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Synergistic behavior of homogeneous ruthenium-rhodium catalysts for hydrogenation of carbon monoxide

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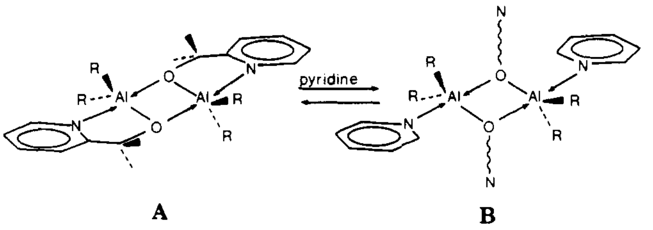

Figure 5. Five-coordination either through *intramolecular* (A) or *intermolecular* (B) pyridine *N*-to-Al coordination.

that the Al center is on the NMR time scale five-coordinate. A plausible explanation is the presence of the equilibrium shown in Figure 5.

Since in pyridine, the ^1H NMR spectra (see Table IV, compound IV) prove that this species is still subject to the on–off movement of the pyridyl N atom, the Al centers remain predominantly five-coordinate as a result of the Al–pyridine solvent interaction. While the (intramolecular) pyridyl N atom is leaving, a pyridine solvent molecule occupies the fifth coordination position.

Conclusions

The present results shows that care should be taken in extrapolating crystallographic information about the structure of five-coordinate diorganoaluminum compounds, both to their structure in solution and to the interpretation of the observed reactivity. Although, in the solid state, the dimeric diorganoaluminum 2-pyridylmethanolate compounds possess five-coordinate aluminum centers, in solution there is an equilibrium between the five-coordinate and a four-coordinate dimeric species via an on–off movement of the neutral pyridyl N donor site. In addition to ^1H and ^{13}C NMR spectroscopy, ^{27}Al NMR is shown to be extremely useful for the study of the changing coordination number at the metal center. The chemical shift values for the present series of five-coordinate (in the slow exchange limit) diorganoaluminum compounds in solution are in the range of 35–45 ppm (cf. ref 19b).

Acknowledgment. The X-ray data were kindly collected by Dr. A. J. M. Duisenberg. Investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO) (A.L.S. and B.K-P). Mr. J. M. Ernsting and Dr. D. M. Grove are thanked for recording and discussions of the NMR spectra.

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Supplementary Material Available: Tables of positional and thermal parameters for all atoms, a list of observed and calculated structure factors, a complete list of bond lengths and bond angles (Table SI), and an ORTEP plot of $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$, cryoscopic molecular weight determinations in benzene (Table SII), and elemental analyses (Table SIII) (13 pages). Ordering information is given on any current masthead page.

Synergistic Behavior of Homogeneous Ruthenium–Rhodium Catalysts for Hydrogenation of Carbon Monoxide

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Homogeneous solutions containing complexes of both ruthenium and rhodium are shown to exhibit good selectivity for the catalytic hydrogenation of carbon monoxide to ethylene glycol. Reactions were studied at pressures from 400 to 850 atm and temperatures from 190 to 240 °C. Iodide ion is an effective promoter for this reaction. The total activity of the bimetallic system does not depend on the amount of rhodium present, but addition of this metal affects product selectivity. Metal complexes observed in catalytic solutions are $[HRu_3(CO)_{11}]^-$, $[Ru(CO)_3I_3]^-$, and $[Rh(CO)_2I_2]^-$. A mechanism consistent with these results is presented, which involves hydride transfer from $[HRu(CO)_4]^-$ to an electrophilic carbonyl ligand on a rhodium complex. A correlation of CO stretching force constants of metal carbonyls with their reactivities toward $[HRu(CO)_4]^-$ suggests that the rhodium complex involved in this reaction is likely to contain Rh(III) and may be $[Rh(CO)_2I_4]^-$.

Introduction

The hydrogenation of carbon monoxide to oxygenates by homogeneous catalysts has been most extensively studied for complexes of cobalt, rhodium, and ruthenium.[1] These catalytic systems produce varying amounts of methanol, ethylene glycol, ethanol, and other minor products. Several recent reports have indicated that mixtures of ruthenium and rhodium complexes provide an effective bimetallic catalytic system with enhanced selectivity for ethylene glycol,[2-6] the most valuable product. We now wish to report our independent discovery[7] and studies of a ruthenium–rhodium–halide catalytic system for homogeneous CO hydrogenation. A mechanistic scheme is also presented which is consistent with the catalytic observations.

