HYDROFORMYLATION OF OLEFINS
BY WATER SOLUBLE AND ASYMMETRIC COBALT AND PLATINUM COMPLEXES

by

Ipin Guo

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APPROVED:

Brian E. Hanson
B.E. Hanson, Chairman

Mark R. Anderson
M.R. Anderson

Mark E. Davis
M.E. Davis

John G. Mason
J.G. Mason

Joseph S. Merola
J.S. Merola

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Blacksburg, Virginia

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Committee Chairman: B.E. Hanson

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(ABSTRACT)

Hydroformylation of olefins (OXO synthesis), one of the oldest organometallic catalytic reactions, continues to be of interest because of its commercial significance. Great interest recently has been placed on the development of immobilized homogeneous catalysts that combine the virtues of conventional heterogeneous and homogeneous catalysts.

The objective of this dissertation is to investigate novel phosphine modified water soluble cobalt and platinum complexes as homogeneous and immobilized hydroformylation catalysts. The ligands include (1) Monodentate phosphines: $P[(CH_2)_n-C_6H_4-SO_3Na]_3$ (n = 0~3) and $P[C_6H_4-NMe_3^+BF_4^-]_3$; (2) Bidentate asymmetric phosphines: CHIRAPHOS$(NMe_2)_4$ (CHIRAPHOS = 2,3-bis(diphenylphosphino)butane), SKEWPHOS$(NMe_2)_4$ (SKEWPHOS = 2,4-bis(diphenylphospino)pentane), and DIOP$(NMe_2)_4$ (DIOP = 2,2-dimethyl-4,5-bis(diphenyl(phosphinomethyl)-1,3-dioxolane)). These complexes were immobilized and/or recycled

by four different methods: (1) Two phase catalysis; (2) Supported aqueous phase catalysis; (3) Catalyst supported on ion exchange resins; (4) Extraction of the catalyst from an organic phase into an aqueous phase.

Catalytic results for the hydroformylation of α-olefins shows that n/b (normal:branch of aldehyde product) ratio can be increased if proper alkyl-phosphine ligands are chosen. For example, as high as 18.5 of n/b ratio was obtained in $PtCl[P(C_6H_5)_3]_2-SnCl_3$ system and 5.6 in $Co_2(CO)_6[TRIMAPP]_2$ (TRIMAPP = trimethylamino-phenylphosphine) system.

Metal leaching, from the aqueous phase to the organic phase during the catalytic reaction, was reduced by supporting the water soluble cobalt and platinum complexes onto a high surface area glass (CGP-350). For instance, 5.7% cobalt metal was found in the organic phase when $Co_2(CO)_6(TPPTS)_2$ was used under reaction conditions (TPPTS = triphenylphosphine trisulphonated salt). When the same cobalt complex was immobilized on glass, no cobalt metal leaching was observed.

Asymmetric hydroformylation of styrene catalyzed by $PtCl[SKEWPHOS(NMe_2)_4]-SnCl_3$ shows a very strong temperature dependence on optical selectivity. Enantiomeric excess (ee's) switches sign from *S* to *R* form at 57°C. At 25°C, there is 60.6% ee of *S* product, whereas 56.7% ee in favor of *R* product is observed at 100°C.

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CHAPTER 1. INTRODUCTION

Ever since the development of homogeneous catalysis, it has been recognized that one of its central problems is the separation of the catalyst and the product of reaction. Attempts to overcome this disadvantage have led to the investigation of so called "heterogenized" catalysts.[1-5] A "heterogenized" catalyst is commonly achieved by one of the following methods: (1) the catalyst and substrates are in immiscible phases; (2) the catalyst is bonded to a solid support; and (3) the catalyst is entrapped within a microporous material.[6-10] In this dissertation homogeneous catalysts which have been made heterogeneous by one of the above methods will be said to be immobilized.

A great deal of attention has been focused on the search for water soluble transition metal complexes and related catalyst systems since water has a variety of properties that set it apart from most organic solvents. Immobilization of water soluble catalysts is achieved if the reactants and products are in the organic phase while the metal complex remains in the water phase. Most organometallic compounds however have limited water solubility. Therefore, the synthesis of novel water soluble transition metal complexes is central to the development of new immobilized homogeneous catalyst systems.

