JOURNAL OF CATALYSIS 79, 334–347 (1983)

Ethanol from H_2 and CO via Homogeneous Ruthenium Catalysis

BARBARA K. WARREN AND B. DUANE DOMBEK

Union Carbide Corp., South Charleston, West Virginia 25303

Received July 2, 1982; revised October 22, 1982

Ruthenium carbonyl complexes in the presence of an iodide promoter, an acid, and a phosphine oxide provide an unusually selective catalytic system for the direct conversion of CO and H_2 to ethanol. Reaction conditions studied range from 30 to 87 MPa and 180 to 250°C (1 MPa = 9.87 atm). Other products include methanol, methane, acetaldehyde, ethylene glycol, and *n*-propanol. Much of the ethanol may be derived from initially formed methanol, and the acid component appears to be necessary to facilitate this homologation process. The basic phosphine oxide solvent levels the acidity of the solution, preventing a strong acid from protonating and destroying basic metal complexes involved in the CO hydrogenation process.

INTRODUCTION

As the price of petroleum continues to rise and its future availability becomes uncertain, synthesis gas (H_2/CO) becomes an increasingly attractive alternate feedstock for the chemical industry. The conversion of synthesis gas to organic chemicals has therefore become an important goal for research at both fundamental and applied levels. Homogeneous catalysts offer the potential advantage of forming certain desirable organic products from H_2/CO with high selectivity, but few homogeneous systems are presently known to effectively catalyze such conversions. Soluble cobalt catalysts have been shown to convert synthesis gas to mixtures of products including methanol, ethanol, propanol, glycols, glycerine, and their formate esters (*1–5*). Rhodium complexes produce ethylene glycol and an array of minor products resembling that from cobalt-catalyzed reactions (*3, 6*). Homogeneous ruthenium catalysts have been found to hydrogenate carbon monoxide to methanol and methyl formate (*7*), to methyl, ethyl, and glycol esters in carboxylic acid solvents (*8, 9*), or to methanol, ethylene glycol, and ethanol in the presence of certain promoters (*10, 11*). Several metal complexes in the presence of strong Lewis acids have been found to reduce CO to hydrocarbons (*12, 13*). Low activities for homogeneous hydrogenation of CO have been reported for various other metal complexes (*3, 4*). In the above studies in which ethanol is formed, its rate of production is small, and the selectivity to this product is generally low. We now report the discovery and investigation of a homogeneous catalytic system which produces ethanol directly from CO and H_2 in high yields and at substantial rates (*14*).

EXPERIMENTAL

Materials. Laboratory reactions were carried out under an atmosphere of dry N_2 (or H_2, if noted) using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ immediately before use. Tri-*n*-propylphosphine oxide (Pr_3PO) was prepared by American Cyanamid, Inc. Other phosphine oxides and $Ru_3(CO)_{12}$ were obtained from Strem Chemicals, Inc. PPN[$HRu_3(CO)_{11}$] (PPN = bis(triphenylphosphine)iminium) was prepared by the published method (*15*).

Methods. Infrared spectra were recorded on a Perkin–Elmer 281B spectrophotometer using 0.1-mm CaF_2 cells. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

0021-9517/83/020334-14$03.00/0

When HI was used in reactions, solutions of known concentration were prepared by bubbling gaseous HI into the solvent and recording the weight gain; appropriate amounts of this mixture were then employed in the reactions.

Catalytic experiments were carried out in an Autoclave Engineers stainless-steel autoclave of 125 ml of nominal volume, stirred by a magnetically coupled turbine. The catalyst mixture was charged to the reactor, and the system was purged and pressurized with approximately 2 MPa of CO. The temperature was then raised to the desired reaction temperature before admitting premixed H_2/CO at the specified pressure. As gas was consumed by reaction, incremental amounts were added to maintain the pressure within about ±3.4 MPa of the specified pressure. Reactions were normally allowed to proceed until a standard amount of H_2/CO had been consumed; thus amounts of products formed in most reactions are similar even though reaction times may be different. The reactor was then cooled immediately with circulating cold water. Product amounts were determined by vapor-phase chromatography using internal standard methods. Reported rates are calculated based on product amounts and reaction times. These are therefore average rates, and could differ significantly from instantaneous rates for some products (see Fig. 11, for example). Nevertheless, comparisons among the experiments are believed to be meaningful because of the fact that similar product concentrations were formed in most reactions; conversions are comparable.

$[(C_3H_7)_3POH][CF_3SO_3]$. To a solution of Pr_3PO (3.52 g, 20.0 mmol) in dichloromethane (25 ml) we added dropwise a solution of CF_3SO_3H (3.0 g, 20.0 mmol) in CH_2Cl_2 (5 ml). The solution was evaporated to dryness, and the white solid was washed with pentane and dried under high vacuum to afford a yield of 6.33 g (97%): NMR (CD_2Cl_2) 1.08 (9H, m), 1.30–2.30 (12H, m), 10.80 (1H, s). Anal. calcd. for $C_{10}H_{22}F_3O_4PS$: C, 36.81; H, 6.75; P, 9.51; F, 17.48. Found: C, 35.84; H, 6.66; P, 9.56; F, 16.83.

Reaction of $Ru_3(CO)_{12}$ with HI and Pr_3PO. A solution of $Ru_3(CO)_{12}$ (2.56 g, 4 mmol) and HI (0.67 g of 57% aqueous solution, 3 mmol) in Pr_3PO (30 ml) containing 5 ml of sulfolane (to depress the solvent freezing point) was placed in a Fischer–Porter pressure bottle (Lab-Crest Scientific Glass Co., Warminster, Pa.) and stirred at 65°C under 0.2 MPa of CO. The infrared spectrum was recorded after 46 h, and it indicated the presence of both $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$.

$[(CH_3)_3POH][Ru(CO)_3I_3]$. To a mixture of $Ru_3(CO)_{12}$ (2.56 g, 4 mmol) and $(CH_3)_3PO$ (1.12 g, 12 mmol) in 100 ml of THF we added dropwise aqueous HI (8.08 g of 57% solution, 36 mmol). The solution was then stirred for 2 h and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (80 ml) and diethyl ether (40 ml). Addition of hexane and cooling at −35°C gave large yellow needles which were dried under high vacuum at 70°C to afford a yield of 5.27 g (67%): NMR (CD_2Cl_2) 2.03 (9H, d, J = 13 Hz), 10.12 (1H, s). Anal. calcd. for $C_6H_{10}I_3O_4PRu$: C, 10.93; H, 1.52. Found: C, 11.30; H, 1.63.

An analogous reaction with Pr_3PO produced $[(n\text{-}C_3H_7)_3POH][Ru(CO)_3I_3]$. Anal. calcd. for $C_{12}H_{22}I_3O_4PRu$: C, 19.38; H, 2.96. Found: C, 20.66; H, 3.36.