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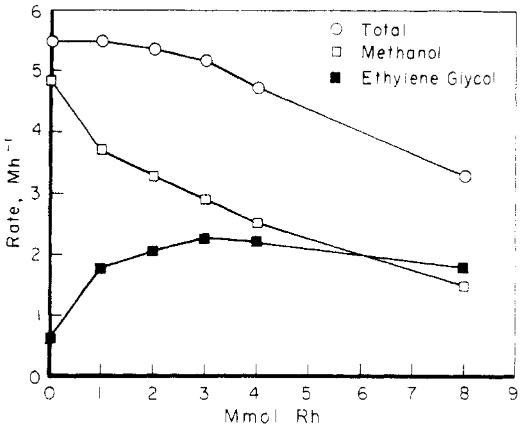

Figure 1. Rates to products with increasing rhodium concentration. Conditions: 75 mL of NMP solvent, 6 mmol of Ru, 18 mmol of NaI, 12 500 psi of 1:1 H_2/CO, 230 °C.

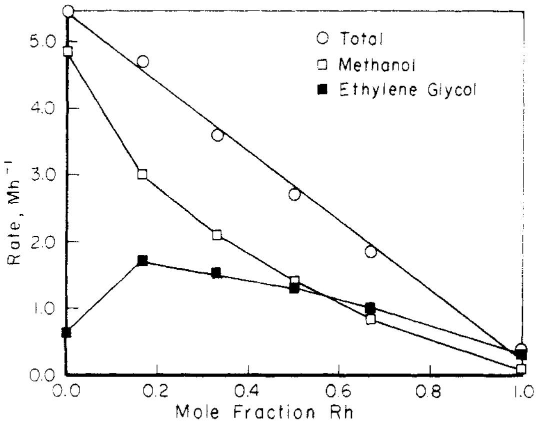

Figure 2. Rates to products vs. mole fraction of ruthenium and rhodium. Conditions: 75 mL of NMP solvent, 6 mmol of total metal, 18 mmol of NaI, 12 500 psi of 1:1 H_2/CO, 230 °C.

Results

Iodide-promoted ruthenium catalysts for homogeneous CO hydrogenation have been studied previously in these laboratories, and results of our catalytic and mechanistic studies have been reported.[8] When small amounts of a rhodium complex (typically Rh(CO)$_2$(acac)) are added to this catalytic system, substantial changes in product selectivity are observed. Figure 1 illustrates the effect of adding increasing amounts of rhodium to several otherwise identical reactions. The ratio of ethylene glycol to methanol is observed to increase significantly, although the total activity of the system remains quite constant up to a rhodium/ruthenium ratio of about 0.5. (Total activity is based on the total moles of methanol and ethylene glycol produced, rather than the amounts of CO or H_2 consumed. This assumes that steps which control activity are early in the CO reduction process before product selectivity is determined.[1]) The loss in total activity seen upon adding larger amounts of rhodium is very probably a result of the decreasing I^- promoter/total metal ratio in this series of experiments. Rate dependences on I^-/Ru ratio in the ruthenium system have been described previously,[8] and the effects of decreasing amounts of iodide on the Ru–Rh system are described below.

To determine in a clearer way the effects of rhodium on the selectivity and activity of the Ru–Rh–I^- system, a series of experiments was then performed in which the total metal/I^- ratio was held constant and the Ru–Rh ratio was varied. Results are shown in Figure 2. This figure clearly depicts the tendency toward improved ethylene glycol/methanol selectivity with an increasing fraction of rhodium. It also makes evident the linear relationship between the total activity of the system and the amount of ruthenium present; i.e., the effect of rhodium is almost entirely that of enhanced selectivity.

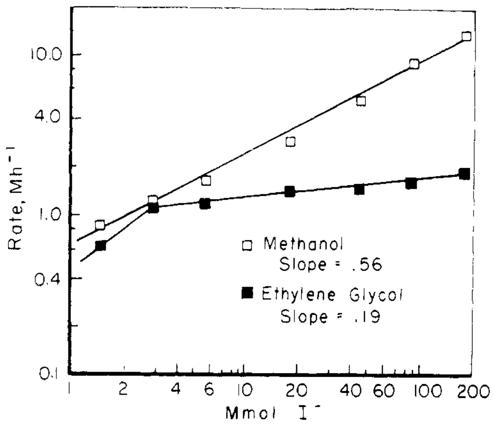

Figure 3. Rates to products with increasing sodium iodide concentration. Conditions: 75 mL of NMP solvent, 6 mmol of Ru, 1 mmol of Rh, 12 500 psi of 1:1 H_2/CO, 230 °C.

