Separation of Gas Mixtures by Supported Complexes

**D. A. Nelson
M. A. Lilga**

December 1986

**Prepared for the U.S. Department of Energy
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SEPARATION OF GAS MIXTURES
BY SUPPORTED COMPLEXES

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under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

RESEARCH SUMMARY

This report covers work performed during the period 1 October 1985 through 30 September 1986 by the Pacific Northwest Laboratory (PNL) for the Department of Energy, Morgantown Energy Technology Center.

The goal of this program is to establish the feasibility of coordination complexes as reactive carriers for facilitated transport membrane systems. Emphasis has been placed on systems which can operate using carriers within immobilized liquid membranes requiring stoichiometric or catalytic amounts of transition-metal complexes to accomplish gas separations. The separation of hydrogen from mixtures, such as low-Btu gas, is the specific objective of this research.

In research conducted last year, we found that $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ shows a 2:1 kinetic preference for H_2 binding over CO , but that these gases are tightly bound. This year in order to find complexes that bind H_2 and CO reversibly, a series of $\text{Ru}(\text{CO})_2\text{L}_3$ complexes, where L is phosphine or phosphite, were examined. Early attempts to prepare these complexes by exchange of various ligands (L) into $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{PPh}_3)_3$ were unsuccessful, yielding oils or showing no reaction at all. A more general route involves the reaction of excess L with $[\text{RuCl}_2(\text{CO})_3]_2$ to afford the complexes $\text{RuCl}_2(\text{CO})_2\text{L}_2$. In analogy to $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$, these complexes undergo reduction with sodium amalgam in the presence of L to give the desired products. Four of the ten complexes prepared form hydrides when exposed to hydrogen. Each of these four complexes also forms a carbonyl adduct in the presence of carbon monoxide. Only $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ was found to rapidly bind hydrogen then release it within 10 minutes with mild heat. The release is complete and only the starting complex is formed. The other complexes which form hydrides require more than 3 hours to remove hydrogen from the metal center.

The $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ complex also shows a 2:1 selectivity for H_2 binding over CO. The equilibrium constant for H_2 binding by $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ is 350 at 25°C . At 25°C , k_{obs} for the binding of CO, H_2 , and O_2 are $6.76 \times 10^{-3} \text{ sec}^{-1}$, $7.54 \times 10^{-3} \text{ sec}^{-1}$, and $5.92 \times 10^{-3} \text{ sec}^{-1}$, respectively. The similarity of these observed rates may indicate that PPh_2py dissociation is limiting. Kinetic measurements at 50° and 60°C are consistent with a two-step mechanism involving initial phosphine dissociation followed by gas addition.

Preparation of cationic dppm and PPh_3 ligands containing a quaternary ammonium group was pursued. These ligands are expected to be of use in attaching complexes to an ion exchange membrane for separations of H_2 and CO. A PPh_3 derivative was prepared, however, the routes to a dppm derivative were complicated and yielded only small amounts of diphosphine materials that could not be purified.

A system was investigated that catalyzes the dehydrogenation of alcohols and the hydrogenation of ketones. Such a catalyst, if used in a membrane containing an alcohol solvent, might be of use in selective H_2 separation from gas mixtures. The dehydrogenation of cyclohexanol and 2-octanol were studied using a $\text{RhCl}_3/\text{SnCl}_2/\text{LiCl}$ catalyst system. These alcohols are dehydrogenated at rates that are initially rapid, but which gradually slow to a stop. The decrease in rate of H_2 evolution is a result of the establishment of an equilibrium between the alcohol and the liberated hydrogen and ketone. At 150°C , cyclohexanol has the fastest rate of dehydrogenation. Several dehydrogenation/hydrogenation cycles have been carried out using this alcohol over a period of one week without serious catalyst deactivation or side reactions. Initial tests of the catalyst dissolved in cyclohexanol within two membranes were inconclusive. An anion exchange membrane was not suitably wetted by the catalyst solution and CelgardTM, which was wetted, could not be kept wet at 150°C under flow conditions in the membrane cell.

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PROGRAM OBJECTIVE AND PURPOSE

The objective of this program is to establish the feasibility of using coordination complexes as agents in facilitated transport membrane systems. Emphasis has been placed on systems which utilize stoichiometric or catalytic amounts of transition-metal complexes to accomplish gas separations. The separation of hydrogen from mixtures, such as low-BTU gas, is the specific objective of this research.

MILESTONE SCHEDULE

The milestones of each task are shown below and in Figure 1. A more complete discussion of each task follows this outline.

TASK A. ION EXCHANGE ATTACHMENT OF A SYNGAS CARRIER

- A.1 Complete preparation of ligand and complex, 2/86.
- A.2 Determine gas uptake and solubilities of complex, 2/86.
- A.3 Attach complex to membrane and examine facilitation, 8/86.

TASK B. CATALYTIC FACILITATED TRANSPORT

- B.1 Examine homogeneous reactions for catalytic hydrogenation and dehydrogenation, 6/86.
- B.2 Measure hydrogen transport of system, 9/86.

FIGURE 1. Milestone Schedule

PROGRAM TASKS

The individual tasks and subtasks are discussed below. Although not identified as a distinct task, there was a considerable effort expended by Pacific Northwest Laboratory to coordinate research activities with the subcontractor and report the research results to DOE-METC. Monthly letter reports, quarterly technical reports, and a final technical report were forwarded to DOE-METC during the normal reporting periods. The 6th Annual Gasification Contractors' meeting was also attended to report the results of this work.

TASK A. ION EXCHANGE ATTACHMENT OF A SYNGAS CARRIER

Subtask A.1. Preparation of Ligand and Complex

The ligand (4-N,N,N-trimethylammoniumphenyl)diphenylphosphine tetrafluoroborate will be prepared and incorporated within complexes of the type $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$. PR_3 in these complexes could be phosphites, such as $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OPh})_3$, or phosphines, such as PPh_3 , $\text{P}(\text{p-CH}_3\text{C}_6\text{H}_4)_3$, PBu_3 , and $\text{P}(\text{cyclohexyl})_3$. In addition, the ligand $[\text{Ph}_2\text{PCH}_2\text{Ph}(\text{C}_6\text{H}_4\text{NMe}_3)]\text{BF}_4$ will be synthesized and used to prepare analogs of the $\text{Pd}_2(\text{dppm})_2\text{X}_2$ complexes.

