Separation of Gas Mixtures by Supported Complexes

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January 1985

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

SEPARATION OF GAS MIXTURES
BY SUPPORTED COMPLEXES

Final Report for the Period
1 October 1982 - 30 September 1984

D. A. Nelson
R. T. Hallen
M. A. Lilga

January 1985

Prepared for
the U.S. Department of Energy
Morgantown Energy Technology Center
under Contract DE-AC06-76RLO 1830

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RESEARCH SUMMARY

This final report covers research performed during the period of 1 October 1982 to 30 September 1984 by the Pacific Northwest Laboratory (PNL) for the Department of Energy, Morgantown Energy Technology Center.

The goal of the program was to identify and demonstrate advantageous procedures for the chemical separation of gases, such as CO, CO₂, and H₂, from medium-Btu gas mixtures by use of supported complexes.

The milestone schedule (Figure 1) indicates the task starting and completion times. All tasks were completed with the two year period.

Three complexes were chosen for rapid gas uptake and selectivity at 25°C from among a group of 22 coordination complexes synthesized during this program. The three complexes showed considerable selectivity toward individual gases. For instance, Pd₂(dpm)₂Cl₂ or bis-μ-(bisdiphenylphosphinomethane)-dichlorodipalladium (Pd-Pd), rapidly bound carbon monoxide from solution. This complex could be regenerated, with the carbon monoxide reversibly removed, by warming to 40°C. The presence of other gases, such as carbon dioxide, oxygen, nitrogen, hydrogen, ethylene, or acetylene, had no effect upon the rapid uptake of carbon monoxide or its removal. Such selectivity was also noted with Ru(CO)₂(PPh₃)₃, biscarbonyltris(triphenylphosphine)ruthenium. Although this complex bound hydrogen, carbon monoxide, and oxygen in solution, the hydrogen was taken up twice as fast as carbon monoxide and seven times faster than oxygen. These gases could be removed from the complex with mild heat or decreased pressure. Crystalline Rh(OH)(CO)(PPh₃)₂, hydroxocarbonylbis(triphenylphosphine)rhodium, rapidly bound carbon dioxide; the complex was regenerated at 50°C under reduced pressure. The rapid uptake of carbon dioxide by this complex was not changed in the presence of oxygen.

In general the three selected crystalline or solvent dissolved complexes performed well in the absence of polymeric support. The stability and favorable kinetics of the three complexes suggest that they could be utilized in a solution system for gas separation (Conceptual Analyses and Preliminary Economics). Further, these complexes appear to be superb candidates as transport agents for facilitated-transport, membrane systems.

PROGRAM OBJECTIVE AND PURPOSE

The objective of this program was to define the most advantageous materials (both the complex and support), methods of material preparation, material properties, and the performance of feasible supported complex systems in applicable gas separations. The overall purpose of the program was to identify and demonstrate advantageous procedures for the chemical separation of gases, such as CO, CO₂, H₂, H₂S, and CH₄, from medium BTU gas mixtures by the use of supported complexes.

The program involved selection and preparation of model complexes capable of reversible sorption of specific gases, attachment of selected complexes to compatible supporting material, and examination of the reversibility, gas capacity and other physical characteristics of such attached complexes.

FIGURE 1. Milestone Schedule

MILESTONE SCHEDULE

The milestone of this program represent the two year research effort. The milestones of each task are shown below and in Figure 1. A full discussion of each task follows this section.

Task A. Selection of Complexes, Supporting Matrices and Separable Mixtures

Complete selection of complexes, supporting matrices and separable mixtures, 11/82.

Task B. Preparation of Model Complexes

Complete synthesis of eight model complexes, 5/83.

Task C. Gas Sorption by Model Complexes

Examine the gas sorption of each model complex, 6/83.

Task D. Preparation of Supported Complexes

D.1 Attachment of Ligands to Supports

Complete attachment of ligands to supports, 8/83

D.2 Supported Complex Formation

Complete supported complex formation, 9/83

D.3 Gas Sorption by Supported Complex

Examine the gas sorption of each supported complex, 11/83

Task E. Sorption-Desorption Cycling

E.1 Desorption Studies

Complete desorption studies, 3/84

E.2 Sorption Studies

Complete sorption studies, 3/84

E.3 Long Term Cycling

Determine the long term cycling stability of the supported complex through at least 10 cycles of gas uptake/release, 9/84

Task F. Thermal Aspects of Supported Complexes

F.1 Heat of Reaction

Determine the heat of gas sorption by the supported complex, 3/84

F.2 Thermal Conductivity of Supported Complex

Determine the thermal conductivity of the supported complex, 4/84

F.3 Thermal Decomposition of Complexes

Establish major decomposition routes of the complexes, 7/84

Task G. Sorption-Desorption Equilibria and Rate

G.1 Sorption-Desorption Equilibria of Supported Complexes

Determine the sorption-desorption equilibria of the supported complex, 5/84

G.2 Rate of Sorption-Desorption of Supported Complexes

Determine the rate of sorption-desorption of the supported complex, 9/84

PROGRAM TASKS

The research is organized into seven major tasks. The individual tasks and subtasks are discussed below. Although not identified as a distinct task, considerable effort was needed to coordinate research activities with the subcontractor and report the research results to DOE during the normal reporting periods. A glossary (p. 111) identifies the abbreviations used for the ligands and complexes in this work.

TASK A. Selection of Complexes, Supporting Matrices and Separable Mixtures

The goal for this task was to identify at least eight complexes which could be useful for reversible sorption of individual components of medium-Btu gas. The gas components of interest were CO_2 , CO , H_2 , H_2S and CH_4 . The type of material to support the coordination complexes was to be determined. Also, a separable mixture which represented medium-Btu gas was to be established. Several complexes have been reported to coordinate one or more of the gases of interest. Those complexes are discussed below in relation to the respective gases.

- CO_2 Separation -- Several mono- and bimetallic complexes have been shown to be reversible carbon dioxide carriers. These include the bifunctional $\text{Co}^{\text{I}}(\text{salen})\text{M THF}$ complex; where M is Li, Na, K, or Cs.⁽¹⁻³⁾ In order to activate CO_2 for coordination, the basic cobalt center, to which the C-atom binds, requires an alkali cation to interact with the O-atoms to complete the acid-base interaction. Carbon dioxide desorption can be achieved by warming the complexes to 30°C or by decreasing the pressure over the mixture of CO_2 -complex and solvent. The three tertiary phosphine-rhodium complexes $\text{Rh}(\text{P}^n\text{Bu}_3)_3\text{Cl}$, $\text{Rh}(\text{PhPMe}_2)_3\text{Cl}$, and $\text{Rh}(\text{Ph}_2\text{PEt})_3\text{Cl}$ have been reported to bind CO_2 .⁽⁴⁾ Only the latter two complexes desorbed CO_2 under vacuum or by heating above 80°C . $\text{Ni}(\text{PCy}_3)_3$ ⁽⁵⁾ and $[\text{NiL}_4]$, where $\text{L} = \text{PEt}_3$ or PBu_3 ,⁽⁶⁾ also

coordinate CO_2 . Heating the CO_2 -adducts of the nickel complexes in vacuo resulted in phosphine decomposition and incomplete CO_2 recovery, while treatment with iodine or sulfuric acid did release CO_2 . Several iridium complexes have been reported to reversibly bind CO_2 . The earliest work was by Flynn and Vaska⁽⁷⁾ who investigated the reactivity of $\text{trans-Ir(OH)(CO)(PPh}_3)_2$. Complete decarboxylation of the CO_2 -complex required 10 hours at 25°C under vacuum. A companion CO_2 -rhodium complex underwent desorption only after several weeks of vacuum exposure. The other iridium systems were claimed in a patent by Herskovitz and Parshall.⁽⁸⁾ Two of the more successful CO_2 carriers were $[\text{Ir(dmpc)}_2]\text{Cl}$ and $[\text{Ir(PMe}_3)_4]\text{Cl}$, both absorbing CO_2 while in hydrocarbon suspension. Desorption was achieved by heat, vacuum, or treatment with dichloromethane. The $[\text{Rh(diars)}_2]\text{Cl}$ complex has also been observed to bind CO_2 .⁽⁹⁾ The CO_2 bonding within this complex is considerably different from that in most others since no metal-oxygen interactions occur; i.e., bonding occurs only between rhodium and the carbon of CO_2 . Carbon dioxide coordination with metallo-systems has also been reviewed recently.^(10,11)

- **CO Separation** -- A considerable number of metal carbonyls, and metal cluster carbonyls⁽¹²⁾ are known to activate small gas molecules such as CO and H_2 and act as homogeneous catalysts for carbonylation and hydrogenation processes, for example. Many of the mononuclear complexes serve also as CO or H_2 carriers under the same conditions. Several complexes have been investigated for their ability to reversibly bind these gases. For instance, $\text{CH}_3\text{Mn(CO)}_5$ was studied as a CO carrier in various solvents, with equilibrium and the forward and reverse kinetics being determined at several temperatures.⁽¹³⁾ Vaska⁽¹⁴⁾ reported the reversible carbonylation of $\text{trans-IrCl(CO)(PPh}_3)_2$ in solution, a system that also reversibly binds oxygen. A series of complexes of structure $\text{Pd}_2(\text{dpm})_2\text{X}_2$ (where dpm bridges the single-

bonded Pd-Pd moiety and X = halogen, SCN, NCO, N₃ or NO₂) has been observed to reversibly bind carbon monoxide,⁽¹⁵⁾ sulfur dioxide,⁽¹⁶⁾ and acetylene.⁽¹⁷⁾

Carbon monoxide inserts directly between the Pd-Pd bond forming a complex described as a molecular A-frame.⁽¹⁵⁾ The reversible reaction between carbon monoxide and phthalocyanatoiron(II) in dimethylsulfoxide has been studied.⁽¹⁸⁾ The equilibrium and rate constants have been determined.

Iron(II) porphyrin systems have been similarly investigated due to their reversible affinity for carbon monoxide.⁽¹⁹⁻²¹⁾

• H₂ Separation — The reversible binding of hydrogen by trans-IrCl(CO)(PPh₃)₂⁽²²⁾ and RhCl(PPh₃)₃⁽²³⁾ are noteworthy since the oxidative addition (+H₂) and reductive elimination (-H₂) processes are common in hydrogenation and homogeneous catalysis generally. Many other complexes add hydrogen at a single metal center to form a dihydride. Decamethyltitanocene reversibly binds hydrogen and nitrogen, but reacts irreversibly with carbon monoxide.⁽²⁴⁾ Several hours under vacuum at 25°C are required to desorb hydrogen. Hydrogen has also been added to IrCl(PCy₃)₃ at 20°C, but a cyclohexyl group of the ligand has been observed to partially dehydrogenate upon desorption.⁽²⁵⁾ The complexes W(CO)₃(PCy₃)₂ and Mo(CO)₃(PCy₃)₂ both reversibly coordinate hydrogen, nitrogen and ethylene.⁽²⁶⁾ The hydrogen-complexes are of considerable interest since H₂ binds as a distinct molecule, (i.e. in a σ^2 -mode) and not as two hydride ligands. A further example of hydrogen binding involves Ru(CO)₂(PPh₃)₃.⁽²⁷⁾ The hydrogen can be removed with either O₂ or CO with concomitant generation of the dioxygen or carbon monoxide complexes. Of further interest, a reversible exchange can be achieved between O₂ and H₂ on the metal center under slight hydrogen pressures. A recent review covers many other examples of hydrogen binding by mono- and polynuclear metallic complexes.⁽²⁸⁾

TASK B. Preparation of Model Complexes

This task required the preparation of at least eight coordination complexes. This involved the preparation of ligands followed by complexation with appropriate metal ions. The initial complex synthesis was performed in solution so that the products could be screened by instrumental techniques (Subtask C.1). However, due to the low aqueous solubility of some gases (10^{-3} M oxygen in water at one atmosphere pressure, for instance) and the ready degradation of many ligands in solution, the useful form of many model complexes was assumed to be crystalline or solid.

Some of the proposed model ligands have been well investigated already as reversible gas sorption agents. In such cases, the appropriate literature data needed only to be compared with that obtained from competing material prepared in the laboratory.

Once the more promising complexes had been determined (Task C), further and more involved syntheses may be required. Since one of the objectives is to attach model complexes to a solid support, complexes with suitable attachment groups had to be prepared. Our experience has shown that such connecting groups may have an important steric effect upon gas sorption. Consequently, complexes with attachment groups were prepared in such a manner that steric hindrance of the coordinating gas-metal ion was minimized.

TASK C. Gas Sorption by Model Complexes

Each of the model complexes, those with and those without attachment groups, were investigated to determine efficiency of gas sorption. In some cases, particularly those of the complexes without attachment groups, gas sorption efficiencies may already have been established. If, however, the information was not directly comparable to competing complexes, the gas sorptions were to be reperformed.

An attempt was made to include representative complexes for each target gas, if possible. The amount of gas adsorbed by the solid or crystalline complexes was to be measured manometrically at or below 25°C. The results from this manometric technique should help confirm (or decide) the type of complexes to be attached to solid support materials.

TASK D. Preparation of Supported Complexes

Subtask D.1. Attachment of Ligands to Support

Model ligand preparation required isolation and purification at each step of the synthesis route. In comparison, polymeric attachments usually occur in high conversion since excess reagents can be utilized and later removed by exhaustive solvent washing.

Our previous experience has shown that the ligand attachment to the support must not allow severe steric hindrance to the coordinating gas-metal ion. Such molecular design will depend upon Task B; however, this subtask may require redesign if the support-attached complex does not meet expectations. This subtask generally involved support attachment of the best ligands as determined in Task C.

Subtask D.2. Supported Complex Formation

Generally, it has been assumed that the reaction between the metal ion and the ligand is quantitative. This may not be true for support-attached ligands. In particular, our experience with cobalt complexation by polymer-attached saltptr indicated that low metal ion coordination could occur. Techniques which use an excess of metal ion or increase the reaction temperature may be useful during the metal-ligand complexation. Each supported complex was to be analyzed to confirm the metal ion uptake. Metal complexation in excess of 80% of the attached ligand (assuming a 1:1 relationship) was a goal so that useful gas capacity could be achieved.

Subtask D.3. Gas Sorption by Supported Complex

This subtask involved examination of the gas coordination by the support-attached complex(es). The bound gas was determined by manometric techniques at or below 25°C. This subtask may be looped back to Subtask D.1 if the supported complex did not meet expectations.

TASK E. Sorption-Desorption Cycling

Subtask E.1. Desorption Studies

This subtask was particularly directed toward methods of gas desorption from the supported catalyst. Temperature, pressure, photolytic and ultrasonic techniques were to be considered. The pressure range at which gas desorption occurs was to be determined during this investigation. The separated gases desorbed by these techniques were to be examined by gas chromatography.

Subtask E.2. Sorption Studies

These studies determined the best temperature for gas sorption as well as the effect of pressure on sorption. Presence of a gas sorption exotherm may require cooling during these studies. If such an exotherm was quite noticeable, then Task F may be conducted before the conclusion of this subtask. Maximum gas sorption at ambient temperature and pressure was an obvious goal, although the characteristics of the complex may not allow this. However, attachment of the complex to a support could moderate radical cooling requirements.

Subtask E.3. Long Term Cycling

Each of the polymer-attached complexes (solid-state) were to have been examined for their ability to sorb gas in Subtask E.2. The gas sorption was determined with manometric equipment. The polymer-attached complex exhibiting the most gas uptake was to be examined through at least 10 sorption-desorption

cycles. If a degradation (irreversible oxidation) trend was not established within 10 cycles, the sorption-desorption study was to be extended to 50 cycles.

TASK F. Thermal Aspects of Supported Complexes

Subtask F.1. Heat of Reaction

The heat of gas sorption of the polymer-attached complexes was determined by dsc (differential scanning calorimetry). The information obtained from solid state was of distinct interest since it was found that the oxygenation of Cosalen evolved 84 KJ/mole of heat.⁽²⁹⁾ Such reactions on the polymer may not necessarily be of that magnitude.

Subtask F.2. Thermal Conductivity of Supported Complex

If the heat of reaction of the polymer-attached complexes and gases was substantial, then information concerning heat transfer would be useful so that adequate cooling could be provided. Thermal conductivity measurements would allow us to establish the amount and efficiency of cooling necessary for the sample vessel. This information could be used to eliminate possible deviations from the rate laws during Task G.

TASK G. Sorption-Desorption Equilibria and Rate

Subtask G.1. Sorption-Desorption Equilibria of Supported Complexes

Equilibrium data were essential to define the limiting fundamental characteristics of the sorption-desorption processes between the gas and the coordinating complex. Thus, the formation and protonation constants of the ligands and complexes were to be determined, if applicable. With this information, quantitative determination of the equilibrium interaction of the molecular gas with the complexes might be computed. Most of the work with the

detached complex may be performed in solution. However, examination of the polymer-attached complex, in solid state, may require a gravimetric and sorption apparatus (McBain balance type).

Subtask G.2. Rate of Sorption-Desorption of Supported Complexes

The kinetics of the complex-gas formation were determined spectrophotometrically in solution with a stopped-flow apparatus. This was to be initially performed with the model complex that best represented the polymer-attached complex having the highest gas uptake. It should be noted that some sorption reactions may be too slow or too fast for use of the stopped-flow equipment. Solid state kinetics may be required for the polymer-attached complexes since the solubility of the polymers (even uncrosslinked types) may be minimal in aqueous solvents.

DISCUSSION

TASK A. Selection of Complexes, Matrices and Mixtures

After thorough examination of the literature and discussions with other investigators, eleven complexes were identified as having potential for reversible gas sorption. The complexes were prioritized, but each was to be considered in Task B to determine ease of synthesis and efficacy of gas sorption. The complexes are presented below in relation to the respective gases.

- CO_2 Separation -- The small linear CO_2 molecule is generally a weak ligand for transition metal complexes, and requires a highly active metal center or assisted center. Several complexes appear to have such characteristics. These include the bifunctional $\text{Co}(\text{salen})\text{Na}$ THF and $\text{Co}(\text{pr-salen})\text{Na}$ THF complexes^(2,3), $\text{Rh}(\text{P}^n\text{Bu}_3)_3\text{Cl}$,⁽⁴⁾ $\text{Rh}(\text{Ph}_2\text{PEt})_3\text{Cl}$,⁽⁴⁾ $[\text{Ir}(\text{dmpe})_2]\text{Cl}$,⁽⁸⁾ and $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$.⁽⁷⁾ Complexes such as $\text{Ni}(\text{PCy}_3)_3$ ⁽⁵⁾ and $\text{Ni}(\text{PBu}_3)_4$ ⁽⁶⁾ were not considered due to the elaborate synthetic procedures necessary to prepare them. The $[\text{Rh}(\text{diars})_2]\text{Cl}$ ⁽⁹⁾ complex was not considered due to its related structure to $[\text{Ir}(\text{dmpe})_2]\text{Cl}$.

- CO Separation -- Although many complexes bind CO, a few appeared to hold more promise due to their potential specificity for CO in the presence of other gases. The $\text{Pd}_2(\text{dpm})_2\text{X}_2$ complex was of considerable interest due to its unusually reactive metal-metal bonds which allowed CO insertion between the two palladium atoms.⁽¹⁵⁾ Phthalocyanatoiron(II)⁽¹⁸⁾ was also interesting since it could be obtained commercially. Complexes such as $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ⁽²⁹⁾ were not investigated further due to their lack of specificity for CO.