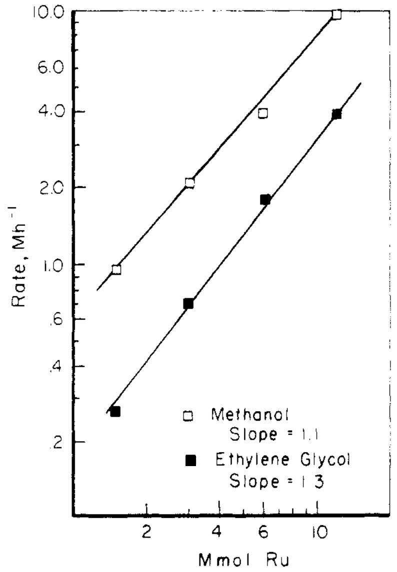

Figure 4. Log–log plot of rates to products vs. catalyst concentration. Conditions: 75 mL of NMP solvent, Ru/Rh/NaI = 1:6:18, 12 500 psi of 1:1 H_2/CO, 230 °C.

A series of experiments whose results are shown in Figure 3 illustrates the effects of increased iodide promoter concentration on the selectivity and activity of the Ru–Rh system. A break in the ethylene glycol rate dependence below a I^-/metals ratio of about 0.5 is similar to that observed in the Ru–I^- system[8] and suggests that the Ru complexes present during catalysis are similar in both cases. (The rhodium component is present in only small amounts in this series of experiments, and its effect on this stoichiometry is expected to be minor.) The observed dependence of the methanol rate on [I^-] is very similar to that observed in the Ru–I^- system, but the glycol rate dependence is substantially less (0.2 vs. 0.45 in the Ru–I^- system). The lower iodide dependence may suggest that there is a step in ethylene glycol formation which is inhibited by free iodide.

Figure 4 illustrates a result similar to that observed for the Ru–I^- system:[8] increased catalyst concentrations lead to higher product ratios of ethylene glycol to methanol.

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[8] B. D. Dombek, *J. Organomet. Chem.*, **250**, 467 (1983); *J. Am. Chem. Soc.*, **103**, 6508 (1981).

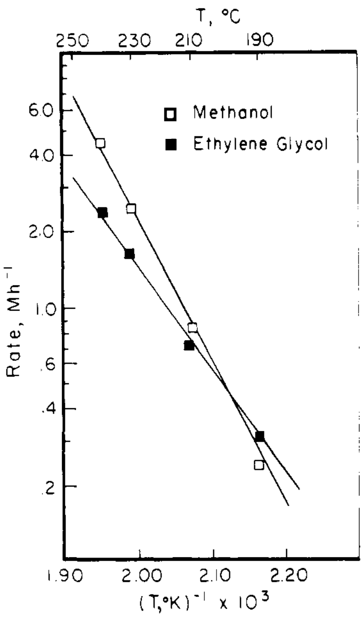

Figure 5. Plot of log (rate) vs. $1/T$ for methanol and ethylene glycol products. Conditions: 75 mL of NMP solvent, 6 mmol of Ru, 2 mmol of Rh, 18 mmol of NaI, 12 500 psi of 1:1 H_2/CO.

This observation suggests that intermolecular processes are involved, especially in the reactions leading to ethylene glycol. The observed dependence of the ethylene glycol rate on catalyst concentration is essentially identical with that found for the Ru-I⁻ system.

Temperature dependences of ethylene glycol and methanol formation rates in *N*-methylpyrrolidone solvent are shown in Figure 5. As estimated from this plot, the observed activation energy for glycol formation is 20 kcal/mol and that for methanol formation is 26 kcal/mol. For the Ru-I⁻ system in the same solvent, observed activation energies for glycol and methanol formation have been found to be 12 and 24 kcal/mol, respectively.[9] On the other hand, observed activation energies of about 18 kcal/mol are seen for both methanol and ethylene glycol production in the rhodium-catalyzed system for CO hydrogenation.[1] Thus the temperature dependence of the ethylene glycol producing pathway in the Ru-Rh-I⁻ system resembles that of the base-promoted rhodium system more than the Ru-I⁻ system.

