in $^{13}$CO to 48% by KH Initiator; Hexane Solution.
Figure 18. Infrared Spectrum of Mn$_2$(CO)$_{10}$ Enriched in $^{13}$CO to 61% by NaBH$_4$ Initiator; Hexane Solution.
Nevertheless, $^{13}\text{CO}$ enrichment initiated by KH was significant in $\text{Cr(CO)}_6$ and $\text{Mo(CO)}_6$. The reaction of KH with $\text{Cr(CO)}_6$ and $\text{W(CO)}_6$ at 25°C is slow. Consequently, no $^{13}\text{CO}$ incorporation was observed at 25°C (Experiments 16 and 20). However, at 60°C $\text{Cr(CO)}_6$ was enriched to a degree of 24% $^{13}\text{CO}$ using KH as an initiator (Experiment 15). The reaction of $\text{Mo(CO)}_6$ with KH is more rapid than that of $\text{Cr(CO)}_6$ or $\text{W(CO)}_6$ with KH. This is consistent with the relative reaction rates of the Group VI hexacarbonyls with nucleophiles [179]. Thus, $\text{Mo(CO)}_6$ can be enriched to 26% at 25°C employing KH as an initiator (Experiment 18).

When $\text{NaBH}_4$ is employed as an initiator, $^{13}\text{CO}$ incorporation occurs readily in $\text{Cr(CO)}_6$ (52% $^{13}\text{CO}$, Experiment 14), $\text{Mo(CO)}_6$ (38%, Experiment 17) and $\text{W(CO)}_6$ (33%, Experiment 19) at 25°C. Figures 19, 20 and 21 show infrared spectra of carbon-13 enriched $\text{Cr(CO)}_6$, $\text{Mo(CO)}_6$, and $\text{W(CO)}_6$, respectively.

It seems reasonably that our observation of $^{13}\text{CO}$ enrichment in the presence of small quantities of KH or $\text{NaBH}_4$ is occurring through chemistry studied in detail by D. J. Darensbourg and M. Y. Darensbourg [180-183].

The reaction of $\text{M(CO)}_6$ ($\text{M} = \text{Cr, Mo, W}$) with hydride donors has been shown to proceed to $\mu^-\text{H[M(CO)}_5\text{]}_2^-$ as a final product, probably through intermediates $\text{M(CO)}_5^-\text{CO}$ and $\mu^-\text{HM(CO)}_5^-$ [180].

$$\text{H}^- + \text{M(CO)}_6 \quad \text{M} = \text{Cr, Mo, W} \quad \rightarrow \quad \mu^-\text{H[M(CO)}_5\text{]}_2^- \quad (4)$$

The $\mu^-\text{H[M(CO)}_5\text{]}_2^-$ dimer has been shown to exchange $^{13}\text{CO}$ rapidly in THF at 66°C and in general, the hydrido-bridged dimers of Cr, Mo, and W have
Figure 19. Infrared Spectrum of Cr(CO)$_6$ Enriched to a Level of 52%, CH$_2$Cl$_2$ Solution
Figure 20. Infrared Spectrum of Mo(CO)$_6$ Enriched to a Level of 38%, CH$_2$Cl$_2$ Solution
Figure 21. Infrared Spectrum of W(CO)$_6$ Enriched to a Level of 33%, CH$_2$Cl$_2$ Solution
been shown to decompose according to Equation 5 [181]:

$$\mu^{-}[M(CO)_5]^2 \quad \xrightleftharpoons{} \quad HM(CO)_5^- + M(CO)_5$$

HCr(CO)$_5^-$ also exchanges CO rapidly at room temperature and reacts with Cr(CO)$_6$ to generate $\mu^-[Cr(CO)_5]_2^-$ [182]. Thus, in our enrichment solutions we would expect the $\mu^-[M(CO)_5]_2^-$ complexes to be present. We have spectroscopically identified (IR) $\mu^-[Cr(CO)_5]_2^-$ and $\mu^-[Mo(CO)_5]_2^-$ in active enrichment solutions. Coupled with known equilibria of M(CO)$_6$ with HM(CO)$_5^-$ and $\mu^-[M(CO)_5]_2^-$ in solution; it is likely that exchange occurs between these hydrido carbonyl anions and free $^{13}$CO and that the M(CO)$_6$ is subsequently formed through Equilibrium 5. This chemistry is summarized in Figure 22.

\[ H^- + M(CO)_6 \xrightarrow{CO} [HM(CO)_5]^+ + CO \]
\[ HM(CO)_5^- + M(CO)_5 \xrightarrow{M(CO)_6} \mu^-[M(CO)_5]_2^- \]

**Figure 22.** Known Chemistry of Group VI Carbonyl Anions
IV. Preparation of Ruthenium Carbonyl Anions

A question which often arises in the area of cluster catalysis is whether or not the cluster remains intact under catalysis conditions. Given the ease with which clusters of different nuclearity interconvert in the catalysis of the WGSR by ruthenium carbonyl clusters in basic solution (Results and Discussion, Sect. I), it was of interest to study the chemistry of mononuclear ruthenium carbonyl anions.

The use of phosphine ligands to enhance the catalytic activity of transition metal catalyzed systems is well known. Although there have been numerous reports on the preparation of neutral phosphine substituted clusters [184-186], little information concerning the synthesis and characterization of phosphine substituted cluster anions has been reported [187]. It was of interest to prepare phosphine substituted derivatives of \([\text{HRu}_3(\text{CO})_{11}]^-\) and study their chemistry relevant to catalysis of the WGSR.

1. Mononuclear Ruthenium Carbonyl Anions

A. Preparation and Characterization of \(\text{K}_2[\text{Ru(CO)}_4]\)

The anion \([\text{Ru(CO)}_4]^{2-}\) was considered to be a good starting point for the study of the chemistry of mononuclear ruthenium carbonyl anions. The synthesis and characterization of \([\text{Ru(CO)}_4]^{2-}\) has not been reported. Stone and coworkers [171] reported that reduction of \(\text{Ru}_3(\text{CO})_{12}\) by sodium in liquid ammonia produced a mixture of \(\text{Na}[\text{HRu(CO)}_4]\) and \(\text{Na}_2\text{Ru(CO)}_4\);
It was thought that carrying out a similar reduction with potassium might produce $K_2[RU(CO)_4]$ free of any $[HRu(CO)_4]^{-}$ impurity. Thus, the reduction of $RU_3(CO)_12$ by potassium in liquid ammonia was performed with the stoichiometry indicated in Equation (1).

$$RU_3(CO)_12 + 6 Na \xrightarrow{NH_3(1), -33^\circ C} Na_2[RU(CO)_4] + Na[HRu(CO)_4]$$

The product is a cream white solid which is extremely sensitive to oxygen and water. It is insoluble in common solvents such as THF, CH$_3$CN, CH$_2$Cl$_2$ or Et$_2$O. The analysis of the solid indicates that solid is genuine $K_2[RU(CO)_4]$, free of potential impurities such as KNH$_2$, K[HRu(CO)$_4]$ or other ruthenium carbonyl anions within the limits of elemental analysis. The infrared spectrum of $K_2[RU(CO)_4]$ as a mujol mull is shown in Figure 23. One strong, broad band at 1720 cm$^{-1}$ is assigned to a C=O stretch of terminally bound carbon monoxide ligands. A second, sharper band at 540 cm$^{-1}$ is assigned to Ru-C stretch. This second assignment is based partially on the following trend in metal-carbon stretching frequencies for known mononuclear carbonyl anions: Mn(CO)$_6^+$, 416 cm$^{-1}$; Cr(CO)$_6$, 441 cm$^{-1}$; V(CO)$_6^-$, 460 cm$^{-1}$. Additionally, the Fe-C stretch in $[Fe(CO)_4]^{2-}$ occurs at 556 cm$^{-1}$ in aqueous solution [188]. Due to the insolubility of $K_2RU(CO)_4$, a carbon-13 NMR spectrum was not attained. The structure of the $[RU(CO)_4]^{2-}$ anion is probably tetrahedral, consistent with the single V(CO) in the infrared spectrum.
Figure 23. Infrared Spectrum of $K_2[Ru(CO)_4]$ as a Nujol Mull
and analogous to the known structure of the isoelectronic \([\text{Fe(CO)}_4]^{2-}\) anion [189]. Attempts to metathesize \(\text{K}_2[\text{Ru(CO)}_4]\) with larger, more symmetrical cations such as \(\text{N}({\text{Et}})_4\text{Br}\) resulted in conversion of the \([\text{Ru(CO)}_4]^{2-}\) to \([\text{Ru}_4(\text{CO})_{13}]^{2-}\) [190].

The preparation and characterization of PPN \([\text{HRu(CO)}_4]\) has been previously reported [186]. The salt \(\text{K}_2[\text{Ru(CO)}_4]\) was used to prepare solutions of \(\text{K}[\text{HRu(CO)}_4]\) so that this latter complex could be studied. Numerous attempts to isolate the salt \(\text{K}[\text{HRu(CO)}_4]\) were unsuccessful [190]. The salt \(\text{K}_2[\text{Ru(CO)}_4]\) dissolves in anhydrous methanol to form a yellow solution of \(\text{K}[\text{HRu(CO)}_4]\), which was slowly converted to \(\text{K}[\text{HRu}_3(\text{CO})_{11}]\) with time (Results and Discussion, Section II). A carbon-13 NMR spectrum of \([\text{HRu(CO)}_4]^-\) has not been previously reported. The carbon-13 NMR proton-decoupled spectrum of \(\text{K}[\text{DRu(CO)}_4]\) in deuterio-methanol at 25°C is shown in Figure 24. The spectrum consists of a single resonance at 211.0 ppm relative to TMS. The spectrum did not change significantly when recorded at -37°C or -88°C, indicating that the molecule is quite fluxional. The proton NMR spectrum of \(\text{K}[\text{HRu(CO)}_4]\) in methanol consists of a single resonance at 18.8 \(\delta\).

2. Preparation and Characterization of \(\left[\text{(CO)}_4\text{Ru-}^{\text{\(\delta\)}}\text{-CH}_3\right]^-\)

The salt \(\text{K}\left[\left(\text{CO}\right)_4\text{Ru-}^{\text{\(\delta\)}}\text{-CH}_3\right]\) was prepared by reaction of \(\text{K}_2[\text{Ru(CO)}_4]\) with \(\text{CH}_3\text{Cl}\) in THF according to Equation (2).

\[
\text{K}_2\text{Ru(CO)}_4 + \text{CH}_3\text{Cl} \xrightarrow{\text{THF}, 25^\circ C} \text{K}\left[\left(\text{CO}\right)_4\text{Ru-}^{\text{\(\delta\)}}\text{-CH}_3\right] + \text{KCl}
\]
Figure 24. Carbon-13 NMR Spectrum, $^1$H-decoupled, of K[DRu(CO)$_4$] in CD$_3$OD at 25°C.
Figure 25. Infrared Spectrum of $\text{K}[(\text{CO})_4\text{Ru-C-CH}_3]$ in THF.
The isolated salt $K[(CO)_4Ru-C-CH_3]$ is sensitive to oxygen and water. The infrared spectrum of $K[(CO)_4Ru-C-CH_3]$ is given in Figure 25. It consists of 4 bands in terminal $\nu$(CO) region and one strong absorption at 1579 cm$^{-1}$ assigned to the acyl carbonyl C-O stretch. The iron analog, $[(CO)_4Fe-C-CH_3]^{-}$, has been reported to exhibit an acyl carbonyl absorption at 1592 cm$^{-1}$ [191]. The $^1$H NMR spectrum of $PPN[(CO)_4Ru-C-CH_3]$ at 25°C is shown in Figure 26. It consists of two sets of resonances, those due to the $PPN^+$ counterion (7.1-7.3 ppm) and, the other to the methyl group (1.93 ppm) of the acyl ligand. Integration of the spectrum gives a 10.1 to 1 ratio for the $PPN^+$ to methyl protons. The carbon-13 NMR spectrum (Figure 27) of $K[(CO)_4Ru-C-CH_3]$ consists of a single resonance at 207.6 ppm and does not change significantly over the temperature range +25°C to -70°C. A second resonance at 265 ppm appears after considerable data accumulation and may be due to the acyl carbon atom which is present in natural $^{13}$C abundance.

3. Preparation of $K[HRu_3(CO)_9(DPPE)]$

The phoshpine substituted cluster $K[HRu_3(CO)_9(DPPE)]$ was prepared by two independent methods:

\[ K[HRu_3(CO)_{11}] + DPPE \xrightarrow{THF, 25^\circ C} K[HRu_3(CO)_9(DPPE)] + 2CO \]

\[ Ru_3(CO)_{10}(DPPE) + K[(CH_3)_3BH] \xrightarrow{THF, 25^\circ C} K[HRu_3(CO)_9(DPPE)] + CO + B(CH_3)_3 \]
Figure 26. Proton NMR Spectrum of PPN[(CO)$_4$RuC-CH$_3$] in CD$_2$Cl$_2$ at 25°C (300.13 MHz).
Figure 27. Carbon-13 NMR Spectrum of $\text{K}[(\text{CO})_4\text{Ru-C-CH}_3]$ in THF-d$_8$ at 25°C (75.4 MHz).
Figure 28. Infrared Spectrum of $\text{K[H}_3\text{Ru}_2(\text{CO})_9(\text{DPPE})]$ in THF.
In both methods, a near quantitative amount of CO gas was evolved. The infrared spectrum of K[HRu₃(CO)₉(DPPE)] in THF is shown in Figure 28. It displays the terminal carbonyl absorptions: 2041 cm⁻¹, m; 2005 cm⁻¹, sh; 1958 cm⁻¹, vs; 1938 cm⁻¹, sh. The bridging carbonyl region consists of two absorptions at 1651 cm⁻¹ and 1718 cm⁻¹. This is very similar to the bridging region of the K⁺, Na⁺, and Li⁺ salts of [HRu₃(CO)₁₁]⁻ in THF, in which a single bridging carbonyl absorption is split by ion-pairing interactions [192]. For K[HRu₃(CO)₁₁], the infrared spectrum contains bridging carbonyl absorptions at 1730 cm⁻¹ and 1680 cm⁻¹ [192], compared to values of 1718 cm⁻¹ and 1651 cm⁻¹ for K[HRu₃(CO)₉(DPPE)]. This shift to lower frequency is consistent with phosphine substitution, resulting in increased electron density on the metal center(s) and thus, increased π-backbonding to the remaining carbonyl groups. The variable temperature proton NMR spectra of K[HRu₃(CO)₉(DPPE)] are shown in Figure 29. At 90 MHz, the ¹H NMR spectrum in the metal-hydride region consists of a triplet (J = 9 Hz) at 21.9 τ. This is consistent with an edge-bridging hydride which is coupling to two equivalent phosphine atoms. At higher magnetic field (300.1 MHz), the triplet structure is not observed unless the spectrum is recorded at higher temperature (47°C). When the temperature of the sample is lowered, the triplet structure is lost and the spectra indicate that a slow exchange limit is achieved at -63°C. The "static" spectrum at -63°C suggests that the salt K[HRu₃(CO)₉(DPPE)] is able to adopt a number of isomeric configurations. This is not surprising in that most of the phosphine substituted carbonyl cluster compounds studied to date have been reported to adopt a number of different isomeric forms [184-187].
Figure 29. Variable Temperature $^1$H NMR Spectra of K[Ru$_3$(CO)$_9$(DPPE)] in THF-d$_8$; (a) 90 MHz; (b)-(h) 300 MHz.
spectrum at -63°C consists of strong resonance at 21.3 τ, a doublet (J = 40 Hz) at 22.1 τ and a triplet (J = 10 Hz) at 22.9 τ. These spectral changes are reversible; when the sample is warmed from -63°C to +47°C, the triplet at 21.9 τ is observed. Additionally, the 1H NMR spectra at 25°C indicated resonances at 2.3 ppm and 7.3-7.4 ppm assigned to the methylene and phenyl protons, respectively, of the DPPE P#P#P#PC^Cl^P^) ligand. Lowering of the sample temperature resulted in a broadening of these signals.

The variable temperature 1H-coupled and 1H-decoupled carbon-13 (75.4 MHz) spectra of Li[HRu₃(CO)₉(DPPE)] are quite complex, and are shown in Figure 30. The slow exchange limit is achieved at -34°C. The 1H-decoupled spectrum at -34°C is not considerably simplified from the 1H-coupled spectrum because (1) there are a number of isomers present; (2) 31P-13C as well as 13C-13C coupling are expected [192,157]. Therefore, a complete analysis of the carbon-13 NMR spectra was not achieved. Examination of the bridging carbonyl region reveals five resonances in the 1H-decoupled spectrum: (1) a doublet (J = 50.1 Hz) at 303.9 ppm; (2) an apparent doublet of doublets (J = 60 Hz) at 310 ppm; (3) a weak doublet (J = 41 Hz) at 315 ppm; and (4) a broad resonance at 327 ppm. The magnitude of these coupling constants is consistent with 31P-13C coupling [184].