Water soluble transition metal complexes can be generated by introducing hydrophilic groups such as -COOH, -OH, $-NH_2$, $-SO_3^-$, and $-NMe_3^+$ into the ligands. Phosphine ligands are often modified with hydrophilic groups may be used to generate water soluble metal complexes.

Many mono- and bidentate water soluble phosphines have been synthesized and reported.[11-16] These phosphines can readily coordinate with group VI, VII, and VIII transition metals.[17-21] Although the electronic and steric effect of neutral phosphine ligands has been thoroughly studied and reviewed.[22] Similar studies of water soluble phosphines are not available.

The availability of water soluble transition compounds with a variety of polar and ionic groups allows for a variety of immobilization techniques to be employed. For example:

1. The catalyst may be ionically exchanged onto an ion exchange resin;
2. As suggested above, the catalyst may be dissolved in a phase that is immiscible with the reactant phase;
3. The catalyst can act homogeneously in one phase,

then be extracted into a second immiscible phase;

4. The catalyst may be dissolved in a water layer which in turn is supported on the surface of a hydrophilic solid.

These immobilized catalysts, in principle, combine the virtues of conventional homogeneous and heterogeneous systems. One problem that often plagues immobilized catalysts is the decline of activity and selectivity due to a significant catalyst leaching. This shortcoming makes immobilized systems unable to compete with most commercial heterogeneous catalysts. Much effort has been put into the development of more efficient water soluble and immobilized liquid phase catalysts which keep high activity and selectivity, easy handling, as well as less metal leaching. One solution is to generate different water soluble phosphine ligands. Evaluation of these phosphine modified transition metal catalysts is best performed by examining their activity and selectivity in catalytic reactions. The catalytic results can then be correlated with the properties of the ligands. Another solution is to search for different and better immobilization techniques in which more efficient bonding between support and catalyst is established.

Asymmetric hydroformylation, another interesting topic, is also drawing widespread attention. The stereo specific addition of dihydrogen and carbon monoxide to a pro-chiral olefin is an important goal in the synthesis of biologically or pharmacologically active molecules, since the process involves both carbon-carbon bond formation and the introduction of a synthetically useful functionality in the molecule. The significance of the asymmetric reaction is that there is the potential for the synthesis of a wide variety of chiral compounds.[23] There are a number of reports of asymmetric hydroformylations of olefins with chiral catalysts, particularly those involving rhodium and platinum complexed to optically active phosphine ligands.[24-27] Although platinum complexes generally give hydroformylation products with higher asymmetric induction than rhodium, the study of platinum related asymmetric hydroformylation is only the story of recent years. To this date less than one hundred platinum complexes have been found to be catalytically active for the reaction. Even fewer are the number of platinum complexes developed for water soluble and supported phase catalysis.

In this work, two new families of alkyl phosphines have been synthesized. The first is a series of phenylalkyl phosphines, $P[(CH_2)_m-C_6H_5]_3$ (m = 0~3) and their phenyl sulfonated analogues. The second set of phosphine ligands are chiral amino biphosphines: CHIRAPHOS$(NMe_2)_4$, SKEWPHOS$(NMe_2)_4$, and DIOP$(NMe_2)_4$. These phosphines are readily coordinated to cobalt and platinum to form the corresponding transition metal complexes. Homogeneous phase catalysis was carried out first with these complexes for hydroformylation of linear and prochiral olefins. Possessing either phenyl or amino group these phosphines can be sulfonated or quaternized and become water soluble. Cobalt and platinum complexes of the modified water soluble phosphines were generated. The resulting water soluble transition metal catalysts were immobilized onto several high surface hydrophilic supports by the aforementioned techniques. The immobilized catalyst systems were then applied to the hydroformylation of linear and prochiral olefins. The influences of phosphine on catalysis were investigated.