Reaction of $Ru_3(CO)_{12}$ with H_2 and Pr_3PO. Hydrogen gas was slowly bubbled through a mixture of $Ru_3(CO)_{12}$ (2.08 g, 3.0 mmol), Pr_3PO (45 ml), and sulfolane (5 ml) at 75°C. After 4 h, the infrared spectrum showed $[HRu_3(CO)_{11}]^-$ (Fig. 6) to be the only metal carbonyl product.

Reaction of $PPN[HRu_3(CO)_{11}]$ with $[Pr_3POH][CF_3SO_3]$. A solution of $PPN[HRu_3(CO)_{11}]$ (1.15 g, 1.0 mmol) in CH_2Cl_2 (45 ml) was treated with $[Pr_3POH][CF_3SO_3]$ (0.33 g, 1.0 mmol). The infrared spectrum, recorded after 15 min, showed $Ru_3(CO)_{12}$ as the only metal carbonyl complex.

RESULTS AND DISCUSSION

Effects of Iodide Ion and HI on Ru-Catalyzed CO Hydrogenation

Ruthenium complexes in the presence of iodide salts such as KI have been found to catalyze the hydrogenation of carbon monoxide to methanol, ethylene glycol, and ethanol (*10*). Particularly effective solvents for this reaction are polar compounds, which include *N*-methylpyrrolidone and sulfolane (Table 1, entries 1 and 2). Phosphine oxides have also been studied as solvents, and give results similar to those obtained in other polar solvents, but yield a somewhat higher proportion of the ethanol product (Table 1, entry 3). (No evidence of phosphine oxide decomposition was found in these experiments; catalytic solutions were examined for possible decomposition products by techniques which included infrared spectroscopy, ^{31}P NMR, and combined gas chromatography–mass spectrometry.) A major difference between the phosphine oxide and other solvents becomes obvious when iodine or HI is added to these reaction mixtures before catalysis. (I_2 is converted to HI or its equivalent under catalytic reaction conditions; the two are found to yield identical results in this work.) Other compounds have also been observed to produce the equivalent of HI by their reaction or decomposition under catalytic conditions. Thus reactions of Ru(0) complexes in phosphine oxide solvents containing quaternary ammonium, phosphonium, and sulfonium iodides have been found to give good selectivities to ethanol (*14*), and mixtures of the same Ru complexes found in HI-promoted reactions (see below) were observed after catalysis. Figure 1 illustrates the consequence of adding increasing amounts of HI to a KI-promoted catalytic system in tri-*n*-propylphosphine oxide (Pr_3PO) solvent. Rates to methanol and ethylene glycol are adversely affected, but the production of ethanol is very substantially increased by the addition of HI. (Similar results have been observed in the oxides of trimethylphosphine, triethylphosphine, and tributylphosphine.) For comparison, Fig. 2 shows the results of

TABLE 1

Catalytic Reactions of H_2 and CO[a]

No.	mmol			Solvent	*P* (MPa)	*T* (°C)	Rates (mmol h^{-1})		
	Ru	KI	I_2				CH_3OH	CH_3CH_2OH	$(CH_2OH)_2$
1	6	18	—	NMP[b]	86.1	230	398	13	48
2	6	18	—	Sulf[c]	86.1	230	270	9	44
3	6	18	0	Pr_3PO[d]	86.1	230	435	50	56
4	6	—	3	Pr_3PO	86.1	230	162	293	<20
5	6	—	3	Sulf	86.1	230	<2	<4	<2
6	3	—	1.5	Pr_3PO	41.3	250	41	86	<4
7	8	—	4	Pr_3PO	41.3[e]	240	81	140[f]	<8
8	8	—	4	Pr_3PO	41.3[e]	210	32	53[g]	<4

[a] Conditions: 75 ml solvent, 1 : 1 H_2/CO, Ru charged as $Ru_3(CO)_{12}$.

[b] *N*-Methylpyrrolidone.

[c] Sulfolane.

[d] Tri-*n*-propylphosphine oxide.

[e] $H_2/CO = 2:1$.

[f] Methane produced at a rate of 164 mmol h^{-1}.

[g] Methane produced at a rate of 22 mmol h^{-1}.

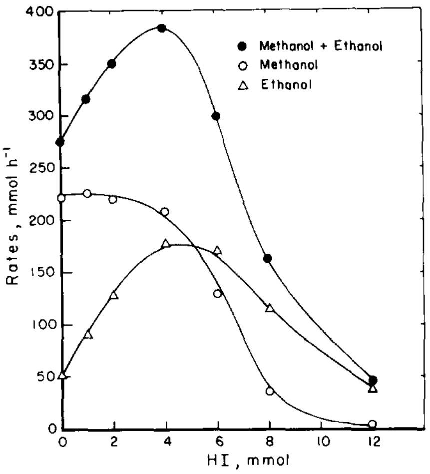


FIG. 1. Effect of adding HI to a mixture of $Ru_3(CO)_{12}$ and KI in Pr_3PO solvent. 75 ml Pr_3PO, 6 mmol Ru, 18 mmol KI, 86.1 MPa, $H_2:CO = 1$, 210°C. Runs are ca. 0.3–1 h.

a similar study in sulfolane solvent; addition of I_2(HI) causes only a small increase in ethanol production, and this compound never becomes a major product constituent. Results comparable to those found in sulfolane have also been observed in other solvents, including 18-crown-6.

Potassium iodide or other added iodide salts are found to be unnecessary in the phosphine oxide–HI reactions. For example, Fig. 3 demonstrates that good selectivity and activity for ethanol formation can be obtained by adding only I_2(HI) to $Ru_3(CO)_{12}$ in phosphine oxide solvent. (In contrast, addition of I_2 to $Ru_3(CO)_{12}$ in sulfolane solvent causes very low catalytic activity; cf. Table 1, entries 4 and 5.) Although it is not required, addition of KI to HI-promoted reactions in phosphine oxide solvent does increase the catalytic activity and alter the selectivity (Fig. 4).

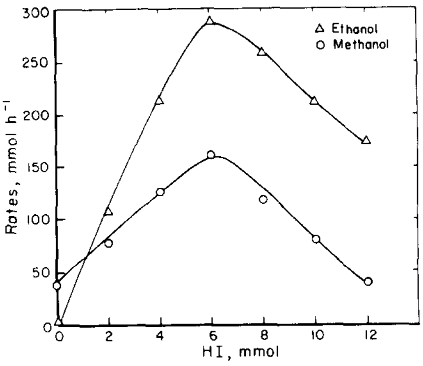


FIG. 3. Effect of adding HI to $Ru_3(CO)_{12}$ in Pr_3PO solvent. 75 ml Pr_3PO, 6 mmol Ru, 86.1 MPa, $H_2:CO = 1$, 230°C (HI added as I_2).