Subtask A.2. Gas Uptake and Solubilities of the Complexes

The derivitized complexes prepared in Subtask A.1 will be examined for their ability to bind both carbon monoxide and hydrogen; i.e., the observed rates will be measured. At the same time the solubilities of the complexes in various solvents suitable for use as an immobilized liquid will be determined. The observed kinetic rates will be measured in the solvent of choice.

Subtask A.3. Attachment of the Complex to a Membrane

Attachment of one of the above complexes to the ion exchange membrane may require aqueous addition to the solvent. Initial exchange may be investigated using resin beads rather than the membrane. Completion of the attachment will be monitored by elemental analyses and ultraviolet spectrophotometry. Success of the exchange will further be examined by initial measurements of facilitated gas separation, particularly binary and ternary mixtures of carbon monoxide, hydrogen, and nitrogen. An immobilized liquid membrane cell, similar to that developed at the National Bureau of Standards, will be used.

TASK B. CATALYTIC FACILITATED TRANSPORT

Subtask B.1. Homogeneous Catalysis

The catalyst system, $\text{RhCl}_6^{3-}/\text{SnCl}_2/\text{Cl}^-$, necessary for the hydrogenation/dehydrogenation of ketones/alcohols will be examined under homogeneous conditions to determine pressure and temperature requirements. Preliminary rate information will be obtained so that comparisons can be made with the heterogenized systems prepared in Subtask B.2. Catalytic runs will be performed with NR_4^+Cl^- present in order to mimic the environment present within the membrane.

Subtask B.2. Hydrogen Transport Measurement

The $\text{RhCl}_6^{3-}/\text{SnCl}_2/\text{Cl}^-$ catalyst system should be easily immobilized within an anion exchange membrane. Addition of excess chloride may not be necessary (depending upon RhCl_6^{3-} loading) since chloride is typically the initial counterion present in these membranes. The flux of H_2 across the membrane will be measured using gc analysis of the sweep and feed gases with and

without the carrier present. A mixed gas feed consisting of N_2 , H_2 , CO_2 , CO , and CH_4 will be studied to determine selectivity for H_2 .

DISCUSSION

TASK A. ION EXCHANGE ATTACHMENT OF A SYNGAS CARRIER

Subtask A.1. Preparation of Ligand and Complex

$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, studied in our previous work [1], was shown to bind H_2 and CO. A 2:1 kinetic preference for H_2 binding was demonstrated. When the complex was used in the dual column reactor with a mixed gas feed, however, it was found that the CO complex was thermodynamically preferred. Under the conditions of those experiments CO could not be stripped because of its tight binding to the Ru center. Since altering the steric and electronic properties of ligands is known to have large effects on complex reactivity (i.e., binding of small molecules such as CO and H_2), a series of phosphine and phosphite substituted complexes, $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$, were desired. Once in hand, these complexes would be subjected to CO and H_2 to determine whether reversible binding occurs and whether there is selectivity for one component.

Three synthetic approaches to these complexes have been attempted. Direct ligand exchange was unsuccessful starting with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and excess $\text{P}(\text{OMe})_3$, $\text{P}(\text{p-tol})_3$, PCy_3 , and $\text{P}(\text{p-ClC}_6\text{H}_4)_3$, where p-tol is p- $\text{CH}_3\text{C}_6\text{H}_4$ and Cy is cyclohexyl. Impure products, usually oils, were obtained. The reaction mixture of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and PCy_3 showed no reaction with H_2 after two days in THF. Phosphine exchange was also attempted with $\text{RuCl}_2(\text{PPh}_3)_3$. PCy_3 and $\text{P}(\text{OMe})_3$ did not exchange; however, $\text{P}(\text{p-tol})_3$ and $\text{P}(\text{OPh})_3$ apparently did.

A more general and successful approach to these materials is the reaction of phosphine with $[\text{RuCl}_2(\text{CO})_3]_2$. With PPh_3 this reaction is known to give $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ which can be reduced with sodium amalgam in the presence of PPh_3 to give $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. The reaction of $[\text{RuCl}_2(\text{CO})_3]_2$ or $\text{RuCl}_2(\text{CO})_2(\text{thf})_2$ (thf = tetrahydrofuran) with PR_3 affords the analogous

$\text{RuCl}_2(\text{CO})_2(\text{PR}_3)_2$ complexes, where PR_3 is $\text{P}(\text{p-tol})_3$, $\text{P}(\text{p-C}_6\text{H}_4\text{OMe})_3$, PCy_3 , PPhCy_2 , $\text{PPh}_2(\text{allyl})$, $\text{PPh}(\text{allyl})_2$, PPh_2py (py = pyridyl), $\text{PPh}(\text{OMe})_2$, $\text{P}(\text{OMe})_3$, and $\text{P}(\text{OPh})_3$. $\text{P}(\text{p-tol})_3$ gave the same material as in the exchange reactions with $\text{RuCl}_2(\text{PPh}_3)_3$ followed by a CO purge and is probably $\text{RuCl}_2(\text{CO})_2(\text{P}(\text{p-tol})_3)_2$. The bulkier PCy_3 and PPhCy_2 gave mixtures of two compounds which may be cis and trans isomers.

Sodium amalgam reduction in the presence of added ligand afforded $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$. Each of these complexes was treated with H_2 gas while in solution (usually thf). The results of the hydrogen reactions are presented in Table 1, Section A.2.

The complex $\text{RuH}_2(\text{CO})_2(\text{PPh}_2\text{py})_2$ (py = pyridyl) has been synthesized, isolated, and characterized. This complex is prepared by precipitation from a hydrogen-saturated thf solution of $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ with hydrogen-saturated hexane. The reaction of H_2 with $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ to form the dihydride is reversible as discussed in Subtask A.2 and it is important to the kinetic determination that the dihydride be isolated and well-characterized.