CHAPTER 2. LITERATURE REVIEW

2.1 Hydroformylation of Olefins

Hydroformylation is one of the oldest and largest homogeneously catalyzed reactions of olefins. The reaction was first discovered in 1938 by Roelen while working for Ruhrchemie in Germany.[28,29] He found that when an olefinic Fischer-Tropsch fraction was recycled over the heterogeneous cobalt based Fischer-Tropsch catalyst in the presence of synthesis gas, a mixture of carbon monoxide and hydrogen, there was a marked increase in the concentration of aldehydic products in the recycle stream. Originally, it was thought that the reaction was due to the heterogeneous cobalt catalyst but later work revealed that the actual catalyst was a soluble cobalt carbonyl species with the reaction taking place in a homogeneous liquid phase. The process is frequently referred to as the "OXO" process, with oxo being short for oxonation, i.e. the adding of oxygen to a double bond. However, the term hydroformylation is descriptively more accurate and probably more useful in characterizing this type of reaction.

Catalyzed by various transition metal complexes, hydroformylation converts an olefin to an aldehyde by the addition of CO and H_2.[30]

$$RCH{=}CH_2 + CO + H_2 \rightarrow \underset{\text{"normal"}}{RCH_2CH_2CHO} + \underset{\text{"branched"}}{RCH(CH_3)CHO} \qquad (2.1)$$

In the absence of isomerization there are, depending on the orientation of H-CHO addition across the double bond, two possible aldehyde products from an unsymmetrical alkene substrate. With a terminal alkene as substrate, (Equation 2.1), the two products are referred to as "normal" and "branched". In all but a few specialized cases the normal isomer is the preferred commercial product and the normal/branched ratio is an important parameter in the industrial hydroformylation process; generally speaking, the higher the ratio the better. In addition to linear terminal olefins, a wide variety of different olefins have been successfully hydroformylated, e.g. linear internal olefins, unsaturated alcohols, phenols, ethers, and amides.[23,24] The largest commercial use is the manufacture of butyraldehyde from propylene.[30] Butyraldehyde is a versatile chemical intermediate produced on a scale of a million tons per year worldwide. Another major application of hydroformylation is the synthesis of fatty alcohols from $C_8 \sim C_{20}$ terminal olefins. The linear alcohols, prepared this way, are used in synthesis of biodegradable detergents.

Furthermore, there is a tremendous increase in attention on asymmetric hydroformylation with current interest for mechanistic studies and for the biological activity of the enantiomerically pure products.[25-27,31]

2.2 Hydroformylation Catalysts

For a long time cobalt carbonyl was regarded as the only catalyst suitable for hydroformylation. Industry has devoted much effort to the search for more active or more selective catalysts. For example, phosphine modified cobalt complexes give rise to much more stable and selective catalysts. Phosphine modified cobalt operates at higher temperature than $Co_2(CO)_8$. More research has been done since 1960's and brought a rapid advance in the number of organic reactions catalyzed by noble metal complexes. One of the most spectacular achievements in this respect was the development of hydroformylation catalysts based on rhodium complexes.[24]

Rhodium carbonyls as catalysts for hydroformylation were first mentioned in a patent of the Chemische Verwertungs

Gesellschaft Oberhausen as early as 1956.[32] Unmodified rhodium carbonyl hydroformylation catalysts are between 10^2 and 10^4 times more active than their cobalt analogues. They are also highly active isomerization catalysts, but give rise to disappointingly low normal/branched ratios which seldom exceed 1:1, even with simple alkenes such as propene (cobalt carbonyl by comparison can give ratios up to 4:1).[30] This low selectivity together with the high price of rhodium, ca. 3500 times that of cobalt, far outweighs the activity advantage of rhodium. The major breakthrough in the commercial application of rhodium based hydroformylation catalysts was the use of triphenylphosphine as a modifying ligand which was achieved independently by Wilkinson's group and Coffey in 1965.[33] Simultaneously researchers at Shell Oil[34] in 1966 found that alkyl phosphines improved the selectivity of cobalt carbonyl as a catalyst. At present, phosphine modified rhodium systems receive great attention because of their high activity and selectivity, as well as high stability (see Table 2.2).

The search for modified hydroformylation catalyst systems has continuous to receive a great deal of attention. The great number of possible combinations offer promising opportunities to find more active and more selective catalysts. Mostly, the interest focuses on complexes of the following noble metals: iridium, ruthenium, osmium, palladium, and platinum.[35-39] Rhodium is by far the most active metal for hydroformylation of linear olefins, surpassing in this respect even the "classical" metal cobalt. Cobalt is still good candidate because of its low cost and good activity for internal olefins and high selectivity for further hydrogenation of aldehyde. Platinum, on the other hand, plays an important role in asymmetric hydroformylations (see section 2.4).