- H_2 Separation -- Hydrogen is rather difficult to bind to complexes with any degree of specificity. There are several complexes that bind H_2 , but most

also bind CO, O₂, or N₂, while some were sensitive to water. Two complexes which did appear to have some possible specificity were Ru(CO)₂(PPh₃)₃⁽²⁷⁾ and RhCl(PPh₃)₃.⁽²³⁾

- H₂S Separation - It is generally conceded that the chemistry of H₂S with metallo-complexes provides complicated and ill-defined sulfides. For instance, [Ru(NH₃)₅(H₂S)]⁺² can be formed, but it spontaneously decomposes to yield dithiolates.⁽³⁰⁾ Only one complex, IrCl(CO)(PPh₃)₂, has been suggested by the literature⁽³¹⁾ to reversibly bind H₂S. The removal of H₂S apparently required 140°C under vacuum for 1 hour to reform IrCl(CO)(PPh₃)₂.

- CH₄ Separation - Extensive research has been directed toward the activation of alkanes with coordination complexes. Unfortunately, the inherent inert character of the alkanes does not allow them ready coordination to metals. Only recently has a complex successfully coordinated alkanes; however, the alkanes were very weakly bound. The weakly solvated complex [IrH₂S₂(PPh₃)₂], where S is acetone, was used to bind cyclic alkanes.⁽³²⁾ Due to the weak alkane ligation most gases (H₂, CO, O₂ and CO₂) and polar solvents readily compete for the coordination sites. There does appear to be considerable activity and advances in this area, but none have led to reversible alkane sorption.

Cross-linked polystyrene was determined to be the best polymeric support for coordination complexes. This was based upon two points. First, polystyrene has been used as the support of choice for polymer-attached homogeneous catalysts. Attachment of the complex to the polystyrene can generally be achieved by covalent bonding. This ensures minimum loss of catalyst from the support surface. Secondly, polystyrene has been found to be excellent for diffusion controlled processes, such as those utilizing supported catalysts or complexes.⁽³³⁾ Although these diffusion controlled

processes implied solid-liquid interaction, the solid-gas interactions necessary for gas separation were presumed to operate in a similar manner. Therefore, since polystyrene has been well characterized as a support for many types of homogeneous catalysts, it was selected as the preferred material for coordination catalyst attachment.

The medium-Btu gas has been defined as having a heating value of 250-550 Btu/ft³(34). A synthetic mixture containing the five gases was attained by normalizing raw gas compositions (eliminating H₂O and N₂) from the Lurgi and Koppers-Totzek processes: 22 mol% CO, 28% CO₂, 39% H₂, 10% CH₄ and 0.3% H₂S.

TASK B. Preparation of Model Complexes

The complexes which were prepared for this project have been placed together according to the gas they were assumed to bind.

CO₂ Coordination

Prior to the preparation of Co(alkyl-salen)Na·THF complexes, where salen=N,N'-ethylene bis(salicylideneimine), it was necessary to prepare two alkyl-salen ligands. The ethyl- and propylsalen ligands (Figure 3) were prepared quantitatively by the reaction of *o*-hydroxypropiophenone and *o*-hydroxybutyrophenone, respectively, with diaminoethane. Although *o*-hydroxypropiophenone is commercially available, *o*-hydroxybutyrophenone had to be synthesized via the Fries rearrangement.⁽³⁵⁾ The cobalt complexes were prepared by reacting cobalt(II) acetate with the salen ligands.

FIGURE 2. Salen Ligands in CO₂ Coordination Complex

The properties of these complexes are typified by the propyl derivative, Co(pr-salen)Na·THF. This light orange complex was dissolved in tetrahydrofuran (THF) and reacted with sodium metal. The reduction of the Co(II) complex was accompanied by a color change (orange to green). The alkali metal reduced the oxidation state of cobalt while remaining bonded as a cation to the oxygen ends of the salen ligand⁽²⁾ as shown below:

where $\text{ONNO} = \text{pr-salen}$

Co(pr-salen)Na·THF was very soluble in THF, but was also exceptionally sensitive to oxygen. Our preliminary experiments suggested that irreversible oxidation occurred at less than 50 ppm oxygen. For this reason, all syntheses were performed in Schlenk (vacuum) glassware. This complex formed a red-brown precipitate in tetrahydrofuran (THF) upon exposure to CO_2 .

Other reported analogs, such as Co(pr-salen)K·THF, formed the CO_2 complex readily at 25° and deposited red crystals.^(1,3) These crystalline complexes released CO_2 in vacuo and redissolved in THF to form the original green solution. Carbon dioxide was also removed from the CO_2 complexes suspended in solvent by partially (in vacuo) distilling the solvent at approximately 30° .⁽²⁾

The Co(salen)Na·THF complex was also prepared in this laboratory. It too was quite sensitive to oxygen. Exposure of a THF solution of Co(salen)Na·THF to CO_2 yielded maroon-colored crystals which were isolated and stored under helium. The oxygen sensitivity of the crystalline CO_2 -complex was considerably diminished. The CO_2 -complex could be handled within a glovebox (helium) without elaborate precautions for oxygen removal.

$\text{RhCl}(\text{PBU}_3)_3$, where Bu = n-butyl, was prepared in a manner similar to that reported previously.⁽⁴⁾ The starting material, $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$, was dissolved in either benzene or pentane followed by addition of tributylphosphine. A red oil, with some crystalline material, was isolated from the pentane solution. The benzene solution was used directly for the gas uptake experiment. However, the CO_2 uptake was nearly nonexistent. It further appeared that the reversibility of the CO_2 uptake may be doubtful.⁽⁴⁾ It has been reported that upon standing $\text{RhCl}(\text{CO}_2)(\text{PBU}_3)_2$ rearranged to form a phosphine oxide with one ligand while leaving CO coordinated to rhodium. The complex may be considered of minimal use for solid state gas separation due to the loss of a ligand in equation (1).

Disregarding equation (2), the complex would require an unattached ligand for CO_2 reversal. Thus, this complex was not considered further.

It had been reported that changing the phosphine ligands of $\text{RhCl}(\text{PBU}_3)_3$ to ethyldiphenylphosphine allowed the complex to bind CO_2 .⁽⁴⁾ Consequently, $\text{RhCl}(\text{EtPPh}_2)_3$ was prepared by reacting $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ with ethyldiphenylphosphine in benzene. In our laboratory $\text{RhCl}(\text{EtPPh}_2)_3$ in benzene solution formed <1% of the assumed CO_2 adduct when exposed to that gas. This complex will not be investigated further.

The complex $[\text{Ir}(\text{dmpe})_2]\text{Cl}$, where dmpe = 1,2-bis(dimethylphosphino)ethane, was prepared from $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$. The cyclooctene complex was prepared by two procedures. The first involved use of IrCl_3 ⁽³⁶⁾ and the second required $(\text{NH}_4)_2\text{IrCl}_6$.⁽³⁷⁾ The latter procedure yielded a much purer cyclooctene product in our hands. In benzene the yellow cyclooctene complex turned orange upon contact with dmpe. The desired crystalline complex was a light yellow color

when solvent was removed. It reacted slowly with air to give a white to pink colored solid. Exposure to CO_2 also gave a white solid. However, the rate of color change in CO_2 appeared more rapidly than that noted when the complex was exposed to air. It was reported that CO_2 can be replaced from $[\text{Ir}(\text{dmpe})_2(\text{CO}_2)]\text{Cl}$ with CO , CS_2 and H_2 .⁽⁸⁾

The complex $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ was prepared in a manner similar to that of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$.⁽⁸⁾ The yellow solid was reported to react with CO_2 in benzene or toluene suspension. In both cases, the color change was yellow to white. This color change also occurs with air exposure. However, some samples were noted to decompose to a brown sinter with gas evolution.

The $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ complex was prepared by reacting $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with AgBF_4 in CH_3CN to produce $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3\text{CN})^+$ which was then exposed to NaOH .⁽⁷⁾ The OH stretch was observed in the ir spectrum at 3610 cm^{-1} while the CO stretch occurred at 1925 cm^{-1} . The crystalline yellow complex was reported to slowly bind CO_2 (five hours was required).⁽⁷⁾ Complex decarboxylation was reported to occur after about 10 hours at 25°C ; we found no CO_2 uptake by crystalline $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ even after 24 hours at 25°C . However, when $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ was dissolved in tetrahydrofuran and exposed to CO_2 , a precipitate was formed which had no vibrational mode at 3610 cm^{-1} . The carbonyl stretch was shifted to 1962 cm^{-1} (shoulder at 1930 cm^{-1}). Related absorbances were observed at 1637, 1620, 1312, and 814 cm^{-1} . These wave numbers were similar to those reported by Vaska⁽²⁾ for $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2(\text{CO}_2)$. When CO_2 was evacuated (partially) from the surface of the mixture, the precipitate redissolved (OH stretch was again visible by ir spectroscopy). Thus, $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ reversibly binds CO_2 in solution.

Crystalline $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ was prepared in a manner similar to $\text{Ir}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ since it was reported to instantly bind CO_2 .⁽⁷⁾ The yellow

complex appeared to be stable in air; a nujol mull of the complex gave no sign of O_2 addition or degradation after 1 week of exposure to air.

The Rh complex rapidly bound CO_2 while in a crystalline state. Infrared spectroscopy indicated that $Rh(OH)(CO)(PPh_3)_2$ had a CO stretch at 1945 cm^{-1} and an OH stretch at 3620 cm^{-1} . After exposure to CO_2 , the OH stretch disappeared and the CO stretch was shifted to 1972 cm^{-1} . Other CO_2 vibrational modes were observed at 1615, 1315 and 815 cm^{-1} . CO_2 was liberated and the starting material regenerated when the sample was heated to 60°C in vacuo for one hour.

CO Coordination

A series of palladium complexes was prepared by a unique synthetic procedure. The complexes were $Pd_2(dpm)_2Cl_2$, $Pd_2(dpm)_2Br_2$, $Pd_2(dpm)_2I_2$, $Pd_2(dpm)_2(NCO)_2$, and $Pd_2(Ph_2AsCH_2AsPh_2)Cl_2$. The starting materials for the complexes were $Pd(PhCN)_2Cl_2$, prepared from $PdCl_2$ and benzonitrile, and $Pd_2(PhCH=CHCOCH=CHPh)_3(CHCl_3)$,⁽³⁸⁾ prepared from $PdCl_2$ and dibenzylideneacetone. These complexes were combined in the presence of the ligand dpm, bis(diphenylphosphino)methane, dissolved in dichloromethane. The complexes $Pd_2(dpm)_2Br_2$,⁽¹⁵⁾ $Pd_2(dpm)_2I_2$, and $Pd_2(dpm)_2(NCO)_2$ were prepared by anion exchange; i.e., exposure of $Pd_2(dpm)_2Cl_2$ with KBr, KI, and NaNCO, respectively.

The $Pd(Me-dpm)Cl_2$ and $Pd_2(Me-dpm)_2Cl_2$ complexes were synthesized using unambiguously prepared $Ph_2PCH(CH_3)PPh_2$ (Me-dpm) ligand (see Task D). The

ligand was combined with $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ to yield $\text{Pd}(\text{Me-dpm})\text{Cl}_2(\text{I})$, while Me-dpm was combined with $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$, where Ph_2Ppy is diphenylpyridylphosphine, to give $\text{Pd}_2(\text{Me-dpm})_2\text{Cl}_2(\text{II})$. The ^1H -nmr spectra (experimental and computer-simulated) for the complexes are presented in Figures 3a and 3b. Computer derivitization involved input of coupling patterns, intensity and splitting, as well as equivalent nuclei, into a program which produced a simulated spectrum based on that data. Close spectral fit helped confirm the assumed structure. The coupling constants and chemical shifts are reported in Table 1. The hand derived coupling constants for the methine hydrogen of I are presented in Figure 4. It should be noted that structure II is represented as the cis isomer, but not enough information has been obtained to distinguish it from a trans configuration. The nmr spectra of Figures 3a, 3b, 4, and those following have been reported in a standard manner with relative intensity as the ordinate and chemical shift as the abscissa. The chemical shift depends upon field strength. Since the field strengths employed in nmr are of the order of millions of cycles per second (as example, 100 MHz), while the difference between the resonance frequencies are in terms of a few cycles, chemical shifts are expressed in terms of parts per million (ppm).

TABLE 1. Proton nmr Spectra of Pd-Complexes

<u>Pd(Me-dpm)Cl₂</u>		<u>Pd₂(Me-dpm)₂Cl₂</u>	
<u>Chemical Shifts</u> (ppm)			
CH ₃	1.12	CH ₃	1.02
H ₁	4.75	H ₁	4.94
<u>Coupling Constants</u> (Hz)			
J _{H, Me}	7.64	J _{H, Me}	6.8
J _{H, P}	12.03	J _{H, P}	6.17
J _{Me, P}	17.53	J _{Me, P}	6.14

FIGURE 3a. ^1H -nmr Spectrum of $\text{Pd}(\text{Me-dpm})\text{Cl}_2$ Where A = Experimental and B = Computer Derived

FIGURE 3b. ^1H -NMR Spectrum of $\text{Pd}_2(\text{Me-dpm})_2\text{Cl}_2$ Where A = Experimental and B = Computer Derived

FIGURE 4. Examination of Coupling Constants for the Methine Hydrogen of $\text{Pd}(\text{Me-dpm})\text{Cl}_2$

The $\text{PdPt}(\text{dpm})_2\text{Cl}_2$ mixed metal complex was prepared since it has been reported to have some unique properties. In particular, $\text{PdPt}(\text{dpm})_2\text{Cl}_2$ binds CO rapidly while in solution and desorbs CO in a solid state at 90°C in vacuo.⁽³⁹⁾ However, SO_2 replaces CO from $\text{PdPt}(\text{dpm})_2(-\text{CO})\text{Cl}_2$, as shown below, and can itself be removed by nitrogen purge. This would suggest that SO_2 would "catalyze" the reversible uptake of CO.

The $\text{PdPt}(\text{dpm})_2\text{Cl}_2$ was prepared by combining $\text{Pt}(\text{dpm})\text{Cl}_2$ and dpm with $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$. The product contained a small amount of residual $\text{Pt}(\text{dpm})\text{Cl}_2$. However, the metal complex was relatively unstable in solution (CDCl_3), since the ^1H -nmr spectrum changed considerably in 16 hours. Due to this presumed instability further work with $\text{PdPt}(\text{dpm})_2\text{Cl}_2$ was curtailed.

Several other palladium complexes were prepared, but they were based upon tri-2-pyridylphosphine (Ppy_3) or diphenylpyridylphosphine (pyPPh_2) ligands. The mono-Pd complexes which were prepared are intermediates for the respective Pd_2 complexes. The ultraviolet spectral absorbances (λ_{max}) and corresponding extinction coefficients (ϵ_{max}) are reported in Table 2.

TABLE 2. Electronic Spectral Values for Some Palladium Complexes in Dichloromethane at 25°C

Complex	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($M^{-1}cm^{-1}$)
$Pd(Ppy_3)_2Cl_2$	338	3,416
$Pd(Ppy_3)_2Br_2$	362 398	2,946 1,861
$Pd(pyPPh_2)_2Br_2$	363	9,734
$Pd(pyPPh_2)_2I_2$	425	3,112
$Pd_2(Ppy_3)_2Cl_2$	335 460	12,048 8,416
$Pd_2(Ppy_3)_2Br_2$	348 375 475	11,599 7,537 10,289
$Pd_2(Ppy_3)_2I_2$	376 410 525	9,709 7,316 11,700
$Pd_2(pyPPh_2)_2Br_2$	348 385 483	13,678 6,307 7,919
$Pd_2(pyPPh_2)_2I_2$	379 415 480 540	1,369 6,836 4,820 10,821

The $Pd_2(Ph_2Ppy)_2I_2$ complex which had been prepared earlier was subjected to crystallographic analyses since it appeared to be one of the complexes of the pyridylphosphine series incapable of binding CO. The standard Oak Ridge National Laboratory crystallographic computer programs were used in this work⁽⁴⁰⁾, see Figure 5. The fractional atomic coordinates will be published later. The P-Pd bond distance was determined as 2.59 nm.

Exposure of $Pd_2(Ppy_3)_2X_2$ and $Pd_2(Ph_2Ppy)_2X_2$ to water presented varying results depending upon the halogen and ligand. The $Pd_2(Ph_2Ppy)_2X_2$ complexes (X = Cl, Br and I) were insoluble in water and appeared to be quite stable in

FIGURE 5. Stereoview (ORTEP) of the $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$. Complex Showing the Labeling Scheme and Atomic Vibrational Ellipsoids of 5% Probability. The Hydrogen Atoms are not Shown

aqueous systems. However, $\text{Pd}_2(\text{Ppy}_3)_2\text{Cl}_2$ was soluble and appeared to react with water, while $\text{Pd}_2(\text{Ppy}_3)_2\text{Br}_2$ was slightly soluble in water, yet also reacted with it. These results were quite interesting in the light of a recent report⁽⁴¹⁾; where a similar complex, $\text{Pd}_2(\text{dmpm})_2\text{Cl}_2$, $\text{dmpm} =$ bis(dimethylphosphino)methane, was soluble in water yet still absorbed CO. Further, this complex seemed to catalyze the water-gas shift reaction at 25° with the presumed mechanism:

This complex inserted a CO molecule between the Pd-Pd bond in typical A-frame fashion; however the reactions noted above occurred to the exterior of this A-frame. The pyridyl-Pd complexes may react in a similar fashion with water and CO.

Hydrogen Coordination

The complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ was prepared by a new and yet unreported procedure. The three step procedure (shown below) gave an overall yield of about 65%.

The complexes $\text{Ru}(\text{CO})_2\text{PPh}_3(\text{dpm})$ and $\text{Ru}(\text{CO})_2(\text{Ppy}_3)_3$ were also prepared to determine the effect of ligand change upon hydrogen sorption. $\text{RhCl}(\text{PPh}_3)_3$ was obtained commercially and will be discussed in Task C.

TASK C. Gas Sorption by Model Complexes

CO₂ Coordination

The isolated green complexes Co(pr-salen)Na·THF and Co(salen)Na·THF in THF rapidly absorbed carbon dioxide dissolved in the solution. In each case, the CO₂ uptake was stoichiometric with Co. Samples of 0.025M of complex in THF absorbed a full complement of CO₂ within 5-10 seconds at 25°C using 1 atm of constant pressure of the gas over the solution. Stopped-flow equipment will be needed to examine this rapid reaction more quantitatively.

Upon exposure to CO₂, THF solutions of Co(Pr-salen)Na·THF formed a red-brown precipitate while Co(salen)Na·THF formed red crystals. These crystals released CO₂, in vacuo, and also redissolved in THF to form the original green solution. Carbon dioxide can also be removed from the CO₂-complexes by suspending them in other solvents and partially vacuum distilling the solvent at 30°C.⁽³⁾ However, due to the extreme oxygen sensitivity of these complexes further work in this area was terminated.

The yellow complexes [Ir(PMe₃)₄]Cl and [Ir(dmpe)₂]Cl were reported to reversibly bind CO₂ in benzene suspension to yield white adducts, and the bound CO₂ of Ir(dmpe)₂(CO₂)Cl could be displaced by CO or H₂.^(8,43) We found that a white complex was formed when either of the precursors was exposed to oxygen.