In a related study, the complex $\text{RuMo}(\text{CO})_5(\text{dppm})_2$ was prepared and examined for reversible H_2 and CO binding. This complex was previously reported to react reversibly with CO but reversibility with H_2 and specificity were not reported [2]. In our study, it was found that both react reversibly. This complex is prepared by the reaction of $\text{RuH}_2(\text{dppm})_2$ with $\text{Mo}(\text{CO})_6$ to afford $\text{RuMo}(\text{CO})_6(\text{dppm})_2$ from which CO is liberated under vacuum. $\text{RuH}_2(\text{dppm})_2$ is prepared from $\text{Ru}(\text{COD})(\text{COT})$ (COD is cyclooctadiene and COT is cyclooctatetraene), dppm, and H_2 in toluene solution.

The preparation of two cationic phosphine ligands was attempted. The target ligands are derivatized PPh_3 and dppm compounds containing trimethylammonium substitution in the para position of a phenyl group. These ligands

could be incorporated into the ruthenium complexes discussed above or into the $\text{Pd}_2(\text{dppm})_2\text{X}_2$ complexes which we have previously shown to be agents for H_2 separation.

An intermediate expected to be of importance in the preparation of both ligands is $\text{PPh}(\text{C}_6\text{H}_4\text{NMe}_2)\text{Cl}$. This phosphine is an air sensitive yellow solid prepared by reaction of PPhCl_2 and $\text{BrMgC}_6\text{H}_4\text{NMe}_2$. The ^1H and ^{31}P -NMR spectra are consistent with the given formula. When this material is reacted with one equivalent of PhMgBr the expected diphenylaminophenyl product [3] is not obtained. Instead, a 24% yield of $\text{PPh}(\text{C}_6\text{H}_4\text{NMe}_2)_2$ is isolated. A redistribution reaction apparently occurs and the desired $\text{PPh}_2(\text{C}_6\text{H}_4\text{NMe}_2)$ could not be obtained.

$\text{PPh}(\text{C}_6\text{H}_4\text{NMe}_2)_2$ is also isolated in the attempted preparation of a derivatized dppm ligand when $\text{PPh}(\text{C}_6\text{H}_4\text{NMe}_2)\text{Cl}$ is reacted with $\text{PPh}_2\text{CH}_2^-\text{Li}^+\cdot\text{TMEDA}$ (TMEDA is tetramethylethylenediamine) [4]. The expected product $\text{Ph}_2\text{PCH}_2\text{PPh}(\text{C}_6\text{H}_4\text{NMe}_2)$ was not detected. An alternative strategy was devised in which $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{PPhCl}$ would be prepared from $\text{OPPh}_2\text{CH}_2^-\text{Li}^+$ and PPhCl_2 , two easily prepared starting materials. While a white precipitate formed rapidly when the lithium reagent was added dropwise to the phosphine chloride, the product was found to be a mixture of compounds. Diphosphine components were present but could not be isolated.

Subtask A.2. Gas Uptake and Complex Solubilities

The reactivity of each of the $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$ complexes with H_2 was tested in thf solution. The results of the tests are summarized in Table 1. Ligand substitution results in complexes with reactivity ranging from no H_2 uptake to reversible and irreversible binding. Our previous work indicated that $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ requires over 7 hours at 65°C (under nitrogen) to release the hydrogen. Further, the hydrogen release is not clean; i.e., at least two major products and two minor products are formed. Similar results were

obtained with complexes containing the *p*-methoxyphenyl and *p*-tolyl phosphine ligands. The hydrogen removal is incomplete after 3 hours, but several products are also evident. After 4 hours at 65°C, $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PCy}_3)_2$ is almost completely intact. Some trace products were detected. Of considerable interest is $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_2\text{py})_2$. This complex totally releases hydrogen within 10 minutes and cleanly reforms the starting complex. Furthermore, $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ shows a preference toward H_2 binding over CO. A solution of the complex reacts with a 50:50 mixture of H_2 and CO to afford a 70:30 hydride to carbonyl adduct product ratio based on ^1H NMR integration. It is not known at this time whether this is a kinetic or thermodynamic product mixture.

TABLE 1. Reaction of $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$ with Hydrogen at 25°C and 1 Atmosphere^(a)

<u>PR₃ or P(OR)₃</u>	<u>Hydride Formation</u>
diphenylpyridylphosphine	yes
tri(<i>p</i> -tolyl)phosphine	yes
tri(<i>p</i> -methoxyphenyl)phosphine	yes
tricyclohexylphosphine	yes
allyldiphenylphosphine	no
diallylphenylphosphine	no
dimethoxyphenylphosphine	no
diphenylmethoxyphosphine	no
trimethoxyphosphite	no
triphenoxyphosphite	no

(a) The complexes were considered inert to hydrogen if no hydride formed within 24 hours.

The kinetics and thermodynamics of H_2 binding to $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ were determined. The ruthenium (0) complex was examined for H_2 uptake in a dimethylacetamide (dma) solution at 25°C. The equilibrium constant for H_2

binding, originally determined by us to be 700, was established by uv/vis spectroscopy at 375 nm and 450 nm (an average of both). However, this value was in error due to impurities in the dma solvent. These impurities reacted with the Ru(0) complex resulting in competing absorptivities. The problem was resolved by performing a final distillation of the dma from some of the Ru(0) complex prior to its use in the equilibrium experiments. Reproducible results were obtained with this solvent, and an equilibrium constant for H₂ binding of 350 at 25°C was confirmed. This small value indicates that release of hydrogen is favored although the hydrogen uptake was quite fast. The original complex which was examined earlier, Ru(CO)₂(PPh₃)₃, had an equilibrium constant of 10⁴-10⁵. This large value favored hydride formation but not hydrogen release.

The kinetics of hydrogen binding by Ru(CO)₂(PPh₂py)₃ were too slow at 25°C for the use of stopped-flow equipment, requiring the use of standard uv/vis methods for work at this temperature. The t_{1/2} for H₂ binding (time required for 50% of the complex to react) was 150 sec at 25°C. Stopped-flow was used at temperatures above 40°C in order to obtain more accurate rate and thermodynamic data. The solvent in these studies was dma.