The variable temperature 1H-decoupled and 1H-coupled phosphorous-31 spectra of Li[HRu₃(CO)₉(DPPE)] are given in Figure 31. A complete analysis of the spectra was not accomplished. Attempts to obtain 31P NMR spectra of highly (> 60%) enriched 13C0 samples resulted in significant broadening and little useful information.
Figure 30. Variable Temperature Carbon-13 NMR Spectra of Li[HRu$_3$(CO)$_9$(DPPE)] at 75.4 MHz in THF-d$_8$; (a) $^1$H decoupled, (b) $^1$H coupled.
Figure 31. Variable Temperature $^{31}$P NMR Spectra of Li[HRu$_3$(CO)$_9$(DPPE)] in THF-d$_8$. 

27°C
EXPERIMENTAL

I. Apparatus

A. Vacuum System

A Pyrex glass high vacuum system similar to that described by Sanderson [193] was used for the quantitative manipulation of volatile compounds.

The vacuum line consisted of two reaction manifolds, a McLeod gauge, a calibrated Toepler system, and a calibrated distillation train. The system was evacuated to a pressure of $10^{-5}$ torr by a two-stage mercury diffusion pump and a Welch Duo-Seal high speed mechanical pump, which were protected by traps cooled to $-196^\circ$C and $-78^\circ$C, respectively.

Each reaction manifold contained six inlets consisting of a Fischer-Porter 4 mm Teflon stopcock and a Fischer-Porter 9 mm Solv-Seal joint, a 9/8 ball joint, or a 14/35 standard taper joint. Mercury blowouts were attached to one half of the inlets and were used for monitoring reaction pressures. Two of the inlets on one manifold were fitted such that a removable Pd thimble (described in detail in Section D) could be attached with 9/8 ball joints. Each manifold included a mercury manometer.
The distillation train consisted of four calibrated U-traps and an isolable mercury manometer. Fischer-Porter 4 mm valves were used in the distillation train.

The electrically controlled Toepler pump, which was calibrated for volume, was capable of measuring noncondensible reaction products in quantities ranging from 0.01 to 7.5 mmoles.

Nitrogen, hydrogen, and carbon monoxide were admitted to the vacuum system through an airtight 10 mm Tygon tubing system. Gasses admitted in this manner were passed through a -196°C U-trap and were found to be free of oxygen.

B. Drybox

Manipulations of non-volatile air sensitive compounds were carried out in a Vacuum Atmospheres glove box in which a nitrogen atmosphere in the range of 10 ppm oxygen was maintained. This was achieved by continual circulation of pre-purified nitrogen through a purification tower which contained Ridox oxygen scavenger (Fischer Scientific Company) and Linde 13-X molecular sieves. The nitrogen atmosphere was monitored by mass spectral analysis and the titanocene test [194]. Design and operation of the glove box has been described previously [195].

C. Parr High Pressure Reactor

Reactions which required greater than two atmospheres of pressure were performed in a 300 mL stainless steel general purpose bomb (Parr Instrument Company). The reactor was equipped with a Teflon inlet valve
for pressurization, a pressure gauge capable of measuring from 0 to 3000 psi, and a rupture disc which would release the contents of the reactor in the event that the pressure reached 3000 psi. The system was pressurized from gas cylinders through flexible 3/16" high pressure tubing (Airco Company). The loading pressure was controlled with a high pressure regulator (Matheson Company) adapted to the gas cylinder. The temperature of the reactor was controlled with a heating mantle and the temperature measured with a calibrated thermocouple. The reaction mixtures were stirred by means of a Teflon-covered magnetic stir bar spun by an external magnetic stir plate. A glassliner was used inside the bomb cylinder to facilitate the handling of reagents.

D. Palladium Thimble

A Palladium thimble (General Electric Company), which was employed in the study of the catalysis of the water-gas shift reaction, is shown in Figure 32. The Palladium thimble is designed to permit entry of pure H₂ into a vacuum system at a controlled rate. The thimble operates on the principle of diffusion, where heating of the Ag (25%) - Pd (75%) alloy frit will permit only H₂ to pass through. The details on the design, specifications, and underlying principles can be found in the following references [196-199].

The Palladium thimble consisted primarily of a heating unit, thermocouple, and silver-palladium membrane.

The heating unit consisted of two flexible wire leads which were a source of input voltage from an external 60 cycle a-c variable power (Variac) supply capable of producing up to 90 volts. These flexible
Figure 32. Palladium Thimble
wire leads were attached to a coil of nichrome heater wire which was wrapped around a porous Al₂O₃ support tube. This Al₂O₃ support tube, in turn, encompassed the Pd-Ag membrane. This allowed homogeneous heating of the Pd-Ag membrane without any direct contact with the heater power source. The temperature of the Pd-Ag leak as a function of applied input voltage is given in Table II.

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<th>Thermocouple Reading \ mv</th>
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<tr>
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\(^{a}\)Reference junction at 0°C.
Table 12
Temperature of the Ag-Pd Membrane in the Presence of H₂
as a Function of Applied Voltage

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Table 13
Temperature of the Ag-Pd Membrane in the Presence of Gas Mixtures as a Function of Applied Voltage

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<th>Membrane Temp.</th>
<th>Thermocouple</th>
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<td>volts</td>
<td>atm.</td>
<td>°C</td>
</tr>
<tr>
<td>0</td>
<td>---</td>
<td>25°C</td>
<td>1</td>
</tr>
<tr>
<td>10V</td>
<td>N₂(0.79), O₂(0.21)</td>
<td>120°C</td>
<td>5</td>
</tr>
<tr>
<td>10V</td>
<td>C₆(0.87), H₂(0.13)</td>
<td>100°C</td>
<td>4.5</td>
</tr>
<tr>
<td>15V</td>
<td>C₆(0.87), H₂(0.13)</td>
<td>170°C</td>
<td>7</td>
</tr>
<tr>
<td>22V</td>
<td>C₆(0.87), H₂(0.13)</td>
<td>240°C</td>
<td>10</td>
</tr>
<tr>
<td>25V</td>
<td>N₂(0.79), O₂(0.21)</td>
<td>275°C</td>
<td>11</td>
</tr>
</tbody>
</table>
Tables 12 and 13 also show that the temperature that the Pd-Ag membrane attained at a given applied potential was very dependent on the gas pressure at the membrane as well as the nature of gas. Thus, a higher voltage input was required to attain the same temperature at the membrane when H₂ gas was present than when the thimble was evacuated (10⁻⁵ mm Hg), or when any other gas (N₂, O₂, CO) was present at an identical pressure. This is a very important practical consideration in operating the Pd thimble. If the system is being baked at a given temperature in the presence of a gas, especially H₂, removal of the gas, (without first decreasing voltage input) will result in a very rapid increase in the temperature of the thimble, which could lead to thermal cracking of the membrane-glass seals.

The temperature of the Pd-Ag leak could be monitored conveniently with a Chromel Alumel Thermocouple referenced at 0°C. A digital voltmeter (O.S.U. Chemistry Dept.) capable of measuring potentials in the range of 0 to 30 millivolts was employed in conjunction with the reference junction (0°C) to obtain reproducible temperature readings at a given input potential (Table 11).

The silver (25%) - palladium (75%) leak was capable of allowing hydrogen to pass through its porous membrane at higher temperatures. Mass spectral analysis of the gas leaked through the frit indicated that the hydrogen was the only gas present within the limits of the mass spectrometer. The Ag-Pd leak operated at optimum conditions when it was regenerated. This regeneration, or conditioning, of the leak was accomplished by heating the Ag-Pd membrane in air at 400 to 450°C for 4-8 hours and then reducing in pure hydrogen at 400°C for 12-16 hours.
The rate of leakage of hydrogen as a function of the temperature of membrane was studied and is shown in Table 14.

In operating the Pd thimble, the experimental setup was such that the Pd-Ag membrane was separated from all Hg sources by U-traps kept at -196°C. Continuous removal of H₂ accelerates the removal of H₂ from the catalytic system because the rate of H₂ diffusion across the membrane should be directly proportional to the pressure differential of H₂ across the membrane. This point was tested so that the H₂ leakage rate across the membrane at various H₂ pressures and membrane temperatures would be known. This information was of importance in determining whether the thimble would be useful in removing H₂ as it formed during catalysis of the water-gas shift reaction. The data is given in Table 14.

Table 14
Rate of H₂ Leakage as a Function of Membrane Temperature and H₂ Pressure Differential

<table>
<thead>
<tr>
<th>ΔH₂ Pressure atm.</th>
<th>Temperature of Membrane °C</th>
<th>Leak Rate millimole H₂/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53</td>
<td>70°C</td>
<td>0.01</td>
</tr>
<tr>
<td>0.53</td>
<td>230°C</td>
<td>2.1</td>
</tr>
<tr>
<td>0.53</td>
<td>250°C</td>
<td>2.7</td>
</tr>
<tr>
<td>0.53</td>
<td>390°C</td>
<td>19.0</td>
</tr>
<tr>
<td>0.36</td>
<td>390°C</td>
<td>12.8</td>
</tr>
<tr>
<td>0.17</td>
<td>390°C</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Figure 33. Rate of Hydrogen Leak Through Pd-Ag Membrane as a Function of Temperature.
Table 14 indicates that the rate of $H_2$ leakage through the membrane was nearly proportional to the $H_2$ pressure differential at $390^\circ C$. Based on diffusion theory, the $\ln$ (leak rate) should be proportional to $1/T_{\text{abs}}$. Earlier data (before the thimble was repaired) indicated that this relationship was true over higher (>200°C) temperatures. The data in Table 14, although insufficient, indicated that the relationship was of some value in determining the temperature at which the desired rate of $H_2$ removal could be achieved. Figure 33 shows a plot of $\ln$ (Leak rate) vs. $1000/T_{\text{abs}}$ based on the data in Table 14.

E. Glassware

Pyrex or Kimax bulbs fitted with 9 mm Fischer-Porter Solv-Seal joints were utilized for most reactions. These vessels were connected to the vacuum line by the use of adaptors with Teflon stopcocks. Sidearms were utilized for removal of samples for NMR and addition of various reactants to the reaction solution. Filtration operations were performed under vacuum in extractors similar to the one shown in Figure 34. NMR sample tubes which contained CO/$H_2$ atmospheres were attached to the reaction vessel via thick walled Pyrex tubing and sealed off along this thick-walled tubing at $-196^\circ C$.

F. Nuclear Magnetic Resonance Spectra

Nuclear Magnetic Resonance Spectra were obtained on Bruker WM-300, Bruker HX-90, and Bruker HX-80 spectrometers operating in the FT mode. The spectrometers were equipped with variable temperature and heteronuclear spin-decoupling capabilities. The operating frequency (MHz) of each spectrometer for the various nuclei is listed below.
Figure 34. Vacuum Extractor.
Proton chemical shifts are reported in tau units, measured relative to tetramethylsilane (TMS) at 10.00 \( \tau \), \( \text{CHCl}_3 \) at 2.76 \( \tau \), \( \text{CH}_2\text{Cl}_2 \) at 4.68 \( \tau \), and tetrahydrofuran (THF) at 8.27 \( \tau \). Carbon-13 shifts are expressed in ppm, also measured relative to TMS at 0.00 ppm. The chemical shifts in \( ^{11}\text{B} \) NMR are reported relative to \( (\text{C}_2\text{H}_5)_2\text{O-BF}_3 \) at 0.00 ppm. Phosphorous-31 chemical shifts are relative to \( \text{H}_3\text{PO}_4 \) at 0.00 ppm.

### G. Infrared Spectra

Infrared spectra were obtained with a Perkin-Elmer 457 grating spectrometer. All spectra were calibrated with polystyrene film, in which a sharp absorption at 1601.4 cm\(^{-1}\) was used as a reference. Solid samples were run as KBr pellets or as Nujol mulls between KBr plates in an airtight holder. Solution spectra were obtained in matched Perkin-Elmer liquid cells with 0.1 or 0.5 mm Teflon spacers and KBr windows. Gaseous samples were either condensed or expanded into an evacuated 10 cm glass cell with KBr windows and a Kontes Teflon vacuum stopcock.

### H. X-Ray Powder Diffraction Patterns

Copper K\(_{\alpha}\) radiation was produced at 32 kilovolts and 12 milliamperes on a North American Phillips X-Ray generator. Powder
diffraction patterns were obtained with a Debye-Scherrer camera, 11.46 cm in diameter, on Eastman Kodak NS-392F X-ray film. Samples were packed into 0.3 or 0.5 mm x-ray capillary and sealed with a flame.

I. Mass Spectra

Mass spectra of gaseous samples were obtained on a modified AEI MS-10 spectrometer. Hydrogen/carbon monoxide ratios were determined by comparison with standard mixtures of known hydrogen/carbon monoxide content. In samples in which the hydrogen/carbon monoxide ratio was very small, the hydrogen peak was measured relative to that of $^{13}\text{C}^{16}\text{O}$ (1.1% abundant).

Mass spectra of samples containing transition metals were analyzed by Mr. C. R. Weisenberger on an AEI MS-9 spectrometer. Heptacosafluorotributylamine was used as a calibrant.

J. Electron Spin Resonance

Electron spin resonance spectra were recorded using a Varian Model 102 ESR Spectrometer on samples prepared as frozen glasses at -196°C using a round quartz sample cell. Spectra were obtained at a microwave frequency of 9.149 GHz and a microwave power of 1 mW. Signal assignments were made relative to a pitch sample of 2.0036 g.

II. Reagents

A. Acetyl Chloride

Acetyl Chloride was purchased from Aldrich Chemical Co. It was purified by reaction with PCl$_5$ at 50°C followed by fractionation through
successive U-traps at -15°C, -78°C, and -196°C to remove primarily HCl and acetic acid impurities.

B. Ammonia

Ammonia was obtained from Matheson Scientific Products. It was purified by condensation onto metallic sodium followed by stirring for several hours. The ammonia was stored at -78°C in a thick-walled Pyrex tube equipped with a Kontes 4 mm stopcock.

C. Benzophenone

Benzophenone was purchased from Fischer Scientific Company was stored in the drybox and used as received.

D. Bis(1,2-diphenylphosphino)ethane

Bis(1,2-diphenylphosphino)ethane was purchased from Strem Chemicals Co. It was recrystallized from hot ethanol (95%), dried at 25°C at 10⁻⁵ mm Hg, and stored in drybox.

E. Bis(diphenylphosphino)methane

Bis(diphenylphosphino)methane was purchased from Strem Chemicals Co., and was used as received.

F. Carbon Monoxide

Carbon monoxide, 99.9%, was purchased from Matheson Scientific Products. It was passed thru a -196°C trap to remove H₂O and CO₂ prior
to use. Mass spectral analysis taken over a period of months indicated that the hydrogen content of the CO decreased from 5.4% to 0.4%.

G. Carbon Monoxide, 99% $^{13}$C

Carbon monoxide, 99% $^{13}$C enriched, was purchased from Monsanto Company (Mound Laboratory) and used as received.

H. Chromium Hexacarbonyl

Chromium hexacarbonyl was obtained from Strem Chemicals and was used as received.

I. Deionized, Distilled Water

Deionized, distilled water was thoroughly degassed by several freeze, pump, thaw cycles on the vacuum line.

J. Deuterium Oxide, 99.96% $^2$D

Deuterium oxide, 99.96% $^2$D, was purchased from Norell, Inc. and degassed on a vacuum line. It was stored at room temperature in a vacuum storage vessel equipped with 4 mm Kontes stopcock.

K. Dimanganese Decacarbonyl

Dimanganese decacarbonyl was obtained from Strem Chemicals and was used as received.
L. Dirhenium Decacarbonyl

Dirhenium decacarbonyl was obtained from Strem Chemicals and was used as received.

M. Ethoxyethanol

Ethoxyethanol, 99%, was purchased from Aldrich Chemical Company. It was purified by distillation from Mg turnings and stored over N₂.

N. Hydrogen

Hydrogen was obtained prepurified from Union Carbide Corporation and was passed through a -196°C trap prior to use. Mass spectral analysis of the hydrogen did not reveal CO, CO₂, or O₂.