2.3 Hydroformylation Kinetics and Mechanisms

According to Natta,[40] the hydroformylation of 1-pentene with $Co_2(CO)_8$ as the catalyst obeys the kinetic equation:

$$\frac{d[\text{aldehyde}]}{dt} = k \times [\text{olefin}] \times [\text{Co}] \times \frac{P_{H2}}{P_{CO}} \tag{2.2}$$

The partial pressure of CO was found to have a detrimental effect on the overall rate of the hydroformylation reaction. However a certain minimum partial pressure of CO, which depends on temperature, is required to stabilize the hydridocobalt carbonyl species in solution.

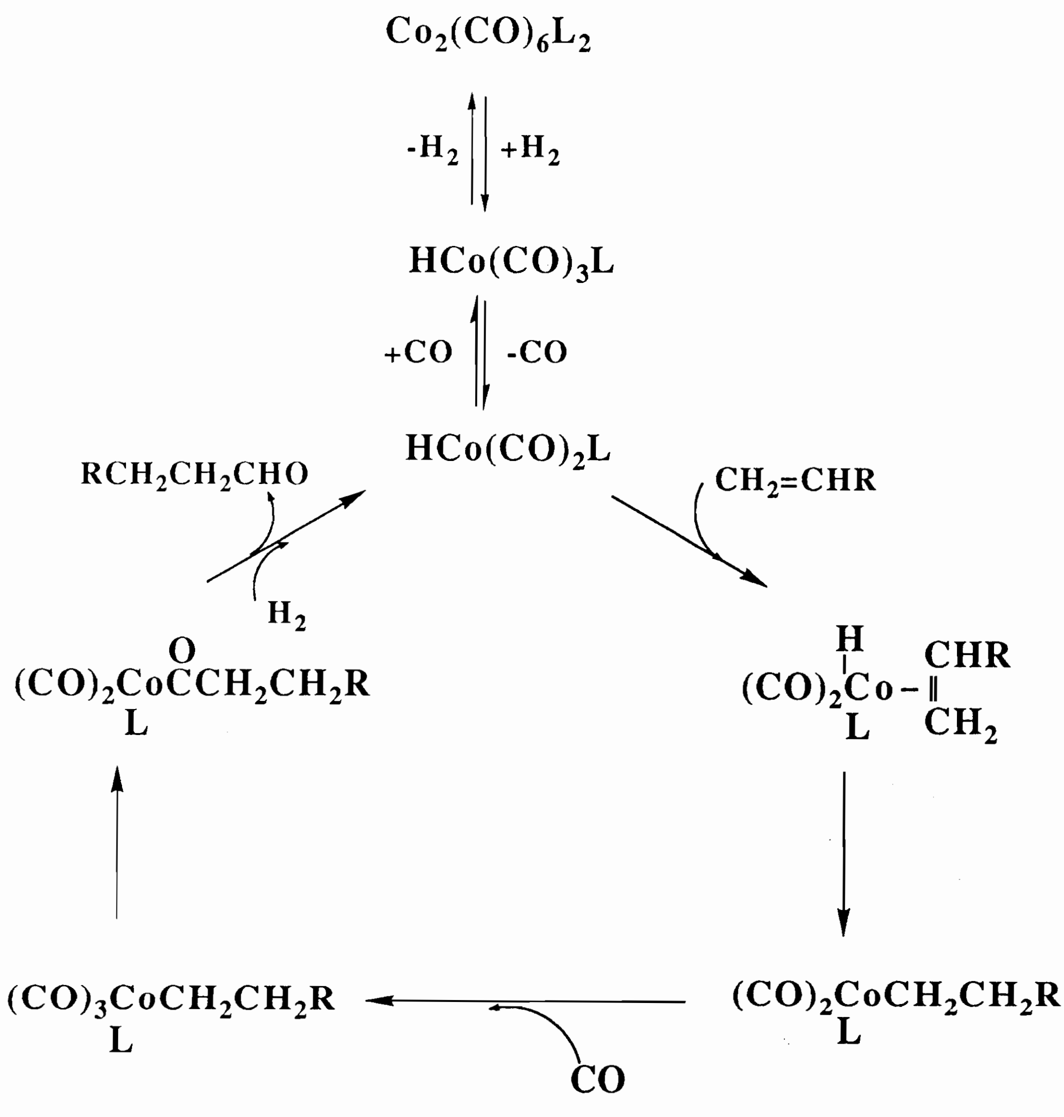
For platinum complexes catalyzed hydroformylation, relation between the rate and reaction variables, i.e. concentrations of the catalyst, olefin, and partial pressure of H_2 and CO, has been established:[30]