Initially, H₂, CO, and O₂ were added individually to dma solutions of Ru(CO)₂(PPh₂py)₃ at 25°C. The results are shown in Table 2. The similarity

TABLE 2. Values for Forward Observed Rate Constants (k_{obs}) at 25°C
and 1 Atmosphere of Gas

$\underline{CO}$ (s^{-1})	$\underline{H_2}$ (s^{-1})	$\underline{O_2}$ (s^{-1})
6.76×10^{-3}	7.54×10^{-3}	5.92×10^{-3}

of k_{obs} values suggests that diffusion of gas into the dma could be limiting or that dissociation of a PPh_2py ligand is required to provide a site for gas binding. A two-step mechanism, an initial phosphine dissociation followed by H_2 addition, was found to operate in gas binding to $Ru(CO)_2(PPh_3)_3$ and probably also operates for the very similar PPh_2py -containing complex. This mechanism is shown below.

The overall observed rate for this process is expressed as:

$$rate = \frac{k_1 k_2 [Ru(CO)_2(PPh_2py)_3] [H_2]}{k_{-1} [PPh_2py] + k_2 [H_2]} \quad (3)$$

First-order kinetics are achieved by holding the complex and H_2 concentrations constant while varying the phosphine concentration. Under these conditions the following relationships describes the observed rate:

$$k_{obs} = \frac{k_1 k_2 [H_2]}{k_{-1} [PPh_2py] + k_2 [H_2]} \quad (4)$$

$$k_{\text{obs}}^{-1} = \frac{k_{-1}[\text{PPh}_2\text{py}]}{k_1 k_2 [\text{H}_2]} + \frac{1}{k_1} \quad (5)$$

By plotting $[\text{PPh}_2\text{py}]$ vs. k_{obs}^{-1} , k_1 is determined from the intercept and the ratio k_{-1}/k_2 is obtained from the slope. Also, k_1 equals k_{obs} at 1 atm H_2 pressure when the $[\text{PPh}_2\text{py}]/[\text{Ru}]$ ratio is less than 20 since the $k_{-1}[\text{PPh}_2\text{py}]$ term is much smaller than the $k_2[\text{H}_2]$ term in equation 3. The dependence of k_{obs} on phosphine concentration was most apparent at a hydrogen pressure of 200 torr. The results of data taken at this pressure at 50° and 60°C with a $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ concentration of $3.7 \times 10^{-4} \text{ M}$ are summarized in Table 3. Values of k_1 at 50° and 60°C obtained graphically from the phosphine variation method agree well with the values obtained when no phosphine is added. This is not the case for data taken at 25°C which indicate a k_1 of 0.0014 sec^{-1} from the phosphine variation method and 0.0059 sec^{-1} from runs where no phosphine was added. The discrepancy may be due to a limitation caused by H_2 diffusion into the solution. A comparison of these kinetics to the kinetics of H_2 binding by the PPh_3 -containing complex (conducted at 25°C) unfortunately cannot be made until the 25°C data reported here are more fully understood.

TABLE 3. Kinetic parameters for the Reaction of H_2 (200 torr) and $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ ($3.7 \times 10^{-4} \text{ M}$) at 50° and 60°C

<u>T°C</u>	<u>k_1</u>	<u>k_{-1}/k_2</u>
50	0.0747	$2.59 \times 10^{-4} [\text{H}_2]$
60	0.2984	$2.34 \times 10^{-3} [\text{H}_2]$

H_2 binding by $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ was found to be first order in the complex and zero order in H_2 . Measurements of k_{obs} were also made at various temperatures with constant hydrogen and Ru complex concentrations with no

added phosphine. The Arrhenius plot of $\ln k_{\text{obs}}$ ($k_{\text{obs}} = k_1$ under these conditions) vs. $1/T$ is linear and yields an activation energy of 87.6 kJ/mole $^{\circ}\text{K}$.

The rate of H_2 release from $\text{RuH}_2(\text{CO})_2(\text{PPh}_2\text{py})_2$, k_{-2} , was determined at 60 $^{\circ}\text{C}$. The ruthenium hydride complex and 100 equivalents of added phosphine were heated in dma under vacuum. At two different complex concentrations the value of k_{-2} was $2.67 \times 10^{-4} \text{sec}^{-1}$ indicating either the expected first order dependence on complex or that the off-rate is controlled by diffusion of H_2 from the solvent.

The binding of both H_2 and CO to $\text{RuMo}(\text{CO})_5(\text{dppm})_2$ was found to be reversible according to eq. 6. Exposure of the complex to a 1:1 mixture of H_2 and CO forms the hydride and carbonyl adducts in 2:3 ratio respectively. Binding of hydrogen and carbon monoxide are very fast. The carbonyl adduct, $\text{RuMo}(\text{CO})_6(\text{dppm})_2$, reforms the pentacarbonyl complex within a 20-minute period at 80 $^{\circ}\text{C}$. Also, the carbonyl adduct is completely converted to the hydride after a 20-minute exposure to hydrogen gas. Approximately 30% of the hydrogen is removed from $\text{RuMo}(\text{H})_2(\text{CO})_5(\text{dppm})_5$ at elevated temperature within 20 minutes.

Subtask A.3. Attachment of the Complex to a Membrane

A $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$ complex derivatized with a cationic phosphine was to have been attached to a membrane. We were unable to prepare the cationic phosphine, however, owing to a more complicated phosphine reaction chemistry than anticipated.

TASK B. CATALYTIC FACILITATED TRANSPORT

Subtask B.1. Homogeneous Hydrogenation and Dehydrogenation

A strategy that we consider promising for H_2 separation, and to our knowledge has not been investigated, is the use of catalysts that will reversibly incorporate hydrogen into a substrate (S) that is also the reaction solvent; i.e., catalyze hydrogenation and dehydrogenation reactions (Equation 7). Such a catalyst/substrate system in an immobilized liquid membrane (ILM)

will give facilitated transport of hydrogen where the carrier is now the substrate rather than the transition metal. The concept is illustrated in Figure 2.

FIGURE 2. Catalytic Facilitated Transport

The ultimate driving force for H_2 permeation in this catalytic system is the differential partial pressure of H_2 on either side of the membrane. Hydrogen entering the membrane is used to hydrogenate an unsaturated substrate. The hydrogenated substrate diffuses across the membrane and is dehydrogenated forming hydrogen, which exits the low pressure side. This allows the substrate to diffuse back across the membrane. The effective hydrogen concentration within the membrane (concentration of dissolved H_2 + concentration of hydrogenated substrate) is not limited by the normal solubility of H_2 in the solvent resulting in high H_2 selectivity. Hydrogen permeability is, in part, a function of the kinetics of the overall reaction.