The effect of reaction pressure on the catalytic system is quite similar to its effect on the Ru-I⁻ system,[8] as shown in Figure 6. Rate dependences of about third- to fourth-order are observed for methanol and glycol products in both systems. Similar dependences are observed in the Rh system.[1]

Infrared spectroscopic studies were carried out in an attempt to determine the form of the rhodium component under reaction conditions. In typical mixed ruthenium-rhodium experiments, the infrared spectra were essentially identical with those of ruthenium catalytic systems, since the amount of rhodium employed was usually relatively small. To determine the state of rhodium under similar conditions in the absence of ruthenium, a solution of $Rh(CO)_2(acac)$ in sulfolane containing 6 equivs of NaI was heated to 175 °C under 8000 psi of 1:1 H_2/CO. Under these conditions, the only complexes observed were $[Rh(CO)_2I_2]^-$ (2055, 1992 cm^{-1}) and $[Rh(CO)_4]^-$ (1898 cm^{-1}). A similar experiment containing 1 equiv of I_2 showed the presence of only $[Rh(CO)_2I_2]^-$. These findings may be contrasted with the results of earlier studies in which much smaller amounts (<1 equiv) of ionic promoters were employed and rhodium clusters were observed under reaction conditions.[10]

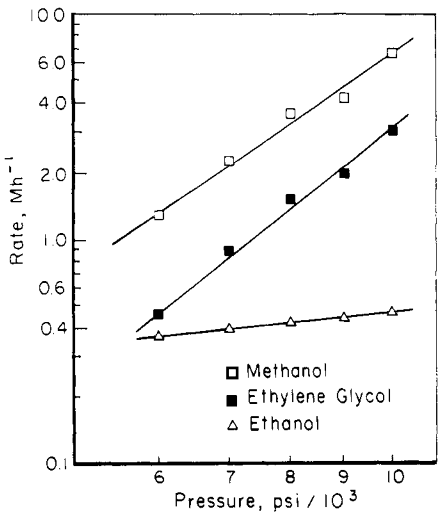

Figure 6. Log-log plot of rates to methanol, ethylene glycol, and ethanol products vs. reaction pressure. Conditions: 75 mL of NMP solvent, 15 mmol of Ru, 3 mmol of Rh, 45 mmol of NaI, 230 °C, 1:1 H_2/CO.

High-pressure infrared studies were also carried out on a mixed ruthenium-rhodium system containing a relatively large proportion of rhodium in an attempt to observe rhodium complexes in the bimetellic system. Absorbances attributable to $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$ were seen, as in Ru-I⁻ systems.[8] In addition, a band at 2055 cm^{-1} was observed which was never found in rhodium-free systems. This band is assigned to $[Rh(CO)_2I_2]^-$; the lower frequency band for this compound was usually obscured by absorptions of the ruthenium complexes. No $[Rh(CO)_4]^-$ was observed, and there was little evidence for rhodium-containing clusters.

Catalytic solutions were routinely analyzed by atomic absorption spectroscopy for Ru and Rh content. No precipitation or loss of either metal component was observed in the catalytic experiments described here.

Discussion

During our study of halide-promoted ruthenium catalysts for CO hydrogenation, it was observed that the addition of rhodium complexes caused a considerable enhancement in the selectivity of the system toward the production of ethylene glycol. Earlier studies of the Ru-I⁻ system supported a reaction scheme which involved intermolecular hydride transfer between two ruthenium complexes as an important step in the CO reduction process.[8] Studies were therefore undertaken to aid in our understanding of the bimetallic Ru-Rh-I⁻ system and the role of the Rh component in its reactions. In order to obtain results as chemically meaningful as possible, catalytic reactions were performed for relatively short periods which reduced the amounts of possible secondary products such as methane, ethanol, ethers, or acetals. Major products were the primary products methanol and ethylene glycol. Other secondary effects, such as reaction rate or selectivity changes due to dilution of the catalyst or reaction medium by products, were also avoided. For these reasons also, the reactions reported here were carried out at relatively high pressures to further enhance the ratio of primary to secondary products. Interpretation of the

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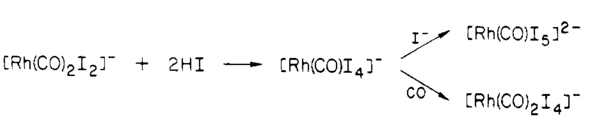
results is therefore simplified, since the total activity of the system is essentially given by the sum of the productivities to methanol and ethylene glycol, and the ratio of these products is close to a true mechanistic selectivity.