Results of the above catalytic studies may be summarized as follows:

(a) KI and other iodide salts are good promoters for Ru-catalyzed hydrogenation of CO to methanol, ethanol, and ethylene glycol in a variety of polar solvents, including phosphine oxides.

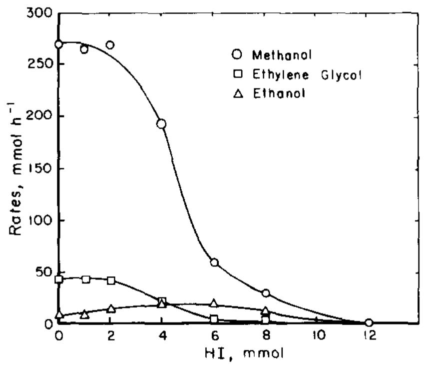


FIG. 2. Effect of adding HI to a mixture of $Ru_3(CO)_{12}$ and KI in sulfolane solvent. 75 ml sulfolane, 6 mmol Ru, 18 mmol KI, 86.1 MPa, $H_2:CO = 1$, 230°C (HI added as I_2).

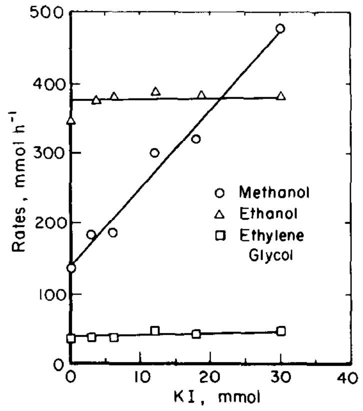


FIG. 4. Effect of adding KI to a mixture of $Ru_3(CO)_{12}$ and HI in Pr_3PO solvent. 75 ml Pr_3PO, 6 mmol Ru, 6 mmol HI (added as I_2), 86.1 MPa, $H_2:CO = 1$, 230°C.

(b) HI in weakly basic solvents (such as sulfolane, $pK_{BH+} = -12.9^{16}$) does not promote CO hydrogenation by Ru complexes nor does it enhance CO reduction when added to Ru–KI mixtures.

(c) Addition of HI to Ru complexes in phosphine oxide solvents promotes CO hydrogenation (and is especially effective for ethanol formation). There is an optimum ratio of HI to Ru for maximum activity.

(d) Addition of HI to a KI-promoted system in phosphine oxide solvents causes increased overall activity up to an optimum HI/Ru ratio, which may differ from the optimum ratio in (c). Selectivity to ethanol is increased as well by the addition of HI.

Ruthenium Complex Chemistry

A. Reactions of $Ru_3(CO)_{12}$ with iodide salts under H_2/CO. Various Ru(O) complexes including $Ru_3(CO)_{12}$ have been found to react under H_2/CO with ionic iodide compounds in a redox process according to Eq. (1) (*10*, *17*).

$$\tfrac{7}{3}Ru_3(CO)_{12} + 3I^- + H_2 \rightarrow \underset{\mathbf{1}}{2[HRu_3(CO)_{11}]^-} + \underset{\mathbf{2}}{[Ru(CO)_3I_3]^-} + 3\,CO \quad (1)$$

The ratio of the two ruthenium complexes formed is found to be fixed by this redox stoichiometry and independent of excess iodide. The reaction occurs in a variety of solvents under mild conditions, and the above two complexes are also observed in catalytic solutions after CO hydrogenation reactions with iodide promoters. Evidence from iodide dependence studies indicates that these complexes are present as well under catalytic conditions, and both **1** and **2** are found necessary to provide optimum reaction rates (*10*). (The individual complexes provide little or no activity, and can be observed unchanged after exposure to conditions normally employed for catalysis.) The maximum activity of these iodide-promoted catalytic systems has been observed at a **1/2** molar ratio of about 2.0 (*10*), even when this ratio is measured (by infrared spectroscopy) at ambient conditions after catalysis. This does not necessarily imply that these complexes are the operating catalysts in such systems. Rather, their presence presumably indicates that they comprise the most stable combination of Ru complexes under these conditions; other, more reactive complexes could be generated by their interaction or combination. For example, a reaction such as the reverse of Eq. (1) would stoichiometrically form Ru(O) products. It can thus be seen that the **1/2** ratio is diagnostic of the average ruthenium oxidation state of the system in any particular reaction, and that the maximum catalytic activity is obtained with an optimum average oxidation state.

The ratio of **1** to **2** can be altered by the addition to catalytic reactions of reagents which have the effect of reducing or oxidizing the system. Addition of a base which can act as a hydrogen halide acceptor was found to have the effect of reducing the system, a change which is manifested by an increase in the **1/2** ratio. Generation of a base *in situ* can also reduce the system and alter the activity. Although Ru(II) complexes such as $[Ru(CO)_3I_3]^-$ are normally inactive for CO hydrogenation, activity develops in an amide solvent such as *N*-methylpyrrolidone, $pK_{BH_+} = -0.9$ (*18*). The basic character of this solvent perhaps contributes to some reduction of the ruthenium complexes. These observations may be relevant to the report that Ru(II) halides (or ruthenium complexes with hydrogen halide promoters) are catalysts for the hydrogenation of carbon monoxide; the "preferred solvents" are organic amides (*19*).

Conversely, addition to an alkali metal iodide-promoted system (containing **1** and **2**) of I_2, HI, or another strong acid oxidizes a corresponding amount of **1** to **2.** Thus addition of HI to a KI-promoted catalytic system in sulfolane solvent (as in Fig. 2) increases the average ruthenium oxidation state, decreases the **1**/**2** ratio from the optimum observed value, and leads to diminished activity.

B. Reactions of $Ru_3(CO)_{12}$ in phosphine oxide solvents. Aside from the high selectivity to ethanol, catalytic reactions in phosphine oxide solvents differ significantly from reactions in many other solvents. One important difference is the observation that addition of HI to a phosphine oxide solution of $Ru_3(CO)_{12}$ alone increases catalytic activity; addition of HI to $Ru_3(CO)_{12}$ in many other solvents does not promote activity, as noted above for sulfolane. Reasons for this behavior were examined by studying the metal complexes formed in the phosphine oxide solutions. When carried out in a sealed reaction vessel, reaction of $Ru_3(CO)_{12}$ with HI in phosphine oxide solvent produces not only the expected oxidized Ru complex, $[Ru(CO)_3I_3]^-$, but also $[HRu_3(CO)_{11}]^-$ (Eq. (2)); the complexes were identified by their characteristic infrared spectra.

$$Ru_3(CO)_{12} + HI \xrightarrow[R_3PO]{CO} \underset{\mathbf{1}}{[HRu_3(CO)_{11}]^-} + \underset{\mathbf{2}}{[Ru(CO)_3I_3]^-} \quad (2)$$

The same complexes could be observed by infrared spectroscopy in reaction solutions of $Ru_3(CO)_{12}$, HI, and Pr_3PO after catalysis under H_2/CO pressure (Fig. 5).