$$\frac{d[\text{aldehyde}]}{dt} = k \times [\text{olefin}] \times [\text{Pt}]^{1.5} \times \frac{P_{H2}}{P_{CO}^{1.5}} \tag{2.3}$$

For all catalysts, the reaction rate decreases as the steric bulk of the olefin increases,[30] i.e.:

r(linear terminal) > r(internal linear) > r(branched)

The mechanism of hydroformylation has been extensively studied and is reasonably well understood. Figure 2.1 shows the accepted reaction cycle for linear olefin hydroformylation with tertiary phosphine modified cobalt as the catalyst.[31] The active species is $CoH(CO)_2L$, formed by dissociation of a carbonyl ligand from $CoH(CO)_3L$ (L = tertiary phosphine ligand). The results of hydroformylation of 1-hexene show



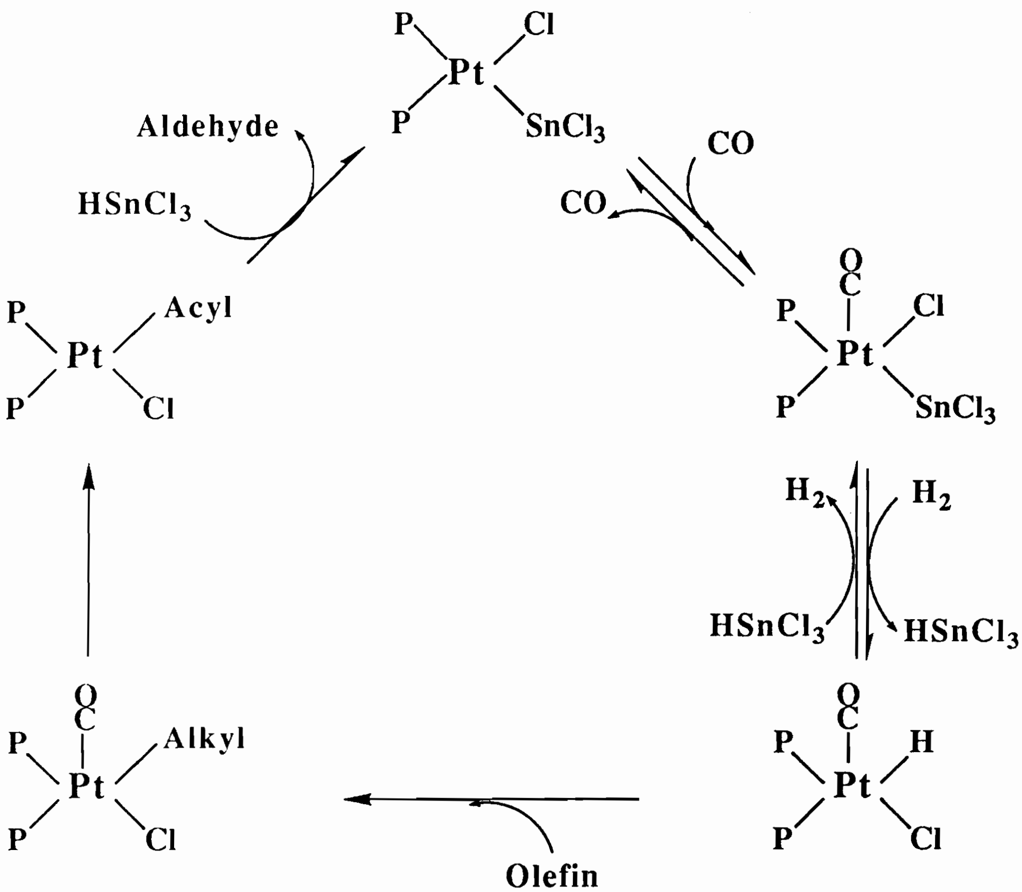
L = tertiary phosphine ligands

ref. 31

Figure 2.1 Mechanism of olefin hydroformylation catalyzed by $Co_2(CO)_6L_2$

that while the product linearity is fairly independent of steric crowding of the tertiary phosphine ligand, but not independent of the ligand basicity. Higher n/b's (normal to branched aldehyde ratio) were obtained when the ligands with larger pK_a were used.[31]

Homogeneous hydroformylation catalysis by platinum-tin complexes was first reported in the mid-seventies.[31] In the absence of tin chloride, complexes of platinum complex containing tertiary phosphine show very low hydroformylation activity. However, when a tin(II) halide, preferably $SnCl_2$, is added to the system, a highly active and very selective hydroformylation catalyst is produced. Figure 2.2 shows the proposed catalytic cycle for the olefin hydroformylation catalyzed by $PtClL_2$-$SnCl_3$ (L = tertiary phosphine).[28] As far as hydroformylation selectivity to n-octanal with $PtH(CO)(PPh_3)_2$-$SnCl_3$ is concerned, there appears to be no significant trend as a function of either the steric or electronic properties of the phosphine donor ligand.[31] Excellent selectivities are obtained with $PtClL_2$-$SnCl_3$, for example when L = PPh_3 normal to branch ratio of up to 20 was observed.[31]



P = tertiary phosphine ligands

ref. 28

Figure 2.2 Mechanism of olefin hydroformylation catalyzed by $PtCl(PPh_3)_2$-$SnCl_3$

2.4 Asymmetric Hydroformylation