The [Ir(dmpe)₂]Cl complex was examined in the present work while dissolved in dimethylacetamide (dma) saturated with CO₂ at 1 atm; a 0.2g sample was dissolved in 25 mL dma with a constant CO₂ pressure which allowed for pseudo-first order conditions. Gas uptake measurements revealed standard first-order absorption curves from which the k_{obs} was found to be $5.9 \times 10^{-3} \text{ s}^{-1}$ at 25°C

and $4.2 \times 10^{-3} \text{ s}^{-1}$ at 0.9°C . A full complement of CO_2 was absorbed with a $t_{1/2}$ of 3 minutes at 0.9°C . Carbon dioxide absorption by $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ in dma was complete in less than one minute at 0.9°C .

Both $[\text{Ir}(\text{depe})_2]\text{Cl}$ and $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ have been shown to metalate and, in the presence of CO_2 , carboxylate activated hydrocarbon solvents.⁽⁴³⁾ Acetonitrile, acrylonitrile, and phenylacetylene all undergo these reactions. The processes and accompanying nmr data were consistent with the following reactions:

$$\text{where } K_2 \gg K_1$$

The reaction of acetonitrile with $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ at 25° was rapid ($t_{1/2} < 10$ min).⁽⁴³⁾ It should be noted that the CO_2 carboxylation reaction with both of these two iridium complexes was reversible, and CO_2 could be removed by gas evacuation at 80° . It seemed plausible that dma also reacted with $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ and $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ via reactions such as (3) and (4), and thus the CO_2 reaction with both complexes was examined in the absence of solvent. The solid phase uptake of CO_2 by $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ did not occur even after 48 hours. However, the solid phase 1:1 uptake of CO_2 by $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ occurred in less than 10 seconds; on heating to 100° under vacuum for 30 minutes, the white CO_2 -complex returned to the orange color of the original complex. Re-exposure of this material to CO_2 instantly (5-10 seconds) turned the complex white again. Thus, $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ retained the rapid CO_2 binding rate even after a single recycle.

The slow or non-existent CO₂ adsorption by [Ir(PMe₃)₄]Cl in the absence of solvent suggests that it possesses a highly-ordered crystalline structure. The reported rapid CO₂ sorption in benzene or toluene slurries by this complex may be explained by solvation of the crystalline complex, which enhances surface structural disorder. The rapid CO₂ sorption by [Ir(dmpe)₂]Cl in solid state suggests that the dmpe ligand confers a definite degree of disorder in the crystalline lattice. It is interesting that the solid phase CO₂ binding was more rapid than that performed in dma solvent; this might be a function of diffusion in the solution reaction or perhaps the solution species is different than that in solid state.

The report that solutions of Rh(PBu₃)₃Cl and Rh(EtPPh₂)₃Cl absorbed CO₂⁽⁴⁾ was not confirmed by later work.⁽⁴⁴⁾ In our laboratory neither complex in solution was found to react with CO₂ even after 24 hours exposure. The reversibility of the reported Rh(PBu₃)₃(CO₂)Cl system was also doubtful in that upon standing, the CO₂-complex was claimed to rearrange to form a species containing both coordinated phosphine oxide and CO.⁽⁴⁾ These complexes were not considered further.

Although Ir(OH)(CO)(PPh₃)₂ did not bind CO₂ while in the solid state, it rapidly absorbed CO₂ while in THF solution. The solid complex may have a closely packed crystalline structure which could reduce CO₂ diffusion to the metal sites. The crystalline Rh(OH)(CO)(PPh₃)₂ rapidly bound CO₂ when exposed to 1 atm of the gas. The CO₂ uptake was 2.41 mL for a 0.102 g sample (theoretical uptake was 3.39 mL). Thus, the CO₂ efficiency was 71%. The 29% loss of efficiency may have been due to air exposure of the sample; CO₂ could have been scavenged from air. Although a prior sample of Rh(OH)(CO)(PPh₃)₂ in nujol was stable to air the viscous oil could have prevented air diffusion to the complex. This seemed to be confirmed when CO₂ was fully desorbed from

$\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2(\text{CO}_2)$ at 56°C under 10^{-4} torr vacuum for 3 hours. The regenerated Rh-complex then bound 83% of the theoretical amount of CO_2 . It should be noted that a prior report indicated that several weeks were required under vacuum at room temperature to desorb CO_2 from the Rh-complex.⁽⁷⁾

CO Coordination

The stoichiometry of the reaction between carbon monoxide and $\text{Pd}_2(\text{dpm})_2\text{X}_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ and } \text{NCO}$, was found to have a 1:1 relationship in solution, as an example see Figure 6. This confirmed previous work reported for some of the palladium complexes.⁽¹²⁾ Further discussion of the CO sorption by $[\text{Pd}(\text{dpm})_2\text{X}_2]$ in solvent will be continued under Task G.

FIGURE 6. Reaction of CO with $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$

In the crystalline state, $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, and presumably the other anion exchanged complexes, did not absorb CO at 25°C . To the contrary, crystalline $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ released CO under vacuum at 78°C . The rigidity of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ within its crystalline lattice probably does not allow separation of the Pd-Pd atoms for CO incorporation (A-frame formation). However, the release of CO from crystalline $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ is not similarly affected. One might assume that the reformation of the Pd-Pd bond is considerably easier in the void left by the leaving CO than Pd-Pd bond breaking in $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. It was assumed that the complex would be susceptible to CO incorporation if the crystalline lattice was partially disrupted by the loss of CO from $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$. However, CO was not inserted into the complex under these conditions.

The electronic (UV) spectra of the palladium complexes and their carbon monoxide insertion products are shown in Table 3.

TABLE 3. Electronic Spectra of Reactants and Carbon Monoxide Insertion Products^a

Compound	λ_{max} , nm(ϵ_{max} , $\text{M}^{-1}\text{cm}^{-1}$) at 25°
$\text{Pd}_2\text{dpm}_2\text{Cl}_2$	416(7550), 347(16800), 293(25900)
$\text{Pd}_2\text{dpm}_2\text{Br}_2$	428(10600), 364(17500), 301(23100), 285(21300), 238(29400)
$\text{Pd}_2\text{dpm}_2(\text{NCO})_2$	394(7390), 326(13500), 290(36300)
$\text{Pd}_2\text{dpm}_2(\mu\text{-CO})\text{Cl}_2^b$	468(0.37), 404(0.20), 306(0.47), 250(1.00)
$\text{Pd}_2\text{dpm}_2(\mu\text{-CO})\text{Br}_2^b$	481(1.00), 410(0.57), 309(0.97), 258(0.57)
$\text{Pd}_2\text{dpm}_2(\mu\text{-CO})(\text{NCO})_2$	444(10500), 410(7590), 292(23200)

a. This was extracted from reference 12; the solvent used was CH_2Cl_2 .

b. The compounds were generated in solution by purging the parent solution with CO gas. Values listed as max are relative absorbance values.

The $\text{Pd}_2(\text{Me-dpm})_2\text{Cl}_2$ complex was dissolved in dichloromethane and exposed to 1 atm of CO; no precipitate was formed. In comparison, $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ formed an insoluble $\mu\text{-CO}$ complex. Manometric measurements indicated that CO was not bound by the alkyl substituted complex. Steric hindrance by the methyl group may reduce articulation (structural bending) of dpm; this could account for the loss of CO binding ability by $\text{Pd}_2(\text{Me-dpm})_2\text{Cl}_2$.

The complexes $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2^{(45)}$ and $\text{Pd}_2(\text{Ppy}_3)_2\text{X}_2$, where $\text{X} = \text{NCO}$, Cl , Br , and I , were reported to bind two moles of CO to one mole of complex. The reaction with CO was presumably reversible as shown below:

Balch⁽⁴⁵⁾ had suggested that two features allowed for this type of linear CO product: the ease by which the pyridyl nitrogen could be displaced from the Pd coordination plane and the lack of articulation available to the Ph_2Ppy ligand. The latter is quite important since the Pd-Pd bond distance must be able to vary from 2.2 to 3.5 nm to accommodate a $\mu\text{-CO}$ bridge in $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$. However, only $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ was found to bind CO within the two series $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{X}_2$ and $\text{Pd}_2(\text{Ppy}_3)_2\text{X}_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{and I}$. Neither ir nor uv spectral evidence could be obtained to indicate CO reaction with any of the other members of those two series. FT-ir was used to substantiate the CO reaction with $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$, but this reaction apparently occurred at substantially less than mole to mole ($\text{Pd}:\text{CO}$). It was estimated to be in the <20% of theoretical range. The CO uptakes were all performed in dichloromethane. There is little evidence to suggest that the CO uptakes would occur more readily in the solid state. At this time it is evident that these phosphinopyridine complexes hold little promise for CO removal from gas mixtures. Further investigation of these complexes has shown that both $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ and $\text{Pd}_2(\text{ppy}_3)_2\text{Cl}_2$ react with one equivalent of dimethyl acetylenedicarboxylate. The yield of the products were 97% for $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ and 92% for $\text{Pd}_2(\text{Ppy}_3)_2\text{Cl}_2$.

The reaction between carbon monoxide and phthalocyanatoiron(II) in dimethylsulfoxide has already been studied.⁽¹⁸⁾ The iron complex adds CO in a one to one ratio. The observed rate, pseudo first-order kinetics, at 20° had the form shown below:

$$k_{\text{obs}} = k_1[\text{CO}] + k_{-1} \text{ where } k_1 = 1.28 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1} \text{ and } k_{-1} = 0.12 \text{ sec}^{-1}$$

Further work was not undertaken with this complex since the $\text{Pd}_2(\text{dpm})_2\text{X}_2$ complexes seemed so promising.

Hydrogen Coordination

Reversible hydrogen and carbon monoxide binding has been previously reported with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$.⁽²⁷⁾ The absorption of CO, H_2 , and O_2 by dma solutions of this complex was initially investigated here. Each gas uptake appeared to be mole to mole with respect to the complex at 25°C in dma. Further discussion of these gas uptakes will be discussed under Task G.

A similar complex was investigated for H_2 binding; $\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$ did bind CO, H_2 , and O_2 on a mole to mole basis. However, the reaction of O_2 with $\text{Ru}(\text{CO})_2(\text{pyPPh}_2)_3$ did not appear to involve simple addition; some of the phosphine ligand was oxidized.

The uptake of hydrogen by $\text{RhCl}(\text{PPh}_3)_3$ had been previously established as a 1:1 relationship in benzene at 25°.⁽²³⁾ The second order rate constant $k_1 = 4.8 \text{ M}^{-1} \text{ sec}^{-1}$ was determined in benzene at 25°. Halpern proposed the following mechanism:

The $\text{RhCl}(\text{PPh}_3)_2$ complex (formed by loss of PPh_3) occurred as the dimer $[\text{RhCl}(\text{PPh}_3)_2]_2$.^(23,46) Further work was not undertaken with this complex.

The gas uptakes of the complexes examined in Task C are presented in Table 4.

Competitive H_2S Coordination

During the investigation of CO uptake by $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ it became apparent that the complex may react with or coordinate H_2S . These possibilities were examined by passing H_2S through a solution of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ in dma. The exit gas, which was monitored by gas chromatography, showed the definite presence of hydrogen. This suggested that the sulfur of H_2S had been inserted into the Pd-Pd bond while H_2 was released. The adduct was isolated and characterized as $\text{Pd}_2(\text{dpm})_2(\mu\text{-S})\text{Cl}_2$; its spectra compared well to the reported complex.⁽¹⁶⁾ The isolated complex gave a singlet at 6.2 ppm (with respect to H_3PO_4) with ^{31}P -nmr. The ^1H -nmr indicated two sets of a doublet of quintets, one at 2.81 ppm ($J_{\text{H-H}}=12.7$ Hz), ($J_{\text{P-H}}=3.7$ Hz) and the other at 4.76 ppm ($J_{\text{H-H}}=12.7$ Hz), ($J_{\text{P-H}}=6.1$ Hz).

Bubbling H_2S through a solution of $\text{Pd}_2(\text{dpm})_2\text{I}_2$ did not yield H_2 or the inserted sulfide adduct. Only the starting material was recovered from solution. There appears to be considerable difference in reactivity between $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2\text{I}_2$ for H_2S .

TABLE 4. Gas Uptakes of Coordination Complexes

<u>Complex</u>	<u>Gas</u>	<u>Complex:Gas Ratio*</u>
Co(pr-salen)Na THF	CO ₂	1:1
Co(salen)Na THF	CO ₂	1:1
Ir(dmpe) ₂ Cl	CO ₂	1:1
Ir(PMe ₃) ₄ Cl	CO ₂	1:1
Rh(PBu ₃) ₃ Cl	CO ₂	1:0
Rh(EtPPh ₂) ₃ Cl	CO ₂	1:0
Pd ₂ (dpm) ₂ X ₂	CO	1:1
Pd ₂ (Ph ₂ Ppy) ₂ Cl ₂	CO	1:0.2
phthalocyanatoiron(II)	CO	1:1
Ru(CO) ₂ (PPh ₃) ₃	H ₂	1:1
Ru(CO) ₂ (pyPPh ₂) ₃	H ₂	1:1
RhCl(PPh ₃) ₃	H ₂	1:1

* The ratio reflects the mole to mole composition of the final product.

TASK D. Preparation of Supported Complexes

Subtask D.1. Attachment of Ligands to Support

Several schemes for the attachment of dpm, bis(diphenylphosphino)methane, and dmpe, 1,2-bis(dimethylphosphino)ethane, to polystyrene were investigated in this laboratory. The best scheme for the dmpe attachment involved the following steps:

Preparation of allyl lithium required the reaction of tetra(allyl)tin with butyl lithium. The model ligand $\text{PhCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ was prepared by an analogous route in 94% yield. It was quantitatively brominated and reacted with LiPMe_2 . However, the phosphinated product was a mixture containing three major components. This scheme was applied to Amberlite XAD-2 macroporous polystyrene which had been chloromethylated. Polymer III contained 9.3% Br (15.3% of the aryl groups of polystyrene were reacted), while polymer IV contained only 1.5% P (2.7% ligand attachment). The low conversion of polymer III to IV may be due to the use of macroporous resin or to 1,2-elimination of bromine. The elimination of bromine has been observed during $\text{S}_{\text{N}}1$ substitution attempts with Me_3SnLi .⁽⁴⁷⁾ Dibromoethane produced ethylene when exposed to the lithium reagent.

The difficulties encountered with the model ligand suggest that this type of elimination may occur. Regardless of the actual competitive pathways it is evident that phosphination is difficult and incomplete during the preparation of polymer-attached ligands.

Polymeric attachment of the dpm ligand either required direct alkylation of dpm or the use of geminal groups such as CHCl_2 or CHBr_2 which can undergo substitution to form $\text{CH(PPh}_2)_2$. Our initial alkylation attempt to prepare ligand III involved the direct reaction of butyl lithium with dpm to prepare the anion $(\text{Ph}_2\text{P})_2\text{CH}^-$.

However, this anion and benzyl chloride or benzyl bromide gave a mixture of products of which one appeared to be VI. Although V has been reported as easily prepared by this route,⁽⁴⁸⁾ several attempts via the reported procedure were unsuccessful. The reaction was also performed with dpm-dioxide on the assumption that the pentacoordinated phosphorous would not be available for substitution. Spectral evidence again indicated that several products were formed, but none fit the requirements of the desired ligand. Methylation of dpm was pursued under the presumption that less complex mixtures could be attained. Butyllithium was reacted with dpm in the presence of tetramethylethylene diamine (TMEDA) to form the dpm anion. Iodomethane consistently produced the phosphonium salt (VII). The ¹H-nmr spectrum is presented in Figure 7. However, if trimethylchlorosilane or dimethylallylchlorosilane were used in place of iodomethane the respective mono adducts were formed.

The desired ligand (VIII) was finally obtained by reacting Ph₂PH with methyllithium in benzene to form LiPPh₂ followed by addition of 1,1-dichloroethane. The ligand was isolated in 80% yield. The ¹H-nmr spectrum of this product is presented in Figure 8. Of interest is a recent report that VIII had been prepared by the direct addition of iodomethane to dpm.⁽⁴⁹⁾ However, no spectral evidence was presented to support the claim. An attempt was also made to prepare dimethyl dpm by combining 2,2-dichloropropane and LiPPh₂; the product was highly pyrophoric and rapidly decomposed during isolation attempts. The silicon analog (IX) was prepared using dichlorodimethylsilane

FIGURE 7: ¹H-nmr Spectrum of the Product of Bis(diphenylphosphino)methane and Iodomethane

FIGURE 8. ^1H -nmr Spectrum of Methylbis(diphenylphosphino)methane

and LiPPh_2 . The ^1H -nmr spectrum of this product gave a triplet at 0.22 ppm with a coupling constant, $J_{\text{Me-P}}$, of 4.15 Hz. The ^{31}P -nmr gave a singlet at -51.28 ppm with respect to triphenylphosphine (4.99 ppm with respect to phosphoric acid). The isolated crystals were pyrophoric.

The use of substitutable geminal groups was attempted with benzal bromide and 1,1-dichloro-2-phenylethane. Several reactions were performed with Ph_2PLi . Although crystalline products could be isolated, none were confirmed as mono-substituted dpm.

Another route to dpm attachment was attempted which did not use the direct alkylation or gem-dihalo substitution. Rather, attachment was obtained through one of the phosphorus groups of the ligand. Brominated polystyrene was reacted with butyllithium which formed the lithiated polymer. That

derivatized polymer was combined with bis(dichlorophosphino)methane. The remaining chloro-groups of the ligand were exposed to phenyllithium. Polymer X contained 4.01% P (8.6% of the aryl groups should contain the dpm ligand). There remained a high bromine content within the polymer which indicated that neither the butyllithium nor phenyllithium reactions were complete.

Since the attachment of the phosphine groups through halogen intermediates was obviously a problem, the approach was shifted to more direct reactions on the polystyrene. Macroporous polystyrene (Amberlite XAD-2) was chloromethylated⁽⁵⁰⁾ or brominated⁽⁵¹⁾ and phosphinated with various reagents (Table 5).

TABLE 5. Phosphination of Derivatized Polystyrene Under Various Conditions

Derivative Group on Polymer	Reagents	P Content (%)	Degree of Functionality (%)
CH ₂ Cl	Li/Ph ₂ PCl	3.04	12.6
CH ₂ Cl	BuLi/Ph ₂ PH	2.80	11.5
CH ₂ Cl	Li/Me ₂ PCl	2.48	8.9
Br	BuLi/Ph ₂ PH	1.44	5.4
Br	Li/Ph ₂ PCl	1.44	5.4

The results indicate that phosphination was quite low since the chloromethylated polymer contained 16.8% Cl while the brominated polymer contained 27.6% Br.

It had been assumed that the macroporous polystyrene was only 2% cross-linked with divinylbenzene. Swelling comparisons in a variety of solvents were made with this polymer and a non-macroporous Bio-Rad SX-2 polystyrene (2% cross-linked). For instance, the macroporous resin increased volume by only 50% in benzene; whereas, the SX-2 resin swelled to over 200% in the same solvent. The manufacturing process for macroporous polystyrene requires high surface cross-linking to maintain the average pore size in those beads. This surface cross-linking apparently has hindered ligand attachment. Although both the SX-2 and XAD-2 resins gave similar bromination results, 25.5% Br and 27.6% Br respectively, the phosphination was quite illustrative. Reaction of brominated XAD-2 resin with Ph₂PLi gave a polymer containing 1.4% P and 17.2% Br, while brominated SX-2 resin under similar conditions gave 6.2% P and <0.04% Br. Corresponding results were achieved with Me₂PLi; brominated XAD-2 resin produced 0.9% P and 9.9% Br, while brominated SX-2 resin gave 6.0% P and 0.8% Br. It is of interest to note that chloromethylated SX-2 resin exposed

to Me_2PLi gave less desirable results: 3.3% P and 7.9% Cl. Thus, most of the polymer-complex reactions were performed with phosphinated resins originating from brominated SX-2 polystyrene.