We expect that the transition metal concentration in a catalytic facilitated transport system will be approximately two orders of magnitude less than that in a transition metal carrier system. Thus, the utilization of the transition metal complex is much more efficient since the metal merely acts as a shuttle between dissolved H_2 and the actual substrate carrier. The use of catalytic amounts of complex considerably lowers capital outlay without sacrificing selectivity or permeability.

The simplest approach toward utilization of a hydrogenation/dehydrogenation scheme is one in which a single catalyst, capable of catalysis of both the forward and reverse reactions of Equation 7, is contained in an ILM. Such a catalyst system is hexachlororhodate anion, $RhCl_6^{3-}$, in the presence of $SnCl_2$ and HCl [5-8]. This system catalyzes the dehydrogenation of isopropanol to form H_2 and acetone at $82^\circ C$. Acetone build-up inhibits the reaction owing to reversal of Equation 8. Other alcohols such as ethanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol also have been dehydrogenated. It is

expected that this catalyst could easily be incorporated within an anion exchange resin and used for catalytic facilitated transport of hydrogen.

The dehydrogenation of alcohols appears to be general. Less volatile alcohol/ketone systems, which are desirable in a membrane application in order to minimize evaporative losses, were used in this study. As a result, higher temperatures and faster rates were obtainable. Hydrogenation and dehydrogenation processes were studied separately using a reaction flask connected to a simple gas buret. Dehydrogenation was studied initially. All of the alcohols liberated hydrogen at the maximum rates shown in Table 4. Maximum rates were typically measured within the first hour of commencement of H_2 evolution. H_2 evolution did not start until the solution, which was originally red, turned black.

2,5-hexanediol was initially studied but was abandoned when it was discovered that a resultant mono- or di-ketone product irreversibly cyclized to form a furan ring. 2-octanol dehydrogenates cleanly to 2-octanone and H_2 . The rate of hydrogen evolution gradually slows to a stop after 120 hr. A N_2 flush of the atmosphere over the reaction solution to remove liberated H_2 results in the continuation of H_2 generation at a slow rate, indicating a shift in equilibrium.

Cyclohexanol shows similar behavior (Figure 3) but is dehydrogenated much more rapidly than any of the other alcohols studied. If the atmosphere is swept with N_2 , H_2 evolution continues. The cyclohexanone concentration in

FIGURE 3. Cyclohexanol Dehydrogenation at 150°C

TABLE 4. Maximum Rates of Hydrogen Evolution in Alcohol Dehydrogenation by RhCl₃/SnCl₂/LiCl (a)

<u>Alcohol</u>	<u>ml(H₂)/l (solution)/h</u>	<u>T (°C)</u>
cyclohexanol	28	110
cyclohexanol	2,900	150
cyclohexanol	13,800	170
2-octanol	570	150
2,5-hexanediol	320	150
isopropanol	0.5	83

(a) [RhCl₃] = 0.008 M, [SnCl₂] = 0.07 M, [LiCl] = 0.17 M

the equilibrium mixture is very low, i.e. the equilibrium lies well toward cyclohexanol (eq. 9). If the system is purged with H_2 , an uptake of gas is

noted, indicating that hydrogenation is taking place. The cyclohexanol/cyclohexanone system was cycled through three dehydrogenation/hydrogenation procedures over the course of one week at 150°C without serious loss of catalyst activity or substrate decomposition. Small amounts of cyclohexene and dicyclohexyl ether were detected by GC/mass spectrometry but their concentrations were low and did not change appreciably over the course of the reaction. Although these results are promising, the high temperatures necessary to achieve reasonable rates are not compatible with currently available membranes. For this reason, long-term use in a membrane is probably not immediately possible, however, tests in membranes will be conducted over short periods to determine the feasibility of such a system.

As discussed above, dehydrogenation of cyclohexanol gives a reaction mixture in which the ketone can be hydrogenated again. However, if pure cyclohexanone or 1:3 cyclohexanone/cyclohexanol mixtures are used with the same $\text{RhCl}_3/\text{SnCl}_2/\text{LiCl}$ catalyst concentration, hydrogenation occurs extremely slowly and is not the major reaction pathway. A product that has been identified is 2-(cyclohexylidene)cyclohexanone, formed by dimerization and dehydration (eq. 10). The route to this product is unknown at this time but it

also forms under a nitrogen atmosphere. CO_2 and a trace of CO are detected in the gas phase (H_2 or N_2 atmosphere). These gases are also detected in the attempted hydrogenation of 2-octanone. A control run without RhCl_3 but containing SnCl_2 and LiCl in cyclohexanone also generated CO_2 and a trace of CO . CO_2 may be formed by decarboxylation of a carboxylic acid intermediate. The lack of hydrogenation activity may be due to coordination of ketone which might render the Rh complex unreactive with H_2 . This could explain why hydrogenation takes place at very low ketone concentrations but not at higher concentrations.

Subtask B.2. Membrane Attachment and Transport Measurements

A cell used for the membrane separation experiments was designed and constructed. The design is a modification of one used at the National Bureau of Standards [9]. Since our applications require contact with organic solvents, Teflon was used as the construction material. Teflon is chemically resistant and machinable. Overall dimensions are 6 in. x 9.25 in. with an exposed membrane area of about 200 cm^2 . Gas dispersion ports were machined into the 3/4 in. thick blocks. A Teflon mesh is used as the membrane backing and butyl rubber gaskets make the cell leak-tight. Heating is accomplished using heating tape wrapped around the cell and insulating with KaowoolTM. Tests were performed to determine controller setpoints to maintain desired internal temperatures achieved by external control. Nitrogen gas flows through the cell of 50 ml/min feed and 90 ml/min sweep did not affect the internal temperature. Gas flows were regulated using calibrated flowmeters. The membrane used was a Teflon-based anion exchange membrane obtained from RAI Research Corporation. The hydroxide counterion in this membrane was replaced with chloride by contacting the membrane with a concentrated aqueous solution of NaCl followed by several water rinses. The dried membrane was

then 'wetted' with either pure cyclohexanol or a solution of the $\text{RhCl}_3/\text{SnCl}_2/\text{LiCl}$ catalyst solution in cyclohexanol which had been previously activated by heating to 150°C for 24h. The membrane was treated with the catalyst solution and placed in the cell under a N_2 atmosphere in a glove bag. Flows of 50 ml/min H_2 feed and 50 ml/min N_2 sweep were used in tests. The membrane with cyclohexanol was heated to 50° , 100° , 128° , 137° , and 149°C and H_2 transport measured by gas chromatography. H_2 transport increased with increasing temperatures and the membrane maintained its integrity throughout the experiment. The membrane with the catalyst solution was tested at 149° and 128°C with results virtually identical to the runs with cyclohexanol. This may be because the membrane did not appear to be actually wetted by either solution but rather a film of solution over the membrane was formed.