O. Hydrogen Bromide

Anhydrous hydrogen bromide obtained from Matheson Gas Products was passed through a -78°C trap and stored in a thick-walled Pyrex tube with a Kontes 4 mm stopcock at -78°C.

P. Hydrogen Chloride

Anhydrous hydrogen chloride from Matheson Gas Products was stored in a manner identical to hydrogen bromide. It was purified by passage through successive U-traps at -111°C and -126°C.

Q. Iron Pentacarbonyl

Iron pentacarbonyl was obtained from Alfa Division, Ventron Corporation and was purified prior to use by trap to trap distillation
on a vacuum line (0°C; -15°C). It was stored in a light-proof vacuum storage vessel.

R. Kryptofix™ 222

The compound 4,7,13,16,21,24-hexaoxa-1,10,15,20-tetraazabicyclo(8.8.8.)hexacosane was purchased from PCR Research Chemicals under the name of Kryptofix™ 222. This light sensitive compound was stored in a light-proof container in the drybox.

S. Lithium Aluminum Hydride

Lithium aluminum hydride was purchased from Alfa Division, Ventron Corporation and was used as received.

T. Lithium Borohydride

Lithium borohydride was obtained from MCB Manufacturing Chemists and was used as received. It was stored in the drybox.

U. Molybdenum Hexacarbonyl

Molybdenum hexacarbonyl was obtained from Strem Chemicals and was used as received.

V. Osmium Tetroxide

Osmium tetroxide was obtained from Alfa Division, Ventron Corporation in one gram ampoules and used as received.
W. Potassium

Potassium metal, in mineral oil, was obtained from Mallinckrodt, Incorporated. It was cut, washed with dried hexane, and stored in the drybox.

X. Potassium Deuteride

Potassium deuteride, 99%, was obtained from Aldrich Chemical Company. It was treated in an identical manner to potassium hydride, described below.

Y. Potassium Hydride

Potassium hydride was obtained from Alfa Division Ventron Corporation as a 50% mineral oil dispersion. It was washed repeatedly with dry hexane in a vacuum extractor until a free-flowing powder was obtained. It was stored in the drybox. Methanolysis of 2 samples indicated that the KH was 93.5% active.

Z. Potassium Hydroxide

Potassium hydroxide was obtained from MCB Manufacturing Chemists in pellet form. The pellets were ground to a powder with an agate mortar and pestle and dried at 130°C under dynamic vacuum. It was stored in a vacuum storage vessel.

AA. Silica Gel

Silica gel (80-200 mesh) was purchased from Davison Chemical and was used as received.
BB. Silver Tetrafluoroborate

Silver tetrafluoroborate was obtained from Alpha Division, Ventron Corporation and stored in the drybox without further purification.

CC. Sodium

Sodium metal, in mineral oil, was obtained from Mallinckrodt, Incorporated. It was cut, washed with dried hexane, and stored in the drybox.

DD. Sodium Borohydride

Sodium borohydride was obtained from MCB Manufacturing Chemists and used as received. It was stored in the drybox.

EE. Sodium Hydroxide

Sodium hydroxide was obtained from MCB Manufacturing Chemists in pellet form. It was treated in an identical manner to potassium hydroxide described above.

FF. Tetraethylammonium Bromide

Tetraethylammonium bromide was generously donated by Mr. Michael Banks and was handled in the drybox.

GG. Tetramethylammonium Chloride

Tetramethylammonium chloride was generously donated by Mike Banks and was handled in the drybox.
HH. Triethylboron

Triethylboron was purchased from Alpha Division, Ventron Corporation. It was transferred to a vacuum storage vessel with a Kontes 4 mm valve and stored at -78°C.

II. Triiron Dodecacarbonyl

Triiron dodecacarbonyl was purchased from Strem Chemicals. It was recrystallized from CH₂Cl₂, dried under vacuum at 25°C, and stored under N₂ at -15°C.

JJ. Trimethoxyboron

Trimethoxyboron was obtained from Metal Hydrides, Inc. It was purified by stirring over KH at 25°C until hydrogen evolution ceased. It was transferred to a vacuum storage vessel and stored at room temperature.

KK. Trimethylboron

Trimethylboron was generously donated by Dr. William Dorogy. It was stored at -78°C in a vacuum storage vessel with a Kontes 4 mm valve.

LL. Triphenylmethyltetrafluoroborate

Triphenylmethyltetrafluoroborate was kindly donated by Dr. Colleen C. Nagel. It was stored in the drybox.
MM. Triphenylphosphineiminium Chloride

Triphenylphosphinium chloride was purchased from Alfa Inorganics, recrystallized from CH₂Cl₂/Et₂O, and dried at 130°C to remove solvated CH₂Cl₂.

NN. Triosmium Dodecacarbonyl

Triosmium dodecacarbonyl was purchased from Strem Chemicals and used as received.

OO. Triruthenium Dodecacarbonyl

Triruthenium dodecacarbonyl was purchased from Strem Chemicals and used as received.

PP. Tungsten Hexacarbonyl

Tungsten hexacarbonyl was obtained from Strem Chemicals and was used as received.

III. SOLVENTS

Tetrahydrofuran, dimethyl ether, diethyl ether, glyme, hexane and toluene were dried by stirring over LiAlH₄ for several days. The dried solvents were vacuum distilled into storage bulbs equipped with Kontes 4 mm stopcocks and containing benzophenone and sodium metal.
Dichloromethane and acetonitrile were dried by stirring over P₂O₅ for two to three days followed by vacuum distillation into storage bulbs equipped with Kontes 4 mm stopcocks.

Deuterated solvents were dried and stored in the same manner as their proton containing analogues.

IV. Preparation of Starting Materials

A. Tetraphytetaruthenium Dodecacarbonyl, H₄Ru₄(CO)₁₂

The cluster H₄Ru₄(CO)₁₂ was prepared by the hydrogenation of Ru₃(CO)₁₂ as described in the standard literature method [200].

B. Carbon-13 Enriched Tri ruthenium Dodecacarbonyl, Ru₃(CO)₁₂

Carbon-13 enrichment of Ru₃(CO)₁₂ was accomplished according to the standard literature procedure [201].

C. Diiron Enneacarbonyl, Fe₂(CO)₉

Diiron enneacarbonyl was prepared according to the standard literature procedure [202,203] with the assistance of Dr. Wen-Liang Hsu. A photochemical reaction apparatus similar to the one shown in Figure 35, was assembled in a vented hood. It consisted of a Mercury vapor ultra violet lamp (450 watt Hanovia lamp) with a water-cooled quartz sheath.

All operations were carried out in a vented hood. Approximately 50 mL of Fe(CO)₅ (0.36 mole) was added to 150 mL of glacial acetic acid in the photochemical cell. A stream of nitrogen gas was passed through the solution to eliminate oxygen and to stir the solution. The solution was
Figure 35. Apparatus for Photosynthesis of Fe\(_2\)(CO)\(_9\).
also stirred magnetically with a Teflon coated stir bar. Cold water was circulated through the outer-sheath of the reactor and the ultraviolet lamp was inserted into the sheath. The apparatus was shielded to protect the eyes from the ultraviolet light and the lamp was turned on. After approximately 12 hours the reaction was complete and the lamp turned off. The Fe$_2$(CO)$_9$ product was collected on a sintered-glass filter and washed with ethanol and then diethyl ether. The major by-product, Fe$_3$(CO)$_{12}$, was removed by the washings. The product was dried for 24 hrs. under vacuum at 25°C. Approximately 10 grams (77% yield) of Fe$_2$(CO)$_9$ was obtained as orange platelets. The Fe$_2$(CO)$_9$ was stored at -78°C under nitrogen.

D. Triosmium Dodecacarbonyl

Triosmium dodecacarbonyl was prepared by the method of Sievert and Shapley [204].

E. K$_2$[Ru$_4$(CO)$_{13}$]

The metal cluster carbonylate K$_2$[Ru$_4$(CO)$_{13}$] was prepared by the potassium-benzophenone reduction of triruthenium dodecacarbonyl as reported by Bhattacharyya, Nagel, and Shore [124].

F. K[HRu$_4$(CO)$_{13}$]

The metal cluster K[HRu$_4$(CO)$_{13}$] was prepared by the protonation of K$_2$Ru$_4$(CO)$_{13}$ with anhydrous HCl as reported by Bhattacharyya, Nagel, and Shore [124].
G. K[H₃Ru₄(CO)₁₂]  

The preparation of [H₃Ru₄(CO)₁₂]⁻ was accomplished by deprotonation of H₄Ru₄(CO)₁₂ with KH as reported by Inkrott and Shore [150]. The isolation of the potassium salt which had not been previously reported, is described below.

In the drybox, 12.8 mg (0.319 mmole) of KH (93.5% active) and 220.6 mg (0.296 mmole) of H₄Ru₄(CO)₁₂ were weighed in the drybox. After degassing, 3 mL of THF was distilled into the reaction flask at -78°C. The reaction mixture was heated in an oil bath to 60°C for 2.5 hrs. The non-condensables released during the reaction were measured to be 0.286 mmoles (97%) which analyzed for greater than 99% H₂ by mass spectrometry. The THF was removed at 25°C under vacuum to give a red oil. Approximately 4 mL of CH₂Cl₂ was distilled onto the oil at -78°C. Upon warming to room temperature, precipitation of a deep red solid occurred. The solvent mixture was removed under vacuum and 5 mL of fresh CH₂Cl₂ was distilled onto the precipitate. Filtration in a vacuum extractor gave 197 mg (85%) of K[H₃Ru₄(CO)₁₂]. Proton NMR and infrared spectra of the isolated solid were identical to those reported [151]. ¹H NMR (THF) 27.0 τ, IR (THF): 2059 cm⁻¹, wv; 2037 cm⁻¹, s; 2030 cm⁻¹, s; 2017 cm⁻¹, s; 2008 cm⁻¹, m; 1977 cm⁻¹, m; 1948 cm⁻¹, m; 1928, cm⁻¹, w.

H. K₂[H₂Ru₄(CO)₁₂]  

The preparation and isolation of K₂[H₂Ru₄(CO)₁₂] were accomplished according to the procedure reported by Inkrott and Shore [151].
I. $\text{K}_2[\text{Fe}(\text{CO})_4]\$

The preparation and isolation of $\text{K}_2[\text{Fe}(\text{CO})_4]$ were accomplished according to the procedure by Medford and Shore [205].

J. $\text{K}[\text{HFe}(\text{CO})_4]\$

The preparation and isolation of $\text{K}[\text{HFe}(\text{CO})_4]$ were accomplished according to the procedure of Medford and Shore [205].

K. $\text{K}[\text{HOs}_3(\text{CO})_{11}]$

The preparation and isolation of $\text{K}[\text{HOs}_3(\text{CO})_{11}]$ were accomplished with a slight modification of the literature procedure [157]. In the drybox, 108.0 mg (0.119 mmol) of $\text{Os}_3(\text{CO})_{12}$ and 11.3 mg (0.117 mmol) of $\text{K}[(\text{CH}_3)_3\text{KH}]$ were weighed into a reaction vessel. THF, 4 mL, was added at $-78^\circ\text{C}$ and the reaction was allowed to proceed at $28^\circ\text{C}$. After 18 hrs., 0.121 mmol (102%) of non-condensable gas had been evolved which analyzed for CO. The THF was removed under vacuum and the resulting oil was taken up in a minimum volume of $\text{CH}_2\text{Cl}_2$ (2 mL). Addition of hexane, 5 mL, resulted in precipitation of a yellow solid which was filtered in a vacuum extractor and washed with fresh hexane. An 80 mg (73%) yield of $\text{K}[\text{HOs}_3(\text{CO})_{11}]$ was obtained. The $^1\text{H}$ NMR spectrum consisted of a singlet at 23.9 $\tau$ (THF) at $25^\circ\text{C}$ and the infrared spectrum showed a striking similarity to that of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$. IR (THF): 2088 cm$^{-1}$, w; 2022 cm$^{-1}$, s; 1990 cm$^{-1}$, s; 1950 cm$^{-1}$, s; 1708 cm$^{-1}$, w; 1658 cm$^{-1}$, w.
L. H₂Ru(CO)₄

The unstable complex H₂Ru(CO)₄ was prepared in high yield from K₂Ru(CO)₄ by protonation with a large excess of HCl (g) at -95°C. In a typical experiment, 446 mg (1.53 mmole) of K₂[Ru(CO)₄] was weighed in the drybox in a reaction vessel equipped with a magnetic stirbar. Approximately 3-5 mL of anhydrous HCl (g) was condensed into the reaction vessel at -196°C. The reaction was carried out at -95°C under vigorous stirring for approximately 1-1/2 hours. The unreacted HCl was removed at -78°C. H₂Ru(CO)₄ was isolated by pumping it under dynamic vacuum into a collection trap at -196°C. Isolation of the KCl from the reaction vessel yielded 3.0 mmole of KCl which was slightly contaminated by H₂Ru₃(CO)₁₂. The H₂Ru(CO)₄ product was a colorless liquid which melted at -60°C as previously reported. Although the formation of H₂Ru(CO)₄ based on KCl recovery was essentially quantitative, the yield of isolated H₂Ru(CO)₄ was somewhat less (85%) due to decomposition during transfer from the reaction vessel.

M. K[HFe₃(CO)₁₁]

K[HFe₃(CO)₁₁] was prepared directly from the reaction of KH with Fe₃(CO)₁₂. In a nitrogen filled glovebox, 24.8 mg (0.618 mmole) of KH and 315 mg (0.625 mmol) of Fe₃(CO)₁₂ were weighed and placed in a reaction vessel. A 4 mL quantity of THF was distilled onto the reactants at -78°C and the reaction was allowed to proceed at 24°C. Carbon monoxide generated as the reaction proceeded was periodically removed (-78°C) and measured using a Toepler pump. After 8 hrs. the CO gas evolution indicated that the reaction was 95% complete. The THF was
removed at 25°C and 3 mL of dry CH₂Cl₂ was distilled onto the red oil at -78°C followed by 7-8 mL of dry hexane. The vessel was then warmed slowly to room temperature. Deep red K[HFe₃(CO)₁₁] precipitated from solution and was filtered in a vacuum extractor and washed with dry hexane. An 88% yield of K[HFe₃(CO)₁₁] (280 mg) was obtained. ¹H NMR 18.9 (THF); IR (THF) 2045 cm⁻¹ v; 1992 cm⁻¹, m; 1950 cm⁻¹, s; 1904 cm⁻¹, sh; 1745 cm⁻¹, w; 1688 cm⁻¹ w.

N. Ru₃(CO)₁₀(DPPE)

The compound Ru₃(CO)₁₀(DPPE) was generously donated by Dr. A. B. Bhattacharyya, who developed a high-yield synthesis of the complex.

O. Ru₃(CO)₈(DPPM)₂

The preparation and isolation of Ru₃(CO)₈(DPPM)₂ was accomplished by the procedure of Lauigme and Bonnet [206].

Preparation of Salts of [HRu₃(CO)₁₁]

P. K[HRu₃(CO)₁₁]

The preparation and isolation of K[HRu₃(CO)₁₁] were accomplished according to Nagel [192] with the following modification. The K[(CH₃)₃BH] was generated in situ for reaction with Ru₃(CO)₁₂, as described below.

In the drybox, 45.2 mg (1.12 mmol) of KH and 686 mg (1.07 mmol) of Ru₃(CO)₁₂ were weighed into a reaction vessel equipped with a Teflon covered stirbar. THF, 10 mL, and approximately 0.5 mmol of B(CH₃)₃ were
added to the reaction vessel at -196°C. Upon warming to 25°C, vigorous gas evolution occurred and the solution turned bright red in color. After 1 hr. at 25°C, the non-condensable gas evolved amounted to 0.93 mmol (87%) and was analyzed to be CO. The reaction was continued until complete CO evolution had occurred (4 hrs). The THF and B(CH₃)₃ were removed under vacuum and the resulting red oil pumped on at 10⁻⁵ mm Hg (25°C) for 1-3 hours. The K[Ru₃(CO)₁₁] was precipitated by dissolving the oil in a minimum volume of CH₂Cl₂ (2 mL) and adding hexane (7 mL). The K[Ru₃(CO)₁₁] was filtered in a vacuum extractor and washed with fresh hexane to remove unreacted Ru₃(CO)₁₂. The yield of K[Ru₃(CO)₁₁] was 580 mg (83%). The ¹H NMR spectrum consisted of a single peak at 22. 6 τ (THF) at 25°C. IR (THF): 2075 cm⁻¹, w; 2018 cm⁻¹, s; 1985 cm⁻¹, s; 1948 cm⁻¹, m; 1730 cm⁻¹, w; 1680 cm⁻¹, w.