As shown in Figures 1 and 2, the enhanced selectivity toward ethylene glycol observed upon adding rhodium complexes to the Ru–I$^-$ system is a result of both an increased rate of ethylene glycol production and a decrease in methanol productivity. It can be seen in the initial part of Figure 1 and in Figure 2 that the total productivity of the system is primarily dependent on the amount of ruthenium present, and not on the rhodium component. (Indeed, adding large amounts of $Rh(CO)_2(acac)$, as shown in Figure 1, leads to a decline in total activity, presumably because of its coordination and removal from solution of free iodide promoter.) These results show that there is no single Ru/Rh ratio which can be identified as indicating a significant or unique stoichiometry: rates to methanol and ethylene glycol exhibit smooth changes across the spectrum of Ru/Rh ratios.

The concept of synergism in homogeneous catalysis has been discussed by Golodov.[12] Synergism may be defined as a disporportionate increase in reaction rate observed upon mixing two catalytic systems, both of which will individually catalyze the reaction in question. (A cautionary note on the interpretation of enhanced rate effects caused by added metal complexes has also been published.[13]) The plot of Figure 2 demonstrates that this system possesses synergism between the Ru and Rh components for ethylene glycol production, a negative synergism (antagonism) for methanol production, and essentially no synergism in the total rate of CO hydrogenation.

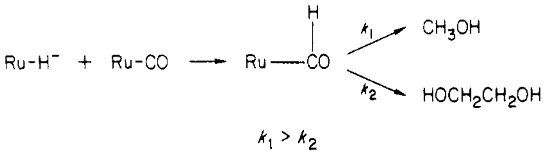
Our catalytic and spectroscopic results suggest that the mechanism(s) of methanol formation by the Ru–I$^-$ system is little changed by the addition of rhodium. Although the rate to methanol is reduced, the dependences of this rate on the reaction variables investigated are essentially unchanged. Such a result would be expected if the essential role of the rhodium additive occurs at the stage of a catalytic intermediate which can partition to form either methanol or ethylene glycol. The effect of rhodium could then be to increase the proportion of this intermediate which is converted to the glycol product, thus simultaneously decreasing the rate to methanol.

Complexes present in the Ru–I$^-$ system during catalysis have been identified as $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$, derived from Ru(0) precursors by a hydrogen-driven redox process.[8] Spectroscopic and stoichiometric studies (e.g., Figure 3) indicate that the same complexes are present after addition of $Rh(CO)_2(acac)$ to the system. Infrared spectroscopic studies suggest that the rhodium added to this system is converted largely to $[Rh(CO)_2I_2]^-$. A number of other catalytic studies have also been reported which show that the predominant rhodium species present in neutral or slightly acidic iodide-containing systems under CO or H_2/CO is $[Rh(CO)_2I_2]^-$.[13-15] In more highly acidic media, this complex is oxidized to Rh(III) species[11,14-16] (eq 1).



(1)

A mechanism for the initial steps leading to CO reduction has been proposed for the Ru–I$^-$ system.[8] It is postulated that important steps in the CO reduction process are the following: (1) equilibrium declusterification of $[HRu_3(CO)_{11}]^-$ to produce the more active mononuclear hydride $[HRu(CO)_4]^-$; (2) equilibrium substitution by CO of an iodide ligand in $[Ru(CO)_3I_3]^-$ to yield the neutral $Ru(CO)_4I_2$ molecule; and (3) hydride transfer from $[HRu(CO)_4]^-$ to an electrophilic CO ligand on $Ru(CO)_4I_2$ (eq 2). Subsequent steps would convert the formyl complex thus formed into methanol or ethylene glycol as products. It is conceivable that rhodium complexes could become involved after the initial stage of formyl formation through, e.g., formyl or hydride transfer from the Ru formyl complex or by the generation of free formaldehyde by the Ru complexes which could be coordinated by the Rh species in solution. Further product-forming steps would then assume the selectivity characteristics and rate and temperature dependences of the specific metal complex involved in these steps. However, free formaldehyde does not appear to be a viable intermediate in CO hydrogenation reactions;[1] it is not a thermodynamically favorable product, and catalytic systems for CO hydrogenation which convert added formaldehyde to CO reduction products have been observed to do so with a product selectivity different from that observed when H_2/CO alone is converted.[17,18] Our experiments with the Ru–Rh–I$^-$ system indicate that added *p*-formaldehyde (which is readily depolymerized at reaction temperatures) is not converted effectively to the alcohol products observed from CO hydrogenation. Transfer of a formyl group from one metal atom to another could be envisioned to occur by several pathways. One possibility is that formyl iodide, ICHO, could be eliminated from one metal center and added to the second. Direct formyl group transfer would seem less likely in a catalytic system under high H_2/CO pressure than hydride transfer from the formyl ligand to a carbonyl ligand on the second metal atom. However, the formyl ligand initially generated by hydride transfer from a metal hydride is unlikely to be as strong a hydride donor as the metal hydride which originally produced it. Thus, the possibility must be also considered that direct transfer of hydride from $[HRu(CO)_4]^-$ to a rhodium carbonyl complex produces a rhodium formyl complex which then forms the alcohol products (eq 3).