Since iodide was added to these reactions only in the form of HI, it was postulated that the above anionic complexes were present as their $[R_3POH]^+$ salts. The pK_{BH^+} of $(CH_3)_3PO$ has been estimated to be -0.5 (*18*), and several $[R_3POH]^+$ salts have been reported (*20–25*). We also prepared stable $[R_3POH]CF_3SO_3$ salts from phosphine oxides and CF_3SO_3H (see Experimental). The formation of the salts observed in Eq. (2) then appears to result from a combination of the two reactions shown in Eqs. (3) and (4):

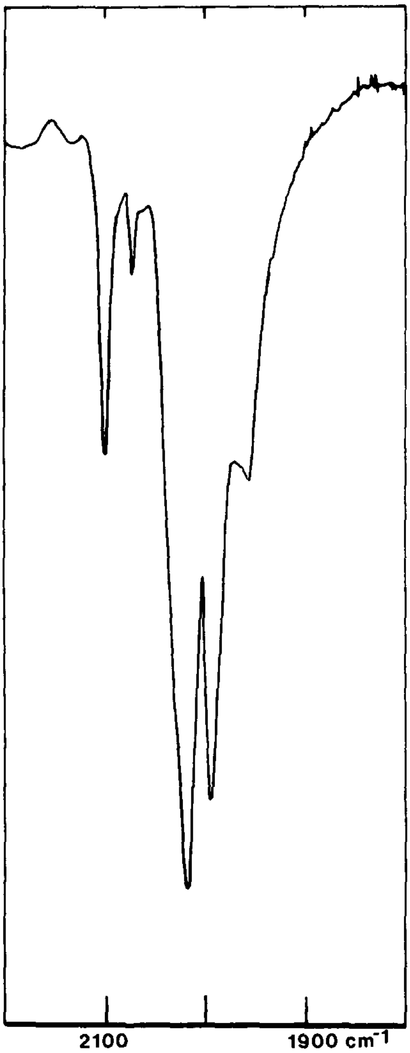


FIG. 5. Infrared spectrum of solution obtained from Pr_3PO, $Ru_3(CO)_{12}$, and HI, after catalysis. 75 ml Pr_3PO, 6 mmol Ru, 6 mmol HI. Conditions of reaction: 86.1 MPa, $H_2:CO = 1$, 230°C. Band at 2100 cm^{-1} and shoulder at 2030 cm^{-1} are assigned to $[Ru(CO)_3I_3]^-$.

$$Ru_3(CO)_{12} + H_2 + R_3PO \rightleftharpoons [R_3POH][HRu_3(CO)_{11}] + CO, \quad (3)$$

$$\tfrac{1}{3}Ru_3(CO)_{12} + 3[R_3POH]I \rightleftharpoons [R_3POH][Ru(CO)_3I_3] + H_2 + CO + 2R_3PO. \quad (4)$$

The reaction of Eq. (3) was found to proceed in Pr_3PO solvent at 70°C under 1 atm of H_2; quantitative formation of $[HRu_3(CO)_{11}]^-$ was observed by infrared spectroscopy (Fig. 6). (Although this product was not isolated, an analogous reaction with Et_3N in THF solvent produced isolable $[Et_3NH][HRu_3(CO)_{11}]$ (*17*). An attempt to carry out the reaction of Eq. (3) in THF solvent using a stoichiometric amount of Pr_3PO did not produce $[HRu_3(CO)_{11}]^-$; instead we found that the reverse (*26*) of Eq. (3) was observed when stoichiometric amounts of $[PPN][HRu_3(CO)_{11}]$ and $[Pr_3POH][CF_3SO_3]$ were mixed. It thus appears that a substantial concentration of phosphine oxide is required to shift Eq. (3) to the anionic Ru complex.

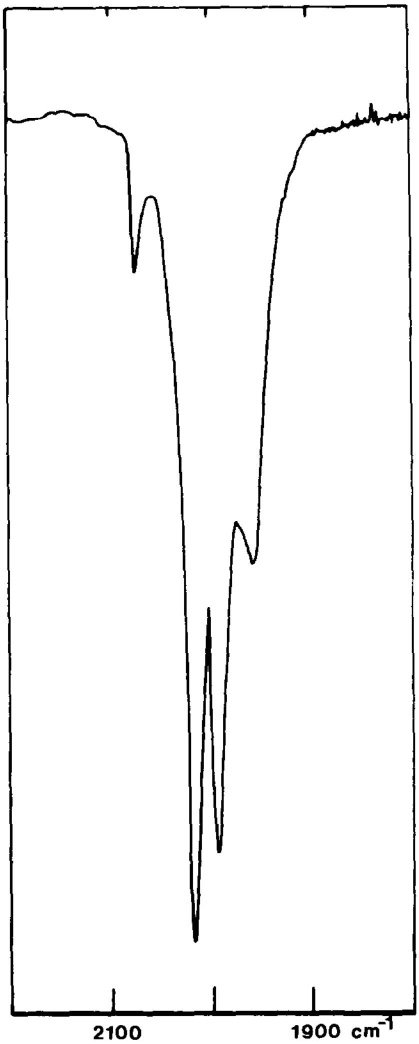


FIG. 6. Infrared spectrum of $[Pr_3POH][HRu_3(CO)_{11}]$ in Pr_3PO solvent.

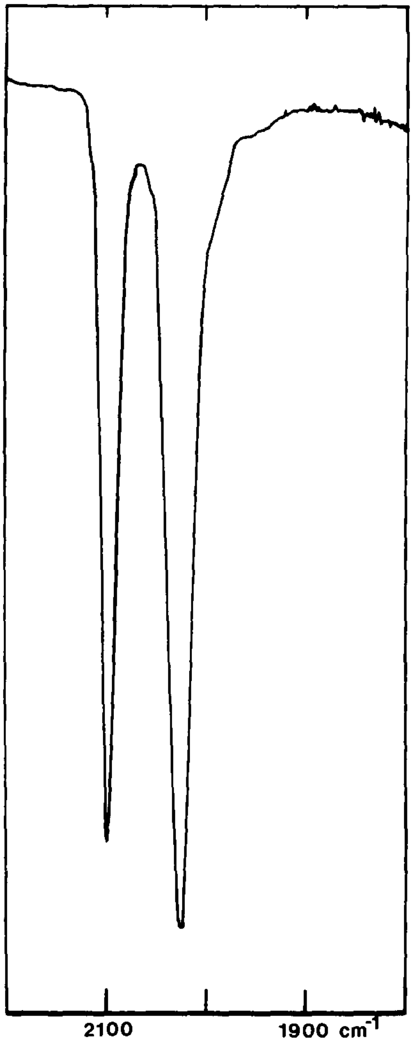


FIG. 7. Infrared spectrum of $[Me_3POH][Ru(CO)_3I_3]$ in THF solvent.