Q. K[Ru₃(CO)₁₁]

The preparation and isolation of K[Ru₃(CO)₁₁] was accomplished according to the procedure described above with the exception that KD (99%) was employed instead of KH. The infrared spectrum of K[Ru₃(CO)₁₁] in THF was indistinguishable from that of K[Ru₃(CO)₁₁].

R. Na[Ru₃(CO)₁₁]

The preparation of Na[Ru₃(CO)₁₁] was performed according to the procedure of Johnson and Lewis [157] with some modification. In the drybox, 37.0 mg (0.978 mmole) of sodium borohydride and 625 mg (0.978 mmole) of Ru₃(CO)₁₂ were weighed in a reaction vessel equipped with a Teflon covered stirbar. THF, 4 mL, was distilled onto the
reactants and the mixture warmed slowly to 28°C under stirring. After 3 hrs. at 28°C, complete CO evolution had occurred (0.97 mmole) and the solvent was removed under vacuum. Hexane, 5 mL, was distilled onto the red oil at -78°C and the mixture was stirred at 28°C. A deep red solid precipitated from solution and was filtered in a vacuum extractor. The Na[HRu₃(CO)₁₁] was washed with fresh hexane to remove unreacted Ru₃(CO)₁₂. The yield of Na[HRu₃(CO)₁₁] was 615 mg (99%). The infrared spectrum of the Na⁺ salt was very similar to that of the K⁺ salt. In the terminal CO stretching region, the IR spectrum of the Na⁺ salt in THF was identical to that reported for the Na⁺ salt in CH₃CN [157]. However, the bridging region in THF consists of 2 absorptions, while in CH₃CN only a single absorption was observed. IR (THF): 2075 cm⁻¹, vw; 2016 cm⁻¹, vs; 1984 cm⁻¹, vs; 1947, m; 1728 cm⁻¹, 2; 1680 cm⁻¹, w.

S. Li[HRu₃(CO)₁₁]

The preparation of Li[HRu₃(CO)₁₁] was performed in a fashion similar to that of Na[HRu₃(CO)₁₁]. In the drybox, 23.3 mg (1.07 mmol) of LiBH₄ and 695 mg (1.09 mmol) of Ru₃(CO)₁₂ were weighed in a drybox. THF, 7 mL was distilled onto the reactants at -78°C and the mixture warmed to 25°C. After 24 hrs., the CO evolved was measured with the aid of a Toepler pump to be 1.11 mmole (103%). The THF was removed under vacuum at 25°C and 5 mL of dry hexane was added at -78°C. Warming the mixture resulted in precipitation of a deep red solid which was filtered in a vacuum extractor and washed with fresh hexane. The yield of Li[HRu₃(CO)₁₁] was 660.2 mg (98%). The infrared spectrum of the Li⁺
salt was very similar to the Na⁺ and K⁺ salts. IR (THF): 2073 cm⁻¹, vw; 2015 cm⁻¹, s; 1985 cm⁻¹, s; 1949 cm⁻¹, m; 1730 cm⁻¹, w; 1678 cm⁻¹, w.

T. \((\text{CH}_3\text{CH}_2)_4\text{N}[\text{HRu}_3(\text{CO})_{11}]\)

The salt \(\text{NET}_4[\text{HRu}_3(\text{CO})_{11}]\) was prepared and isolated by metathesis of the \(\text{K}[\text{HRu}_3(\text{CO})_{11}]\) salt with \([(\text{CH}_3\text{CH}_2)_4\text{N}]\text{Br}\). In a drybox, 580 mg (0.891 mmol) of \(\text{K}[\text{HRu}_3(\text{CO})_{11}]\) and 186 mg (0.885 mmol) of \(\text{[NET}_4\text{]Br}\) were weighed in a drybox. A THF:CH₂Cl₂ (3:1) mixture of 5 mL was distilled onto the mixture at -78°C. The reaction was stirred for 2 hrs. at 25°C and a fine white precipitate formed. The mixed solvent was removed under vacuum and fresh CH₂Cl₂ was added to reaction flask. The KBr precipitate was filtered off in a vacuum extractor. The \(\text{Et}_4\text{N}[\text{HRu}_3(\text{CO})_{11}]\) product was recrystallized from CH₂Cl₂/Et₂O and recovered in ~600 mg (~90%) yield as deep red crystals. The infrared spectrum was identical to that reported previously \([157]\) for \(\text{NET}_4[\text{HRu}_3(\text{CO})_{11}]\) prepared by a different method. IR (CH₂Cl₂): 2075 cm⁻¹, vw; 2018 cm⁻¹, vs; 1985 cm⁻¹, vs; 1948 cm⁻¹, m; 1695 cm⁻¹, w.

U. \((\text{CH}_3\text{CH}_2)_4\text{N}[\text{HRu}_3(\text{CO})_{11}]\)

The salt \(\text{NMe}_4(\text{CH}_3)_2\text{N}[\text{HRu}_3(\text{CO})_{11}]\) was prepared by metathesis of \(\text{K}[\text{HRu}_3(\text{CO})_{11}]\) with \([(\text{CH}_3)_2\text{N}]\text{Cl}\). In a drybox, 584 mg (0.897 mmol) of \(\text{K}[\text{HRu}_3(\text{CO})_{11}]\) and 98.2 mg (0.897 mmol) of \([\text{Me}_4\text{N}]\text{Cl}\) were weighed. A THF:CH₂Cl₂ (2:1) mixture of 7 mL was distilled onto the mixture at -78°C. The reaction was stirred at 25°C for 4-½ hours. The solvent mixture was removed in vacuum and fresh CH₂Cl₂ was distilled onto the products. The KCl was filtered off in a vacuum extractor and the
Me$_4$N[HRu$_3$(CO)$_{11}$] was recrystallized from a CH$_2$Cl$_2$:Et$_2$O mixture (2:7).
The yield of Me$_4$N[HRu$_3$(CO)$_{11}$] was 492 mg (72%). IR (CH$_2$Cl$_2$): 2075 cm$^{-1}$, vw; 2018 cm$^{-1}$, s; 1984 cm$^{-1}$, s; 1945 cm$^{-1}$, m; 1720 cm$^{-1}$, w.

V. Reactions

A. Preparation of New Compounds

1. Preparation of K$_2$[Ru(CO)$_4$]

In a typical experiment, 188.7 mg (0.295 mmole) of Ru$_3$(CO)$_{12}$ and 70.1 mg (1.79 mmole) of potassium were weighed in the drybox in a reaction vessel which was equipped with a stirbar. Anhydrous ammonia was condensed onto the reactants at -78°C and the reaction was allowed to proceed at -36°C until the deep blue color of the ammonia solution dissipated. On this scale, the reaction was usually complete in 1 hr. at -36°C. The reaction was carried out successfully at -78°C as well, but it was 3-4 times slower at this temperature. The ammonia was removed at ambient temperature under dynamic vacuum. The cream white solid product was kept at 25°C at 10$^{-5}$ mm pressure under dynamic vacuum for 2-3 hours. The product was filtered in a vacuum extractor and washed with THF to remove any unreacted Ru$_3$(CO)$_{12}$. The cream white K$_2$[Ru(CO)$_4$] was obtained in 86% yield (221 mg). K$_2$[Ru(CO)$_4$] is extremely sensitive to O$_2$ and H$_2$O and may be stored in the drybox for weeks without decomposition. Elemental analysis. Found: C, 16.68; K, 26.89; Ru, 34.46; N, 0.0; H, 0.0. Calculated for C$_4$K$_2$O$_4$Ru: C, 16.49; K, 26.84; Ru, 34.69; N, 0.0; H, 0.0. IR (Nujol Mull) 1720 cm$^{-1}$, br; 540 cm$^{-1}$, sh.
2. Preparation of $\text{H}_2\text{Ru}_3(\text{CO})_{12}$

The compound $\text{H}_2\text{Ru}_3(\text{CO})_{12}$ was prepared by controlled thermal decomposition of $\text{H}_2\text{Ru}(\text{CO})_4$. $\text{H}_2\text{Ru}(\text{CO})_4$ in a storage vessel at $-78^\circ\text{C}$ was warmed slowly to $25^\circ\text{C}$ in the absence of light. Hydrogen gas was rapidly evolved and the initially colorless $\text{H}_2\text{Ru}(\text{CO})_4$ rapidly yielded a dark red precipitate. A 2.05 mmole quantity of $\text{H}_2\text{Ru}(\text{CO})_4$ gave off 1.31 mmole of $\text{H}_2$. Carbon monoxide was not in the evolved gas. $\text{H}_2\text{Ru}_3(\text{CO})_{12}$ was isolated as a red solid in 80% yield, 345 mg. Elemental Analysis. Found: C, 22.13; H, 0.34; Ru, 47.00. Calculated for $\text{C}_{12}\text{H}_2\text{O}_{12}\text{Ru}_3$: C, 22.47; H, 0.314; Ru, 47.27.

3. Preparation of $\text{K}_2[\text{Os}_3(\text{CO})_{11}]$

The preparation and isolation of $\text{K}_2[\text{Os}_3(\text{CO})_{11}]$ was accomplished according to the procedure by Nagel, Bricker, Alway, and Shore [152] as described below.

A tip tube containing 18.9 mg (0.483 mmole) of potassium was connected to a reaction vessel containing 219.2 mg (0.242 mmol) of $\text{Os}_3(\text{CO})_{12}$ and 92.3 mg (0.505 mmol) of benzophenone. THF, 5 mL was distilled onto the reactants at $-78^\circ\text{C}$ and the potassium was tipped in. The reaction was stirred at room temperature for 3 hours, at which time a clear orange solution was present. The gas evolved during the reaction amounted to 0.231 mmoles (95%) and analyzed for CO. $\text{K}_2[\text{Os}_3(\text{CO})_{11}]$ was isolated by removing the THF to leave a red oil. Dimethyl ether, 5 mL, was distilled onto the oil at $-78^\circ\text{C}$ and care was taken to ascertain that the oil was dissolved. $\text{CH}_2\text{Cl}_2$, 5 mL, was distilled onto the $\text{Me}_2\text{O}$ at $-78^\circ\text{C}$ and the mixture was kept at $-50^\circ\text{C}$ while
the Me$_2$O was removed under vacuum. An orange precipitate of
K$_2$[Os$_3$(CO)$_{11}$] formed and was filtered in a vacuum extractor, washed with
fresh CH$_2$Cl$_2$, and dried for 6 hrs at 25°C and 10$^{-5}$ mm Hg. Elemental
Analysis. Found: C, 13.60; K, 8.62; Os, 59.27. Calc. for
C$_{11}$K$_2$O$_{11}$Os$_3$: C, 13.80; K, 8.17; Os, 59.62.

4. Preparation of K[(CO)$_4$RuC(CH$_3$)$_3$]

In the drybox, 57.3 mg (0.197 mmol) of K$_2$[Ru(CO)$_4$] was weighed into
a reaction vessel containing a Teflon covered stirbar. On the vacuum
line, 3 mL of THF and 0.19 mmol of purified acetyl chloride were
condensed into the reaction vessel. The reaction mixture was stirred at
25°C for 1 hr. at which time the solution was clear orange in color with
a whitish precipitate. The THF solution was filtered in a vacuum
extractor to remove KCl. The THF solvent was removed under vacuum and
the brown oil was dissolved in a minimum volume of CH$_2$Cl$_2$. Addition of
hexane caused precipitation of a brown solid which was washed with fresh
hexane. The yield of product was 51 mg (88%). The K$^+$ salt may be
metasethized to the PPN$^+$ salt with [PPN]Cl. IR (K$^+$ salt, THF) 2029
cm$^{-1}$, w; 1990 cm$^{-1}$, br; 1940 cm$^{-1}$, sh; 1901 cm$^{-1}$, s; 1582 cm$^{-1}$, s.

5. Preparation of K[HRu$_3$(CO)$_9$(DPPE)]

The phosphine substituted cluster anion could be prepared by two
different methods, each of which is described below.

In the first and the more convenient procedure, 49.0 mg
(0.0753 mmol) of K[HRu$_3$(CO)$_{11}$] and 30.1 mg (0.0756 mmol) of
recrystallized bis(1,2-diphenylphosphino)ethane (DPPE) were weighed into
a reaction vessel in the drybox. THF, 5 mL, was distilled in at -78°C and the reaction mixture warmed to 25°C. Rapid gas evolution occurred such that after 4 min. at 25°C, 0.118 mmole or 78% of theoretical CO had been evolved. The reaction was continued for 30 minutes at which time 0.149 mmole (99%) of the CO had been evolved. The product was precipitating from the THF solution as the reaction progressed. Complete precipitation was caused by addition of hexane (4 mL). The product was washed in a vacuum extractor with dry CH₂Cl₂. The yield of K[Ru₃(CO)₉(DPPE)] was 70.2 mg (91%).

A second method for preparation of K[Ru₃(CO)₉(DPPE)] is described below. In the drybox 35.2 mg (0.0363 mmol) of Ru₃(CO)₁₀(DPPE) and 3.4 mg (0.036 mmol) of K[(CH₃)₃BH] were weighed into a reaction vessel equipped with a Teflon covered stirbar. THF, 3 mL, was distilled onto the reactants at -78°C and the reaction mixture warmed to room temperature. After 1 hour, 0.038 mmol (105%) of non-condensable gas had been evolved. The gas analyzed for CO. The THF and B(CH₃)₃ were removed under vacuum and the product was precipitated from CH₂Cl₂ (1 mL) and hexane (3 mL). The K[Ru₃(CO)₉(DPPE)] was filtered in a vacuum extractor and washed with fresh hexane. The product prepared in this manner gave IR and ¹H NMR spectra identical to the product prepared by the first method. The yield was 26 mg (75%).

For variable temperature NMR experiments, [HRu₃(CO)₉(DPPE)]⁻ was prepared as the Na⁺ or Li⁺ salt because of greater solubility. These salts were prepared by the first method described above with Li[Ru₃(CO)₁₁] and Na[Ru₃(CO)₁₁] employed in place of K[Ru₃(CO)₁₁].
B. Reactions

1. Reactions of K[HRu$_3$(CO)$_{11}$]

a. With CO

The reaction of CO with K[HRu$_3$(CO)$_{11}$] was monitored by $^1$H NMR, $^{13}$C NMR, and performed on a large scale as described below. The reactions are described by Dr. Colleen Nagel [192].

In the drybox, 20 mg (.03 mmol) K[HRu$_3$(CO)$_{11}$] was placed in a reaction tube with NMR tube side arm constructed for sealing under pressure, and a Kontes stopcock adaptor. After evacuation, 0.4 mL THF-d$_8$ was condensed onto the salt, warmed to dissolve the salt, and the resulting solution tipped into the NMR tube. With the tube at $-196^\circ$C, CO was expanded through a U-trap held at $-196^\circ$C into the vessel. Keeping the tube at $-196^\circ$C assured slightly greater than one atm. CO in the tube after sealing. The solution was warmed in the NMR spectrometer probe. Spectra were recorded from $-80^\circ$C to $0^\circ$C. Only [HRu$_3$(CO)$_{11}$]$^-$ was visible - no intermediate terminal hydride could be detected. After a total of two hours at temperatures below $0^\circ$C, Ru$_3$(CO)$_{12}$ was crystallizing on the tube walls and additional spectra could not be recorded.

In the drybox, 74 mg (0.12 mmol) of K[HRu$_3$(CO)$_{11}$] which was $-25\%$ $^{13}$C enriched was placed in a reaction vessel with a 10 mm NMR tube side arm constructed for sealing under pressure, and a Kontes stopcock adaptor. A 50:50 mixture of THF:THF-d$_8$, 3 mL, was condensed onto the salt, warmed to dissolve the salt, and the resulting deep red solution tipped into the NMR tube. One atmosphere of CO pressure was expanded into the reaction system, the 10 mm NMR tube was kept at $-196^\circ$C, and the
NMR tube was sealed off. The CO pressure in the NMR tube was calculated to be "1.8 atm. (25°C). The solution was warmed to 25°C and placed in the Bruker-300 NMR spectrometer probe. Spectra were recorded in the temperature range +25°C to -25°C. Only signal(s) attributed to K[HRu₃(CO)₁₁] and Ru₃(CO)₁₂ were visible at 206 ppm and 199.6 ppm, respectively. A slight Ru₃(CO)₁₂ precipitate was evident in the NMR tube.