Tests with a CelgardTM membrane were also inconclusive. This membrane is wetted by cyclohexanol. However, the membrane could not be kept wet at 150°C with flows of 50 ml/min N_2 sweep and 50 ml/min H_2 feed through the cell.

CONCLUSIONS

In our continuing effort to develop new agents for selective gas separation, a series of complexes of the type $\text{Ru}(\text{CO})_2\text{L}_3$ (L is a phosphine or phosphite) have been prepared. These complexes show a wide range of reactivity with H_2 . When L is PCy_3 , the reaction is irreversible, forming $\text{RuH}_2(\text{CO})_2(\text{PCy}_3)_2$. Hydrides are not formed when L is $\text{PPh}_2(\text{allyl})$, $\text{PPh}(\text{allyl})_2$, $\text{PPh}_2(\text{OMe})$, $\text{PPh}(\text{OMe})_2$, $\text{P}(\text{OMe})_3$, and $\text{P}(\text{OPh})_3$. Complexes that reversibly react with H_2 are those containing PPh_3 , $\text{P}(\text{p-tol})_3$, $\text{P}(\text{p-MeOC}_6\text{H}_4)_3$, and PPh_2py . The complexes containing the first three of these ligands show very similar properties; the reaction with H_2 is favorable, but removal of hydrogen from the hydride products is relatively difficult. Previous work with $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ indicated that with a stoichiometric amount of PPh_3 , over 7 hours at 65°C is required to release the bound H_2 and that the reaction is not clean. $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ binds H_2 quickly and also releases it cleanly within 10 minutes under mild heating. This complex shows a 2:1 selectivity for H_2 binding over CO when exposed to a 1:1 H_2/CO mixture.

The kinetics of H_2 binding by $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ were investigated. The results indicate a probable two-step mechanism involving initial phosphine dissociation followed by H_2 addition. This type of mechanism was also found for gas binding to $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. Phosphine dissociation appears to be rate limiting in both cases. The equilibrium constant of 350 for H_2 binding by the PPh_2py complex indicates that H_2 is released much more easily than the PPh_3 complex ($K = 10^4$ - 10^5). The PPh_2py complex could be of value as a H_2 -separation agent in a dual column or membrane application.

The hydrogenation of ketones and the dehydrogenation of alcohols by a $\text{RhCl}_3/\text{SnCl}_2/\text{LiCl}$ catalyst were studied. Catalysis of the equilibrium between an alcohol and the corresponding ketone and H_2 could be utilized within a

membrane for selective H_2 separation. The relatively nonvolatile alcohols cyclohexanol and 2-octanol were rapidly dehydrogenated at $150^\circ C$ liberating H_2 . H_2 evolution continued until an equilibrium was established. Increasing the gas-phase H_2 concentration over the solution at equilibrium results in H_2 uptake caused by hydrogenation of the ketone. With cyclohexanol, three dehydrogenation/hydrogenation cycles at $150^\circ C$ over the course of one week were carried out with no appreciable catalyst deactivation or side reactions. Although the cyclohexanol system possesses good characteristics its applicability in the membrane separation of H_2 could not be shown by our initial tests. The major problem encountered was in maintaining a wetted membrane at $150^\circ C$. Since a temperature of $150^\circ C$ appears to give reasonable rates an even less volatile alcohol than those studied is necessary.

FUTURE DIRECTIONS

Hydrogen is expected to play an increasingly important role in the future as a chemical feedstock and as an energy carrier. Hydrogen currently is produced primarily by steam hydrocarbon reforming of natural gas. However, as the price of natural gas feedstocks increases as they are projected to, the use of other feedstocks, such as coal, will become increasingly competitive. In addition, efficient methods to separate H_2 from coal gasification streams will be very important.

The Pacific Northwest Laboratory (PNL) has been involved for some time in the development of procedures to specifically separate gases using coordination complexes. Research in the past has focused on hydrogen and CO separation. A palladium dimer $Pd_2X_2(dppm)_2$ is selective for CO and a ruthenium complex $Ru(CO)_2(PPh_2py)_3$ shows a 2:1 preference for H_2 over CO. The ultimate end is to develop complexes suitable for use in membrane systems.

While the cost of facilitated transport membrane systems competes favorably with other separation techniques, advances in selectivity and permeability using cheaper materials will make their use more compelling. Specificity for H_2 in the presence of CO is not always possible using coordination complexes. Our experience suggests that complexes which bind hydrogen also bind CO and oxygen. This nonspecificity is due to the very active nature of the metal center that is necessary to coordinate hydrogen. In order to increase the specificity for hydrogen, coordinatively saturated, dimeric systems that react by metal-metal bond cleavage are sought. Such a system is represented by the cyclopentadienylchromium tricarbonyl dimer, $[CpCr(CO)_3]_2$, where Cp is the cyclopentadienyl group. Research at PNL has shown that quantitative hydrogen uptake occurs at 10 atm and 25°C. The hydride loses H_2 to regenerate the dimer at 80°C. The reversible reaction is shown below:

Future work is directed toward determination of the dependence of the equilibrium constant on temperature. The uptake of H_2 by the chromium complex could be improved by substitution of a carbonyl ligand by an alkylisocyanide. The cost to prepare the chromium complex is projected to be about eight times less than the palladium complex and 80 times less than the ruthenium complex.