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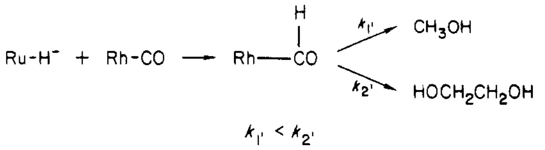

(3)

As shown by Figure 2, a Rh–I$^-$ catalyst system in the absence of Ru does produce small amounts of methanol and ethylene glycol, and the glycol product is formed with quite high selectivity. This may be taken as evidence of the high glycol/methanol selectivity possible at a rhodium

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Table I. CO Stretching Force Constants and Reactivity

compd	CO force const[a], Mdyn/Å	reactn with $[HRu(CO)_4]^-$
cis-$Ru(CO)_4I_2$	18.3 (ax)	*b*
trans-$[Rh(CO)_2I_4]^-$	18.3[c]	
cis-$[Rh(CO)_2I_4]^-$	17.9	
$[(MeCp)Mn(CO)_2(NO)]^+$	17.7	formyl
$[CpRe(CO)_2(NO)]^+$	17.6	formyl
$[Re(CO)_5(PPh_3)]^+$	17.4 (eq)	no reactn
$[Rh(CO)I_4]^-$	17.4	
$[Ru(CO)_3I_3]^-$	17.0	*d*
$Fe(CO)_5$	17.0 (ax)	no reactn
$[Rh(CO)I_5]^{2-}$	16.9	
$[Rh(CO)_2I_2]^-$	16.6	no reactn

[a] When more than one type of carbonyl ligand is present, that having the higher force constant is listed; ax = axial, eq = equatorial. [b] Reaction observed, but unstable formyl intermediate could not be detected. Evidence for the existence and instability of the formyl product has been reported.[19] [c] Assuming a typical value for k_i (0.30 Mdyn/Å), since the A_{1g} band is IR inactive. [d] Redox reaction observed.

center, as in eq 3. (Other studies have also shown the high ethylene glycol selectivities possible with rhodium catalysts.[1] A Ru–I$^-$ system in the absence of Rh exhibits a low ethylene glycol/methanol product ratio. The glycol is postulated to be formed by the process of eq 2; the methanol may be formed by other pathways as well.[8] As increasing amounts of rhodium are added to the Ru system, it would appear that a substantial portion of the process of eq 2 is replaced by a reaction involving rhodium, such as that of eq 3, which produces the glycol product with higher selectivity.

Since $[HRu(CO)_4]^-$ is postulated to be involved in the Ru catalytic system as a hydride donor, its reactivity toward several metal carbonyl complexes has been studied. This hydride reacts with $[CpRe(CO)_2(NO)]^+$ to afford the known rhenium formyl product, as we reported earlier.[19] We have also found that reaction with $[(MeCp)Mn(CO)_2(NO)]^+$ yields the corresponding manganese formyl product. However, $[HRu(CO)_4]^-$ does not react with $[Re(CO)_5(PPh_3)]^+$, with $[CpRe(CO)(NO)(PPh_3)]^+$, or with $Fe(CO)_5$. Its reaction with $Ru(CO)_4I_2$ may proceed through a formyl complex, although we were not able to detect such an intermediate.[19] It is informative to view these results in light of the CO stretching force constants of the metal carbonyl complexes concerned, as shown in Table I.