Subtask D.2. Supported Complex Formation

The SX-2 resin containing diphenylphosphino ligands (6.23%P, degree of functionality = 33.8%) was swelled with tetrahydrofuran and added to $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ dissolved in THF. After two hours much of the yellow orange color of the ligand had transferred to the polymer beads. The suspension was allowed to stand for 42 hours; the pale yellow color of the solution above the beads was similar to that observed after two hours. After solvent washing and vacuum drying the polymer beads were an intense yellow orange color. The elemental analyses indicated that there was 5.61% Ru and 5.94% P present on the polymer. The Ru/P ratio was 0.94 for the polymer and 1.09 for crystalline $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. This suggests nearly a complete exchange of complex to the polymer; i.e., 11.4% of the aryl groups of the polymer contain $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$.

The SX-2 resin containing dimethylphosphine groups (5.96% P, d.f. = 23.1%) was swelled in dimethylacetamide and added to a solution of $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ in dma. The $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ solution was deep red suggesting metalation of dma similar to that noted with acetonitrile.⁽⁴³⁾

The transfer of the red color from the dma to the polymer beads was evident after 15 minutes and appeared to be complete within two hours. After two hours the beads were intense red and the solvent coloration was light yellow. The beads were washed with THF which reduced the red coloration to orange. Presumably the dma metalation was reversed. It should be noted that $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ is not soluble in THF. The elemental analyses indicated that

there was 3.67% Ir and 4.62% P present in the polymer for an Ir/P ratio of 0.79. The ratio of Ir/P is 1.55 for crystalline $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$. This exchange only accounted for 2.2% of polymer aryl group involvement with the complex.

Attachment of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ to SX-2 resin containing diphenylphosphino groups (d.f. = 33.8%) was performed in THF. A rather rapid color transfer occurred within two hours (solvent to beads). The deep yellow beads were washed and vacuum dried. Analyses of the polymer-attached complex indicated 6.1% Rh and 6.6% P for a Rh/P ratio of 0.92. The ratio of Rh/P is 1.66 for crystalline $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$. The degree of polymer-complex functionality was 7.0%.

Subtask D.3. Gas Sorption by Complex

The macroporous polystyrene had exhibited a further unexpected result. The void volumes of a small sample tube packed with Amberlite XAD-2 (macroporous) resin were quite similar whether determined with He, H_2 , Ar, CO, or N_2 . However, the void volume was consistently three times larger when determined with CO_2 . Quite similar values were obtained with brominated macroporous resin and polymer-attached diphenylphosphine as well as SX-2 resin (see Table 6). This suggests that a very specific and rapid adsorption of CO_2 has occurred on the macroporous polystyrene. The CO_2 was readily removed within

TABLE 6. CO_2 Adsorption by Polystyrene^(a)

Polymer Type	N_2 Void Volume (mL)	CO_2 Uptake (mL)	CO_2 Adsorption (mL/g polymer)
XAD-2	1.22	3.15	4.49
XAD-2 Br	1.13	3.23	3.48
XAD-2 PPh_2	1.18	3.24	4.08
20% X-linked (macroporous)	1.04	2.83	3.47
Styron (ground)	0.82	1.51	1.16
Biorad SX-2	1.22	1.58	1.88

(a) Empty volume of the sample holder was 1.33 mL.

seven minutes under vacuum (a normal pump-down cycle). If CO_2 does adsorb to polystyrene, the adsorption is quite weak as illustrated by the ease of its removal. The volume of CO_2 adsorbed by polystyrene was always larger than the empty volume of the sample tube. It was interesting that 20% cross-linked polystyrene (Aldrich Chemical) also adsorbed a significant amount of CO_2 . Uncross-linked polystyrene (Styron) was ground to increase the surface area. It too adsorbed more CO_2 than any of the other gases. Thus, there seemed to be a relationship between the surface area of the polystyrene and the amount of CO_2 adsorbed; the surface area of the XAD-2 resin was $300 \text{ m}^2/\text{g}$.

The CO_2 uptake by SX-2 polymer-attached $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ was performed in the absence of solvent. However, no CO_2 uptake of consequence was noted after normalizing for the polymer adsorption. There was no color change observed during CO_2 exposure. This lack of CO_2 binding was not surprising considering possible steric hindrance by the polymeric support. It may be presumed that the polymer attachment has hindered the ability of the complex to rearrange from an ionic square planar to an octahedral form.

The SX-2 polymer-attached $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ was also examined for CO_2 binding in the absence of solvent. The amount of CO_2 adsorbed beyond normalization was 0.6 mL. This indicated that 52% of the complex was involved in CO_2 binding.

In order for the SX-2 resin-attached $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ to bind hydrogen, one phosphine ligand had to be removed to free a coordination site. This is achieved readily in solution with the formation of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$ which can then bind H_2 . However, the phosphine ligand removal cannot be thermally or photolytically obtained while the complex is in solid state. The crystalline $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ was prepared to determine if H_2 could be thermally removed to obtain $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$. Unfortunately, this was achieved only at 195°C , far

above convenient temperatures (<150°C) for polystyrene use. Neither the oxygen nor carbon monoxide adducts could be reversed at lower temperatures. Consequently, the uptake of hydrogen was examined with polymer-attached $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ in dma suspension. The results are reported in Task G.

TASK E. Sorption-Desorption Cycling

Subtask E.1. Desorption Studies

The preparation of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ under laboratory lights was reported to cause cyclometalation of the dmpe ligand.⁽⁵²⁾ Infrared spectroscopy of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ prepared in this laboratory without exclusion of light confirmed the formation of the cyclometalation product (see Subtask F.3). Thus, CO_2 uptake and differential scanning calorimetry (dsc) had to be performed with $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ prepared in the dark or very subdued light.

The dsc results (Subtask F.1) indicated that solid $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ must be kept below 116°C to avoid the formation of $[\text{IrH}(\text{Me}(\text{CH}_2\text{CO}_2)\text{PC}_2\text{H}_4\text{PMe}_2)(\text{dmpe})]\text{Cl}$ by cyclometalation. This had been previously noted by Herskovitz after heating a solution or suspension of the complex to ~120°C.⁽⁷⁾ This cyclometaled product does not lose CO_2 upon further heating and its production is therefore undesirable. Since desorption of CO_2 from $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ occurs at 177°C, as indicated by our dsc results, heating alone is not an effective regeneration method. We did observe by dsc that a N_2 flow (30°C) across a sample of $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ for 14 hr at 18 mL/min removed about 12% of the CO_2 without cyclometalation. Also, evacuation of a sample of the CO_2 adduct under high vacuum for 75 minutes at room temperature resulted in 5% decarboxylation. Thus, vacuum in combination with less heat may be more effective for CO_2 desorption.

Differential scanning calorimetry was also applied to $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ and its CO_2 adduct. Those results are reported in Subtask F.1.

Manometric measurements had indicated that crystalline $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ at 78°C . A 60 mg sample of solid $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ was completely decarbonylated, as indicated by the infrared spectrum, after heating at 75°C for 18 hours. Upon exposure of this sample to 1 atm of CO at 75°C for 24 hours, 31% (1.78×10^{-3} mmole CO) of the sample was recarbonylated. Prior experience indicated that crystalline $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ (not prepared by the above method) did not bind CO at 24°C even after 3 days. Since the carbonylation of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ in solution is unusually fast because of the low activation enthalpy ($\Delta H_1 = 15 \text{ kJmol}^{-1}$), it is assumed that the lack of CO uptake in crystalline $\text{Pd}_2(\text{dpm})_2$ is due to the rigidity and steric constraints of the lattice. The loss of CO from $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ by heating apparently disrupts this lattice and allows at least some degree of carbonylation upon re-exposure to CO. A sample of the $\text{Pd}_2(\text{dpm})_2(\mu\text{-CO})\text{Cl}_2$ complex was exposed to differential scanning calorimetric conditions to determine the extent of decarbonylation by heat alone. Unfortunately, the dsc pattern indicates that three endothermic events occurred at 102° , 133° , and 180°C . The exothermic event is the melt-decomposition of the complex at about 203°C . The major endothermic peak (133°) was equivalent to 5.46 cal/mole. The only solvent that could be present within the crystals was dichloromethane (bp, 44°C). It is assumed that one of the peaks corresponds to decarbonylation. The cause of the other endotherms is inexplicable at this time.

The complexes $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$, and $\text{Ru}(\text{O})_2(\text{CO}_2)(\text{PPh}_3)_2$ were prepared by bubbling the respective gases through solutions of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. Hydrogen could be removed from $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ in solution by reducing the pressure; the solution color changed from clear/white to yellow. Gas chromatography

confirmed that H_2 was released. Hydrogen was eliminated from $Ru(H)_2(CO)_2(PPh_3)_2$ at $195^\circ C$, while CO was eliminated from $Ru(CO)_3(PPh_3)_2$ at $253^\circ C$. Decomposition of this latter complex occurred at $175^\circ C$. No endothermic event occurred prior to decomposition.

In order for polymer-attached $Ru(CO)_2(PPh_3)_3$ to be available for hydrogen binding, one PPh_3 ligand must be removed. This can normally be achieved in solution by preparing the dihydride. The product, $Ru(H)_2(CO)_2(PPh_3)_2$, needs only to have hydrogen removed to produce an active complex which should bind hydrogen. The dsc results indicated that neither the O_2 nor the CO complexes are useful for direct thermal desorption. Unfortunately, the $195^\circ C$ requirement for hydrogen desorption precludes its use for polymer-attached $Ru(CO)_2(PPh_3)_3$ since polystyrene decomposition occurs beyond $150^\circ C$. It has become apparent that a phosphine ligand may have to be available in order to desorb hydrogen, oxygen or carbon monoxide from the respective complexes. This also requires solvent to maintain the phosphine in proximity of the polymer-attached complex. Further work concerning the polymer-attached $Ru(CO)_2(PPh_3)_3$ in solvent is presented in Task G.

Subtask E.2. Sorption Studies

The bindings of CO_2 by $[Ir(dmpe)_2]Cl$ and $Rh(OH)(CO)(PPh_3)_2$, CO by $Pd_2(dpm)_2Cl_2$, and H_2 by $Ru(CO)_2(PPh_3)_3$ were all performed at approximately $25^\circ C$ and one atmosphere (Task C). Gas binding exotherms for these complexes are reported in Subtask F.1. An example of this involved the dsc results obtained at $35^\circ C$ with crystalline $[Ir(dmpe)_2]Cl$. The CO_2 uptake was complete and quantitative 21 ± 6 sec after gas introduction. This time period may be slightly shorter since N_2 was present in the gas lines prior to CO_2 introduction. Carbon dioxide uptake within 21 sec at $35^\circ C$ indicated that ambient

temperature binding can be achieved. The enthalpy of CO₂ binding ($\Delta H = -18.1 \pm 1.55 \text{ KJ mol}^{-1}$) did not appear large enough to require cooling for bench scale-up of the [Ir(dmpe)₂]Cl system.

Subtask E.3. Long Term Cycling

Polymer attachment did not provide obvious advantage for several of the complexes examined during this work. For instance, Pd₂(dpm)₂Cl₂ could not be attached to polystyrene due to steric hindrance (increase in molecular rigidity), while Ru(CO)₂(PPh₃)₃ could not release a phosphine ligand while in the solid state. There also did not appear to be an obvious advantage, other than improved cycling stability, for the attachment of Rh(OH)(CO)(PPh₃)₂ to polystyrene. Subsequently, the crystalline Rh(OH)(CO)(PPh₃)₂ was examined for cycling stability. If the crystalline complex had shown evidence of degradation or diminished CO₂ uptake within 10 sorption-desorption cycles, the polymer-attached complex would have been examined. The dsc results with the crystalline complex indicated minimal degradation with cycling (Subtask F.1). This was confirmed after 50 cycles with crystalline Rh(OH)(CO)(PPh₃)₂ monitored by manometric equipment. Uptake of CO₂ was performed at 25°C and CO₂ desorption was attained by applying 60°C and 10⁻⁴ torr to the sample for one hour. The crystalline complex (0.04 g) bound 1.7 ± 0.1 mL of CO₂ throughout the 50 cycles. It should not be assumed that similar stability can be obtained with the dissolved complex.

TASK F. Thermal Aspects of Supported Complexes

Subtask F.1. Heat of Reaction

Application of dsc could not be achieved with Pd₂(dpm)₂Cl₂ and Ru(CO)₂(PPh₃)₃ since neither complex quantitatively bound CO or H₂ while in solid state. Differential scanning calorimetry was successfully applied to

both $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ and $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ to determine the enthalpy of CO_2 binding as well as thermal stability of the complexes. Due to the rapid oxygenation of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ all transfers and handling of the complex were done under N_2 . The CO_2 binding was performed at 35°C since lower temperatures were difficult to maintain with the calorimeter. The instrument normally is used with a programmed temperature increase, but an isothermal plateau could be established above 30°C . The binding enthalpy was determined by exposing $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ to CO_2 at 18 mL/min (Figure 9) as well as by desorbing CO_2

FIGURE 9. CO_2 Binding Exotherm of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ at 35°C ; The Time Scale was Started with CO_2 Introduction

from $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ and re-subjecting the complex to a stream of CO_2 . The enthalpy of CO_2 binding from five attempts was $-18.1 \pm 1.55 \text{ KJ mol}^{-1}$.

Differential scanning calorimetry was applied to $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{OH})(\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$. The binding enthalpy was determined by maintaining the complex at 35°C and exposing it to CO_2 (see Figure 10). The initial

FIGURE 10. DSC Thermogram at 35°C of the Uptake of CO₂ by Rh(OH)(CO)(PPh₃)₂; the Time Scale was Started with CO₂ Introduction

endotherm designates the point of CO₂ substitution for N₂ as the sweep gas. The enthalpy of CO₂ binding was calculated as -68.9 KJmol⁻¹ at 35°C. The CO₂ was endothermically eliminated at 92°C (+69.4 KJmol⁻¹), see Figure 11.

Subtask F.2. Thermal Conductivity of Supported Complex

Heat capacity (C_p) is defined as the capacity of a substance to store heat between two temperature levels. The C_p is quite important in this work since it can suggest whether auxiliary cooling of the system is necessary or not during gas uptake. The results for macroporous XAD-2 and 2% cross-linked SX-2 polymer supports were determined by dsc, see Table 7.

Thermal conductivity is a consequence of the transport of kinetic energy across a temperature gradient (heat flow across a surface area per unit time, divided by the negative of the rate of change of temperature with distance in a direction perpendicular to the surface). The accepted value for solid polystyrene is 4.17×10^{-4} cal/sec-cm-°C. Since the polymer supports are highly porous, this number may not be accurate, particularly for macroporous XAD-2.

TABLE 7. Heat Capacity of Polystyrene in Relation to Temperature

<u>Temperature (°C)</u>	<u>C_p of XAD-2^P(cal/g °C)</u>	<u>C_p of SX-2^P(cal/g °C)</u>
40	0.449	0.279
50	0.513	0.305
60	0.584	0.325
70	0.666	0.304
80	0.741	0.390
90	0.745	0.422
100	0.895	0.429
110	0.966	0.474
120	1.041	—

FIGURE 11. DSC Thermogram of $\text{Rh(OH)(CO)(PPh}_3)_2\text{(CO}_2\text{)}$

Subtask F.3. Thermal Decomposition of Complexes

Desorption of CO_2 from $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ examined by dsc was highly variable since cyclometalation appeared to occur at 116° (Figure 12). A sample of this material was examined by ir after the exotherm at 116°C (19.7 kJ mol^{-1}). The ir of the product had absorbances at 2180 cm^{-1} (Ir-H) and 1640 cm^{-1} (carbonyl of a monodentate carboxyl). These absorbances previously had

FIGURE 12. Cyclometalation Exotherm of $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ at 116°C

been reported to arise from cyclometalated products.⁽⁴²⁾ The presumed pathways to these products are shown in Figure 13. The cyclometalated product of $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ can be formed either by heating $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ to 116°C or exposing the cyclometalated product of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ to CO_2 . The cyclometalated $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$ does not appear to lose CO_2 at elevated temperature; little uptake of CO_2 by the "regenerated" material was noted. Regeneration of $\text{IrCl}(\text{CO}_2)(\text{dmpe})_2$, which was prepared in the dark (not cyclometalated), desorbed CO_2 at $\sim 177^\circ\text{C}$. The endotherm of desorption was

FIGURE 13. Pathways for the Formation of Cyclometalated $\text{Ir}(\text{dmpe})_2\text{Cl}$

nearly equal to the exotherm of CO_2 binding for the initial regeneration. However, the second and third regenerations always showed cyclometalation at 116°C and were accompanied by three other endotherms in the $170\text{--}180^\circ\text{C}$ range indicating further (but uncharacterized) decomposition.

The differential scanning calorimetric recycles of Subtask F.1 had been performed by exposing $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ to CO_2 at 35°C and observing the exotherm due to gas evolution occurred; the maxima of the endotherm occurred

at 92°C. Approximately 16% of the CO₂ binding ability of Rh(OH)(CO)(PPh₃)₂ was lost after five dsc cycles when the complex was exposed to direct thermal regeneration (116°C maximum).

The yellow Rh(OH)(CO)(PPh₃)₂ yielded a brown powder if it was kept at 116°C for 1 hour under N₂. Although the brown powder had an ir pattern similar to Rh(OH)(CO)(PPh₃)₂ (CO stretch at 1942 cm⁻¹ rather than 1945 cm⁻¹), it had very low activity toward CO₂. The ir spectrum of this brown powder was quite similar to a product found after an attempt to prepare Rh(OH)(CO)(PPh₃)₂ from RhCl(CO)(PPh₃)₂. New bands in the ir spectrum were observed at 1118, 720, and 542 cm⁻¹. The brown product may be a dimer with a Rh-O-Rh structure, but this is based only upon supposition. Further work will be necessary to determine the structure of the thermally degraded Rh(OH)(CO)(PPh₃)₂.

TASK G. Sorption-Desorption Equilibria and Rate

The two subtasks have been combined in this discussion to increase coherence between rates and equilibria since both are so inter-related.

Solid state kinetics with crystalline Rh(OH)(CO)(PPh₃)₂ and gaseous CO₂

was attempted using a differential scanning calorimetric procedure which involved a Perkin Elmer DSC-2c unit with a thermal analyses data station, equipped with a TADS, DSC Kinetics Program. While this kinetics program proved to be unsuitable for our application, we were able to obtain satisfactory data regarding the extent of reaction (percent reaction) as a

function of time. From this data, the rate of CO_2 uptake could be calculated based upon the number of moles rather than the concentration of reactant as per equation (6). Two experimental difficulties were recognized during this

$$\text{rate} = k_1[\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2] \quad (6)$$

procedure. The first involved changing the gas from N_2 to CO_2 immediately before the kinetics run was initiated. The difference of the specific heats of N_2 and CO_2 was sensed by the instrument and an endotherm acknowledging this difference was imposed over the exotherm of the CO_2 -complex reaction. The specific heat difference was complicated by the gas stream splitter which had uneven gas restrictors necessary for a backflow mechanism. This endotherm was partially eliminated by using a scanning auto baseline. For this reason data taken at the very start of the reaction (10s after the introduction of CO_2) were not included in the kinetics analysis. Plots of $\ln A$ (A =moles of unreacted starting material) versus time were linear. Thus the uptake of CO_2 follows pseudo-first order behavior as expected since measurements were made with a continuous flow of CO_2 over the sample.