GLOSSARY

The abbreviations for ligands and complexes used in this report are shown below with their chemical nomenclature.

thf	tetrahydrofuran
dma	N,N-dimethylacetamide
py	pyridyl
p-tol	<u>para</u> -tolyl
PPh ₃	triphenylphosphine
P(p-CH ₃ C ₆ H ₄) ₃	tri(<u>para</u> -tolyl)phosphine
P(p-ClC ₆ H ₄) ₃	tri(<u>para</u> -chlorophenyl)phosphine
P(p-MeOC ₆ H ₄) ₃	trianisylphosphine
PBu ₃	tributylphosphine
PCy ₃	tricyclohexylphosphine
P(OMe) ₃	trimethylphosphite
P(OPh) ₃	triphenylphosphite
PPh ₂ (allyl)	diphenylallylphosphine
PPh(allyl) ₂	phenyldiallylphosphine
PPhCy ₂	phenyldicyclohexylphosphine
PPh ₂ py	diphenylpyridylphosphine
PPh(OMe) ₂	phenyldimethoxyphosphine
PPh ₂ Cl	diphenylchlorophosphine
PPh(C ₆ H ₄ NMe ₂)Cl	phenyl(<u>para</u> -(dimethylamino)phenyl)chlorophosphine
PPh ₂ (C ₆ H ₄ NMe ₂)	diphenyl(<u>para</u> -(dimethylamino)phenyl)phosphine
PPh(C ₆ H ₄ NMe ₂) ₂	phenyldi(<u>para</u> -(dimethylamino)phenyl)phosphine
dppm	bis(diphenylphosphino)methane

$\text{Pd}_2(\text{dppm})_2\text{X}_2$	dihalobis[μ -bis(diphenylphosphino)methane]- dipalladium (Pd-Pd)
RhCl_6^{3-}	hexachlororhodate anion
$\text{RuCl}_2(\text{PPh}_3)_3$	dichlorotris(triphenylphosphine)ruthenium
$[\text{RuCl}_2(\text{CO})_3]_2$	dichlorotricarbonylruthenium dimer
$\text{RuCl}_2(\text{CO})_2(\text{thf})_2$	dichlorodicarbonylbis(tetrahydrofuran)ruthenium
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	dichlorodicarbonylbis(triphenylphosphine)ruthenium
$\text{RuCl}_2(\text{CO})_2(\text{P}(p\text{-tol})_3)_2$	dichlorodicarbonylbis(tri(<i>p</i> -tolyl)phosphine)ruthenium
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$	dicarbonyltris(triphenylphosphine)ruthenium
$\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$	dicarbonyltris(diphenylpyridylphosphine)ruthenium
$\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$	dihydridodicarbonylbis(triphenylphosphine)ruthenium
$\text{RuH}_2(\text{CO})_2(\text{PPh}_2\text{py})_2$	dihydridodicarbonylbis(diphenylpyridylphosphine)- ruthenium
$\text{RuH}_2(\text{CO})_2(\text{PCy}_3)_2$	dihydridodicarbonylbis(tricyclohexylphosphine)- ruthenium
$\text{RuMo}(\text{CO})_5(\text{dppm})_2$	pentacarbonylbis(μ -bis(diphenylphosphino)methane)- ruthenium molybdenum
$\text{RuMo}(\text{CO})_6(\text{dppm})_2$	hexacarbonylbis(μ -bis(diphenylphosphino)methane)- ruthenium molybdenum
$\text{RuMo}(\text{H})_2(\text{CO})_5(\text{dppm})_2$	dihydridopentacarbonylbis(μ -bis(diphenylphosphino)- methane)ruthenium molybdenum
$\text{RuH}_2(\text{dppm})_2$	dihydridobis(bis(diphenylphosphino)methane)ruthenium
$\text{Ru}(\text{COD})(\text{COT})$	cyclooctadienecyclooctatetraeneruthenium
$\text{Mo}(\text{CO})_6$	hexacarbonylmolybdenum

EXPERIMENTAL

All work reported below was performed under inert atmosphere conditions.

Ligand Exchange Reactions with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$

The following procedure is typical of the method used to exchange PPh_3 in $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with $\text{P}(\text{OMe})_3$, $\text{P}(\text{p-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(\text{cyclohexyl})_3$, and $\text{P}(\text{p-ClC}_6\text{H}_4)_3$. $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (500 mg, 0.53 mmol) in 20 ml thf was refluxed 0.5h with at least a 10-fold excess of phosphine. The volume was reduced to 10 ml, hexane added, and cooled to -60°C . Solid products obtained from the reactions with $\text{P}(\text{p-CH}_3\text{C}_6\text{H}_4)_3$ and PCy_3 were filtered and dried. Oils were obtained from the other preparations.

Ligand Exchange Reactions with $\text{RuCl}_2(\text{PPh}_3)_3$

In a typical experiment, $\text{RuCl}_2(\text{PPh}_3)_3$ (500 mg, 0.52 mmol) in 100 ml hexane was refluxed with at least a 10-fold excess of either $\text{P}(\text{p-tol})_3$, PCy_3 , $\text{P}(\text{OMe})_3$, or $\text{P}(\text{OPh})_3$ for 17 hours. Solutions of the ruthenium reaction mixtures were purged with CO . ^{31}P NMR indicated new materials were obtained from $\text{P}(\text{p-tol})_3$ and $\text{P}(\text{OPh})_3$ while reactions with PCy_3 and $\text{P}(\text{OMe})_3$ were unsuccessful.

$[\text{RuCl}_2(\text{CO})_3]_2$

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (10g) in 500 ml MeOH was placed in a 1L autoclave. The autoclave was purged for 20 min. with CO , pressurized to 10 atm, and heated to $60\text{--}65^\circ\text{C}$ for 30h. After venting, the solution was filtered and evaporated to dryness to give a green-yellow solid (9g, 72%).

$\text{RuCl}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3]_2$

To 0.2 g, 8.4 mmol of $[\text{RuCl}_2(\text{CO})_3]_2$ dissolved in 30mL of CH_2Cl_2 was added 0.53 g, 1.76 mmol of $\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3$. The solution was refluxed for 2

hours. The light yellow solution was reduced to 10mL and diluted with ether. The white precipitate was filtered and vacuum dried, 0.6 g for 91% yield.