The reaction of Eq. (4) was also demonstrated individually. Reactions of the stoichiometric amounts of $Ru_3(CO)_{12}$, R_3PO ($R = CH_3$, $n\text{-}C_3H_7$), and aqueous HI at 25°C under N_2 yield stable complexes of the formula $[R_3POH][Ru(CO)_3I_3]$ (Fig. 7). The presence of the $[R_3POH]^+$ ion is confirmed by a $\nu(OH)$ in the infrared spectrum (*20*), and by observation of the unique proton in the ^1H NMR spectrum.

Reactions (3) and (4) can operate jointly under H_2/CO; this can be illustrated by combining Eqs. (3) and (4):

$$\underset{\mathbf{2}}{3[R_3POH][Ru(CO)_3I_3]} + 7R_3PO + 2CO + 4H_2 \rightleftharpoons \underset{\mathbf{1}}{[R_3POH][HRu_3(CO)_{11}]} + 9[R_3POH]I. \quad (5)$$

The catalytic activity (Fig. 3) and the relative proportions of the two ruthenium complexes observed, **1** and **2**, are dependent on the amount of HI added to the system. A **1**/**2** ratio of about 2.0 is associated with maximum activity in the closely related I^--promoted sulfolane-solvent system (*10*), and infrared spectra of HI-promoted phosphine oxide solutions show a similar ratio of complexes at optimum activity (cf. Figs. 5 and 8). (It should be noted that increased pressures of H_2 and CO are expected to alter this ratio somewhat in the acid-promoted phosphine oxide system, as seen in Eq. (5).) Addition of more HI to an optimum system causes the activity to drop as increasing amounts of **2** are formed at the expense of **1**. Essentially complete conversion to **2** is observed in infrared spectra of catalytic reaction solutions with high levels of HI, and these solutions are practically inactive for CO hydrogenation (see Figs. 1 and 3).

As expected from Eq. (5), the ratio of **1** to **2** is also dependent on the concentration of R_3PO. Figure 9 illustrates the increase in activity by an HI–$Ru_3(CO)_{12}$ system as the proportion of R_3PO to sulfolane is increased. In this study solutions with low activity are found to contain a high proportion of **2**, and those with improved activity have a **1**/**2** mole ratio closer to the value of 2.0 noted above.

When added to a KI-promoted Ru catalyst in sulfolane, HI causes only decreased activity (Fig. 2), but, as described previously, the acid enhances overall activity when added in proper amounts to KI-containing phosphine oxide catalyst solutions (Fig. 1). This difference is also apparently a result of the higher basicity of the phosphine oxide. Upon reaction with H_2/CO and KI in a weakly basic solvent such as sulfolane, $Ru_3(CO)_{12}$ can produce **1** and **2** only in a 2 : 1 ratio (Eq. (1)). However, in the more basic phosphine oxide solvent, additional **1** is formed via an acid–base equilibrium related to Eq. (3). Therefore a

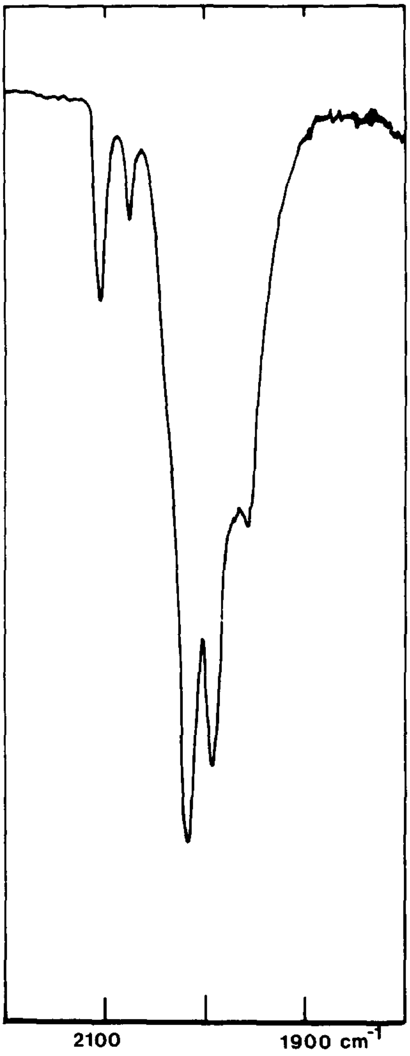


FIG. 8. Infrared spectrum of sulfolane solution of $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$. Complexes are the PPN^+ salts and are present in a 2 : 1 molar ratio. Band at 2100 cm^{-1} is assigned to $[Ru(CO)_3I_3]^-$.

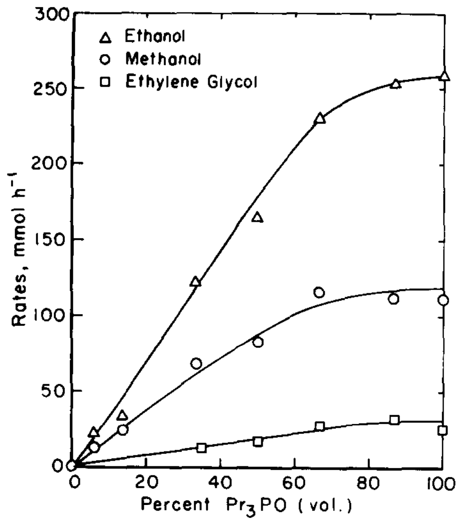


FIG. 9. Effect of Pr_3PO concentration on catalysis by mixtures of $Ru_3(CO)_{12}$ and HI. 75 ml solvent, 6 mmol Ru, 8 mmol HI (added as I_2), 86.1 MPa, $H_2 : CO = 1$, 230°C.

phosphine oxide system promoted with only KI is expected to contain a higher-than-optimum proportion of **1** to **2**, and this is confirmed by infrared spectroscopy (cf. Figs. 8 and 10). Addition of HI alters this ratio in the direction of the optimum and increases overall activity; further additions cause the expected diminished activity.

As seen in Fig. 4, addition of KI to an HI–R_3PO system has the effect of increasing the rates to methanol and ethylene glycol. These increases in rate are similar to those observed upon addition of excess iodide salts to the Ru system in other solvents (*10*). However, in the R_3PO–HI reactions of Fig. 4 the amount of $[R_3POH]I$ (i.e., HI) remains constant, and it is interesting to observe that the rate of ethanol formation also remains essentially unchanged.