A solution of K[HRu₃(CO)₁₁] in THF (1.2 mmol in 4 mL) in a 100 mL bulb attached to an extractor was frozen at -196°C and CO was expanded into the apparatus to ~2 atm. pressure. Stirring the reaction at 0°C afforded precipitation of Ru₃(CO)₁₂ within ten minutes but the reaction did not go to completion. The reaction was filtered and the CO and THF were removed, leaving a yellow precipitate of Ru₃(CO)₁₂ on the frit. An X-ray powder pattern indicated the presence of Ru₃(CO)₁₂ but the presence of KH was not definitive. Previously [192], a sublimation of some of the Ru₃(CO)₁₂ from the frit, followed by an X-ray powder pattern of the residue did not reveal the presence of KH. If the reaction mixture with precipitated Ru₃(CO)₁₂ was quenched at -196°C and the CO pressure removed, warming of the reaction solution resulted in a disappearance of the Ru₃(CO)₁₂ with concurrent CO evolution.

b. With ¹³CO

In the drybox, 106 mg (0.163 mmole) of K[HRu₃(CO)₁₁] was weighed into a 100 mL reaction vessel. THF, 3 mL, was distilled onto the solid at -78°C and 1 atm. of ¹³CO (99%) was expanded over the solution. Stirring the reaction solution at 25°C resulted in some Ru₃(CO)₁₂
precipitate and mass spectral analysis of the gas over solution indicated that significant exchange had occurred after 2 hrs. After 48 hrs., the gas above the solution was collected (6.17 mmoles) and analyzed: 74% $^{13}$CO and 26% $^{12}$CO; which was indicative of complete scrambling of $^{13}$CO and $^{12}$CO.

c. With $\text{H}_2\text{O}$ and CO

An addition tube was filled with 3 mL doubly distilled, demineralized water and degassed on the vacuum line. In the drybox, a 100-mL 2-neck bulb was charged with 20 mg (.03 mmol) K[Ru$_3$(CO)$_{11}$] and the addition tube attached. After evacuation, CO was expanded into the bulb to one atm. pressure. The $\text{H}_2\text{O}$ (pH = 7) was added and the vessel was placed in a 60°C bath and the reaction stirred. After 1.5 hours, Ru$_3$(CO)$_{12}$ was precipitating from solution. The total reaction time was eight hours. The gas was collected, measured, and the $\text{H}_2$ evolution found to be ~0.1 mmol. The $\text{H}_2\text{O}$ was distilled from the vessel, the solid dissolved in hexane, and dried over MgSO$_4$. An infrared spectrum revealed it to be Ru$_3$(CO)$_{12}$.

The water reaction was carried out at 25°C under otherwise identical conditions as described above. After 12 hrs., significant Ru$_3$(CO)$_{12}$ precipitation could be observed. After 48 hrs. the Ru$_3$(CO)$_{12}$ was isolated in ~80% yield with formation of $\text{H}_2$ evident from mass spectral analysis.
d. With H$_2$O

The "blank" reaction of K[HRu$_3$(CO)$_{11}$] with H$_2$O was performed as described in V.B.I.C. above with the exception that no CO was added (Table 6). Approximately 20 mg (0.03 mmol) of K[HRu$_3$(CO)$_{11}$] was dissolved in 3 mL of doubly distilled, demineralized water as above. Stirring at 60°C for 8 hrs. produced no Ru$_3$(CO)$_{12}$ precipitate and only a trace of hydrogen gas (0.002 mmole). A solution IR in H$_2$O revealed only a single strong absorption at 1966 cm$^{-1}$ and no Ru$_3$(CO)$_{12}$. Removal of the H$_2$O followed by dissolution of the reaction product in THF also showed no Ru$_3$(CO)$_{12}$ by IR. If the reaction is allowed to proceed at 60°C for extended periods of time (> 30 hrs.), noncondensible gas (0.005 mmole) which analyzed for 97% CO, 2.9% O$_2$, and 0.1% H$_2$ was evolved.

The reaction performed at 25°C under otherwise identical conditions resulted in no detectable Ru$_3$(CO)$_{12}$ and insignificant H$_2$C as determined by IR and mass spectrometry, respectively.

e. With CO and [Ph$_3$C][BF$_4$]

The reaction has been described by Dr. C. C. Nagel [192] in CH$_2$Cl$_2$ solvent. The reaction was repeated in THF solvent. In the drybox, 48.5 mg (0.0745 mmole) of K[HRu$_3$(CO)$_{11}$] and 23 mg (0.070 mmole) of [Ph$_3$C][BF$_4$] were weighed into a 100 mL reaction vessel. At -78°C, 3 mL of THF and 1 atm. of CO (4.6 mmole) were added to the reaction vessel. The solution was warmed to 27°C under stirring. After 5 minutes at 27°C, the reaction had become much lighter in color and Ru$_3$(CO)$_{12}$ was precipitating from solution. After 30 minutes the reaction appeared to be complete since the solution was orange in color. The solution was
filtered to remove KBF₄ and Ru₃(CO)₁₂ and an IR of the THF solution indicated that only Ru₃(CO)₁₂ (no K[Ru₃(CO)₁₁]) was present. The THF was removed and a solution IR of the precipitates in hexane indicated that Ru₃(CO)₁₂ and Ph₃CH (756 cm⁻¹, 705 cm⁻¹) were the only products.

The reaction above was performed in an ESR tube so that the role of potential radical species could be examined. The ESR tube was adapted to a solv-seal adapter with a Kontes 4 mm Teflon stopcock in such a manner that CO could be added or removed reversibly from the system. In the drybox, 57.1 mg (0.0877 mmole) of K[Ru₃(CO)₁₁] and 28.1 mg (0.0852 mmole) of [Ph₃C][BF₄] were weighed directly into the adapted ESR tube. The reaction apparatus was assembled in the drybox and degassed on the vacuum line. THF, 1 mL was distilled onto the reactants at -78°C and the solution was warmed to 25°C rapidly and maintained at that temperature for 10 minutes. Visually, the reaction was taking place during this period of time. The reaction mixture in the ESR tube was rapidly quenched at -196°C and the ESR spectrum taken at -196°C. The spectrum obtained was consistent with a single-electron and was assigned a relative intensity of one. Based on radical trapping experiments and a lack of fine structure in the ESR spectrum, this radical signal was tentatively assigned to [Ph₃C⁺]. At -78°C, 0.95 atm. of CO was expanded above the reaction solution and the sample was warmed rapidly to 25°C. After 10 minutes the reaction was quenched at -196°C and the ESR spectrum was recorded. Only a slight (~5%) increase in the intensity of the radical signal was observed under identical accumulation parameters. The CO was removed under vacuum at -78°C and the reaction warmed to 25°C for 10 more minutes. After quenching at -196°C, the ESR
spectrum was indistinguishable from the first spectrum taken above. If the reaction between K[HRu₃(CO)₁₁] and [Ph₃C][BF₄] was performed at -78°C, only the radical signal due to Ph₃C was observed. No signal attributable to HRu₃(CO)₁₁⁺ was observed under 1 atm. CO pressure or in the absence of CO. The "blank" reaction between [Ph₃C][BF₄] and THF at 25°C produced only a very weak radical (Ph₃C⁺) signal.

The ESR experiment described above was performed in the presence of the radical trapping agent N-t-butyl α-phenyl nitrone. In the drybox 58.5 mg (0.0899 mmol) of K[HRu₃(CO)₁₁], 30.0 mg (0.0909 mmole) of [Ph₃C][BF₄], and 10 mg (0.056 mmole) of n-t butyl α-phenyl nitrone were weighed into an ESR tube. THF, 1 mL, was added at -78°C followed by .9 atm. of CO. Upon warming to 25°C (2 minutes) an immediate reaction occurred and Ru₃(CO)₁₂ precipitated from solution. The reaction was quenched at -196°C and the ESR spectrum recorded. The spectrum indicated the presence of a radical with 1 unpaired electron but the lack of fine structure in the radical signal showed that the radical trap was not the source of the signal. The ESR spectrum was recorded again after the sample had been kept at 25°C for 4 days. No change in the ESR spectrum had occurred.

f. With [Ph₃C][BF₄]

The blank reaction has been described by Dr. C. C. Nagel [192] in CH₂Cl₂ solvent. The reaction in THF was done as in V.b.1,3, above with the exclusion of CO gas. In the drybox, 48.2 mg (0.0740 mmol) of K[HRu₃(CO)₁₁] and 229 mg (0.0697 mmole) of [Ph₃C][BF₄] were weighed into a reaction vessel. At -78°C, 3 mL of THF was distilled onto the
reactants and the solution was warmed to 27°C. Stirring for a period of hours did not result in Ru$_3$(CO)$_{12}$ precipitation as in V.b.1.e. above. The solution was stirred for a period of 72 hrs. Only after an extended period of time (> 48 hrs) was a Ru$_3$(CO)$_{12}$ precipitate evident.

g. With CH$_3$I and CO

In the drybox, 78 mg (0.12 mmol) of K[HRu$_3$(CO)$_{11}$] was weighed into a 100 mL reaction vessel. After degassing, 3 mL of THF and a slight stoichiometric excess of CH$_3$I (0.15 mmol) were added at -78°C. One atmosphere of CO was expanded above the solution at -78°C and the reaction was warmed to 28°C. Stirring in the absence of light resulted in complete Ru$_3$(CO)$_{12}$ precipitation over a period of 72 hrs. The solution after this time consisted of Ru$_3$(CO)$_{12}$ and a fine white precipitate (KI). Mass spectral analysis of the gas over the reaction solution indicated the presence of only CO and CH$_4$ (0.1 mmole). This reaction was repeated in a similar manner and was followed by $^1$H NMR. Proton NMR spectra of the reaction solution indicated that K[HRu$_3$(CO)$_{11}$] was the only metal hydride species in solution.

h. With CH$_3$I

The blank reaction was done as described above in V.b.1.g. with the exclusion of CO. After 72 hrs, the reaction solution was quenched at -78°C and the noncondensible gas products were measured to be 0.094 mmoles (1.1 equivalent). Mass spectra indicated a 50-50 mixture of CH$_4$ and CO although Ru$_3$(CO)$_{12}$ precipitation was not evident. An infrared spectrum of the reaction solution indicated the presence of
K[HRu3(CO)11] and K[HRu4(CO)13] but no Ru3(CO)12. The reaction was repeated using 1H NMR as a probe. 1H NMR recorded as a function of time at 25°C indicated that K[HRu3(CO)11] (85%) and K[HRu4(CO)13] (15%) were present. 1H NMR studies also indicated that the rate of disappearance of K[HRu3(CO)11] in the absence of 1 atm. CO was 3-4 times slower than when CO at 1 atm. was present.

i. With B(OCH3)3 and CO

In the drybox, 300 mg (0.461 mmole) of K[HRu3(CO)11] was weighed into a 120 mL reaction vessel. THF, 4 mL, and 0.8 mmole of B(OCH3)3 were added at -78°C. One atmosphere of CO was expanded above the reaction solution at -78°C and the reaction was stirred at 0°C. Considerable Ru3(CO)12 sublimed from solution as the reaction progressed. The originally deep red reaction solution was only very lightly colored after 90 hours at 0°C, indicating that most of the K[HRu3(CO)11] was consumed. A 11B NMR spectrum at 96.27 MHz indicated only the presence of B(OCH3)3. A 1H NMR at 90 MHz indicated the presence of K[HRu3(CO)11] (90%) and K2[HRu4(CO)12] (10%) as the only metal hydride species. The considerable precipitate obtained from the reaction was dried at 27°C and 10⁻⁵ mm Hg and was taken into the dry box. A Nujol Mull IR was prepared of the solid products. The infrared spectrum indicated the presence of KBH4 and Ru3(CO)12 by comparison with a standard sample. The reaction of KH with B(OCH3)3 in THF produced a sample which contained KBH4 as identified by IR. However, KBH4 was too insoluble to be observed by 1H or 11B NMR even at high field strengths.
j. With B(OCH₃)

The blank reaction was done as described above in V.B.i.i. To a 100-mL reaction bulb containing 303 mg (0.465 mmole) of K[H₃Ru₃(CO)₁₁] was added 0.8 mmole of B(OCH₃)₃ and 4 mL of THF at -78°C. The reaction mixture was kept at 0°C and stirred for 96 hrs. At no time during the course of the reaction was any Ru₃(CO)₁₂ product evident. A ¹H NMR of the reaction solution indicated that the major components were unreacted B(OCH₃)₃ and K[H₃Ru₃(CO)₁₁].

2. Reactions of K[DRu₃(CO)₁₁]

a. With CO and H₂O

In the drybox, 17.0 mg (0.026 mmole) of K[DRu₃(CO)₁₁] was weighed into a 100 mL reaction vessel. Pure H₂O, 3.3 mL, was tipped onto the K[DRu₃(CO)₁₁] at -78°C. CO was expanded into the vessel at -78°C and the system was warmed to 50°C. The reaction was slower than the analogous reaction employing K[H₃Ru₃(CO)₁₁]. After 32 hrs., considerable Ru₃(CO)₁₂ had precipitated from solution but the reaction was not complete (60%). A mass spectrum of the gas over the reaction solution indicated that only HD (>95%) was formed. No H₂ or D₂ was observed. The reaction was continued by expanding fresh CO over the solution and heating to 50°C. After a total reaction time of 48 hrs., the mass spectrum of the gas over the solution indicated that HD (90%) and H₂ (10%) were present. At reaction times greater than 48 hrs., the HD/H₂ ratio decreased with time due to the near complete consumption of K[DRu₃(CO)₁₁] and the onset of some back reaction.
b. With $\text{H}_2\text{O}$

The blank reaction was done as described above in V.B.2.a. In the drybox 20.0 mg (0.0307 mmole) of $\text{K}[[\text{DRu}_3(\text{CO})_{11}]]$ was weighed into a 100 mL reaction vessel. Pure $\text{H}_2\text{O}$, 4 mL, was tipped onto the solid at $-78^\circ\text{C}$ and the reaction vessel allowed to warm to 50$^\circ\text{C}$. Stirring for 32 hrs did not afford a $\text{Ru}_3(\text{CO})_{12}$ precipitate and the reaction was quenched at $-78^\circ\text{C}$. Mass spectral analysis of the gas over the solution indicated that of the 0.068 mmole of gas evolved, 98% was CO, 2% O$_2$, and only a trace of H$_2$, HD or D$_2$ was present. The reaction was continued for 50 hrs at 60$^\circ\text{C}$ but no significant H$_2$ was observed in the evolved gas.

3. Reactions of $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$

a. With CO

The reaction was performed similarly to the reaction of the potassium salt as described in V.B.1.a. above. From a THF solution (4 mL) containing 761 mg (1.20 mmol) of $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$ under 1.5 atm. of CO pressure (7.4 mmol) was observed a slight $\text{Ru}_3(\text{CO})_{12}$ precipitate at 0$^\circ\text{C}$. Removal of the CO gas at $-78^\circ\text{C}$ followed by stirring at 25$^\circ\text{C}$ led to a consumption of the $\text{Ru}_3(\text{CO})_{12}$ and concurrent CO (0.06 mmole) evolution.

b. With $^{13}\text{CO}$

In the drybox, 12.9 mg (.020 mmole) of $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$ was weighed into a 20 mL reaction vessel. At $-78^\circ\text{C}$, 3.0 mL of THF and approximately 0.1 atm. of CO pressure were added to the system. The reaction was warmed to 27$^\circ\text{C}$ and stirred for 1.5 hrs. A mass spectrum of the gas over
the solution indicated that significant exchange had occurred (51% $^{13}\text{CO}$, 49% $^{12}\text{CO}$).

c. With $\text{H}_2\text{O}$ and CO

The reaction was performed as described in V.B.1.c. above with the exception that Na[HRu$_3$(CO)$_{11}$] was employed in place of K[HRu$_3$(CO)$_{11}$]. A reaction employing 23.0 mg (0.036 mmole) of Na[HRu$_3$(CO)$_{11}$] in 3.7 mL of $\text{H}_2\text{O}$ under 1 atm. CO produced a Ru$_3$(CO)$_{12}$ precipitate at 28°C. After 48 hrs the reaction appeared to be complete. A mass spectrum of the gas above solution indicated that H$_2$ (~0.04 mmole) had been evolved. The precipitate was confirmed as Ru$_3$(CO)$_{12}$ by its infrared spectrum.

d. With $\text{H}_2\text{O}$

The blank reaction of Na[HRu$_3$(CO)$_{11}$] with $\text{H}_2\text{O}$ was performed as described in V.B.3.c. above with the exception that CO was not added. Approximately 20 mg (0.03 mmole) of Na[HRu$_3$(CO)$_{11}$] was dissolved in 3 mL of $\text{H}_2\text{O}$. Stirring at 25°C over a period of 48 hrs did not result in Ru$_3$(CO)$_{12}$ formation. A mass spectrum of the gas evolved during the reaction revealed that H$_2$ had not been formed.

e. With $\text{B(OCCH}_3)_3$ and CO

In the drybox, 278 mg (0.438 mmole) of Na[HRu$_3$(CO)$_{11}$] was weighed into a 120-mL reaction vessel. THF, 4 mL, and 0.9 mmole of B(OCCH$_3)_3$ were added at -78°C. One atmosphere of CO was expanded above the reaction solution at -78°C and the reaction was stirred at 0°C. No apparent reaction occurred after 48 hours at 0°C. The reaction was
warmed to 27°C and no Ru₃(CO)₁₂ precipitate was evident after 24 hrs. An infrared spectrum of the reaction solution indicated only unreacted Na[HRu₃(CO)₁₁].