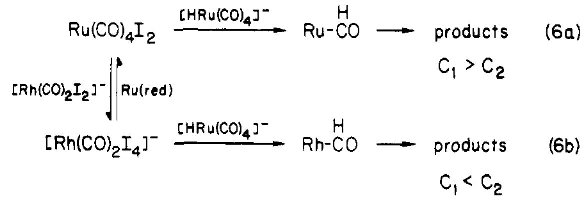
Correlations of CO stretching force constants with reactivities of carbonyl ligands toward nucleophiles have been shown in work by Angelici[20] and Darensbourg.[21] Higher force constants imply greater reactivity toward nucleophilic reagents as a result of less metal-to-carbon π-bonding. Thus, for reaction with a particular nucleophilic reagent, there is a threshold range of CO force constants above which nucleophilic attack occurs and below which the ligand is unreactive. Carbonyl complexes which we have observed to yield formyl products upon reaction with $[HRu(CO)_4]^-$ have CO force constants with a minimum value of 17.6 Mdyn/Å. Compounds with force constants of 17.4 Mdyn/Å and below, even though some were cationic, did not react. Although a reaction was observed between $[HRu(CO)_4]^-$ and $[Ru(CO)_3I_3]^-$, this is a redox process; the position of $[Ru(CO)_3I_3]^-$ in Table I makes it seem unlikely that a metal formyl intermediate is involved. This demonstrates the usefulness of the correlation shown in Table I, since the likelihood of a formyl intermediate in such a reaction can be determined. Likewise, for $Ru(CO)_4I_2$ (whose formyl product would contain labile iodide ligands and must decompose very rapidly if formed[19]) the plausibility of a formyl intermediate is evident.

Model reactions of $[HRu(CO)_4]^-$ with the rhodium halide complexes shown in eq 1 are expected to be at least as complex and inconclusive as those of the ruthenium halide complexes. Difficulties would arise from the instability of some of these complexes under low CO pressures, redox reactions, and the reactivity of possible iodide-containing formyl products. Nevertheless, Table I suggests that $[Rh(CO)_2I_4]^-$ (either cis or trans) will react with $[HRu(CO)_4]^-$ under catalytic conditions to produce a rhodium formyl complex; other rhodium complexes shown in eq 1 appear unlikely to yield a formyl in such reactions. Since $[Rh(CO)_2I_4]^-$ is accessible from $[Rh(CO)_2I_2]^-$ (eq 1), its presence in the catalytic system at low levels seems quite plausible. One might therefore wish to increase the concentration of Rh(III) species in the system, especially $[Rh(CO)_2I_4]^-$, as much as possible. An attempt to do so through eq 1 by increasing the acidity of the solution is unproductive, however, since increased acidity causes oxidation of the reduced ruthenium hydrides required for CO hydrogenation.[22] Oxidation of Rh(I) to Rh(III) in the operating catalytic system would probably result largely from reduction of Ru(II) species. ($Ru(CO)_4I_2$ is expected to be a relatively strong oxidizing agent in the system, as indicated by its highly electrophilic carbonyl ligands.) A minor amount of rhodium oxidation could involve reduction of transient Ru(0) species to anionic ruthenium hydrides. Such processes could involve direct electron transfer but would appear more likely to proceed through the intermediacy of HI, by combination of reactions such as those shown in eq 1, 4, and 5.

$$Ru(CO)_4I_2 + H_2 \rightarrow \text{“Ru(0)”} + 2HI \qquad (4)$$

$$\text{“Ru(0)”} + {}^1/_3H_2 \rightarrow {}^1/_3[HRu_3(CO)_{11}]^- + {}^1/_3HI \qquad (5)$$

A simplified scheme for the involvement of redox equilibria between Ru and Rh complexes involved in catalysis is shown in eq 6. The amount of Rh(III) present in an active system is therefore controlled by this equilibrium process. Increasing the total amount of rhodium in the system is expected to lead to an increase in reaction 6b at the expense of (6a), thus maintaining a constant total activity while changing the selectivity. A scheme of this type is therefore consistent with the results of Figures 1 and 2, as well as other observations. Thus the low dependence of the glycol-forming process on [I$^-$] may be expected, since free iodide can inhibit reaction 6b by converting $[Rh(CO)_2I_4]^-$ to $[Rh(CO)I_5]^{2-}$ (eq 1).



Conclusions

The constant total activity of Ru–I$^-$ solutions observed upon adding Rh is a strong indication that the second metal is primarily involved in a step which determines the

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selectivity of the process rather than the activity. Since a rhodium center appears to offer greater selectivity than a ruthenium center for ethylene glycol formation, an increased amount of product formation is postulated to occur on rhodium as its relative concentration increases. Mechanisms suggested by these general catalytic observations could involve rate-determining formyl or formaldehyde formation on Ru followed by transfer of this group to Rh. However, all of the results are consistent with the transfer of a hydride ligand from $[HRu(CO)_4]^-$ to a carbonyl ligand on a Rh(III) complex formed largely by redox equilibria with $Ru(CO)_4I_2$. This reaction would generate directly a rhodium formyl intermediate which could produce the glycol product with enhanced selectivity.