These observations are consistent with the following generalizations: (a) Rates to all CO reduction products are dependent on the Ru oxidation state of the system, as reflected by the **1**/**2** ratio. This parameter may be adjusted by the addition of acid (or base) to the system, and an optimum value of this ratio is observed at about 2.0. (b) Rates to methanol and ethylene glycol (but not ethanol) are additionally dependent on the concentration of I^-, present as alkali metal iodides and also as $[R_3POH]I$ under some conditions in R_3PO solvent. (c) The selective formation of ethanol requires the presence of acid (e.g., see Figs. 1, 3, and 4), but the addition of excess acid can reduce or destroy the activity of the system by oxidizing the catalyst, as described in (a).

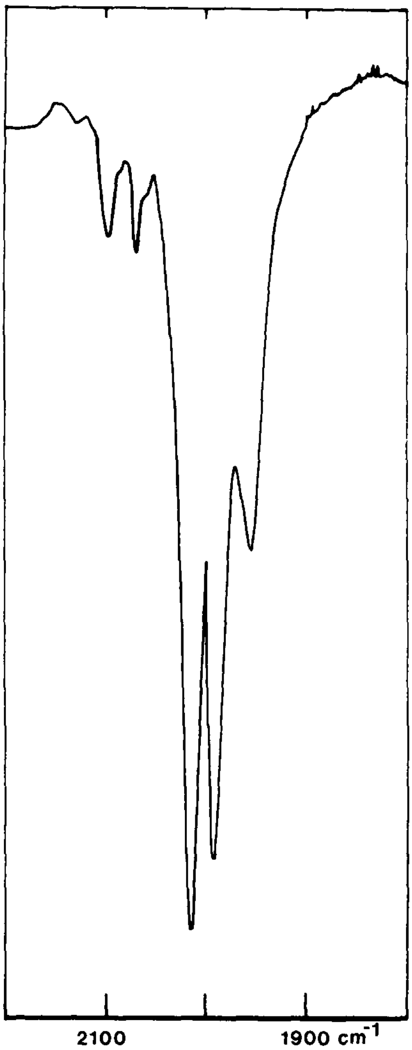


FIG. 10. Infrared spectrum of solution obtained from Pr_3PO, $Ru_3(CO)_{12}$, and KI, after catalysis. 75 ml Pr_3PO, 6 mmol Ru, 18 mmol KI. Conditions of reaction: 86.1 MPa, $H_2 : CO = 1$, 230°C. Band at 2100 cm^{-1} is assigned to $[Ru(CO)_3I_3]^-$.

Consideration of the last point raises what is perhaps the critical difference between reactions in phosphine oxide solvents and in other, less basic media. Reaction mixtures in R_3PO solvent can contain relatively high concentrations of an acid (in the form of the acidic cation $[R_3POH]^+$) which appears necessary to promote ethanol formation, and can simultaneously contain ruthenium complexes in the optimum average oxidation state for CO reduction. Indeed, the complexes **1** and **2** are present in some of these R_3PO solutions exclusively as the $[R_3POH]^+$ salts. In contrast, addition of strong acids to solutions containing **1** in more weakly basic solvents leads to destruction of this complex and a net oxidation of the metal catalyst system. Thus the phosphine oxide solvent appears to serve at least two purposes in the conversion of H_2/CO to ethanol; it is a sufficiently strong base to allow the formation of reduced ruthenium complexes (e.g., Eq. (3)) necessary for CO hydrogenation, and its conjugate acid is a sufficiently strong acid to promote ethanol formation via an apparently acid-catalyzed process.

Although we believe that it should be possible to find other solvents or additives of the proper basicity to simulate the behavior of phosphine oxides in this system, high stability of the compound under reaction conditions and appropriate solvent properties are also requirements.

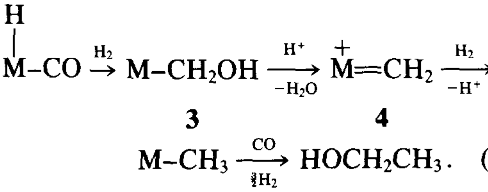
Pathways of Ethanol Formation

In addition to ethanol, methanol, and ethylene glycol, this catalytic system in R_3PO solvent also yields smaller amounts of other compounds which are useful in defining the pathways of product formation. Methane is observed in most reactions; indeed it is interesting to note that this is a rare example of a homogeneous catalytic system which produces substantial amounts of methane directly from H_2/CO. Other minor products include acetaldehyde, *n*-propanol, and longer straight-chain alcohols. It thus appears plausible that the alcohol products are formed in a chain-growth process from aldehyde intermediates.

Several other catalytic systems, especially those containing cobalt, have previously been shown to form at least small amounts of ethanol from H_2/CO (*1–5*). It has been inferred that the ethanol observed in these reactions is a secondary product derived from initially formed methanol via homologation (*2*, *3*).

$$CH_3OH + CO + 2H_2 \rightarrow CH_3CH_2OH + H_2O. \quad (6)$$

Indeed, cobalt carbonyl complexes are well known to homologate alcohols with synthesis gas (*27*). Ruthenium complexes in the presence of iodide promoters and H_2/CO have also been reported to homologate methanol to ethanol (*28–31*), as well as to catalyze similar reactions of esters, ethers (*29–31*), and carboxylic acids (*32*). The importance of an acid component in these reactions has been noted (*29–31*), and its purpose may be to facilitate conversion of the substrate to alkyl iodide or activate it in other ways for addition to a metal center. These acid-promoted catalytic mixtures have been reported to contain the Ru(II) iodide complexes $[Ru(CO)_3I_3]^-$ and $Ru(CO)_4I_2$ or $[Ru(CO)_3I_2]_2$ (*29–32*). Since one of these Ru(II) complexes, $[Ru(CO)_3I_3]^-$, is observed in HI-promoted phosphine oxide solutions, it is reasonable to assume that at least some of the ethanol produced in these reactions could be derived from methanol. However, since this system and others closely related produce ethylene glycol directly from H_2/CO, it seemed plausible that ethanol could also be formed in an analogous manner, i.e., without the intermediacy of methanol. A possible outline of such a process in an acid medium is depicted as



3 **4**

$$\overset{H}{\overset{|}{M}}\text{–}CO \xrightarrow{H_2} M\text{–}CH_2OH \xrightarrow[-H_2O]{H^+} \overset{+}{M}{=}CH_2 \xrightarrow[-H^+]{H_2} M\text{–}CH_3 \xrightarrow[\frac{3}{2}H_2]{CO} HOCH_2CH_3. \quad (7)$$