In addition to the simple hydroformylation of normal and substituted olefins as described in the previous section, hydroformylation can be used for the synthesis of optically active aldehydes.[46-49] For example, hydroformylation of internal olefins such as 2-butene generates a chiral center as shown in Equation 2.5. When the aldehyde synthesis is done with a transition metal complex that bears chiral ligands, asymmetric induction can occur to yield optically active aldehydes. Involving as they do more ligand migration steps, Since asymmetric hydroformylation catalysis involves more ligand migration steps, there is more opportunity for racemization than in asymmetric hydrogenation. Optical yields in asymmetric hydroformylation reactions have not yet reached those achieved by asymmetric catalytic hydrogenation.[28]

$$CH_3CH{=}CHCH_3 + CO + H_2 \rightarrow CH_3CH_2\overset{\overset{\displaystyle CHO}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}}CH_3 \qquad (2.5)$$

Most commonly, monodentate and bidentate chiral phosphine ligands are effective for this purpose. Figure 2.2 shows some frequently used mono- and bidentate chiral phosphine ligands.[49]

Since the early 1970's there has been a great increase in research on new methods for the preparation of optically pure compounds. Asymmetric hydroformylation is a very attractive option because highly designed products can be produced by choosing right olefin and chiral catalysts. For a long time it was a rare event to approach this goal but progress has been good and now optical yields of up to 80 to 99% are frequently obtained, although conversions are typically low.[23]

Bidentate phosphine ligands are normally preferred because of their strong complexation to metals and relative rigid conformation of the complex formed. Complexes derived from asymmetric bidentate ligands can have useful differences in chemical stability and catalytic activity compared to complexes containing only monodentate asymmetric ligands.

The discovery that biphosphines yield more selective catalysts than monophosphines can be credited to Kagan and his group.[49] They developed one of the most efficient ligands (-)-DIOP which is easily prepared from natural tartaric acid in five steps.