The rates of reaction are strongly dependent upon the physical condition of the samples. An unground crystalline sample showed virtually no CO_2 uptake while the same sample ground to a fine powder took up CO_2 with a rate of $8.33 \times 10^{-3} \text{ s}^{-1}$. The same material when dissolved in CH_2Cl_2 followed by rapid solvent removal gave a sample of low crystallinity. This sample reacted with CO_2 with a rate of $2.13 \times 10^{-2} \text{ s}^{-1}$ at 37°C . While both samples reacted to the same extent with CO_2 , as determined by the measured H values, the essentially noncrystalline sample reacted 2.6 times faster than the finely ground crystalline sample. The reduced rates for the crystalline samples may indicate diffusion and lattice effects in these samples.

Exposure of the orange solutions of $\text{Pd}_2(\text{dpm})_2\text{X}_2$ to CO rapidly resulted in a darkening of the color and a red-shift of the absorption maxima (Figure 14). The carbonyl adduct, which has been isolated previously and well characterized,⁽⁵³⁾ results from a direct insertion of CO into the Pd-Pd bond. Such a complex is described as a molecular A-frame.⁽⁵⁴⁾ The binding of CO was confirmed by measurement at 24°C as 1:1 stoichiometry with $\text{Pd}_2(\text{dpm})_2\text{X}_2$ (Task C). Decarbonylation was accomplished by purging the solutions with Ar or by exposure to vacuum.

The rate law for equation (7) is a standard one given in equation (8), and an integrated form is given in equation (9).⁽⁵⁵⁾

$$\frac{-d[\text{XI}]}{dt} = \frac{d[\text{XII}]}{dt} = k_1[\text{XI}][\text{CO}] - k_{-1}[\text{XII}] \quad (8)$$

$$\ln \left[\frac{A_0 - A_\infty}{A_t - A_\infty} \right] = (k_1[\text{CO}] + k_{-1})t \quad (9)$$

Under the stopped-flow conditions the [CO] is effectively constant and the observed first-order rate constant k_{obs} equals $(k_1' + k_{-1})$ where $k_1' = k_1[\text{CO}]$. The k_{obs} values at a fixed [CO] were independent of the initial $[\text{Pd}_2]$, confirming the first-order dependence on $[\text{Pd}_2]$. Plots of k_{obs} vs. [CO] are linear (Figures 15 and 16), thus showing the first-order dependence on [CO], the slope of the line yielding k_1 ; data at lower temperatures (4–24°C) for the X = Cl, Br, and NCO systems are typified by those in Figure 15. That

FIGURE 14. Determination of Equilibrium Constants by Varying Temperature,
Where A is 100% $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and F is 100% $\text{Pd}_2(\text{dpm})_2(\text{CO})\text{Cl}_2$

FIGURE 15. Plots of k_{obs} vs. $[\text{CO}]$ (Given as Partial Pressure for Reaction of CO with $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ ($\blacksquare$, 24°C , $\bullet$, 16°C , $\blacktriangle$, 4°C) and with $\text{Pd}_2(\text{dpm})_2(\text{NCO})_2$ ($\circ$, 24°C , Δ , 16°C , $\square$, 10°C) in dma

FIGURE 16. Plots of k_{obs} vs. $[\text{CO}]$ (Given as Partial Pressure for Reaction of CO with $\text{Pd}_2(\text{dpm})_2\text{I}_2$ in dma at Several Temperatures

the plots go through the origin implies that k_{-1} (the intercept) is negligible on the scale used for k_{obs} . For the iodide system (Figure 16) and the bromide system at higher temperatures (45–55°C), k_{-1} may be evaluated at least approximately as a measurable intercept, as well as k_1 ; thus the equilibrium constant K is determined indirectly as the k_1/k_{-1} ratio. All the kinetic and thermodynamic parameters listed in Table 8 for the iodide system were evaluated from the stopped-flow data alone; excellent Arrhenius and Van't Hoff plots were obtained. The stopped-flow k_1 data for the chloro, bromo, and cyanato systems also gave excellent Arrhenius plots.

Figure 15 shows a typical equilibrium plot according to eq 9, and the thermodynamic parameters listed for the $X = \text{Cl}, \text{Br}, \text{and NCO}$ systems (Table 8) were determined again from excellent Van't Hoff plots. For the bromo system, values for K at lower temperatures, determined by using eq 9 and electronic spectral data, were very compatible with values measured at the higher temperature by the stopped-flow k_1/k_{-1} data (Figure 17). The k_{-1} values for these three systems could be estimated from the ratio of k_1/K or measured directly (see Experimental Section). The agreement between such k_{-1} values for the carbonyl cyanato complex, which gave the lowest "off-rate", was excellent, but as the decarbonylation rates increased (with $t_{1/2} \leq 25\text{s}$ at 24°C as judged from the k_1/K values), the discrepancy between the sets of k_{-1} values became greater. The technique used for decarbonylation (evacuation/shaking) was clearly not efficient enough to remove the CO, or, in other words, there is at least partial diffusion control of CO loss from the solution. The k_{-1} values calculated from k_1/K are considered correct, and the $\Delta H_{-1}^\ddagger$ values listed in Table 8 were thus estimated from $(-\Delta H + \Delta H_1^\ddagger)$ for these exothermic reactions. For the bromo and iodo systems, $\Delta H_{-1}^\ddagger$ values were also determined directly from Arrhenius plots for the intercept k_{-1} values estimated from the stopped-flow data (see Figure 16).

FIGURE 17. Dependence of Equilibrium Constant on Temperature for Reaction of CO with $\text{Pd}_2(\text{dpm})_2\text{Br}_2$: ●, Data from Static Method (Equation 13) at 24-40°C; ■, Data from Stopped-Flow at 44-55°C

TABLE 8. Thermodynamic and Kinetic Data for the Reaction of $\text{Pd}_2(\text{dpm})_2\text{X}_2$ with CO in dma Solution^a

X	$10^{-4}K,^b$ M^{-1}	$P_{1/2},$ torr	$10^{-3}k_1,$ $\text{M}^{-1} \text{ s}^{-1}$	$k_{-1},^c$ s^{-1}	$\Delta H,^d$ kJ mol^{-1}	$\Delta S,^d$ J mol^{-1} K^{-1}	$\Delta H_1^+,^e$ kJ mol^{-1}	$\Delta S_1^+,^e$ J mol^{-1} K^{-1}	$\Delta H_{-1}^+,^f$ kJ mol^{-1}	$\Delta S_{-1}^+,^g$ J mol^{-1} K^{-1}
NCO	37	0.47	3.15	8.5×10^{-3}	-48	-55	26	-92	74	-38
Cl	24	0.71	6.6	2.7×10^{-2}	-57	-85	15	-120	72	-34
Br	3.5	4.9	6.0	0.17	-61	-113	15	-121	76	-8
I	0.13	130	4.2	3.2	-48	-100	23	-100	71	0

^a Equilibrium and rate constants are values at 24°C. ^b Measured by static method, except for X = I when stopped-flow kinetic data were used (Figure 16). ^c Estimated from k_1/K ; directly measured values at 24°C were (s^{-1}) 9.0×10^{-3} (NCO), 1.4×10^{-2} (Cl), and 3.8×10^{-2} (Br). ^d Values of ΔH and ΔS were obtained from a least-squares analysis of the data points; errors are estimated to be $\pm 6 \text{ kJ mol}^{-1}$ and $\pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$. ^e Arrhenius $\Delta E^\ddagger$ measured from stopped-flow data (4–24°C); $\Delta H^\ddagger = \Delta E^\ddagger - RT$, $T = 297^\circ\text{K}$; errors $\pm 3 \text{ kJ mol}^{-1}$ ($\Delta H_1^\ddagger$) and $\pm 10 \text{ J Mol}^{-1} \text{ K}^{-1}$ ($\Delta S_1^\ddagger$). ^f Estimated from $-\Delta H + \Delta H_1$, except for the direct measurement for the iodo system (Figure 16); an experimental value from limited stopped-flow data for the bromo system (cf. Figure 16) was $\sim 60 \text{ kJ mol}^{-1}$. ^g Estimated from $\Delta S_1^\ddagger - \Delta S$.

Some stopped-flow experiments for the carbonylation of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ at 150 torr and 24°C (Figure 15) were modified in that other gases at a partial pressure of 280 torr were added also: the k_{obs} values in the presence of Ar, H_2 , C_2H_2 , C_2H_4 , CO_2 , O_2 , or air were $5.4 \pm 0.1 \text{ s}^{-1}$, compared to a value of 5.8 s^{-1} with just pure CO. At 100 torr of CO ($k_{\text{obs}} = 4.0 \text{ s}^{-1}$), addition of 280 torr of Ar, 280 torr of C_2H_4 , or a 280 torr 1:1 mixture of Ar/ C_2H_4 , resulted in a measured k_{obs} value of 3.2 s^{-1} in each case. The conclusion is that the system shows very high selectivity for CO binding in the presence of these gases. The somewhat lower rate constants in the presence of other gases is almost certainly due to a somewhat lower solubility of the CO.⁽⁵⁶⁾ There was, of course, no reactivity of the chloro dimer toward any of the above gases alone at 760 torr. The $\text{Pd}_2(\text{dpm})_2\text{X}_2$ complexes are, however, known to bind SO_2 reversibly by insertion into the Pd-Pd bond⁽¹⁶⁾ and to react with activated acetylenes to yield cis dimetalated olefinic species also having no metal-metal bond.⁽¹⁷⁾

Addition of chloride ($\text{Cl}^-:\text{Pd}_2 = 40$) had no effect on the k_1 value for the $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ carbonylation, which is consistent with the one-stage concerted process shown in equation 7 with no involvement, for example, of halide dissociation. Addition of dpm to a solution of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ caused decomposition to $\text{Pd}(\text{dpm})\text{Cl}_2$ (detected by ^1H and ^{31}P NMR²⁷) and other unidentified complexes, and so any possible kinetic/mechanistic role for the diphosphine ligand (e.g., dissociation at one end) remained undetectable; monodentate dpm complexes are known.⁽⁵⁷⁾ It seems unnecessary to invoke such pathways, however, and a simple transition state such as XIII is strongly favored.

XIII

The kinetic and thermodynamic enthalpy and entropy parameters, together with selected rate and equilibrium constants, are given in Table 8. The $P_{1/2}$ values are the pressures required for 50% carbonylation and are simply the inverse of K expressed as torr^{-1} . Since the ratio of carbonylated species to starting complex present ($[\text{XII}]:[\text{XI}]$) is given by $(\text{CO partial pressure}/P_{1/2})$, it is seen that carbonylation is essentially complete at relatively low pressures for the $\text{X} = \text{NCO}$ and Cl systems, the XII:XI ratio being 50 at about 23 and 36 torr, respectively. The corresponding ratio is reached at about 245 torr for the bromo dimer, while for the iodo complex the ratio is only about 5.75:1 even at 1 atm (and 11.5:1 at 2 atm). The "on-rates" (k_1) for all four systems are fast and within a factor of about 2; even at the lowest temperature studied (4°C) with about 50 torr of CO, half-lives are of the order of a second. The carbonylation are fast because of the quite low activation enthalpies ($\Delta H_1^\ddagger$) required; indeed, the $\Delta H_1^\ddagger$ values are among the lowest reported for addition of gases to metal centers and are similar, for example, to those measured for binding of CO (and O_2) to myoglobin and protein-free models.^(58,59) The myoglobin and model reactions are even faster, however, ($k_1 \approx 10^5\text{--}10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C) because the $\Delta S_1^\ddagger$ values are considerably less negative than those measured for the Pd dimers (Table 8); the steric requirements for fixing the gas between two metal centers in a transition state such as XIII must be severe.

The equilibrium constants decrease in the order $X = \text{NCO} > \text{Cl} > \text{Br} > \text{I}$, in complete agreement with a qualitative trend noted by Balch and co-workers;^(15,60) the order is clearly governed by the off-rates (k_{-1}) that decrease in the reverse order ($\text{I} > \text{Br} > \text{Cl} > \text{NCO}$). Assuming that the structure of the carbonyls are analogous to that of $\text{Pd}_2(\text{dam})_2(\mu\text{-CO})\text{Cl}_2$,⁽⁶¹⁾ the X ligands are trans to the bridging carbonyl, and the order corresponds to their trans effects.⁽⁶²⁾ Balch and co-workers surmised that the higher trans effect would give a weaker metal-metal bond in complexes such as XI but also a weaker metal-carbonyl bond in XII and that the latter effect must be predominate.^(15,60) Our data show that there is no correlation of the CO lability with the $\nu(\text{CO})$ stretch of the complexes (Cl , 1705, Br , 1712, I , 1713, NCO , 1720 cm^{-1}),^(15,60) but this is not unusual.⁽¹⁹⁾ Indeed, the variation in k_{-1} values, which decrease by a factor of 400 on going from the iodo to cyanato system, is generally reflected largely by differences in $\Delta S_{-1}^\ddagger$. The transition state must be something akin to XIII with approximate trigonal-bipyramidal geometry at each Pd; in the reverse reaction continued formation of the metal-metal bond eventually forces out the CO to leave essentially square-planar coordination at each Pd.⁽⁶¹⁾ The relatively small values of ΔS_{-1} are reasonable for a uni-molecular reaction such as this requiring little rearrangement to form the transition state. The forward reaction, involving fixing the free (solvated) gas molecule at metal centers, shows the expected unfavorable entropy of reaction as well as entropy of activation. The findings here on relative ΔS , $\Delta S^\ddagger$, and $\Delta S_{-1}^\ddagger$ values appear to be quite general for reversible binding of CO^(58,63) (to give a terminal M-CO species) and also for reversible binding of H_2 ⁽⁶⁴⁾ and O_2 .^(58,59) To the best of our knowledge, all solution reactions involving simple coordinative addition of a gas molecule give substantially negative ΔS values, and the property of the binding results from

the exothermicity of the process. This is seen again in Table 8. All the experimental data are consistent with the formulation of the product as shown, XII; there is not dissociation of halide to give an ionic product that has been observed with corresponding platinum systems in methanol solution.⁽⁶⁵⁾

The ruthenium complex, $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, was examined for its ability to bind CO , H_2 , and O_2 . The yellow complex turns colorless in solution when exposed to each of these gases. The ir spectra of $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$,⁽⁶⁶⁾ $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$,⁽⁶⁷⁾ and $\text{Ru}(\text{O}_2)(\text{CO})_2(\text{PPh}_3)_2$ ⁽⁶⁸⁾ corresponded to previous reports. The uv spectrum of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ had no distinct absorbance bands. However, there was a definite elimination of a broad sloping band in the 389 nm region when H_2 , O_2 , or CO was added to the dissolved complex. This band was utilized for the stopped flow measurements.

The reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with H_2 can be expressed as:

The overall observed rate can be shown as:

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{Ru}(\text{CO})_2(\text{PPh}_3)_3] [\text{H}_2]}{k_{-1} [\text{PPh}_3] + k_2 [\text{H}_2]} \quad (12)$$

By holding the H_2 concentration constant and varying the triphenylphosphine concentration, first order kinetics were achieved with the following relationships:

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{H}_2]}{k_{-1} [\text{PPh}_3] + k_2 [\text{H}_2]}$$

$$k_{\text{obs}}^{-1} = \frac{k_{-1}[\text{PPh}_3]}{k_1 k_2 [\text{H}_2]} + \frac{1}{k_1}$$

These kinetic relationships, under stopped flow conditions at 24°C in dma, were utilized by measuring k_{obs} while varying the concentration of PPh_3 . By plotting the information in Table 9 as k_{obs} vs. $[\text{PPh}_3]$ an intercept of the ordinate determined k_1 as 0.12s^{-1} and $k_1/k_2 = 1.57 \times 10^{-2}$ for hydrogen binding. This indicates that the $k_2[\text{H}_2]$ term of equation (11) is quite larger than $k_{-1}[\text{PPh}_3]$. Thus, the rate determining step of equations (10) and (11) involves the loss of phosphine governed by k_1 . This was confirmed for O_2 and CO bindings (see Table 10). Although the overall reaction rates for hydrogenation, carbonylation, and oxygenation are very similar (governed by the common k_1 step), selectivity can still result from differences in k_2 . The kinetics of the reactions of O_2 and CO were examined in a manner similar to that of H_2 with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. The results are presented in Table 10.

TABLE 9. Values for Forward and Reverse Observed Rates with $2.67 \times 10^{-4} \text{ M}$ $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ at 24° in Dimethylacetamide and $1.78 \times 10^{-3} \text{ M}$ Hydrogen (1 atm)

$[\text{PPh}_3] \text{ (M)}$	$k_{\text{obs}} (\text{s}^{-1})$	$k_{\text{obs}} (\text{s}^{-1})$
0	0.1248	8.01
5.58×10^{-3}	0.1158	8.64
1.95×10^{-2}	0.0970	10.31
2.49×10^{-2}	0.0877	11.40
3.32×10^{-2}	0.0787	12.71
4.14×10^{-2}	0.0734	13.62
4.77×10^{-2}	0.0689	14.52

TABLE 10. Kinetic Values for the Binding of CO, H₂ and O₂ to Ru(CO)₂(PPh₃)₃ in Dimethylacetamide at 24°C

Addend	$k_1(\text{s}^{-1})$	k_{-1}/k_2
H ₂	0.12	1.57×10^{-2}
CO	0.12	4.30×10^{-2}
O ₂	0.12	1.09×10^{-1}

Comparison of the k_{-1}/k_2 -values for carbonylation, hydrogenation, and oxygenation indicates that H₂ can be bound twice as fast as CO and five times faster than O₂. Consequently, there should be considerable selectivity for H₂ with Ru(CO)₂(PPh₃)₃ in gas mixtures containing CO and O₂. It should also be noted that O₂ can be displaced from Ru(O₂)(CO)₂(PPh₃)₂ with H₂.⁽²⁷⁾

Polymer-attached Ru(CO)₂(PPh₃)₃ containing 5.4% Ru was examined in dimethylacetamide suspension for H₂ uptake. Equation 12 was modified assuming that low conversion would occur; the term $k_{-1}[\text{PPh}_3]$ was negated since [PPh₃] would be very low. This basically left a first order rate expression. From a plot of $\ln ([\text{Ru}_0]/[\text{Ru}])$ vs. time the k_1 was determined as $6.9 \times 10^{-3} \text{ min}^{-1}$. This was exceedingly slow compared to the crystalline complex dissolved in dma where $k_1 = 0.12 \text{ sec}^{-1}$. This would suggest that k_{-1} could be significant for the supported complex, especially at high conversion. It should be noted that the type of phosphine release was not established during hydrogenation; i.e., if the polymer-PPh₂ was released rather than PPh₃, a free complex would be involved in gas coordination.

The Ru(CO)₂(Ph₂Ppy)₃ complex was investigated for its ability to bind CO, O₂, and H₂. It was assumed that the reaction was similar to that discussed for Ru(CO)₂(PPh₃)₃. The results of the solution kinetics for CO binding are presented in Table 11, and Figures 18 and 19. The intercept of Figure 18 is

FIGURE 18. Plot of k_{obs}^{-1} vs. Phosphine Concentration in dma with 1 atm CO at 26°C

FIGURE 19. Determination of k_{obs} with $1.62 \times 10^{-4} \text{ M Ru(CO)}_2(\text{Ph}_2\text{Ppy})_3$ and 1 atm CO in Dimethylacetamide with $[\text{Ph}_2\text{Ppy}]$ as A, 0; B, $8.5 \times 10^{-3} \text{ M}$; C, $1.23 \times 10^{-2} \text{ M}$; and D, $1.76 \times 10^{-2} \text{ M}$

$1/k_1 = 149$ while the slope = 5.32×10^3 (equivalent to $k_{-1}/k_1k_2 [\text{CO}]$). For CO binding the value of $k_{-1}/k_2 = 1.44$ and $k_1 = 6.70 \times 10^{-3} \text{ s}^{-1}$.