4. Reactions of Li[HRu₃(CO)₁₁]

a. With CO

The reaction of Li[HRu₃(CO)₁₁] with CO in THF was performed similarly to the potassium salt described in V.B.1.a. above. In the drybox, 748 mg (1.21 mmole) of Li[HRu₃(CO)₁₁] was weighed into a 120 mL reaction vessel. THF, 4 mL, was condensed onto the salt followed by expansion of 1 atm. of CO at -78°C. Stirring at -10°, 0°C, and 25°C for several hours at a time did not result in an observable Ru₃(CO)₁₂ precipitate. The reaction was quenched at -196°C and additional CO was added such that the pressure in the vessel would be 2.5 atm. at 0°C. Stirring at 0°C for 40 minutes did not result in a Ru₃(CO)₁₂ precipitate.

b. With CO and H₂O

The reaction was performed similarly to that of the potassium salt described in V.B.1.c. In the drybox, 21.0 mg (0.034 mmole) of Li[HRu₃(CO)₁₁] was weighed into a 120 mL reaction vessel. Pure H₂O, 3.6 mL, was added from a tip tube at -78°C and 1 atm. of CO was expanded over the solution. The reaction was warmed to 28°C and Ru₃(CO)₁₂ precipitated from solution with time. After 48 hrs., the reaction appeared complete. A mass spectrum of the gas above solution revealed that H₂ (0.03 mmol) had been evolved. The orange precipitate was confirmed to be Ru₃(CO)₁₂ by its infrared spectrum.
c. With H₂O

The blank reaction was performed as described in V.B.4.b. above with the exception that CO was not added. A solution containing 20 mg (0.03 mmole) of Li[HRu₃(CO)₁₁] in 3 mL of H₂O was stirred at 28°C for 48 hrs. A Ru₃(CO)₁₂ precipitate was not formed and a mass spectrum of the gas evolved during the reaction failed to reveal any H₂ product as well.

5. Reactions of [N(CH₂CH₃)₄][HRu₃(CO)₁₁]

a. With CO

The reaction of [NET₄][HRu₃(CO)₁₁] with CO was performed in CH₃CN because [NET₄][HRu₃(CO)₁₁] was insoluble in ether solvents. In the drybox, 350 mg (0.465 mmol) of [NET₄][HRu₃(CO)₁₁] was weighed into a 120 mL reaction vessel. CH₃CN, 2 mL, was condensed onto the solid at -78°C followed by CO at -196°C (2 atm). The reaction was warmed to 0°C under stirring. A Ru₃(CO)₁₂ precipitate was not observed after 2 hrs at -10°C, 1 hr at 0°C, or after 3 hrs at 25°C. A ¹H NMR of the reaction solution indicated that only unreacted [NET₄][HRu₃(CO)₁₁] was present.

b. With CO and H₂O

The reaction between [NET₄][HRu₃(CO)₁₁] and H₂O under CO pressure required a cosolvent because [NET₄][HRu₃(CO)₁₁] was very insoluble in H₂O. The reaction was performed with CH₃CN as a cosolvent but no formation of Ru₃(CO)₁₂ was observed. The high solubility of Ru₃(CO)₁₂ in CH₃CN suggested that CH₃CN was not a suitable cosolvent. The reaction was repeated using a methanol:H₂O (95:5) mixture as solvent. In the drybox, 25.0 mg (0.033 mmole) was weighed into a 120 mL reaction
vessel. A solvent mixture of CH\textsubscript{3}OH:H\textsubscript{2}O (95:5), 4 mL, was tipped onto the solid at \(-78^\circ\text{C}\) and CO at 1 atm. was expanded over the solution. The reaction was stirred at 60\(^\circ\text{C}\) for 36 hrs. No Ru\(_3\)(CO)\(_{12}\) precipitate was evident and the reaction was continued at 28\(^\circ\text{C}\) for days. After 5 days, an infrared spectrum of the reaction mixture indicated a slight Ru\(_3\)(CO)\(_{12}\) product. However, mass spectra of the gas over the reaction solution indicated that significant H\(_2\) had not been formed.

c. With H\(_2\)O

The blank reaction of [NEt\(_4\)][HRu\(_3\)(CO)\(_{11}\)] with H\(_2\)O was performed with a CH\textsubscript{3}OH:H\textsubscript{2}O (95:5) solvent mixture. A CH\textsubscript{3}OH:H\textsubscript{2}O (95:5) solution, 3 mL, containing 20 mg (0.03 mmol) of [NEt\(_4\)][HRu\(_3\)(CO)\(_3\)] was stirred at 60\(^\circ\text{C}\) for 24 hrs. No Ru\(_3\)(CO)\(_{12}\) precipitation was observed and a mass spectrum of the gas evolved during the reaction indicated that H\(_2\) was not formed. A similar result was obtained with a H\(_2\)O:CH\textsubscript{3}CN (1:1) solvent mixture.

6. Reactions of [N(CH\textsubscript{3})\(_4\)][HRu\(_3\)(CO)\(_{11}\)]

a. With CO

The reaction of [N(CH\textsubscript{3})\(_4\)][HRu\(_3\)(CO)\(_{11}\)] with CO was performed in CH\textsubscript{3}CN because [N(CH\textsubscript{3})\(_4\)][HRu\(_3\)(CO)\(_{11}\)] was insoluble in ether solvents. In the drybox, 395 mg (0.546 mmol) of [NMe\(_4\)][HRu\(_3\)(CO)\(_{11}\)] was weighed into a 120 mL reaction vessel. CH\textsubscript{3}CN, 2 mL, was condensed onto the solid at \(-78^\circ\text{C}\) followed by 1 atm. of CO at \(-196^\circ\text{C}\). The solution was stirred at 25\(^\circ\text{C}\), 0\(^\circ\text{C}\), and \(-13^\circ\text{C}\) successively for periods of 1 hr. During this time (3 hrs), no Ru\(_3\)(CO)\(_{12}\) precipitate was observed.
b. With CO and H\textsubscript{2}O

The reaction of [NMe\textsubscript{4}][HRu\textsubscript{3}(CO)\textsubscript{11}] with H\textsubscript{2}O under CO pressure required a cosolvent of methanol:H\textsubscript{2}O (90:10). A CH\textsubscript{3}OH:H\textsubscript{2}O (90:10) solution, 3 mL, containing 23 mg (0.034 mmol) of [NMe\textsubscript{4}][HRu\textsubscript{3}(CO)\textsubscript{11}] was stirred under 1 atm. CO for 96 hrs. at 28\textdegree C. During this period of time, only a slight Ru\textsubscript{3}(CO)\textsubscript{12} precipitate formed and a mass spectrum of the gas above the solution indicated only a very slight H\textsubscript{2} product.

c. With H\textsubscript{2}O

The blank reaction of [NMe\textsubscript{4}][HRu\textsubscript{3}(CO)\textsubscript{11}] with H\textsubscript{2}O was performed with a CH\textsubscript{3}OH:H\textsubscript{2}O (90:10) solvent mixture. A CH\textsubscript{3}OH:H\textsubscript{2}O (90:10) solution, 3 mL, containing 25 mg (0.03 mmol) of [NMe\textsubscript{4}][HRu\textsubscript{3}(CO)\textsubscript{11}] was stirred at 28\textdegree C for 90 hrs. No Ru\textsubscript{3}(CO)\textsubscript{12} was observed and a mass spectrum of the evolved gas indicated that H\textsubscript{2} had not been formed.

7. Reactions of [H\textsubscript{3}Ru\textsubscript{4}(CO)\textsubscript{12}]-

a. With H\textsubscript{2}

In the drybox, 40 mg (0.051 mmol) of K[H\textsubscript{3}Ru\textsubscript{4}(CO)\textsubscript{12}] was weighed into a 120 mL reaction vessel. THF, 3 mL, was condensed into the vessel at -78\textdegree C and 694 mm Hg of H\textsubscript{2} was expanded over the solution. The solution was heated at 60\textdegree C for 13 hrs. under stirring and was tipped into an NMR sidearm. The NMR tube was sealed off under the H\textsubscript{2} pressure at -196\textdegree C. Proton NMR spectra at 28\textdegree C indicated that only unreacted K[H\textsubscript{3}Ru\textsubscript{4}(CO)\textsubscript{12}] was present. A mass spectrum of the gas over the solution indicated that it had not changed over the course of the reaction (100% H\textsubscript{2}).
b. With CO

The reaction of $K[H_3Ru_4(CO)_{12}]$ with CO was performed numerous times under a variety of conditions in order to determine the nature of the reaction pathway.

In the drybox, 68 mg (0.086 mmol) of $K[H_3Ru_4(CO)_{12}]$ was weighed into a 120 mL reaction vessel. Glyme, 3 mL, was condensed into the vessel at -78°C and 1 atm. of CO was expanded over the solution. The reaction was stirred at 80°C and monitored by $^1H$ NMR with time. Results are given in Table 15.

Table 15

Reaction of $[H_3Ru_4(CO)_{12}]^-$ with CO at 80°C

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>$[H_3Ru_4(CO)_{12}]^-$</th>
<th>$[HRu_4(CO)_{13}]^-$</th>
<th>$[HRu_3(CO)_{11}]^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0. hr</td>
<td>100%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4.5 hr</td>
<td>65%</td>
<td>10%</td>
<td>25%</td>
</tr>
<tr>
<td>12.0 hr</td>
<td>38%</td>
<td>14%</td>
<td>48%</td>
</tr>
<tr>
<td>22.0 hr</td>
<td>14%</td>
<td>14%</td>
<td>72%</td>
</tr>
<tr>
<td>59. hr</td>
<td>2%</td>
<td>0%</td>
<td>98%</td>
</tr>
</tbody>
</table>
Table 15 indicates that the reaction of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ produces $[\text{HRu}_3(\text{CO})_{11}]^-$ as a final product. Infrared spectra indicated that $\text{Ru}_3(\text{CO})_{12}$ was also a product of the reaction. The mass spectrum of the gas over the solution (in a parallel experiment) revealed that $\text{H}_2$ (0.08 mmole) was also produced.

If the reaction between $[\text{H}_3\text{Ru}_4(\text{CO})]_{12}^-$ and CO was performed at temperatures below 60°C, no $[\text{HRu}_4(\text{CO})_{13}]^-$ intermediate could be observed by $^1\text{H}$ NMR and the reaction did not get to completion. If this incomplete reaction mixture was subjected to a $\text{H}_2$ atmosphere, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ was regenerated quantitatively with the concurrent formation of CO gas. This suggested a CO/$\text{H}_2$ dependent equilibrium between $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and the trinuclear clusters which is discussed in V.B.9. below.

8. Reactions of $[\text{HRu}_4(\text{CO})_{13}]^-$

a. With $\text{H}_2$

The reaction has been described by Dr. C. C. Nagel [192] at 60°C in THF. Essentially the same reaction was repeated at 80°C in glyme. In the drybox, 30 mg (0.037 mmol) of K$[\text{HRu}_4(\text{CO})_{13}]$ was weighed into a 100 mL reaction vessel. Glyme, 4 mL, was added at -78°C and 1 atm. of $\text{H}_2$ was expanded over the solution. Stirring at 80°C for 25 min. resulted in quantitative formation of K$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ ($^1\text{H}$ NMR) and evolution of 0.04 mmol of CO gas (mass spectra).
b. With CO

The reaction of K\(\text{HRu}_4(\text{CO})_{13}\) with CO at 1 atm. has been described by Dr. C. C. Nagel [192]. The reaction was explored in greater detail. When 40 mg (0.050 mmole) of K\(\text{HRu}_4(\text{CO})_{13}\) was subjected to 1 atm. CO pressure in glyme (4 mL) at 80°C, complete consumption of the K\(\text{HRu}_4(\text{CO})_{13}\) occurred in 1 hr. No \(\text{H}_2\) gas was produced and K\(\text{HRu}_3(\text{CO})_{11}\) and Ru\(\text{3(CO)}_{12}\) were the only metal carbonyl products. If the reaction products were heated to 80°C in the absence of CO, K\(\text{HRu}_4(\text{CO})_{13}\) was formed quantitatively and 2 equivalents (0.10 mmole) of CO were evolved if the CO product was removed continuously.

c. With \(\text{H}_2\text{O}/[\text{OH}]^-\)

The reaction of K\(\text{HRu}_4(\text{CO})_{13}\) with \(\text{H}_2\text{O}/[\text{OH}]^-\) solutions were performed in \(\text{H}^1\) NMR tubes. In the drybox, 32.0 mg (0.040 mmole) of K\(\text{HRu}_4(\text{CO})_{13}\) was weighed into a \(\text{H}^1\) NMR tube adapted such that a KOH/\(\text{H}_2\text{O}/\text{Ethoxyethanol (112 mg/0.36 mL/2.9 mL)}\) solution could be added to the solid. Addition of the basic solution to K\(\text{HRu}_4(\text{CO})_{13}\) was done at -78°C. Warming in the NMR probe to 25°C with spectral acquisitions indicated that only K\(\text{H}_2\text{Ru}_4(\text{CO})_{12}\) was present minutes after the solution had reached ambient temperature.

The reaction of K\(\text{HRu}_4(\text{CO})_{13}\) with \(\text{H}_2\text{O}/[\text{OH}]^-\) under less basic conditions was performed using KOH/\(\text{H}_2\text{O}/\text{Ethoxyethanol (8.4 mg/0.27 mL/1.5 mL)}\). \(\text{H}^1\) NMR spectra at 25°C indicated a mixture of K\(\text{H}_3\text{Ru}_4(\text{CO})_{12}\) (20%) and K\(\text{H}_2\text{Ru}_4(\text{CO})_{12}\) (80%) after five minutes. The spectrum did not change significantly with time.
The reaction of $\text{K}[\text{HRu}_4(\text{CO})_{13}]$ with pure $\text{H}_2\text{O}$ in THF was reported by Dr. C. C. Nagel [192] to give an equimolar mixture of $[\text{HRu}_4(\text{CO})_{13}]^-$ and $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ which did not change with time.

The presence of 1 atm. CO did not significantly alter the reaction products observed in the reactions described here.