There are a number of reports of asymmetric hydroformylation of olefins with chiral catalysts. Most of these involve rhodium or platinum complexes with optically

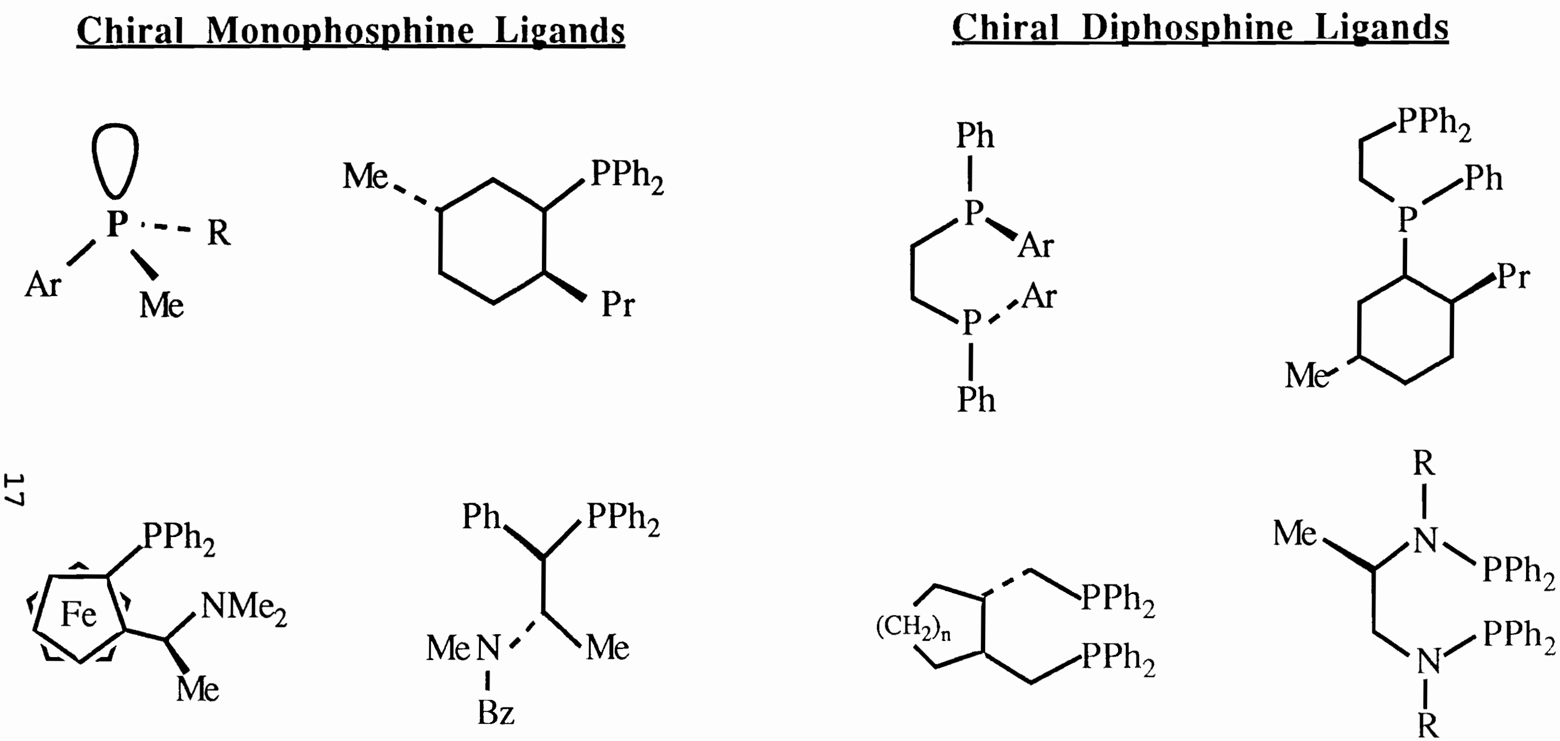


Figure 2.2 Selected mono- and bidentate chiral phosphine ligands

active phosphine ligands.[49-50] Platinum complexes generally give hydroformylation products with a higher degree of asymmetric induction than those of rhodium.[51] The enantiomeric excesses (ee) achieved in hydroformylation with either platinum or rhodium catalysts are generally lower than that obtained in hydrogenation. For example, the hydroformylation of 2-butene in the presence of a platinum catalyst bearing the ligand [(-)-DIOP]2,3-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane gave the corresponding aldehyde in 46.7% ee, while a similar catalyst gave 90.0% ee for the hydrogenation of N-acyl α-amino acids.[49]