The results of the oxygenation of $\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$ are presented in Table 12. The formation of $\text{Ru}(\text{O}_2)(\text{CO})_2(\text{Ph}_2\text{Ppy})_2$ was accompanied by oxidation of the phosphine ligand to phosphine oxide, detected by ^{31}P -nmr. There appeared to be two competing simultaneous reactions occurring during oxygenation; i.e., oxygenation and phosphine oxidation. No further work concerning oxygenation was undertaken.

The results of the hydrogenation of $\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$ are presented in Table 13. Additional amounts of the phosphine ligand did not seem to affect the observed rate constant. Although this should be a second order reaction it had the characteristics of a pseudo first order type. The hydrogenation possibly may proceed through a different mechanism than that for $\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3 + \text{CO}$: i.e., the rate determining step may be different than that of carbonylation and oxygenation. Further, the k_{-1}/k_2 may be extremely small (k_2 very large) which could suggest that hydrogenation is very fast. If this second possibility is correct, then the hydrogenation reaction could be much faster than CO or O_2 addition to $\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$.

TABLE 11. Values for Forward and Reverse Observed Rate Constants with $1.62 \times 10^{-4} \text{ M}$ $\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$ at 26°C in Dimethylacetamide and 1 atmosphere of CO

$[\text{Ph}_2\text{Ppy}] \text{ (M)}$	$k_{\text{obs}} (\text{s}^{-1} \times 10^{-3})$	$k_{\text{obs}} (\text{s}^{-1})$
0	6.46	154
8.50×10^{-3}	5.50	182
1.23×10^{-2}	4.60	217
1.76×10^{-2}	4.05	246

TABLE 12. Values for $^{44}\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$ at 26°C in Dimethylacetamide and 1 atmosphere of O_2

$[\text{Ph}_2\text{Ppy}] (\text{M} \times 10^{-3})$	$k_{\text{obs}} (\text{s}^{-1} \times 10^{-3})$
0	7.01
7.28	3.57
11.9	3.98
16.6	4.07
24.6	4.04

TABLE 13. Values for $^{44}\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$ at 26°C in Dimethylacetamide and 1 Atmosphere of H_2

$[\text{Ph}_2\text{Ppy}] (\text{M})$	$k_{\text{obs}} (\text{s}^{-1} \times 10^{-3})$
0	4.18
8.79×10^{-3}	4.48
1.56×10^{-2}	3.87
1.88×10^{-2}	4.45
2.24×10^{-2}	4.41
3.63×10^{-2}	4.15

Conceptual Analyses and Preliminary Economics

The purification of gases is often one of the most difficult and energy intensive separation processes encountered. For the separation of components from coal gasification streams several promising procedures have been recently investigated including pressure swing adsorption and immobilized liquid membranes. However, most recent separation techniques have been directed toward acid gas removal. These include the use of alkanolamine solutions, carbonate absorbents, physical solvents, and membrane separation.

Another procedure, utilizing coordination complexes, has been examined at Pacific Northwest Laboratory and reported herein. Of the three promising complexes, $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$, $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, the latter seems to be particularly applicable to coal gasification streams. This is due to the ability of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ to bind both H_2 and CO , but with a 2:1 preference for H_2 . The kinetics for CO and H_2 binding is also favorable, fast forward rates and easily achieved reverse rates. At this time the effect of H_2S on $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ has not been determined. Thus, desulfurization costs have been considered in the scheme discussed below.

Due to the favorable results achieved with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ two potential processes have been examined which utilize the advantages of the complex. The more direct of the two processes involves solvent-dissolved complexes while the latter process, discussed in Future Directions, uses this complex and the others for facilitated transport within liquid swollen membranes.

Use of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ for the recovery of CO and H_2 from a low-Btu gas is expected to offer an economic advantage for production of synthesis gas. With such a system air gasification could be substituted for the generation of synthesis gas in place of oxygen gasification as is now used. Thus, synthesis gas could be generated without the expense of an oxygen plant. Not only would the recovery system reduce capital outlay, it would also improve design flexibility relative to plant scale. Presently, plant concepts for synthesis gas generation are extremely large, on the order of 20,000 tons of coal per day, to maximize the economics of scale (including the cost of an oxygen plant).

The recovery of H_2 and CO from low Btu gas is expected to benefit production of synthesis gas for fertilizer and methanol manufacture. In these systems, CH_4 is an inert gas in the synthesis process.

Information on the relative cost of producing a low-Btu gas and an intermediate-Btu gas is not readily available. For the comparison shown in this analysis, the costs of a Westinghouse gasification system for use in molten carbonate fuel cell power plants⁽⁶⁹⁾ were adapted to the proposed application. Costs presented for air and oxygen operation of the Westinghouse gasifier were also used.⁽⁶⁹⁾

A schematic flowsheet of the proposed system is shown in Figure 20. An oxygen system for generation of synthesis gas would require sulfur polishing to remove trace amounts of sulfur from the synthesis gas; no such system is needed in the proposed concept. Also, it may be possible to avoid shifting of the bulk of the synthesis gas by staged operation of the elution column. That is, a H₂-rich stream and a CO-rich stream may be recoverable. The CO-rich stream would then be shifted to produce additional H₂, if needed. No cost for a shift reactor was developed for this estimate. Cost of the shift reactor for an oxygen system will be higher than for the proposed system since a larger fraction of the gases must be shifted in the oxygen system.

The waste gases from the absorber may contain sufficient hydrocarbons to require treatment for recovery of energy values. We assume operation of the gasifier to minimize generation of hydrocarbons.

The cleaned fuel gas from the air-blown Westinghouse gasifier was reported as 2% CH₄, 13.9% H₂, 26.3% CO, 3.8% CO₂, and 54% N₂ (ref. 69, p. 357). Some H₂ and CO may also be lost with the N₂ stream. We expect recovery to be about equivalent to the efficiency of a conventional system.

Relevant installed costs for the Westinghouse gasifiers for air and oxygen operation are shown in the following table. Coal throughput is about 2000 tons/day. It should be noted that these are capital costs for plants to generate an intermediate-Btu gas for the oxygen-blown case and a mixture of CO

FIGURE 20. CO/H₂ Recovery from Low-Btu Gas for Synthesis Gas Production

and H_2 for the air-blown case. Cost of the absorption system containing $Ru(CO)_2(PPh_3)_3$ for the air-blown system was estimated to be equivalent to the sulfur polishing cost.⁽⁶⁹⁾ The costs in Table 14 show a 16% savings in the installed cost for the proposed system relative to oxygen-blown generation of an intermediate-Btu gas.

TABLE 14. Installed Costs for Generation of Synthesis Gas

	\$MM (1982)	
	<u>W/O₂</u>	<u>W/Air</u>
Coal Receiving and Preparation	18.1	20.0
Coal Gasification, Heat Recovery and Bulk Gas Desulfurization	56.5	61.0
Sulfur Polishing, or H_2/CO Recovery by $Ru(CO)_2(PPh_3)_3$	4.4	6.2
Air Compression, or Air Separation and Oxygen Compression	45.8	14.8
BFW and Condensate Treatment	1.6	1.6
General Facility	<u>25.0</u>	<u>23.1</u>
Total	151.4	126.7

Relative operating costs were not estimated for this preliminary analysis. It was assumed that the absorption columns can be operated with a minimal loss of material. The petroleum refining industry routinely handles large quantities of expensive Pt catalyst without significant losses. The depleted Ru should be recoverable. Operating costs for air-blown operation with H_2/CO recovery should not be significantly higher than oxygen-blown operation. Further, power costs will be less for the proposed system.

CONCLUSIONS

Several coordination complexes were examined for their ability to reversibly bind CO_2 , CO, or H_2 . Three of these complexes appeared worthy of further consideration. Carbon dioxide at 1 atm was rapidly bound by crystalline $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ and could be desorbed by mild heat and vacuum. The Rh-complex was subjected to 50 sorption-desorption cycles without loss of activity. The series $\text{Pd}_2(\text{dpm})_2\text{X}_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or NCO}$, was found to be of considerable interest for CO coordination. Absorption of CO was rapid, and the kinetics, which appeared to be quite favorable, were not influenced by the presence of CO_2 , N_2 , O_2 , H_2 , ethylene or acetylene. Thus, $\text{Pd}_2(\text{dpm})_2\text{X}_2$ showed exceptional specificity for CO. Hydrogen and carbon monoxide both formed adducts with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, the complex releasing a phosphine ligand prior to gas coordination. Hydrogen was bound twice as fast as CO and seven times faster than O_2 ; there is definite selectivity for H_2 with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$.

A major thrust of this research was to attach promising complexes to polymeric supports. Unfortunately, attachment of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ to polystyrene eliminated CO uptake. This was due to steric hindrance at the connecting site of the dpm ligand and to the inability of crystalline $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ to bind CO at 25°C . The requirement that a phosphine ligand must be released by $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ prior to H_2 or CO binding could not be achieved under crystalline or supported conditions. The H_2 binding was markedly slowed with polymer-attached $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ in dma suspension. However, the CO_2 binding activity of polymer-attached $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ compared well to its crystalline form. Crystalline $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ had excellent stability over 50 sorption-desorption cycles. There could be an advantage for this polymer-attached complex due to the heat dissipation of the polystyrene support; 49 KJ mol^{-1} was emitted during CO_2 binding.

In general, the crystalline or solvent dissolved complexes chosen in the latter phase of this research performed extremely well without polymeric support. At this time there does not appear to be an advantage for polymeric support when considering $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, or $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$. We would suggest they be considered in solution or crystalline state for gas separation. These complexes appear to be superb candidates as transport agents for facilitated-transport, membrane systems.

FUTURE DIRECTIONS

Due to the favorable results gained with $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$, $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, and $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ two potential processes had been considered which utilize their gas separation advantages. One process, using $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ in solution, was discussed in Conceptual Analyses and Preliminary Economics. The other process concerns gas separations with facilitated-transport membranes.

Membrane separations are inherently low energy processes, but have failed in many applications because the flux and selectivity of conventional polymeric membranes have been too low. An example of the selectivity problem is shown with Prism separators produced by Monsanto; they cannot separate H_2 from CO_2 due to the high diffusivity of H_2 and the high membrane solubility of CO_2 .

A considerable improvement in performance results from using an immobilized liquid (sorbed within a polymer matrix) as the membrane. This system enhances solubilities and diffusivities of permeating gases since the separations are occurring in a liquid phase rather than a polymer. A more significant feature of immobilized liquid membranes is the ability to further enhance permeability and selectivity, often by several orders of magnitude, through facilitated transport. This involves a nonvolatile carrier in the polymer supported liquid which reversibly reacts with the permeating gas. The reactive carrier shuttles back and forth between opposite sides of the membrane carrying the desired gas with it in one direction. This process is very common in biological systems.

The coordination complexes have already shown their potential for separating specific gases from mixed gas streams. Thus, these complexes are excellent candidates for the separation of CO_2 , CO and H_2 . The advantage of facilitated transport with coordination complexes is the dramatic increase in

selectivity due to the complexes. However, this can be combined with the selectivity of specific solvents. For instance, N-methylpyrrolidone has been used in the Purisol® process to separate acid gases. Moreover, the solubility of H_2S is higher than CO_2 in N-methylpyrrolidone which enhances selectivity. It should be emphasized that the use of specific coordination complexes within facilitated membranes should provide tremendous permeability and selectivity increases which are unattainable by the polymers or sorbed solvents alone.

Two potential areas have been noted during the progress of this research with coordination catalysts. The first involved the solubility of $Pd_2(Ppy_3)_2Cl_2$ in water. The complex and its bromo-analog were both soluble and appeared to react with water. Yet, they still absorbed CO. This suggested that these complexes may catalyze the water-gas shift reaction at 25° . Such a catalyst under homogeneous conditions may not seem comparable to heterogeneous shift systems which operate at or near gasifier temperatures. However, these coordination complexes could lead to improved shift catalysts. Further, it might be assumed that the rate of homogeneous shift catalysis may increase with increasing temperature, at least to the decomposition point of the complex.

The second lead involved the ability of macroporous polystyrene to selectively absorb CO_2 . Up to three times the anticipated void volume of CO_2 was absorbed by polystyrene. Only standard void volumes were obtained with N_2 , He, CO, and H_2 . The CO_2 was readily removed from the polystyrene under a slight vacuum. These observations are significant since an inexpensive adsorbent material might be developed which has definite selectivity toward CO_2 .

Listed below are several processes directly or indirectly related to coal gasification which could benefit by enhanced separations with coordination complexes.

- Fuel cell feed streams could be improved by gas separation with complexes. The acid fuel cells, phosphoric acid for instance, can utilize only H_2 and require shift conversion of CO to H_2 . The $Pd_2(dpm)_2Cl_2$ complex can remove CO even in concentrations as low as 0.5 ppm. Thus, CO removal could be performed with the feed stream prior to fuel cell use. The molten carbonate fuel cell prefers a hydrogen rich feed. Partial removal of CO from the feed could improve efficiency, assuming shift reaction limitation. It should be noted that although molten carbonate cells operate at about 1200°F, feed stream cleanup might be economically performed at considerably lower temperatures where coordination complexes could be used.
- The Exxon catalytic gasification process currently assumes a cryogenic process for methane separation. The complexes (all three in series, perhaps) could be used to remove pure streams of CO_2 , CO, and H_2 so that a pipeline quality gas (CH_4) remained.
- The separation of CO from gasification streams can be used to adjust CO/ H_2 ratios for the shift reaction. However, purified streams of CO could be used in the reverse Boudouard process or the BEACON process. Further, CO from gasification streams could be used in processes such as that developed by Union Carbide and the Ube Industries for the manufacture of ethylene glycol. The largest current chemical use of CO is for phosgene production. Gas separation with complexes could be of great use for by-product gas recycle. The COSORB process (Tenneco), currently used for CO

separations, is drastically inhibited by the presence of water and methanol. A process based upon $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ should not encounter similar inhibition.

- There are currently no processes which can remove H_2 from gasification streams. The combined use of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ may allow H_2 to be obtained for chemical manufacture or gas upgrading.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Brian James and Dr. Chung-Li Lee of the University of British Columbia for their considerable effort with the investigation of the Pd and Ru complexes. Their consultations and assistance throughout this project are greatly appreciated. Thanks are also extended to Dr. Lyle Mudge and Eddie Baker for their insight toward the development of the dissolved complex concept and the preliminary economics. We thank Ross Gordon and Bill Riemath for the results obtained by differential scanning calorimetry.

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EXPERIMENTAL

Materials

Carbon Monoxide (C. P. grade), carbon dioxide, hydrogen, ethylene and acetylene were used as received from Matheson. Bis(diphenylphosphino)methane, 1,2-bis(dimethylphosphino)ethane, trimethylphosphine, tetraphenylarsonium chloride, and chlorodiphenylphosphine were obtained from Strem Chemicals or Alfa Products. Solvents such as tetrahydrofuran, deoxygenated and dried with benzophenone ketyl and dimethylacetamide, dried over CaH_2 , were distilled prior to use. All other solvents, especially those in contact with complexes, were distilled prior to use. Syntheses of transition metal complexes were performed in a helium filled glovebox or with the use of standard Schlenk methods.

o-Hydroxybutyryophenone

To 117 g (1.1 mole) of butyryl chloride in a three-necked flask equipped with stirrer, dropping funnel and condenser was added 108 g (1.15 mole) phenol dissolved in ether. The solution was refluxed one hr, washed with aqueous Na_2CO_3 followed by water, then dried over anhydrous sodium sulfate. After solvent removal, the product was distilled (80–85°/10 torr).

To 250 g (1.87 mole) AlCl_3 was added dropwise 164 g (1.0 mole) of phenylbutyrate at room temperature. The mixture was heated at 150° for 20 min, then cooled. To this mixture was added 125 g ice and 75 mL conc. hydrochloric acid. The mixture was allowed to stand 18 hr followed by ether extraction. The ether layer was dried over MgSO_4 . After solvent removal, the product was distilled (140–145°/37 torr); yield, 60 g or 57%. Infrared and mass spectral data were consistent with the structure.

N,N'-Ethylenebis(o-Hydroxybutyrophenylideneimine)

The ligand pr-salen was prepared by combining 54 g (0.33 mole) o-hydroxybutyrophenone and 10 g (0.17 mole) diaminoethane in ethanol. The reagents were refluxed 8 hr, then cooled. No crystalline product formed. The solvent was removed, and the yellow oil was placed in a freezer. Crystals which formed under these conditions were recrystallized from 8% aqueous methanol, mp 119-122°. The infrared spectrum was consistent with the assigned structure.

N,N'-Ethylenebis(o-Hydroxypropiophenylideneimine)

The ligand Et-salen was prepared by combining 50 g (0.33 mole) o-hydroxypropiophenone and 10 g (0.17 mole) diaminoethane in ethanol. The reagents were refluxed 2 hr, then cooled. The crystalline product was recrystallized from 8% aqueous methanol, mp 198-200°. The infrared spectrum was consistent with the assigned structure.

N,N'-Ethylenebis(o-Hydroxybutyrophenylideneiminato)cobalt(II)

To 10 g (29.7 mmol) of pr-salen dissolved in 130 mL 95% ethanol was added 7.4 g (29.7 mmol) of cobalt(II) acetate in 30 mL water. Then, 2 g (49.3 mmol) of sodium hydroxide in 15 mL of water was added. The solution was stirred for 4 hr and refluxed for an additional 45 min. The red orange solid was filtered and washed with water followed by ethanol. The solid complex was recrystallized from 450 mL THF. A microcrystalline solid was recovered: 3.6 g for 30% yield.

N,N'-Ethylenebis(salicylideneiminato)cobalt(II)

To 10 g (37.3 mmol) of salen in 75 mL of DMF was added 9.3 g (37.3 mmole) of cobalt acetate in 25 mL of DMF. The mixture was stirred for 4 hrs, heated to 100° for 30 min., then cooled. The red crystalline precipitate was filtered, washed with DMF and dried in vacuo for 24 hrs. The yield was 10.6 g (82%).

Sodium[N,N'-Ethylenebis(salicylideneiminato)]cobalt(I), Co(salen)Na·THF

This reaction was performed in Schlenk glassware to avoid air exposure. To 0.5 g of Co(II)salen was added 0.1 g sodium metal. Degassed THF (20 mL) was transferred to the solid Co(II)salen and Na. The mixture was magnetically stirred for 18 hrs., then filtered (sintered glass) to remove excess Na metal. In a number of cases excess Na metal was necessary to evoke the reaction (color change red to green). The green solution was transferred to a vacuum vessel to remove the solvent. The remaining dark green solid could be transferred to storage vessels within the He glovebox. Transfer of THF solutions of the bimetallic complex within the glovebox generally involved immediate oxidation (color change green to brown). The yield was 0.4 g (50%). The green solution, when exposed to CO₂, produced a quantitative amount of the red microcrystalline adduct.

Sodium[N,N'-Ethylenebis(0-Hydroxybutyrophenyldieneiminato)]cobalt(I), Co(pr-salen)Na·THF

This reaction was performed in a manner similar to Co(salen)Na·THF. The yield was also 50%. The green THF solution, when exposed to CO₂, produced a quantitative amount of reddish brown adduct.