$\text{Ru(H)}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_2]$

Both of 0.66 g, 0.79 mmol of $\text{RuCl}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3]_2$ and 0.48 g, 1.58 mmol of $\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3$ were suspended in 150 mL of thf. An excess amount of sodium amalgam was added and the resulting mixture was stirred for 48 hours. The sodium amalgam was removed by decantation and filtration through celite. The clear orange solution was reduced to 10 mL and diluted with 150 mL of hexane. Hydrogen gas was bubbled through the solution. A white precipitate slowly formed and was filtered, 0.48 g. The ^1H -nmr spectrum in CDCl_3 indicated a triplet at -4.47 ppm with a coupling constant of $J_{\text{P-H}} = 19.4$ Hz. The ^{31}P -nmr (PPh_3) spectrum gave a singlet at 75.26 ppm.

$\text{RuCl}_2(\text{CO})_2(\text{PCy}_3)_2$

The dimer $[\text{RuCl}_2(\text{CO})_3]_2$ was refluxed in thf to give 0.4 g, 1.07 mmol of $\text{RuCl}_2(\text{CO})_2(\text{thf})_2$. This was combined with 0.69 g, 2.42 mmol of tricyclohexylphosphine in 40 mL of CH_2Cl_2 and refluxed for 2 hours. The yellow solution was reduced to 10 mL and diluted with ether. The yellow product was filtered and dried, 0.64 g for 75% yield.

$\text{Ru(H)}_2(\text{CO})_2(\text{PCy}_3)_2$

The preparation was similar to that used for $\text{Ru(H)}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3]_2$. The ^1H -nmr spectrum in CD_2Cl_2 indicated a triplet at -8.51 ppm with $J_{\text{P-H}} = 22.56$ Hz. The ^{31}P -nmr (PPh_3) spectrum gave a singlet at 44.75 ppm.

$\text{RuCl}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{OCH}_3)_3]_2$

Both 0.25 g, 0.67 mmol of $\text{RuCl}_2(\text{CO})_2(\text{thf})_2$ and 0.53 g, 1.51 mmol of trianisylphosphine were dissolved in 30 mL of CH_2Cl_2 and refluxed for 1 hour.

The solution volume was reduced to 10 mL and pentane was added to precipitate the white product, 0.58 g for 92%.

To 0.4 g, 0.43 mmol of $\text{RuCl}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{OCH}_3)_3]_2$ and 0.19 g, 0.54 mmol of trianisylphosphine suspended in 150 mL of thf was added an excess of sodium amalgam. The reaction was performed in a manner similar to those noted above. The white hydride product gave a ^{31}P -nmr (PPh_3) spectrum with a singlet at 55.82.

$\text{Ru}(\text{CO})_2(\text{PPh}_2\text{py})_3$ (200 mg; 0.2112 mmol) in 20 ml thf was saturated with 1 atm. H_2 for 1 h. The volume of the solution was reduced to 10 ml under vacuum and the solution again exposed to H_2 . Hexane (150 ml), saturated with hydrogen, was added to precipitate the brown-yellow product which was filtered and dried. Yield: 147 mg; 70%, ^1H NMR: δ -7.14 ppm, triplet, $J_{\text{P-H}}=24$ Hz. ^{31}P NMR: 562.83 ppm (with respect to PPh_3).

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.7g) was dissolved in 20 ml degassed EtOH. Cyclooctadiene (COD; 17 ml) was added and the solution refluxed for 15-20 min. Zn dust (7.0 g) was added slowly and the resulting mixture refluxed for 3 h and filtered. The resulting yellow solution was evacuated to dryness overnight and the residue extracted with 100 ml pentane. The mixture was filtered through neutral alumina, reduced to 5 ml and cooled to -80°C . Yellow needles formed and were filtered cold.

$\text{Ru}(\text{COD})(\text{COT})$ (300 mg) and dppm (750 mg) were dissolved in 20 ml toluene. H_2 was bubbled through the solution for 1 h and the solution sealed under H_2

for 15h. Hexane (50 ml) was added to precipitate a pale yellow solid which was filtered and vacuum dried.

$\text{RuMo(CO)}_6(\text{dppm})_2$

$\text{RuH}_2(\text{dppm})_2$ (300 mg, 0.344 mmol) and Mo(CO)_6 (90.8 mg, 0.344 mmol) were heated to 80°C in 10 ml toluene for 3.5 h. The pale yellow suspension dissolved and a red solid formed. The solution was cooled to -80°C and filtered under nitrogen. The precipitate was vacuum dried.

$\text{PPh(C}_6\text{H}_4\text{NMe}_2\text{)Cl}$

To Mg (2.17g, 0.0893 moles) in 10 ml thf was added dropwise a solution of $\text{Me}_2\text{NC}_6\text{H}_4\text{Br}$ (7.40 g, 0.0370 moles) in 30 ml thf. After stirring 1 h the resulting solution was added dropwise over a 1.5h period to PhPCl_2 (5.0 ml, 3.69×10^{-2} moles) dissolved in 10 ml thf and cooled to 0°C. The solution was reduced in volume to 10 ml and a total of 20 ml Et_2O added to precipitate a white solid which was filtered and washed with CH_2Cl_2 . The solvent was removed from the filtrate and a minimum amount of thf was added to dissolve the residue. A yellow solid that precipitated on standing was filtered and washed with thf and vacuum dried (3.68g).

$\text{PPh(C}_6\text{H}_4\text{NMe}_2\text{)}_2$

To Mg (0.23g) in 10 ml Et_2O was added dropwise PhBr (0.4 ml, 5.6 mmol) dissolved in 5 ml Et_2O . After stirring for ca. 1h the solution was added slowly to a suspension of $\text{PPh(C}_6\text{H}_4\text{NMe}_2\text{)Cl}$ (0.50 g, 1.9 mmol) in 10 ml thf. The yellow solid dissolved immediately to give a colorless solution. The reaction was quenched with saturated aqueous NH_4Cl and extracted with benzene. The benzene layer was dried with MgSO_4 and reduced in volume to ca. 1 ml. Addition of 80 ml EtOH and cooling resulted in the precipitation of a white solid which was filtered, washed, and vacuum dried (0.16 g), mp 154-155°C.

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