9. The Tetranuclear/Trinuclear Cluster Equilibrium Studies

a. Reaction of $[\text{HRu}_3(\text{CO})_{11}]^-$ with $\text{Ru}_3(\text{CO})_{12}$

In the drybox, 78.8 mg (0.121 mmol) of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and 26.0 mg (0.0407 mmol) of $\text{Ru}_3(\text{CO})_{12}$ were weighed into a 50 mL reaction vessel. Glyme, 4 mL, was distilled onto the reactants at $-78^\circ\text{C}$ and the system was warmed to $80^\circ\text{C}$. Noncondensible gasses were removed from time to time as the reaction progressed. After 4 hrs., 0.24 mmole of CO gas had been evolved and a $^1\text{H}$ NMR of the reaction solution showed only $\text{K}[\text{HRu}_4(\text{CO})_{13}]$. An infrared spectrum confirmed that $\text{K}[\text{HRu}_4(\text{CO})_{13}]$ had been formed and $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and $\text{Ru}_3(\text{CO})_{12}$ completely consumed.

b. Reaction of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ with $\text{Ru}_3(\text{CO})_{12}$ under $\text{H}_2$

In the drybox, 45.0 mg (0.069 mmole) of $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ and 15.0 mg (0.023 mmole) of $\text{Ru}_3(\text{CO})_{12}$ were weighed into a 100 mL reaction vessel. Glyme, 3 mL, was distilled into the vessel at $-78^\circ\text{C}$ and $\text{H}_2$ (1 atm.) was expanded over the solution. Stirring at $80^\circ\text{C}$ resulted in quantitative formation of $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ after 16 hrs as evidenced by $^1\text{H}$ NMR. Mass spectral analysis of the gas over the solution indicated that CO had been evolved (~0.14 mmole).
c. Reaction of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) with CO/H\(_2\) Mixtures

The reaction of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) with CO/H\(_2\) mixtures was performed in a 120 mL reaction vessel at 60°C under a total gas pressure of 1 atm. The species present in solution were determined by \(^1\text{H}\) NMR taken as a function of time. In the drybox, 91.5 mg (0.117 mmole) of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) was weighed into the reaction vessel adapted with a \(^1\text{H}\) NMR tube sidearm. Glyme, 3 mL, was condensed onto the solid at -78°C and a CO/H\(_2\) mixture of approximate known composition was expanded over the solution. The reaction vessel was stirred at 60°C for at least 24 hr. periods and the gas above the solution was analyzed by mass spectrometry. Proton NMR spectra of the reaction solution were recorded under the CO/H\(_2\) atmosphere. This process was reported to ensure that equilibrium had been achieved during the time frame of the experiment. The results are given in Table 16. A number of solvents were employed, as shown in Table 16, and the notion of an equilibrium was tested by starting with a 3:1 ratio of \([\text{HRu}_3(\text{CO})_{11}]^-:\text{Ru}_3(\text{CO})_{12}\) under CO/H\(_2\) mixtures, described in V.B.9.d. below.

d. Reaction of \([\text{HRu}_3(\text{CO})_{11}]^-:\text{Ru}_3(\text{CO})_{12}\) (3:1) with CO/H\(_2\) Mixtures

The reaction of a 3:1 mixture of \([\text{HRu}_3(\text{CO})_{11}]^-:\text{Ru}_3(\text{CO})_{12}\) with CO/H\(_2\) mixtures was performed identically to those of \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) as described above in V.B.9.c. For the experiments performed in this manner, 75.1 mg (0.117 mmole) of \([\text{HRu}_3(\text{CO})_{11}]^-\) and 24.9 mg (0.039 mmole) of \(\text{Ru}_3(\text{CO})_{12}\) was employed. Results are given in Table 16. Irrespective
Table 16

Relative Concentrations of \([H_3Ru_4(CO)_{12}]^-\) and \([HRu_3(CO)_{11}]^-\) Under Varying CO/H\(_2\) Ratios

<table>
<thead>
<tr>
<th>CO/H(_2)</th>
<th>Temperature, °C</th>
<th>Solvent(s) (^b)</th>
<th>([H_3Ru_4(CO)<em>{12}]^-/[HRu_3(CO)</em>{11}]^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>60°C</td>
<td>THF, glyme, EE</td>
<td>2.3</td>
</tr>
<tr>
<td>11.5</td>
<td>60°C</td>
<td>glyme</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>60°C</td>
<td>glyme</td>
<td>6.3</td>
</tr>
<tr>
<td>0</td>
<td>60°C</td>
<td>THF, glyme, EE</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>

\(^a\)determined by mass spectrometry  
\(^b\)EE = Ethoxyethanol

of the starting point, the same ratio of \([H_3Ru_4(CO)_{12}]^-\) to \([HRu_3(CO)_{11}]^-\) was achieved at a given CO/H\(_2\) ratio.

10. Reactions of K\(_2[H_2Ru_4(CO)_{12}]\)

a. With CO

In the drybox, 50 mg (0.060 mmol) of K\(_2[H_2Ru_4(CO)_{12}]\) was weighed into a 120 mL reaction vessel. THF, 3 mL, was condensed onto the solid at -78°C and 598 mm Hg of CO was expanded over the solution. Stirring at 60°C for 13 hrs. did not produce a change in the infrared spectrum of the solution or in the mass spectrum of the gas over the solution.

b. With H\(_2\)

In the drybox, 50 mg (0.060 mmol) of K\(_2[H_2Ru_4(CO)_{12}]\) was weighed into a 120 mL reaction vessel. THF, 3 mL, was condensed onto the solid
at -78°C and 1 atm. of H₂ was expanded over the solution. Stirring at 60°C for 18 hrs. did not produce a change in the infrared spectrum of the solution.

11. Reactions of K₂[Ru(CO)₄]

a. With CH₃OH:H₂O

In the drybox, 73.2 mg (0.251 mmole) of K₂[Ru(CO)₄] was weighed and placed in an NMR tube. Approximately 1.5 mL of dry CH₃OH was condensed onto the K[HRu(CO)₄] at -78°C and the NMR tube was sealed off under vacuum at -196°C. The sample was allowed to warm to room temperature and proton NMR spectra were observed as a function of time. Initially the major component (> 95%) was K[HRu(CO)₄] (18.8 τ). With time, the solution changed from yellow to red in color and the signal due to K[HRu₃(CO)₁₁] grew in intensity while that for K[HRu(CO)₄] decreased. After 14 hrs. at 25°C, the ratio of K[HRu(CO)₄] to K[HRu₃(CO)₁₁] was 1:2.

The above reaction was performed identically with the exception that 1.0 mL of H₂O (pH = 7.0) was added to the methanol solution of K[HRu(CO)₄]. A rapid (~20 sec.) conversion to K[HRu₃(CO)₁₁] occurred. One atmosphere of CO pressure had no observable effect on the conversion of K[HRu(CO)₄] to K[HRu₃(CO)₁₁] in anhydrous methanol or a methanol:water (3:2) mixture.

In a number of experiments, H₂O was added directly to K₂[Ru(CO)₄]. The reaction was so vigorous that substantial H₂Ru(CO)₄ was formed and this underwent some thermal decomposition to produce H₂Ru₃(CO)₁₂. Consequently, gas evolution was somewhat less than
expected (88%). $\text{K[HRu}_{3}(\text{CO})_{11}]$ was the only soluble metal carbonyl product. No $\text{K[HRu(CO)}_{4}]$ was detected by $^1\text{H}$ NMR in any of the above reactions which contain $\text{H}_2\text{O}$.

b. With $\text{HCl}$

In the drybox, 73.0 mg (0.250 mmole of $\text{K}_{2}[\text{Ru(CO)}_{4}]$) was weighed in a reaction vessel. After it was degassed, 3-4 mL of THF was distilled onto the solid at -78°C. The vessel was kept at -196°C and 0.418 mmole of anhydrous HCl was condensed into the vessel. Upon slow warming to room temperature, a rapid (~1 min.) reaction took place. The THF solution turned deep red and $\text{H}_2$ and CO gas were evolved. After 1.0 min. at 25°C, 0.254 millimoles of non-condensible gas was given off (Analysis: 66% $\text{H}_2$, 34% CO). This result corresponded to 2.0 equivalent of hydrogen and 1.0 equivalent of carbon monoxide evolved per 3.0 equivalent of $\text{K[HRu(CO)}_{4}]$ consumed. The infrared spectrum of the reaction solution indicated that $\text{K[HRu}_{3}(\text{CO})_{11}]$ of very high purity was formed. Isolation of $\text{K[HRu}_{3}(\text{CO})_{11}]$ yielded 50 mg (92%) of product. In a second experiment, 97.5 mg (0.385 mmole) of $\text{K[HRu(CO)}_{4}]$ and 0.571 mmole of anhydrous HCl were reacted under less than stoichiometric conditions in which insufficient HCl was available (3:1.76). Gas evolution was less than stoichiometric according to Equation (1), and the solution consisted of a mixture of $\text{K[HRu(CO)}_{4}]$ and $\text{K[HRu}_{3}(\text{CO})_{11}]$.

c. With Ethoxyethanol/$\text{H}_2\text{O}/\text{KOH}$

In the drybox, 73.3 mg (0.250 mmole) of $\text{K}_{2}[\text{HRu(CO)}_{4}]$ was weighed into an NMR tube. An adapter containing 2 mL of 5.6 molar aqueous KOH
solution and 1 mL of ethoxyethanol was attached. The solution was tipped into the NMR tube at -78°C which was sealed off at -196°C. The NMR spectra were recorded as a function of time at 25°C. These proton spectra showed that K[HRu(CO)] was formed initially but was transformed into K[HRu₃(CO)₁₁] over a period of less than 2 minutes. After 5 minutes at 25°C, the H NMR spectrum indicated that the solution consisted of primarily [HRu₃(CO)₁₁⁻] (80%), and [H₂Ru₄(CO)₁₂]²⁻ (20%). No K[HRu(CO)]⁻ was observed. This experiment was repeated under 1 atm. CO pressure (0.41 mmol) under otherwise identical conditions. No observable difference in the rate of conversion from mononuclear to trinuclear species was observed by H NMR.

12. Reactions of Ru₃(CO)₁₂

a. With KH

In the drybox, 91.6 mg (0.143 mmol) of Ru₃(CO)₁₂ and 5.7 mg (0.14 mmol) of KH (93% active) were weighed into a reaction vessel. THF, 3 mL, was condensed onto the reactants at -78°C and the reaction allowed to proceed at 25°C. The reaction solution turned deep red and 0.139 mmol of CO gas was evolved over a period of 14 hrs. An infrared spectrum of the reaction solution indicated that K[HRu₃(CO)₁₁] had been formed cleanly.

b. With KH and Kryptofix 222

In the drybox, 6.0 mg (0.15 mmole) of KH, 59 mg (0.15 mmole) of Kryptofix 222, and 94 mg (0.15 mmole) of Ru₃(CO)₁₂ were weighed in a 25 mL reaction vessel. THF, 3 mL, was distilled onto the reactants at
-78°C. The mixture was stirred at -36°C for 45 minutes and a slow reaction occurred as judged by a color change. At 25°C, 90% of the theoretical CO was evolved in less than 10 minutes. H₂ was also in the evolved gas. A ¹H NMR spectrum of the reaction solution indicated that [HRu₃(CO)₁₁]⁻ had been formed.

A subsequent blank reaction of KH with Kryptofix 222 in THF gave H₂ gas as a product at 25°C.

c. With KH and ¹³CO

In the drybox, 6.3 mg (0.150 mmole) of KH (95% active) and 96.0 mg (0.150 mmole) of Ru₃(CO)₁₂ were weighed into a 125 mL reaction vessel. THF, 4 mL, was added at -78°C and ¹³CO (95.7% ¹³C) was expanded over the solution to a pressure of 745 mm Hg. The reaction mixture was stirred at 25°C for 43 hrs. During this time, the characteristic deep red color of K[HRu₃(CO)₁₁] was not observed and the reaction appeared to be inhibited. After 48 hrs, the gas over the solution was measured to be 5.68 millimoles and was analyzed for 71.9% ¹³CO and 28.1% ¹²CO. Removal of the CO gas over solution also led to a net reaction between KH and Ru₃(CO)₁₂. After 12 hrs. at 25°C, 0.109 mmoles of CO had been evolved and the formation of K[HRu₃(CO)₁₁] was evident by infrared spectroscopy. The mass spectrum of the evolved CO indicated a distribution of 72% ¹³CO and 28% ¹²CO.

The inhibition of the reaction between KH and Ru₃(CO)₁₂ by an atmosphere of CO gas was also observed with natural abundance CO.

Later experiments revealed that ¹³CO-¹²CO exchange in this reaction was statistical after 10.5 hrs at 27°C.
d. With NaH and $^{13}\text{CO}$

In the drybox, 11.3 mg (0.471 mmole) of NaH (95% active) and 286 mg (0.448 mmole) of Ru$_3$(CO)$_{12}$ were weighed into a 120 ml reaction vessel. THF, 4 ml was added at -78°C and $^{13}\text{CO}$ (99% $^{13}\text{C}$) was expanded over the solution to a pressure of 750 mm Hg. The reaction was stirred at 27°C for 10.5 hrs and the gas in the system collected (5.37 mmole) and analyzed. A mass spectrum revealed that the carbon monoxide consisted of 52% $^{13}\text{CO}$ and 48% $^{12}\text{CO}$.

e. With LiH and $^{13}\text{CO}$

In the drybox, 3.8 mg (0.48 mmole) of LiH and 288 mg (0.451 mmole) of Ru$_3$(CO)$_{12}$ were weighed into a 120 ml reaction vessel. THF, 4 ml, was added at -78°C and $^{13}\text{CO}$ (99% $^{13}\text{C}$) was expanded over the solution to a pressure of 750 mm Hg. The reaction was stirred at 27°C for 10.5 hrs. Collection of the gas in the system yielded 5.41 mmole of carbon monoxide which analyzed for 70% $^{13}\text{CO}$ and 30% $^{12}\text{CO}$ by mass spectrometry.

f. With $^{13}\text{CO}$

The blank reaction between Ru$_3$(CO)$_{12}$ and $^{13}\text{CO}$ was performed under identical conditions as described in V.B.12.c. above with the exception that KH, NaH, and LiH were excluded. In a 125 mL reaction vessel was weighed 96.0 mg (0.150 mmole) of Ru$_3$(CO)$_{12}$. THF, 4 mL, was added at -78°C and 760 mm Hg pressure of $^{13}\text{CO}$ (95.7% $^{13}\text{C}$) was expanded over the solution. The reaction solution was stirred at 25°C for 48 hrs. The gas above the solution was measured to be 6.02 mmoles which analyzed for 95.7% $^{13}\text{CO}$. 
13. Reactions of K[HFe(CO)₄]

With CO

In the drybox, 160 mg (0.805 mmole) of K[HFe(CO)₄] was weighed into a 130 mL reaction bulb. THF, 2 mL, was condensed onto the solid at -78°C and 1 atm. of CO gas was expanded over the solution. The reaction was stirred at 0°C for 19 hrs. The volatile components of the reaction system were rapidly removed under dynamic vacuum and the condensable components collected in a U-trap at -196°C. An infrared spectrum of the condensable components in THF indicated that Fe(CO)₅ was a product of the reaction. Comparison of this infrared spectrum with standard spectra of samples of known concentration [Fe(CO)₅ in THF] indicated that 0.04 mmole of Fe(CO)₅ had been produced. A ¹H NMR of the nonvolatile reaction products showed only K[HFe(CO)₄] (18.9 τ). No intermediate formyl species could be detected by ¹H NMR or infrared spectroscopy.

A blank reaction of K[HFe(CO)₄] in THF in the absence of CO revealed that K[HFe(CO)₄] is stable under the reaction conditions.

The salt K[HFe(CO)₄] was found to exchange its carbonyls with free ¹³CO rapidly in THF at 25°C.

b. With HCl

In the drybox, 27.3 mg (0.111 mmole) of K₂[Fe(CO)₄] was weighed into a 30 mL reaction vessel. THF, 2 mL, was condensed into the vessel at -78°C. The THF solution was cooled to -196°C and 0.185 mmole of HCl gas was condensed into the system. The reaction mixture was warmed to 25°C under stirring. The CO gas evolved during the reaction was removed
periodically with the Toeploer pump. Based on CO evolution, the reaction was judged to be 75% complete after 22 hrs. at 25°C. After 30 hrs., 0.105 mmole (95%) of CO had been evolved. An infrared spectrum of the reaction mixture indicated that K[HFe₃(CO)₁₁] was formed in high yield. A ¹H NMR spectrum of the reaction mixture confirmed that K[HFe₃(CO)₁₁] was the predominant product.

c. With H₂O

In the drybox, 31 mg (0.15 mmole) of K[HFe(CO)₄] was weighed into a ¹H NMR tube. Pure H₂O, 1 mL, was tipped onto the solid at -78°C and the reaction was warmed to 25°C. A slow reaction occurred as evidenced by a color change from yellow to red. Proton NMR spectra were recorded as a function of time at 25°C. With time the signal due to K[HFe(CO)₄] decreased in intensity while that of K[HFe₃(CO)₁₁] increased. After 10 hrs., the reaction was complete as judged by ¹H NMR. The NMR tube was attached to the vacuum line through an adaptor with tubing such that the noncondensable gas could be removed and measured. A mass spectrum of the collected gas (~1 mmole) indicated the presence of both H₂ (70%) and CO (30%).

14 Reactions of [Os(CO)₄]²⁻

a. With H₂O

In the drybox, 73.6 mg (0.194 mmole) of K₂[Os(CO)₄] was weighed into a ¹H NMR tube. Pure H₂O, 1.5 mL, was condensed onto the solid at -196°C. The reaction was warmed to 25°C and ¹H NMR spectra were recorded as a function of time. Within minutes, the spectra indicated
that the solution consisted of primarily $\text{H}_2\text{Os(CO)}_4$ (17.8 τ, 86%) and $\text{K}[\text{HOs(CO)}_4]$ (20.3 τ, 14%). No other species were observed by $^1\text{H}$ NMR even after 12 hrs at room temperature. $[\text{HOs}_3\text{(CO)}_{11}]^-$ could be observed after 160 hrs as a minor product. Measurement of the gas evolved in the NMR experiment indicated that only 0.002 mmole of non-condensible gas had evolved.