μ-Dichlorotetrakis(cyclooctene)diiridium(I)

To 20 g (5.7 mmol) of IrCl₃·3H₂O dissolved in 30 mL of degassed 27% aqueous isopropanol was added 4 mL (30.7 mmol) of cyclooctene. The solution was stirred at reflux for 3 hr; the color changed from dark red to orange. The precipitate was filtered and washed with cold methanol. The dried yellow crystals were dried in vacuo: 18.5 g for 63% yield.

Chlorobis(dimethylphosphino)ethaneiridium(I)

To 2.0 g (2.23 mmol) Ir₂Cl₂(C₈H₁₄)₄ in 20 mL of benzene was added 1.34 g (8.93 mmol) of 1,2-bis(dimethylphosphino)ethane. The mixture darkened to deep orange. It was stirred for 18 hr, then filtered. The orange precipitate

(2.3 g) was dried in vacuo, yield 99%. Exposure of the powder to air yielded a white to pink solid. Exposure to CO₂ gave a white solid within 5–10 sec. Calcd. for IrC₁₂H₃₂P₂Cl: C, 27.29; H, 6.06. found: C, 27.30; H, 6.13.

Chlorotetrakis(trimethylphosphino)iridium(I)

To 2.0g (2.23 mmol) Ir₂Cl₂ (C₈H₁₄)₁₄ in 50 mL toluene was added 1.4 g (18 mmol) trimethylphosphine in 10 mL in toluene. The yellow solution darkened to orange and was held at -25° for 3 days. The product was filtered with a medium sintered glass filter and washed with 50 mL of degassed hexane. The yellow solid was dried in vacuo for 18 hr, 2.37 g for 77.5% yield.

Chlorotris(tri-n-butylphosphino)rhodium(I)

To 1 g (2.57 mmol) of [RhCl(C₂H₄)₂]₂ dissolved in 50 mL benzene was added 3.1 g (15.43 mmol) of tributylphosphine. Gas was evolved and a very slight darkening of the red solution occurred. The solution was stirred 18 hr, then transferred to Schlenk glassware in order to remove the solvent by cryogenic (vacuum) distillation. A red oil with some crystalline material remained. This mixture was used for CO₂ sorption studies.

Chlorotris[tri(ethyldiphenylphosphino)]rhodium(I)

The reaction was performed in an analogous manner with that of RhCl(PBu₃)₃. A solid-oil mixture was also obtained after vacuum removal of the solvent.

Pd(PhCN)₂Cl₂

PdCl₂ (2.00 g) was dissolved in 100 mL of benzonitrile over a steam bath during 24 hr. The color of the solution changed from colorless to dark red. The resulting solution was filtered into 500 ml of n-pentane. The yellow crystals that precipitated out were collected by filtration; the yield was 3.75 g, 90%.

$\text{Pd}_2(\text{Ph}-\text{CH}=\text{CH}-\text{CO}-\text{CH}=\text{CH}-\text{Ph})_3(\text{CHCl}_3)_2$

PdCl_2 (1.05 mg, 5.92 mmol) was refluxed in 150 mL of methanol which contained dibenzylideneacetone, dba, (4.60 g) and sodium acetate (3.90 g). The mixture was refluxed with stirring for four hours to give a dark purple precipitate and allowed to cool to room temperature to complete the precipitation. The precipitate was collected by filtration, washed with 250 mL of methanol and dried under vacuum. The product was purified by dissolving in 200 mL of hot chloroform and reprecipitating with 600 mL of ethyl ether. Dark purple crystals were collected by filtration and dried in vacuum; the yield was 4.9 g, 80%.

$\text{Pd}_2(\text{dpm})_2\text{Cl}_2$

A mixture of $\text{Pd}(\text{dba})_3\text{CHCl}_3$ (0.54 g, 0.52 mmol) $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (0.41 g, 1.08 mmol), and bis(diphenylphosphino)methane (0.82 g, 2.13 mmol) in 50 mL of dichloromethane was refluxed for 30 min. The red solution was filtered and concentrated by rotary evaporator to 15 mL. Excess methanol was added to precipitate the red crystals, which were recrystallized from dichloromethane/methanol. The product was collected by filtration and dried under vacuum; the yield was 0.9 g, 80%.

$\text{Pd}_2(\text{dpm})_2\text{Br}_2$

Potassium bromide (0.68 g, 5.7 mmol) was dissolved in a 20% aqueous methanol solution and added to a solution of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ (0.60 g, 0.57 mmol) in 25 mL of dichloromethane. The color of the solution changed immediately from orange red to dark red. Further addition of aqueous methanol caused the precipitation of a dark red product which was collected by filtration. Recrystallization from dichloromethane/aqueous methanol, followed by vacuum drying, yielded 0.68 g (95%) of the product.

$\text{Pd}_2(\text{dpm})_2(\text{NCO})_2$

This compound was prepared by the same method described above for $\text{Pd}_2(\text{dpm})_2\text{Br}_2$ but using sodium isocyanate instead of potassium bromide.

$\text{Pd}_2(\text{dpm})_2\text{I}_2$

Potassium iodide (0.62 g, 3.74 mmol) was dissolved in a 30% aqueous methanol solution and added to a solution of $\text{Pd}_2(\text{cpm})_2\text{Cl}_2$ (0.50 g, 0.75 mmol) in 25 mL of dichloromethane. The color of the solution turned from orange to dark red. Addition of methanol caused precipitation of the deep red crystalline product. The solid was recrystallized from dichloromethane with additions of 10% aqueous methanol. The crystals were dried in vacuo, 0.60 g for 94% yield.

Tri(2-pyridyl)phosphine

To 12.6 g, (86.3 mmol) of 2-bromopyridine in 30 mL of ether cooled to -90° was added 50 mL (80 mmol) of 1.6 M butyl lithium also kept at -90° . The solution immediately turned red. After 30 min, a solution of 2.3 mL (26 mmol) of phosphorus trichloride in 50 mL of ether (-90°) was added dropwise over 1 hr. After 2 hr, the solution was warmed to 25° and extracted with 100 mL of 2 M H_2SO_4 . The aqueous extract was made alkaline with saturated NaOH solution. The deep red layer which separated was distilled under vacuum, bp $180-200^\circ/1.5$ torr. The product crystallized, and was recrystallized from acetone-petroleum ether; pale yellow crystals for 60% yield.

Diphenylphosphine

To 50 g (0.19 mole) triphenylphosphine in 150 mL tetrahydrofuran under N_2 was added 2.75 g (0.40 mole) of lithium shavings. The deep red solution was stirred 14 hr at 25° , then cooled in an ice bath. To the solution was added 200 mL of degassed water. The colorless solution was extracted with 200 mL of ether. The ether layer was washed with dilute HCl , then water. The ether

layer was dried over Na_2CO_3 . Solvent was removed and the product was vacuum distilled, bp 112–115°/1.5 torr. The yield was 85%. ^1H -nmr (CDCl_3): $\text{Ph}_2\text{P}-^1\text{H}$, δ 6.36 ppm ($J_{\text{P-H}}$, 218 H_z).

(2-Pyridyldiphenyl)phosphine

To a solution of 10 g (54 mmol) diphenylphosphine in 200 mL of tetrahydrofuran at 25° was added 33.8 mL (54 mmol) of 1.6 M butyl lithium. The red solution was stirred for 2 hr. To this was added 5.0 g (54 mmol) of 2-chloropyridine in 40 mL of tetrahydrofuran over 1 hr. The red color dissipated. After 18 hr, 50 mL of methanol was added. The solvents were removed in vacuo, and 1 L of hot hexane mixed with charcoal was added to the yellow product. After filtration and partial solvent removal, white crystals formed, 90% yield. A ^{31}P singlet was observed at 3.36 ppm in CDCl_3 (referenced to H_3PO_4).

$\text{Pd}(\text{Ppy}_3)_2\text{Cl}_2$

To a solution of 0.5 g (1.30 mmol) of $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ in 10 mL dichloromethane was added 0.72 g (2.74 mmol) of tripyridylphosphine in 10 mL dichloromethane. The bright solution turned to a yellow color in 10 min. Solvent volume was reduced to 10 mL, and yellow crystals were precipitated with ether. A total of 0.15 g (92% yield) of product was recovered.

$\text{Pd}(\text{Ppy}_3)_2\text{Br}_2$

To a solution of 0.5 g (0.71 mmol) of $\text{Pd}(\text{Ppy}_3)_2\text{Cl}_2$ in 150 mL dichloromethane was added slowly a solution of 0.73 g (6.14 mmol) of potassium bromide dissolved in a minimum amount of water containing 0.39 g (12 mmol) of methanol. The solution was stirred 2 h, then the solvent volume was reduced by half. The precipitated yellow product was washed with 20 mL of ethanol. After vacuum drying, 0.43 g of crystals were recovered (yield, 88%). The uv spectrum had two absorbances at 362 nm and 398 nm. Calcd. for

$\text{PdC}_{30}\text{H}_{24}\text{N}_6\text{P}_2\text{Br}_2$: C, 45.23; H, 3.04; N, 10.55. Found: C, 42.75; H, 2.95; N, 9.62.

Pd(Ppy₃)₂I₂

To a solution of 0.5 g (0.56 mmol) of Pd(Ppy₃)₂Cl₂ in 150 mL of dichloromethane was added slowly a solution of 1.59 g (9.6 mmol) of potassium iodide dissolved in a minimum amount of water containing 0.58 g (18 mmol) of methanol. The solution was stirred for 2 h. The color of the solution changed from yellow to brown during this period. The volume was reduced to 15 mL, and the reddish brown crystals were washed with 100 mL water and 100 mL of ethanol. After vacuum drying, 0.58 g of crystals were recovered for a 91% yield. Calcd. for PdC₃₀H₂₄N₆P₂I₂: C, 40.45; H, 2.72; N, 9.44. Found: C, 39.57; H, 2.68; N, 9.13.

Pd₂(Ppy₃)₂Br₂

To 0.30 g (0.38 mmol) of Pd(Ppy₃)₂Br₂ suspended in 20 mL dichloromethane was added 0.20 g (0.19 mmol) of Pd₂(dba)₃CHCl₃ in 20 mL dichloromethane. The mixture was stirred for 4 h, then the solvent was reduced to 15 mL. The addition of ether caused precipitation of deep red crystals; the yield was 94%. The ³¹P-nmr spectrum (CDCl₃) gave a singlet at 8.99 ppm (relative to triphenylphosphine). The uv spectrum had absorbances at 348 nm, shoulder at 375 nm, and 475 nm. Calcd. for Pd₂C₃₀H₂₄N₆P₂Br₂: C, 39.90; H, 2.68; N, 9.31. Found: C, 39.63; H, 2.27; N, 9.00.

Pd₂(Ppy₃)₂Cl₂

To 0.30 g (0.42 mmol) Pd(Ppy₃)₂Cl₂ suspended in 20 mL dichloromethane was added 0.22 g (0.21 mmol) Pd₂(dba)₃CHCl₃ in 20 mL dichloromethane. The mixture was stirred for 1 hr, whereupon the color changed from yellow to red. The solvent was vacuum reduced to 10 mL, and ether was added to give red crystals. These were recrystallized from dichloromethane-ether for 94% yield. The ³¹P-nmr spectrum (CDCl₃) gave a singlet at 11.11 ppm relative to triphenylphosphine. Calcd. for Pd₂C₃₀H₂₄N₆P₂Cl₂: C, 44.25; H, 2.97; N, 10.32. Found: C, 44.28; H, 3.01; N, 10.26.

$\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$

To a solution of 0.41 g (1.05 mmol) of $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ in 10 mL dichloromethane was added 0.74 g (4.0 mmol) tris(2-pyridyldiphenyl)phosphine in 10 mL dichloromethane. Yellow crystals were collected after ether trituration. They were washed with ethanol and vacuum dried for a quantitative yield.

$\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$

To a stirred suspension of 120 mg (0.18 mmol) of $\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ in 20 mL dichloromethane was added 94 mg (0.09 mmol) of $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ in 20 mL dichloromethane. After stirring for 1 hr the solvent was reduced to 5 mL. Trituration with ether gave dark red crystals which were washed with ether. The yield was 90%.

$\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Br}_2$

To 0.30 g (0.39 mmol) of $\text{Pd}(\text{pyPPh}_2)_2\text{Br}_2$ suspended in 20 mL of dichloromethane was added 0.20 g (0.19 mmol) of $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ in 20 mL of dichloromethane. The mixture was stirred for 2 h, then the solvent was reduced to 15 mL. Ether caused precipitation of reddish brown crystals; the yield was 92%. The ^{31}P -nmr spectrum (CDCl_3) gave one singlet at 8.99 ppm (upfield with respect to triphenylphosphine) and a second singlet at 7.67 ppm (downfield with respect to PPh_3). It was assumed that these were isomers. The uv absorbances were 348 nm, 385 nm, and a shoulder at 483 nm. Calcd. for $\text{Pd}_2\text{C}_{34}\text{H}_{28}\text{N}_2\text{P}_2\text{Br}_2$: C, 45.42; H, 3.14; N, 3.11. Found: C, 45.31; H, 3.15; N, 2.95.

$\text{Pd}_2(\text{Ph}_2\text{Ppy})_2(\text{NCO})_2$

To 0.50 g (0.17 mmol) of $\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ in 100 mL dichloromethane was added 0.46 g (7.1 mmol) of sodium isocyanate in minimal water containing two equivalents of methanol. After stirring for 1.5 hr, the solvent volume was reduced to 15 mL. The precipitated product was washed with 20 mL of water. After recrystallization with dichloromethane-ether, a yield of 90% orange

crystals was recovered. The ^{31}P -nmr spectrum (CDCl_3) gave two singlets, 8.92 ppm and 23.16 ppm relative to Ph_3P . These represent the trans and cis forms of the complex.

$\text{Pd}_2(\text{Ph}_2\text{Ppy})_2\text{I}_2$

To 0.32 g (0.34 mmol) $\text{PdPh}_2\text{PpyI}_2$ suspended in 25 mL of dichloromethane was added 0.18 g (0.17 mmol) of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ in 20 mL of dichloromethane. The color of the mixture changed from orange to purple after 2 h of stirring. The solvent volume was reduced to 20 mL, and hexane was used to precipitate the purple crystals. The yield was 99% (0.66g). The ^{31}P -nmr spectrum (CDCl_3) gave a singlet at 4.72 ppm relative to Ph_3P . The uv spectrum gave absorbances at 379 nm, 415 nm, 480 nm, and 540 nm. Calcd. for $\text{Pd}_2\text{C}_{34}\text{H}_{28}\text{N}_2\text{P}_2\text{I}_2$: C, 41.11; H, 2.84; N, 2.82. Found: C, 41.47; H, 3.07; N, 2.76.

Dichlorotris(triphenylphosphino)ruthenium

To RuCl_3 (1.0 g, 3.18 mmol), dissolved in 500 mL hot methanol and cooled, was added triphenylphosphine (5.0 g, 19 mmol). The solution was refluxed 6 hr, cooled and filtered. The precipitate was washed three times with methanol, then vacuum dried. The brown crystals were air stable. A quantitative yield was achieved (3.03 g).

Dichlorodicarbonylbis(triphenylphosphino)ruthenium

The $\text{RuCl}_2(\text{PPh}_3)_3$ crystals from the previous reaction were dissolved in 50 mL dichloromethane and stirred 20 hr under 1 atm of CO. The solvent volume was reduced to 20 mL under a slow flow of CO. To this solution was added 30 mL of methanol to precipitate the white crystals. They were filtered and dried in vacuo for 24 hrs, 1.91 g for 80% yield.

Dicarbonyltris(triphenylphosphino)ruthenium

To $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (2.0 g, 2.65 mmol) dissolved in 400 mL of dry, degassed THF was added triphenylphosphine (1.39 g, 2.65 mmol). After stirring

for a few minutes, an excess of sodium amalgam was added. The clear color of the mixture turned orange. After 2 days the mixture was filtered through Celite.[®] The solvent was removed from the filtrate under vacuum. The residue was extracted with degassed benzene and filtered through Celite.[®] After solvent removal, the residue was dissolved in a minimum amount of degassed THF. The solvent volume was reduced until yellow-orange crystals appeared. Hexane was added to facilitate crystallization. The crystals were filtered and dried in vacuo, 2.0 g for 80% yield.

Ruthenium trichloride (5.0 g) dissolved in 250 mL of dried methanol was placed in a 0.5 L autoclave containing a glass liner. The autoclave was charged with 10 atm of CO and heated to 60–65°C for 30 h. After cooling and venting, the liner containing the yellow-green solution was removed. This solution was filtered, and the solvent was removed to give a pale yellow green solid.

A dichloromethane solution (50 mL) containing 0.30 g (0.59 mmol) $\text{[RuCl}_2(\text{CO})_3\text{]}_2$ and 0.69 g (2.64 mmol) of pyridyldiphenylphosphine was refluxed under Ar for 18 h. Carbon monoxide was evolved vigorously during the reaction. The solvent volume was reduced to 10 mL, and ether was added. The white precipitate was recrystallized from dichloromethane-ether for a yield of 0.62 g (70%). The ^{31}P -nmr spectrum (benzene- d^6) gave a singlet at 26.48 ppm.

A dichloromethane solution (50 mL) containing 0.30 g (0.59 mmol) of $\text{[RuCl}_2(\text{CO})_3\text{]}_2$ and 0.70 g (2.64 mmol) of tripyridylphosphine was refluxed under Ar for 18 h. The solvent volume was reduced to 10 mL, and white crystals were filtered from the mixture. Recrystallization from dichloromethane gave 0.64 g

(72% yield). The ^{31}P -nmr spectrum (CDCl_3) gave a singlet at 38.50 ppm.

Calcd. for $\text{RuC}_{32}\text{H}_{24}\text{P}_2\text{N}_6\text{O}_2\text{Cl}_2$: C, 50.67; H, 3.19; N, 11.08. Found: C, 50.04; H, 3.19; N, 10.74.

$\text{Ru}(\text{CO})_2(\text{Ph}_2\text{Ppy})_3$

A suspension of 1.0 g (1.33 mmol) of $\text{RuCl}_2(\text{CO})_2(\text{pyPPh}_2)_2$ and 0.77 g (2.92 mmol) of pyridyldiphenylphosphine was prepared in 400 mL of degassed, dried THF under Ar. An excess amount of sodium amalgam was added to the mixture with stirring. After 24 h of stirring, the unreacted amalgam was removed by decantation of the solvent. The reddish brown solution was filtered three times through Celite® and allowed to stand overnight. A grey precipitate was removed by filtration. The clear red solution was added to 400 mL of hexane, and the solvent volume was vacuum reduced. Bright red crystals were recovered (1.07 g for 85% yield). The ^{31}P -nmr spectrum (benzene-d_6) gave a singlet at 56.9 ppm.

$\text{Ru}(\text{CO})_2(\text{Ppy}_3)_3$

This complex was synthesized in a manner similar to that described above; i.e., two equivalents of tripyridylphosphine was added to $\text{RuCl}_2(\text{CO})_2(\text{Ppy}_3)_2$. The brown product was recovered for a 88% yield. The carbonyl stretching frequency (ir) was 1920 cm^{-1} .

$\text{Ru}(\text{CO})_2(\text{Ppy}_3)_2$

An excess of sodium amalgam was added to a suspension of 1.0 g (1.32 mmol) of $\text{RuCl}_2(\text{CO})_2(\text{Ppy}_3)_2$ in 400 mL of dry THF under Ar. The mixture was stirred 18 h, then decanted from the unreacted amalgam. After three Celite® filtrations, hexane was added to the clear red solution. Reddish-brown crystals were removed by filtration. They were very air sensitive. The ^{31}P -nmr spectrum (benzene-d_6) gave a singlet at 65.9 ppm. The spectrum suggested that a rapid chelation between Ru and the pyridyl nitrogen may occur.