Complexes containing the hydroxymethyl ligand (**3**) are postulated intermediates in the formation of ethylene glycol from H_2/CO (*2–4, 33*). A number of studies have indicated that methylidene complexes such as **4** are formed in reactions of $M-CH_2OH$ (*34*) and $M-CH_2OR$ complexes (*35–39*); in some cases such electrophilic methylidene complexes have been observed spectroscopically (*40, 41*) and isolated (*42, 43*). (A referee has suggested that the work of Cutler *et al.* (*44*) might lead one to expect ethers as products by reaction of **4** with alcohols present in the system, to give $M-CH_2OR$ intermediates. Indeed, dimethyl ether and methyl ethyl ether have been detected as trace products in these catalytic reactions, but we do not take this as evidence for the intermediacy of **4**. Protonolysis of $M-CH_2OR$ to give **4** might be expected to be even more favorable than protonolysis of hydroxymethyl complex **3**.) Heterolytic activation of hydrogen by a process such as that of Eq. (2) would generate a proton and create a hydride ligand which could be transferred to the electrophilic methylidene ligand. (See Ref. (*45*) for studies of hydride donation by $[HRu_3(CO)_{11}]^-$.) The resulting methyl ligand could then be converted to ethanol as in methanol homologation (*27*). The process of Eq. (7) thus involves donation and removal of protons, steps which could involve the phosphine oxide molecule and its conjugate acid. It is also conceivable that proton donation could be even more extensively involved in the CO reduction process by this system; the proton-induced reduction of CO on an anionic iron cluster has recently been demonstrated stoichiometrically (*45, 46*). However, there are many similarities in the behavior and characteristics of the HI-promoted phosphine oxide system with those of related iodide-promoted systems in other solvents (overall reaction rates, temperature and pressure dependences, complexes observed in solution, etc.). These observations lead us to believe that the rate-determining steps for initial CO hydrogenation in this system are essentially the same as in solvents of very different basicity, under conditions such that the concentration of proton donors will be much different.

Experiments with ^{13}C-labeled methanol were carried out to gain information about its possible conversion to ethanol in this system. Shown in Table 2 are the results of one such experiment in which a known amount of $^{13}CH_3OH$ was added to a standard reaction solution before catalysis. The amounts of liquid products derived from the labeled methanol were determined by ^{13}C NMR using as standards solutions from identical catalytic experiments without added methanol and synthetic solutions containing known amounts of products. Methane containing the ^{13}C label was analyzed by gas-phase infrared spectroscopy. It is clear that methanol is converted to ethanol (and methane, as well as other minor products) under reaction conditions. Although in principle a kinetic analysis of these or similar data could yield information concerning the extent of ethanol formation from methanol, experimental difficulties associated with high-pressure operation precluded this type of analysis.

TABLE 2

Results of a Catalytic Experiment Containing Added $^{13}CH_3OH$[a]

	$(CH_2OH)_2$	CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	CH_4
Total (mmol)	5.2	95	149	8.3	34
From $^{13}CH_3OH$ (mmol)	0	1.3	13	0.5	6.2

[a] Reaction conditions: 75 ml Pr_3PO, 15 mmol Ru, 7.5 mmol I_2, 86.1 MPa, H_2/CO = 1, 230°C, 0.30 h, 0.85 g of 93% ^{13}C-labeled CH_3OH added before run.

Therefore, to gain further information about the mechanism of ethanol formation by this system, a study was undertaken of the distribution of products as a function of reaction time. Identical reactions were run for differing periods of time, which avoided several potential problems involved in sampling a single reaction during catalytic operation. Results of this series of experiments are plotted in Fig. 11; instantaneous net rates of product formation are given by the slopes of the appropriate curves.

It is found that rates to ethanol, methane, ethylene glycol, and *n*-propanol are linear within experimental error over the reaction time investigated. (Although an upward curvature is expected in the plots for secondary products, this will occur only in the early stages of the reaction before extinction of the apparent methanol rate. Experimental uncertainties in both the short reaction times and small amounts of products could easily mask such initial curvature.) The apparent rate of methanol formation decreases markedly with time, and levels off to a net methanol rate of zero. Extrapolation of this curve to the beginning of the reaction gives an estimate of the initial rate of methanol formation. This rate (≥650 mmol h^{-1}) is in very good agreement with the sum of the rates (646 mmol h^{-1}, as determined from Fig. 11) to the products possibly derived from methanol (as shown by the separate experiment with $^{13}CH_3OH$), i.e., ethanol (420 mmol h^{-1}), methane (200 mmol h^{-1}), and *n*-propanol (26 mmol h^{-1}). It is therefore evident that much or all of these products could have been derived from initially formed methanol via homologation or hydrogenolysis. (Even if ethanol is formed in this system via methanol homologation, this represents "direct" production of ethanol from H_2/CO in the sense that no methanol is charged to the reaction; it is formed and consumed *in situ*.) Although it is not required by these results, the possible operation of a second pathway to ethanol related to Eq. (7) cannot be discounted. The extent to which such a pathway contributes to total ethanol formation under various reaction conditions is not known.

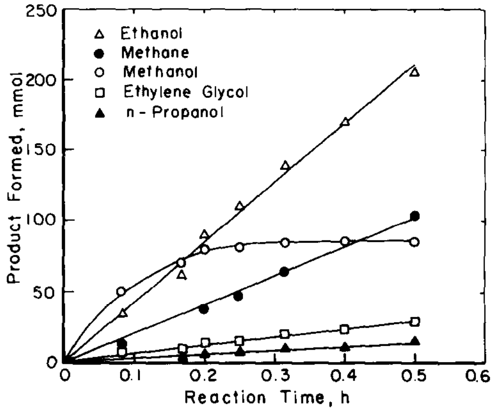


FIG. 11. Product distribution vs reaction time. 75 ml Pr_3PO, 15 mmol Ru, 15 mmol HI (added as I_2), 86.1 MPa, $H_2:CO = 1$, 230°C.

CONCLUSIONS

Research on this catalytic system has again demonstrated the importance of medium effects in homogeneous catalysis. This phenomenon is perhaps especially significant in complex catalytic processes which may involve consecutive conversions or multiple catalytic components. Formation of ethanol from H_2/CO in this phosphine oxide solvent system and from CH_3OH in related processes appears to be dependent upon the presence of an acid component. However, addition of strong acids to halide-promoted ruthenium catalytic systems can also disrupt the initial CO hydrogenation process, evidently by protonation and destruction (oxidation) of anionic Ru complexes involved in that step. The phosphine oxide solvent can level the acidity of added strong acids, providing a medium of appropriate acidity for certain acid-catalyzed conversions while still permitting the presence of basic metal complexes required in other steps. The precise nature of the acid-catalyzed process is not known. Since many of the observed products are possibly derived from methanol, it is reasonable to suggest that the acid facilitates formation of a methyl ligand from methanol, perhaps through an iodomethane intermediate. The selectivity to ethanol will then be determined largely by factors also involved in the extensively studied methanol homologation process (*27*). Alternatively, some of the ethanol may be selectively formed in a direct route from H_2/CO, e.g., via methylidene complexes. The roles of specific metal complexes involved in the various stages of product formation have not been addressed in this report. Research is continuing with the goal of clarifying these issues and extending to other catalytic processes the concepts generated by this study.