Experimental Section

The complexes $PPN[HRu(CO)_4]$[23] (PPN = bis(triphenylphosphine)nitrogen(1+)), $[(C_5H_5)Re(CO)_2(NO)]PF_6$,[24] $[(C_5H_5)Re(CO)(PPh_3)(NO)]PF_6$,[24] $[(CH_3C_5H_4)Mn(CO)_2(NO)]PF_6$,[25] and $[Re(CO)_5(PPh_3)]BF_4$[26,27] were prepared by using literature procedures or modifications thereof. $Ru_3(CO)_{12}$ was obtained from Strem Chemicals, Inc., and $Rh(CO)_2(acac)$ (acac = acetonylacetonate) was supplied by Johnson Matthey, Inc. *N*-Methylpyrrolidone (NMP) was used as obtained from Burdick and Jackson.

Catalytic experiments were performed in an Autoclave Engineers stainless steel autoclave of 125-mL nominal volume, stirred by a magnetically coupled turbine. After the catalyst mixture was charged, the autoclave was purged with CO and pressurized to about 500 psi. The system was then heated to the desired reaction temperature before admitting H_2/CO at the desired pressure. As reactant gas was consumed by the reaction, incremental amounts were added to maintain the pressure within ±500 psi of the initial pressure. Reactions were allowed to proceed until a standard amount of H_2/CO had been consumed. The reactor was then rapidly cooled with circulating water. Product amounts were determined by gas chromatography using internal standard methods. Reported rates were calculated based on product amounts and reaction times. Time dependence studies showed that the rates obtained at these levels of H_2/CO conversion are linear and are representative of initial rates; secondary reactions are very minor under these conditions.

High-pressure infrared spectra were recorded on a Digilab FTS-10 spectrometer using a high-pressure cell described elsewhere.[28] In a typical experiment studied by high-pressure infrared spectroscopy, a solution of 0.33 mmol of $Ru_3(CO)_{12}$, 1 mmol of $Rh(CO)_2(acac)$, and 6 mmol of NaI in 125 mL of sulfolane was heated to 175 °C under 8000 psi of 1:1 H_2/CO. Spectra were recorded at this temperature and at 100 °C after the system was cooled.

Reactions between $[HRu(CO)_4]^-$ and metal carbonyls were followed by ^2H NMR using the deuterated ruthenium hydride. Spectra were obtained with a 200-MHz Nicolet instrument using 20-mm tubes. A spectrum of the $PPN[DRu(CO)_4]$ (0.82 mmol in 20 mL of acetone) was recorded at −40 °C. The solution was then warmed to 0 °C, and 0.64 mmol of the metal carbonyl was added. After being mixed at 0 °C for 1.5 min, the solution was cooled to −40 °C and the ^2H NMR recorded. If no reaction was evident, the solution was allowed to warm to 25 °C before again recording the NMR spectrum. If a reaction was evident but a metal formyl resonance could not be detected, the reaction was repeated, maintaining the temperature at −60 °C. Formyl resonances were observed in reactions with $[CpRe(CO)_2(NO)]^+$ (δ 16.18) and $[(MeCp)Mn(CO)_2(NO)]^+$ (δ 14.60). Reported positions for the formyl resonances in CpRe(CO)(NO)(CHO) and CpMn(CO)(NO)(CHO) are δ 16.20 and 14.77, respectively.[29] Metal carbonyl stretching force constants were calculated by using the Cotton–Kraihanzel approximation.[30]

Registry No. CO, 630-08-0; Ru3(CO)12, 15243-33-1; PPN[HRu(CO)4], 79408-52-9; Rh(CO)2(acac), 14874-82-9; $[(C_5H_5)Re(CO)_2(NO)]PF_6$, 12306-73-9; $[(C_5H_5)Re(CO)(PPh_3)(NO)]PF_6$, 79919-50-9; $[(CH_3C_5H_4)Mn(CO)_2(NO)]PF_6$, 52202-14-9; $[Re(CO)_5(PPh_3)]BF_4$, 70083-75-9; *cis*-$Ru(CO)_4I_2$, 18475-75-7; *trans*-$[Rh(CO)_2I_4]^-$, 44769-93-9; *cis*-$[Rh(CO)_2I_4]^-$, 44769-94-0; $[Rh(CO)I_4]^-$, 44494-08-8; $[Rh(CO)_3I_3]^-$, 32423-83-9; $Fe(CO)_5$, 13463-40-6; $[Rh(CO)I_5]^{2-}$, 38840-34-5; $[Rh(CO)_2I_2]^-$, 38255-39-9; $HO(CH_2)_2OH$, 107-21-1.

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