15. Reactions of $[\text{HFe}_3\text{(CO)}_{11}]^-$

a. With CO

In the drybox, 225 mg (0.437 mmole) of $\text{K}[\text{HFe}_3\text{(CO)}_{11}]$ was weighed into a 120 mL reaction vessel. THF, 4 mL, was condensed into the vessel at $-78^\circ\text{C}$ and 1 atm. of CO was expanded over the solution. The reaction was stirred at 23°C for approximately 10 hrs. During this time the reaction solution changed in color from deep red to orange-yellow. The volatile components of the reaction mixture were removed and an infrared spectrum indicated that Fe(CO)$_5$ had been formed. An infrared spectrum of the nonvolatile reaction products indicated that $\text{K}[\text{HFe(CO)}_4]$ was the major product. A $^1\text{H}$ NMR spectrum indicated that $\text{K}[\text{HFe(CO)}_4]$ was present and that $\text{K}[\text{HFe}_3\text{(CO)}_{11}]$ had been consumed.

16. Reactions of $[\text{HOs}_3\text{(CO)}_{11}]^-$

a. With CO

In the drybox, 50 mg (0.054 mmole) of $\text{K}[\text{HOs}_3\text{(CO)}_{11}]$ was weighed into a 120 mL reaction vessel. THF, 1.5 mL, was condensed into the vessel at $-78^\circ\text{C}$. CO was expanded over the solution at $-78^\circ\text{C}$ to a pressure of 1 atm. The reaction was stirred at 25°C for a period of 48
hours without any Os₃(CO)₁₂ precipitate evident. The system was kept at 0°C for 24 hrs without evidence of a reaction. An infrared spectrum of the reaction solution indicated that only unreacted K[HO₅(CO)₁₁] was present in significant concentration.

17. Reactions of "H₂Ru₃(CO)₁₂"

a. In Solution

The compound H₂Ru₃(CO)₁₂ was unstable at 25°C in a variety of solvents including THF, CH₂Cl₂, CHCl₃ and hexane. If 20 mg (0.03 mmole) of H₂Ru₃(CO)₁₂ was stirred in THF at 25°C, H₂ gas (0.03 mmole) and Ru₃(CO)₁₂ (IR) were formed in high yield in 20 minutes. This decomposition was followed by variable temperature ¹³C NMR. Below 0°C the H₂Ru₃(CO)₁₂ was stable but warming the NMR tube to room temperature resulted in a rapid and clean conversion to Ru₃(CO)₁₂.

b. With KH

In the drybox, 30 mg (0.047 mmole) of H₂Ru₃(CO)₁₂ and 2.0 mg (0.049 mmole) of KH (93% active) were weighed into a reaction vessel. THF, 3 mL, was condensed into the vessel at -78°C and the mixture was stirred at 25°C. After 54 hrs. the noncondensibles were measured to be 0.035 mmole which analyzed for 52% H₂ and 48% CO. An infrared spectrum of the THF soluble products indicated that K[HRu₃(CO)₁₁] was formed almost exclusively.
c. With KD

The reaction of $\text{H}_2\text{Ru}_3(\text{CO})_{12}$ with KD was performed as described in V.B.17.b. above. Stirring for 120 hrs at $25^\circ\text{C}$ gave $\text{K}[	ext{HRu}_3(\text{CO})_{11}]$ and a gas mixture consisting of 47% CO, 30% HD and 23% H$_2$ as products.

d. With H$_2$O/[OH]$^-$

The reaction of 20 mg (0.03 mmole) of $\text{H}_2\text{Ru}_3(\text{CO})_{12}$ with 2 mL of a 0.07 M aqueous KOH solution was very slow, yielding a deep red solution after 3-4 hrs at $25^\circ\text{C}$. A $^1\text{H}$ NMR of this solution indicated that $\text{K}[	ext{HRu}_3(\text{CO})_{11}]$ was the major species present. If the basicity of the solution was increased to 0.5 M [OH]$^-$ the rate of reaction increased, but the system became heterogeneous. When a 5.6 M KOH solution was employed, a reaction occurred within minutes but considerable insoluble products were formed.

18. Reactions of $\text{K}[	ext{HRu}_3(\text{CO})_9(\text{DPPE})]$  

a. With CO

In the drybox, 184 mg (0.185 mmole) of $\text{K}[	ext{HRu}_3(\text{CO})_9(\text{DPPE})]$ was weighed into a 120 ml reaction vessel. THF, 1 ml, was condensed onto the solid at $-78^\circ\text{C}$. The reaction was warmed to $0^\circ\text{C}$ and stirred for several hours. No precipitate was observed at $0^\circ\text{C}$ or after several hours at $25^\circ\text{C}$. An infrared spectrum of the reaction solution indicated only the presence of $\text{K}[	ext{HRu}_3(\text{CO})_9(\text{DPPE})]$. 
b. With CO and H$_2$O

In the drybox, 45 mg (0.045 mmole) of K[Ru$_3$(CO)$_9$(DPPE)] was weighed into a 120 ml reaction vessel equipped with a sidearm containing 4 ml of degassed H$_2$O and a Kontes stopcock. After degassing, a very slight quantity of THF (>1 ml) was condensed onto the salt at -78°C and 1 atm. of CO was expanded into the system. The H$_2$O was tipped onto the K[Ru$_3$(CO)$_9$(DPPE)] and the reaction was stirred at 25°C. Ru$_3$(CO)$_{10}$(DPPE) began precipitating from solution immediately. After approximately 6 hrs the reaction was complete. The gas over the reaction was collected with a Toeploer pump and a mass spectrum revealed that H$_2$ (0.05 mmol) was a product. An infrared spectrum of the reaction precipitate revealed that it was Ru$_3$(CO)$_{10}$(DPPE).

c. With H$_2$O

The blank reaction was performed as described in V.B.18.b. above with the exception that no CO was added. After 6 hours at 25°C, no precipitate was evident. Mass spectral analysis of the gas above the solution indicated that H$_2$ was not produced in the reaction.

d. With B(OCH$_3$)$_3$ and CO

In the drybox, 173 mg (0.175 mmole) of K[Ru$_3$(CO)$_9$(DPPE)] was weighed into a 120 ml reaction vessel. THF, 3.5 ml, and 0.27 mmole of B(OCH$_3$)$_3$ were condensed into the vessel at -78°C. One atmosphere of CO was expanded over the solution at -78°C and the system was warmed to 25°C. Stirring at 25°C for 72 hrs did not result in any precipitate
formation. An infrared spectrum of the reaction solution revealed that unreacted K[HRu$_3$(CO)$_9$(DPPE)] was the only metal carbonyl present.

19. Reactions of K[HRu$_3$(CO)$_7$(DPPM)$_2$]

a. With CO

In the drybox, 261 mg (0.196 mmole) of K[HRu$_3$(CO)$_7$(DPPM)$_2$] was weighed into a 120 ml reaction vessel. THF, 1.5 ml, was condensed onto the solid at -78°C and 1 atm. of CO was expanded over the solution. The reaction was warmed to 0°C and stirred for several hours. No precipitate was observed at 0°C or after the reaction had proceeded several hours at 25°C. An infrared spectrum of the reaction solution indicated only the presence of K[HRu$_3$(CO)$_7$(DPPM)$_2$].

b. With CO and H$_2$O

The reaction of K[HRu$_3$(CO)$_7$(DPPM)$_2$] (0.050 mmole) with CO (1 atm) and H$_2$O (4.5 ml) was performed in an identical manner to that of K[HRu$_3$(CO)$_9$(DPPE)] described above in V.B.18.b. Within 6 hrs. at 25°C, complete consumption of K[HRu$_3$(CO)$_7$(DPPM)$_2$] had occurred and a Ru$_3$(CO)$_8$(DPPM)$_2$ precipitate had formed. A mass spectrum of the gas in the system indicated that H$_2$ (0.05 mmol) was a reaction product.

c. With H$_2$O

The blank reaction was performed as described in V.B.19.b. above with the exception that no CO was added. After 6 hrs at 25°C, no Ru$_3$(CO)$_8$(DPPM)$_2$ precipitate was observed. A mass spectrum of the gas in the system indicated that H$_2$ was not a product.
VI. Water-Gas Shift Catalysis Studies

A. Preparation of Catalyst Solutions

1. Neutral Metal Carbonyl Catalyst Precursors

Water-gas shift catalysis studies employing \( \text{Fe}_3(\text{CO})_{12} \), \( \text{Ru}_3(\text{CO})_{12} \), \( \text{H}_4\text{Ru}_2(\text{CO})_{12} \), \( \text{Ru}_3(\text{CO})_{10}(\text{DPPE}) \), \( \text{Ru}_3(\text{CO})_8(\text{DPPH})_2 \), and \( \text{Os}_3(\text{CO})_{12} \) as catalyst precursors were all carried out using the same procedure. In a 120 ml reaction vessel, 0.04 millimole of metal carbonyl was weighed and 3.0 ml of ethoxyethanol was added under a flow of \( \text{N}_2 \). The ethoxyethanol-metal carbonyl mixture was cooled to \(-78^\circ\text{C}\) and 0.36 ml of a \( \text{H}_2\text{O} \) solution which contained 2.0 mmole of the appropriate base (KOH, NaOH, LiOH, NEt\(_3\), Me\(_4\)NOH) was added. The \( \text{N}_2 \) flow was stopped, the vessel evacuated, and the catalysis solution was thoroughly degassed at \(-78^\circ\text{C}\). A known amount of CO pressure (~0.9 atm) was expanded through a \(-196^\circ\text{C} \) U-trap into the catalysis vessel and to a mass-spect. sample bulb simultaneously at \(-78^\circ\text{C}\). The sample bulb was analyzed by mass spectrometry for background \( \text{H}_2 \) in the carbon monoxide. At this stage, the system was prepared for the catalysis, which was performed in two different manners described in VI.1. and VI.b.2. below.

2. Metal Carbonylate Catalyst Precursors

Water-gas shift catalysis studies employing \( \text{K}[\text{HFe}_3(\text{CO})_{11}] \), \( \text{K}[\text{HFe}(\text{CO})_4] \), \( \text{K}[\text{HOs}(\text{CO})_4] \), and \( \text{K}_2[\text{Ru}(\text{CO})_4] \) as catalyst precursors were all carried out using the following procedure. A tip tube containing a solution of ethoxyethanol/\( \text{H}_2\text{O} \)/KOH (3.0 ml/0.36 ml/2.0 mmole) and attached to a Kontes 9 mm stopcock was degassed on the vacuum line. In the drybox, 0.04 mmole of metal carbonylate was weighed into a 120 ml
reaction vessel and the adapter with tip tube was attached. The reaction vessel was degassed and the basic solution in the tip tube was tipped onto the metal carbonylate at -78°C. The system was prepared for catalysis as described in VI.b.1 and VI.b.2 below.

B. Methods of Performing Catalysis

1. Hydrogen Accumulation in a Closed System

In the first method, the closed reaction system was heated to 100°C and stirred for 24 hrs. During this time, the H₂ produced catalytically by the water-gas shift reaction accumulated in the reaction vessel. After 24 hrs, the catalysis solution was quenched by cooling to -78°C and the gas was collected by a Toepler pump. A typical run produced 4.5 mmol of gas (CO + H₂), which generally analyzed (mass spectrometry) for 9 to 10% H₂ (0.5% to 4.5% background H₂ in the CO). If the reaction was to proceed for several days, fresh CO was expanded into the vessel and the entire process was repeated every 24 hrs. At given times, the catalysis solution was analyzed by ¹H NMR by tipping it into an NMR tube which was then sealed.

2. Continuous Removal of H₂ through a Pd Membrane

In the second method, the catalysis vessel was attached to a Pd thimble (Figure ) which continuously removed H₂ from the system. The catalysis vessel was stirred at 100°C and the Pd thimble was operated at 400°C (section I.d.). H₂ continuously diffused through the Pd, leaving CO behind, and was collected with a Toepler pump, which operated continuously. In a typical 24 hr catalysis run, 10 mmole of gas (CO +
H$_2$ was produced which generally analyzed (mass spectrometry) for 2 to 4% H$_2$. A 0.4 to 0.7 mmole quantity of H$_2$ (> 99%) diffused through the Pd membrane over the 24 hr period. If the reaction was to proceed for several days, new CO was expanded into the system and the entire process repeated every 24 hrs. The catalysis solution was analyzed by $^1$H NMR by tipping it into an NH$_2$ tube which was then sealed.

VII. Carbon-13 Enrichment of Metal Carbonyls Initiated by KH and NaBH$_4$

All exchange experiments employing the KH as an exchange initiator were prepared in the drybox. Although the NaBH$_4$ may be handled in air, best results were obtained when a free-flowing powder of NaBH$_4$ was stored and handled in the drybox.

A. Enrichment of Fe(CO)$_5$

In a nitrogen filled drybox 1.0 mg (.025 mmol) of KH was placed in a 140-mL reaction vessel containing a Teflon covered magnetic stirring bar. THF, 2.0 mL, was distilled into the reaction vessel at -78°C followed by distillation of 0.38 mmol of Fe(CO)$_5$ at -196°C. Approximately 1 atm (5.93 mmol) of $^{13}$CO was expanded over the reaction solution at -78°C. The reaction vessel was then allowed to warm to ambient temperature with the exclusion of light and was stirred for 20 hrs. Very brief visual inspection of the reaction solution from time to time indicated that its initially yellow color was maintained throughout the course of the reaction. The gas in the reaction vessel was trapped and measured with the use of a Toepler pump. Mass spectral analysis of
the $^{13}$CO-$^{12}$CO gas mixture revealed that statistical exchange between Fe(CO)$_5$ and free $^{13}$CO had occurred. The Fe(CO)$_5$ was recovered in greater than 90% yield by trap to trap distillation (-15°C, -45°C, -78°C). The infrared spectrum of recovered Fe(CO)$_5$ also indicated that the exchange was complete. In the absence of KH, no measurable (mass spect., IR) $^{13}$CO-$^{12}$CO exchange occurs under identical conditions of time and temperature.

B. Enrichment of Fe$_3$(CO)$_{12}$, Ru$_3$(CO)$_{12}$, Os$_3$(CO)$_{12}$, Group VI, and Group VII Carbonyls:

In a nitrogen filled drybox the KH (Table 10) was placed in a 140 mL reaction vessel containing a Teflon covered magnetic stirring bar and the solid metal carbonyl compound. Generally between 0.1 and 1.0 mmole of metal carbonyl was employed. THF was distilled into the reaction vessel at -78°C and the solution was maintained at this temperature while 1 atm (~6 mmole) of $^{13}$CO (95%) was expanded over the liquid. The solution was allowed to warm to 25°C in the absence of light and was stirred continuously. Mass spectral analysis of the gases over the solution were performed from time to time to determine the extent of isotopic exchange. Quantities of individual metal carbonyls used, conditions, and extent of enrichment are given in Table 10. Isolation procedures for the metal carbonyls are given below. Infrared spectra, carbon monoxide mass spectral analysis, and carbon-13 NMR were employed to determine both the degree of $^{13}$CO incorporation and the purity of the isolated carbonyl. Blank reactions (no hydride initiator) were carried out under identical conditions (Table ) and did not yield a measurable
$^{13}$CO incorporation with the exception of Experiment 6 (Table 10) where Fe$_3$(CO)$_{12}$ was converted to Fe(CO)$_5$ under $^{13}$CO pressure.

C. Isolation of enriched solid metal carbonyls

After gas sampling had indicated significant $^{13}$CO–$^{12}$CO exchange had occurred, the carbon monoxide was removed from the vessel, measured, and analyzed. Ru$_3$(CO)$_{12}$, Os$_3$(CO)$_{12}$, Cr(CO)$_6$, Mo(CO)$_6$ and W(CO)$_6$ are insoluble in THF so that separation from the THF-soluble hydrido carbonyl anions formed was accomplished by cooling the solution to $-78^\circ$C and filtering. Isolated yields of the metal carbonyls are: Ru$_3$(CO)$_{12}$ (85%); Os$_3$(CO)$_{12}$ (88%); Cr(CO)$_6$ (90%); Mo(CO)$_6$ (75%); W(CO)$_6$ (86%).

Isolation of Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$ was accomplished by reducing the volume of THF to 1 mL and cooling to $-78^\circ$C. Crystals of Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$ formed and were collected by rapid filtration. Yield: Mn$_2$(CO)$_{10}$ (84%); Re$_2$(CO)$_{10}$ (79%).
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