ACKNOWLEDGMENTS

We thank Dr. G. L. O'Connor and Dr. J. P. Henry for their support and encouragement throughout this research, and Mr. C. P. Wolfe for his excellent technical assistance.

REFERENCES

1. Gresham, W. F., U.S. Patent 2636046 (to E. I. DuPont) (1953).
2. (a) Rathke, J. W., and Feder, H. M., *J. Amer. Chem. Soc.* **100,** 3223 (1978); (b) Feder, H. M., *Ann. N.Y. Acad. Sci.* **333,** 45 (1980).
3. Fahey, D. R., *J. Amer. Chem. Soc.* **103,** 136 (1981).
4. Keim, W., Berger, M., and Schlupp, J., *J. Catal.* **61,** 359 (1980).
5. Paxson, T. E., Reilly, C. A., and Holocek, D. R., *J. Chem. Soc. Chem. Commun.*, 618 (1981), and references therein.
6. Pruett, R. L., and Walker, W. E., U.S. Patent 3833634 (to Union Carbide Corp.) (1974).
7. Bradley, J. S., *J. Amer. Chem. Soc.* **101,** 7419 (1979).
8. (a) Dombek, B. D., *J. Amer. Chem. Soc.* **102,** 6855 (1980); (b) Dombek, B. D., *in* "Catalytic Activation of Carbon Monoxide" (P. C. Ford, Ed.), ACS Symposium Series, Vol. 152, p. 213. Washington, D.C., 1981.
9. Knifton, J. F., *J. Chem. Soc. Chem. Commun.*, 188 (1981).
10. Dombek, B. D., *J. Amer. Chem. Soc.* **103,** 6508 (1981).
11. Knifton, J. F., *J. Amer. Chem. Soc.* **103,** 3959 (1981).
12. Wang, H.-K., Choi H. W., and Muetterties, E. L., *Inorg. Chem.* **20,** 2661 (1981).
13. Choi, H. W., and Muetterties, E. L., *Inorg. Chem.* **20,** 2664 (1981).
14. Warren, B. K., U.S. Patent 4301253 (to Union Carbide Corp.) (1981); U.S. Patent 4333852 (1982).
15. Johnson, B. F. G., Lewis, J., Raithby, P. R., and Suss, G., *J. Chem. Soc. Dalton Trans.*, 1356 (1979).
16. Hall, S. K., and Robinson, E. A., *Canad. J. Chem.* **42,** 1113 (1964).
17. Dombek, B. D., to be published.
18. Arnett, E. M., Mitchell, E. J., and Murty, T., *J. Amer. Chem. Soc.* **96,** 3875 (1974).
19. Smith, D. W., U.K. Pat. Appl. 2074164 (National Distillers and Chemical Corp.) (1981).
20. Schmidt, A., *Z. Anorg. Allg. Chem.* **362,** 129 (1968).
21. Seel, F., and Bassler, H.-J., *Z. Anorg. Allg. Chem.* **423,** 67 (1976).
22. Cameron, T. S., and Prout, C. K., *J. Chem. Soc. C,* 2289 (1969).
23. Trippett, S., and Walker, D. M., *J. Chem. Soc.*, 2976 (1960).
24. Maciel, G. E., and James, R. V., *Inorg. Chem.* **3,** 1650 (1964).
25. Albright, T. A., Freeman, W. J., and Schweizer, E. E., *J. Org. Chem.* **40,** 3437 (1975).
26. Keister, J. B., *J. Organomet. Chem.* **190,** C36 (1980).
27. Slocum, D. W., *in* "Catalysis in Organic Synthesis" (W. H. Jones, Ed.), p. 245. Academic Press, New York, 1980.
28. Onda, Y., Japan Patent 52-73804 (to Mitsubishi) (1977).
29. Braca, G., Sbrana, G., Valentini, G., Andrich, G. P., and Gregorio, G., *in* "Fundamental Research in Homogeneous Catalysis," Vol. 3, p. 221. Plenum, New York, 1979.
30. Braca, G., Sbrana, G., Valentini, G., Andrich, G. P., and Gregorio, G., *J. Amer. Chem. Soc.* **100,** 6238 (1978).
31. Braca, G., Sbrana, G., Valentini, G., Andrich, G. P., and Gregorio, G., *Ind. Eng. Chem. Prod. Res. Dev.* **20,** 115 (1981).
32. Knifton, J. F., *J. Mol. Catal.* **11,** 91 (1981).
33. Dombek, B. D., *J. Amer. Chem. Soc.* **101,** 6466 (1979).
34. Casey, C. P., Andrews, M. A., McAlister, D. R., and Rinz, J. E., *J. Amer. Chem. Soc.* **102,** 1927 (1980).
35. Jolly, P. W., and Pettit, R., *J. Amer. Chem. Soc.* **88,** 5044 (1966).
36. Green, M. L. H., Ishaq, M., and Whiteley, R. N., *J. Chem. Soc. A,* 1508 (1967).
37. Brookhart, M., and Nelson, G. O., *J. Amer. Chem. Soc.* **99,** 6099 (1977).
38. Davison, A., Krusell, W., and Michaelson, R., *J. Organomet. Chem.* **72,** C7 (1974).
39. Flood, T. C., DiSanti, F. J., and Miles, D. L., *Inorg. Chem.* **15,** 1910 (1976).
40. Brookhart, M., Tucker, J. R., Flood, T. C., and

Jensen, J., *J. Amer. Chem. Soc.* **102,** 1203 (1980).

41. Wong, W.-K., Tam, W., and Gladysz, J. A., *J. Amer. Chem. Soc.* **101,** 5440 (1979).
42. Gladysz, J. A., Kiel, W. A., Lin, G.-Y., Wong, W.-K., and Tam, W., *in* "Catalytic Activation of Carbon Monoxide" (P. C. Ford, Ed.), ACS Symposium Series, Vol. 152, p. 148. Washington, D.C., 1981.
43. Steinmetz, G. R., and Geoffroy, G. L., *J. Amer. Chem. Soc.* **103,** 1278 (1981).
44. Bodnar, T., Coman, E., Menard, K., and Cutler, A., *Inorg. Chem.* **21,** 1275 (1982).
45. Bricker, J. C., Nagel, C. C., and Shore, S. G., *J. Amer. Chem. Soc.* **104,** 1444 (1982).
46. Whitmire, K. H., and Shriver, D. F., *J. Amer. Chem. Soc.* **103,** 6754 (1981).
47. Whitmire, K. H., and Shriver, D. F., *J. Amer. Chem. Soc.* **102,** 1456 (1980).