$\text{Ru}(\text{CO})_2(\text{pyPPh}_2)_2$

Synthesis of this complex was similar to that of $\text{Ru}(\text{CO})_2(\text{Ppy}_3)_2$. A brown product was isolated; it was also quite air sensitive.

$\text{Pt}(\text{PhCN})_2\text{Cl}_2$

To 2.0 g of K_2PtCl_4 dissolved in 15 mL of H_2O was added 30 mL of benzonitrile. The two-phase mixture was heated to 100°C until the aqueous layer was colorless. The two phases were separated and the aqueous layer was discarded. The yellow benzonitrile solution was cooled to 25°C and placed in a freezer for 18 h. The yellow crystals which formed were filtered and vacuum dried, the yield was 55%.

$\text{Pt}(\text{dpm})\text{Cl}_2$

To 0.1 g $\text{Pt}(\text{PhCN})_2\text{Cl}_2$ dissolved in 5 mL of dichloromethane was added with stirring 0.08 g of dpm in 5 mL of dichloromethane. The solution was stirred for 0.5 h, whereupon a white precipitate formed. Ether was added to enhance the precipitation. The solid was vacuum dried, 0.13 g for 98% yield. The dpm methylene proton resonance was observed at 4.44 ppm in the ^1H -nmr spectrum.

The $J_{\text{P-H}}$ was 11 hz.

$\text{PtPd}(\text{dpm})_2\text{Cl}_2$

To 0.2 g $\text{Pt}(\text{dpm})\text{Cl}_2$ and 0.12 g of dpm dissolved in 25 mL of dichloromethane was added 0.16 g of $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$. The mixture was refluxed for 0.5 h, filtered and crystallized with the addition of ether. The product was recrystallized from dichloromethane-ether. The product was contaminated with a small amount of $\text{Pt}(\text{dpm})\text{Cl}_2$.

Silylation of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$

To 7.7 g of dpm dissolved in 50 mL of benzene containing 2.8 g of tetramethylethylenediamine was added 19 mL of 1.6 M butyllithium. The solution was stirred 3 h until a yellow orange color persisted. To this was

slowly added 3.2 g of chlorotrimethylsilane. The solution was stirred for 18 h. The precipitated LiCl was filtered and the solvent was removed from the filtrate. The yellow gum was dissolved in 300 mL of hot ethanol under N_2 , then cooled. The white crystals that formed were filtered and vacuum dried. The yield was 84%. 1H -nmr spectra indicated a singlet at 1.5 ppm (CH_3-Si) and a triplet at 2.9 ppm (methine) with a J_{H-P} of 1.5 H_z . The silylation of dpm with allyldiphenylsilyl chloride also gave the mono-adduct.

1,1-Bis(diphenylphosphino)ethane

This product, Me-dpm, was prepared in the following manner: to a solution of 5.3 g (28 mmol) of Ph_2PH in 15 mL of benzene was added, dropwise, 18 mL of 1.5 M methyllithium in ether. The solution turned yellow and methane was evolved. After 3 hours of stirring, 1.4 g (14.3 mmol) of 1,1-dichloroethane was added to the Ph_2PLi solution. A white precipitate formed immediately. This mixture was stirred 3 hours and filtered through Celite to remove LiCl. The solvent was removed in vacuo to yield a yellow oil. To the oil was added 300 mL of 95% ethanol. White crystals formed which were recrystallized with a solution of dichloromethane and ethanol. The yield (4.5 g) was 80% of theoretical. Calcd. for $C_{26}H_{24}P_2$: C, 78.38; H, 6.07. Found: C, 77.71; H, 6.21.

(1-Diphenylphosphino-1-Diphenylmethylphosphonium)ethane Iodide

To 3.85 g (10 mmol) of dpm dissolved in 50 mL of benzene containing 1.8 mL (12 mmol) of tetramethylethylenediamine was slowly added 9.5 mL of 1.6 M butyllithium in hexane. The color of the solution became yellow. After stirring for 3 hours, 2.5 mL of iodomethane was added. A white precipitate formed. The mixture was stirred 18 hours, then filtered to remove LiI. The solvent was removed under vacuum. Further colloidal LiI was removed after dissolving the product in a solution of dichloromethane and ether. The

recrystallized product was isolated in 79% yield, 4.3 g. Calcd. for

$C_{27}H_{27}P_2I$: C, 60.01; H, 5.04. Found: C, 60.07; H, 5.12.

1,1-Dimethylbis(diphenylphosphino)silane

To 5.3 g (28 mmol) of Ph_2PH in 50 mL of benzene was added 18 mL of 1.6 M methyllithium in ether. After 3 hours of stirring, 1.9 mL (15.6 mmol) of dichlorodimethylsilane was slowly added to the solution. The mixture containing white precipitate was stirred 1 hour, then filtered through Celite. Solvent was vacuum removed. The yellow oil was air sensitive. Thus, 100 mL of hexane was placed over the oil and the two layers were stored in a freezer to induce crystallization. The hexane was decanted while maintaining the crystals at $-77^\circ C$. The crystals were washed with 400 mL of cold hexane to yield 4 g of the pyrophoric product.

$Pd(Me-dpm)Cl_2$

To 0.30 g (0.78 mmol) of $Pd(PhCN)_2Cl_2$ in 10 mL of dichloromethane was added 0.31 g (0.78 mmol) of Me-dpm in 10 mL of dichloromethane. The solution was stirred 2 hours. Ether was added to the solution to induce crystallization. The yellow crystals were recrystallized from ether-dichloromethane for a yield of 0.4 g (89%). Calcd. for $C_{26}H_{24}P_2Cl_2Pd$: C, 54.24; H, 4.20. Found: C, 54.08; H, 4.21.

$Pd_2(Me-dpm)_2Cl_2$

To 0.30 g (0.43 mmol) of $Pd_2(Ph_2Ppy)_2Cl_2$ in 20 mL of dichloromethane was added 0.34 g (0.85 mmol) of Me-dpm in 20 mL of dichloromethane. After stirring for 3 hours, the mixture was filtered and the solvent volume was reduced to 15 mL. Ether was added to induce crystallization. The yellow-orange crystals were recrystallized from chloroform-methanol to give 0.40 g (87% yield). Calcd. for $C_{52}H_{48}P_2Cl_2Pd_2$: C, 57.80; H, 4.48. Found: C, 56.08; H, 4.67.

Chlorodimethylphosphine

To 18.6g (0.1 mol) of tetramethyldiphosphine disulfide was added 53.5 g (0.3 mol) of phenyldichlorophosphine. The mixture was heated to about 200°C to obtain dissolution. A short-path distilling apparatus was used for the very slow product distillation (4 hours); 4.6 g of clear pyrophoric liquid was obtained (23% yield).

Rh(OH)(CO)(PPh₃)₂

To 25 mL of acetonitrile was added 1.49 g (2.1 mmol) of RhCl(CO)(PPh₃)₂ and 0.67 g (3.4 mmol) of AgBF₄. After stirring for 2 days in the dark, the suspension was filtered. Removal of the solvent afforded a yellow solid which was then dissolved in 10 mL of the THF. Addition of 3.5 mL of 0.99 M aqueous NaOH (3.5 mmol) to the THF solution gave a dark yellow solution. Solvent was removed and dichloromethane was added. Insoluble material was removed by filtration. The solvent volume was reduced, and the solution was placed in a refrigerator. Yellow crystals were recovered for 15% yield, 0.22 g.

IR(nujol): 1945 cm⁻¹ (ν_{CO}), 3620 cm⁻¹ (ν_{OH}).

Ir(OH)(CO)(PPh₃)₂

This complex was prepared from IrCl(CO)(PPh₃)₂ in a manner similar to that described for Rh(OH)(CO)(PPh₃)₂. IR(nujol): 1925 cm⁻¹ (ν_{CO}), 3610 cm⁻¹ (ν_{OH}).

Preparation of Polystyrene

Macroporous cross-linked polystyrene was washed with the following solvents and conditions with stirring; 1 M NaOH(60°), 1 M HCl(60°), 1 M NaOH (60°). 1 M HCl (60°), H₂O (25°), DMF (40°), 1 M HCl (60°), H₂O (60°), CH₃OH, CH₂Cl₂-CH₃OH(2:3 v/v), CH₂Cl₂-CH₃OH (3:1 v/v), CH₂Cl₂-CH₃OH (9:1 v/v), and CH₂Cl₂. The exposure period of the polymer to each solvent was 24 hours. At the end of wash period the polymer was dried in vacuo at 100°.

Chloromethylation of Polystyrene

Macroporous polystyrene (50 g), from the previous sequential wash procedure, was allowed to swell in 500 mL trichlorethylene, contained in a 3-necked flask, for 18 hrs. To the three necked flask, equipped with condensor and thermometer, was added 100 g chloromethylmethylether. (Caution, chloromethylmethylether is a potent carcinogen.) The mixture turned dark red upon addition of 60 g of SnCl_4 . The temperature was maintained at 25° for 2 hrs. After filtration, the polymer was washed with dioxane- H_2O (1:1 v/v) dioxane-3M HCl (1:1 v/v), dioxane, dioxane- H_2O (1:1), H_2O and finally methanol. The product was dried at 90°C under vacuum yielding 56 g (5.2% Cl) and 60 g (16.8% Cl), respectively for 20% and 2% cross-linked polystyrene. The solvent containing chloromethylmethylether was decomposed with 6 M NaOH using a quarternary amine to impose phase-transfer conditions.

Preparation of Brominated Polystyrene

To a suspension of 25 g of Amberlite XAD-2 polystyrene in 300 mL of CCl_4 was added 0.73 g of anhydrous FeCl_3 . The mixture was stirred for 30 min before 19.3 g (0.12 mole) of bromine was added. After the addition was complete, the mixture was stirred mechanically for 1 hr. at 25° and 2 hr at reflux. The beads were filtered and sequentially washed with CCl_4 , acetone, acetone-water (2:1 v/v), acetone, benzene, and methanol. Elemental analysis indicated 27.58% Br; thus, 50% of the aryl rings had been brominated.

Diphenylphosphine Attachment to Polystyrene

To 10 g of brominated SX-2 polystyrene (25.55% Br) was added 350 mL of benzene distilled from sodium. To this was added 55 mL of 2.5 M butyllithium in hexane. The mixture was stirred at 60°C for 3 h, then filtered and washed

with benzene followed by THF. The deep red polymer was suspended in 100 mL of distilled THF (from benzophenone ketyl). To this was added 20 mL of chlorodiphenylphosphine. After 18 h, the polymer was filtered and washed with the sequence THF, THF-H₂O (2:1), H₂O, THF, toluene, and finally methanol. After vacuum drying the analyses indicated 6.23% P and <0.04% Br.

Dimethylphosphine Attachment to Polystyrene

To 5.0 g of lithiated SX-2 polystyrene prepared in a manner similar to that above was added 50 mL distilled THF and 9.5 g (98 mmol) chlorodimethylphosphine. After 18 h the beads were filtered and sequentially washed with the solvents noted above. The yellow beads were vacuum dried; analyses were 4.63% P and 3.74% Br.

Bis(diphenylphosphino)methane Attachment to Polystyrene

To 10 g of brominated polystyrene (27.58% Br) was added 50 mL toluene. To this was added 60 mL of 1.6 M butyllithium in hexane. The mixture was heated to 75°C for 15 h, then cooled, and filtered. The beads were washed with toluene and THF. The beads were suspended in 75 mL of THF and 5.0 g (23 mmol) of bis(dichlorophosphino)methane was added. The beads turned red, and were stirred for 24 h. The mixture was filtered and washed with THF.

The polystyrene beads were resuspended in 100 mL of THF and 18.9 mL (34 mmol) of 1.8 M phenyllithium in benzene was added. The black mixture was stirred 48 h, then filtered. The beads were washed with THF and extracted with dichloromethane. After vacuum drying, the beads analyzed for 4.01% P and 0.55% Cl.

[Ir(PMe₃)₄]Cl Attachment to Polystyrene

To 1.0 g of dimethylphosphinated polystyrene suspended in 50 mL of distilled, degassed dma was added 1.0 g (1.8 mmol) of [Ir(PMe₃)₄]Cl. The reaction was performed under He. The yellow orange complex gave a deep red

color when dissolved in dma. Within 2 h, with no stirring, most of the color transferred to the polymer. The red beads were washed with dma. Washing with THF reduced the color of the beads to orange. Elemental analyses indicated 2.76% Ir and 5.66% P.

Attachment of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ to Polystyrene

To 5.0 g of diphenylphosphinated polystyrene swelled in freshly distilled tetrahydrofuran (from benzophenone ketyl) was added 1.5 g $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$. The mixture was mechanically stirred for 5 days under a He atmosphere. The beads were filtered and washed with tetrahydrofuran and benzene. The polymer retained a definite yellow color after vacuum drying. Analyses indicated the presence of 5.61% Ru and 5.94% P.

Attachment of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ to Polystyrene

To 0.40 g of diphenylphosphinated polystyrene (SX-2 resin, 6.23% P) suspended in 75 mL of THF was added 0.32 g (0.8 mmol) of $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$. The beads were stirred briefly and allowed to stand for 3 days under a N_2 atmosphere. The beads were filtered and washed with 3 x 50 mL of thf. The bright yellow beads were vacuum dried and analyzed: 4.80% Rh and 5.30% P.

Kinetic Measurements

The gas-uptake manifold or constant pressure apparatus (Figure 21) was used for preliminary kinetics of $[\text{Ir}(\text{dmpe})_2]\text{Cl}$ and $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$. The procedures for examining $\text{Pd}_2(\text{dpm})_2\text{X}_2$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ are discussed below with $\text{Pd}_2(\text{dpm})_2\text{X}_2$ as an example.

The faster reactions with $t_{1/2} < 5$ min were studied by using a thermostated Durrum 110 stopped-flow apparatus equipped with a 2-cm light path cuvette. The average k_{obs} values were determined by monitoring absorption of the reactant or the carbonyl at their respective λ_{max} values; measurements

FIGURE 21. Constant Pressure Gas-Uptake Apparatus

were made at two wavelengths by using a minimum of three experiments. Conditions were chosen so that reactions followed the first-order rate law $\ln(A_t - A_\infty) - \ln(A_0 - A_\infty) - k_{\text{obs}} t$, where A_0 , A_t and A_∞ are the solution absorbances at $t=0$, time t , and completion of the reaction, respectively. A linear regression analysis was used to obtain k_{obs} from the $\ln(A_t - A_\infty)$ vs. t plot; the plots were linear over at least 3 half-lives and the precision obtained was always better than 10% over the 0–40°C temperature range used.

The $[\text{Pd}_2]$ was varied from 0.33 to 1.75×10^{-4} M, while a concentration range in CO was made available by varying the partial pressures of CO and Ar in a total of 1 atm at 25°C. The effect of other added gases on the carbonylation rates was examined by using gas mixtures with known partial pressures. The solubility of CO in dma was 4.4×10^{-3} M atm $^{-1}$ at 24°C (Henry's law being obeyed) and was about 2% lower at 40°C and 2% higher at 0°C. In the mixing chamber of the stopped-flow instrument, equal volumes of the Pd and gas solutions are mixed; thus the actual concentration of gas in the reaction solution is half that made up and transferred to the storage syringe.

Slower reaction rates, usually the decarbonylation (k_{-1}), were measured in a thermostated Perkin-Elmer 552A spectrophotometer using a specially designed cell consisting of a 1-cm path length cell attached by a side arm to a reservoir bulb, and fitted with a Teflon stopcock and an O-ring joint for attachment to a vacuum/gas-handling line. A solution of XII formed in situ via the carbonylation reaction, was exposed to vacuum with vigorous shaking prior to monitoring the absorbance (loss of solvent during several evacuations was taken into account). The standard log (absorbance difference) vs. time plots gave linearity over several half-lives from which the first-order rate constant k_{-1} was readily evaluated.

Equilibrium Constant Measurements

Samples of $\text{Pd(dpm)}_2\text{X}_2$ (to give 1.5×10^{-4} M solutions) were weighed into the special cell described above, with 5 mL of dma being present in the reservoir bulb. Following degassing by several freeze-pump-thaw cycles, the dma was transferred to dissolve the complex and the apparatus then filled to 1 atm pressure with CO/Ar mixtures in which the CO partial pressure could be varied from 0 to 750 torr at the required temperatures between 0 and 40°C. The solution was then shaken to establish the equilibrium shown in equation 6 and the uv/vis spectrum recorded in the thermostated Perkin-Elmer 552A. The procedure was repeated at varying CO pressures at several temperatures. Corrections for the vapor pressure of dma were negligible (1.0 torr at 15°C, 4.5 torr at 40°C). Pressures of CO were chosen to give a reasonable variation in $[\text{XII}]/[\text{XI}]$, as well as complete formation of excellent isosbestics were observed at any given temperature.

The analysis for equilibrium 6 is standard by using the expressions shown in (13) at any convenient wavelength, where A_0 and A_{CO} are the absorbance of

$$K = [\text{XII}]/[\text{XI}][\text{CO}]$$
$$\log \frac{A_0 - A}{A - A_{\text{CO}}} = \log K + \log [\text{CO}] \quad (13)$$

$\text{Pd}_2(\text{dpm})_2\text{X}_2$ (XI) and $\text{Pd}_2(\text{dpm})_2(\text{CO})\text{X}_2$, respectively; A is the absorbance at some known CO pressure (concentration) when mixtures of XI and XII are present. For the X=Cl, Br, and NCO systems, plots of $\log [(A_0 - A)/(A - A_{\text{CO}})]$ vs. $\log [\text{CO}]$ were linear with slope 1.0 ± 0.10 confirming the 1:1 stoichiometry. The plots were fitted with a linear regression program to determine K ($\pm 10\%$). For the iodide system, the carbonyl was not quite fully formed at up to 2 atm of CO pressure, and A_{CO} could not be determined directly.

GLOSSARY

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

salen	N,N'-ethylenebis(salicylideneimine)
Co(salen)	N,N'-ethylenebis(salicylideneiminato)cobalt(II)
Co(salen)Na·THF	Sodium[N,N'-ethylenebis(salicylideneiminato)]cobalt(I)
PBu ₃	tributylphosphine
Ph ₂ P ^{Et}	diphenylethylphosphine
dmpe	1,2-bis(dimethylphosphino)ethane
PPh ₃	triphenylphosphine
PCy ₃	tricyclohexylphosphine
dpm	bis(diphenylphosphino)methane
Me-dpm	1,1-bis(diphenylphosphino)ethane
Ph ₂ Ppy	diphenylpyridylphosphine
Ppy ₃	tripyridylphosphine
PMe ₃	trimethylphosphine
[Ir(PMe ₃) ₄]Cl	tetrakis(trimethylphosphine)iridium chloride
[Ir(dmpe) ₂]Cl	Bis(1,2-bis(dimethylphosphino)ethane)iridium chloride
Rh(OH)(CO)(PPh ₃) ₂	hydroxocarbonylbis(triphenylphosphine)rhodium
Ru(CO) ₂ (PPh ₃) ₃	Biscarbonyltris(triphenylphosphine)ruthenium
Pd ₂ (dpm) ₂ Cl ₂	Bis-μ-(bisdiphenylphosphinomethane)-dichlorodipalladium (Pd-Pd)

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