In last few years, many platinum complexes with chiral phosphine ligands have been synthesized and applied to hydroformylation of different pro-chiral olefins. Kollar, et al. synthesized several different Pt-Sn catalytic systems. About 88% and 70% ee's have been achieved when hydroformylation of styrene was performed by platinum-BDP-DIOP/$SnCl_2$ (BDP-DIOP = (-)-(4R, 5R)-2,2-dimethyl-4,5,-bis(5-dibenzephosphinol-5-methyl)-1,3-dioxane) and platinum-BPPM/$SnCl_2$ (BPPM = (2S,3S)-N-(tert-butoxycarbonyl)-[2,4-(diphenylphosphino)methyl]pyrrolidine) respectively.[25,52,57]

In addition to the asymmetric hydroformylation of linear and aromatic olefins, vinylidene esters have been also hydroformylated with the DIOP-containing Pt catalyst.[53-55] In the hydroformylation of dimethyl itaconate, the corresponding aldehyde enantiomer was formed in 88% ee.[54] More recently, various vinyl aromatics, vinyl acetate, and N-vinyl phenthalimide have been asymmetrically hydroformylated with Pt-Cl[(S,S)-BPPM]/$SnCl_2$ catalyst with ee up to 80%.[55]

Styrene has been the most popular and successful substrate in studies of asymmetric hydroformylation. This is due mainly to the fact that the reaction does not suffer from isomerization of the olefinic bond which is a harmful side reaction in that it decreases stereo selectivity, especially when using cobalt and platinum catalysts. In the asymmetric hydroformylation of styrene three products are usually formed: 2-phenylpropanal, 3-phenylpropanal, and ethyl benzene which arises from the hydrogenation of styrene. From a synthetic point of view, high selectivity in producing the chiral 2-phenylphopanal as well as high optical purity of 2-phenyl propanal is desirable.

2.5 Immobilization of Water Soluble Catalysts

The preparation of water soluble transition metal catalysts by immobilizing active transition metal complexes on solid supports such as organic polymers, inorganic oxides, and related materials (so called SLP, Supported Liquid Phase) has recently become a topic of interest.[56] The hope is that the immobilization eventually will give superior hybrid catalysts possessing the advantages of both traditional homogeneous and heterogeneous catalyst systems. Two phase catalysis with a water soluble catalyst can be considered as a special immobilization of active species if substrates and products are both in the organic phase. Recently, a novel immobilization catalyst system, Supported Aqueous Phase Catalyst (SAPC), has become an area of increasing interest.[57]

Water solubility is usually achieved by introducing highly polar substituents e.g. $-SO_3^-$, $-COOH$, $-OH$, $-NH_2$, $-NMe_3^+$, etc. into the phosphine molecules. Sulphophenyl phosphine dissolves in aqueous media at any pH, while carboxyl and amino substituted phosphines dissolve only in basic and acidic solutions respectively. On the other hand, the sulfonation of different phosphines has been reported with reasonable yields.[15,16] Different sulfonated phosphine modified transition metal complexes have been used as catalysts in several reactions.[13,17] Therefore, more attention has been focused on the development of sulfonated phenyl phosphine modified transition metal complexes.

Borowski, et al.[11] first successfully synthesized a number of Ru, Pd, and Pt complexes with sodium diphenyl phosphinobenzene sulphonate (dpm) as ligands and applied them for catalytic hydrogenation and hydroformylation of alkenes under two-phase conditions. Several Rh, Pt, Co, Mo, Ru, Ir, and Ni complexes of trisulphonated triphenylphosphine salt (TPPTS) have been synthesized.[12-17] Compared to dpm, TPPTS has a much higher water solubility. TPPTS is one of the most popular phosphine ligands for the preparation of water soluble phosphine modified transition metal complexes.

In addition to sulphonated phosphines, other water soluble phosphine metal complexes such as $-NMe_3^+$, -COOH, -OH have been reported.[18-20] For example, rhodium complexes with $Ph_2PCH_2CH_2NMe_3^+$ were shown to have hydrogenation and hydroformylation activity under two-phase reaction conditions.[18]

Water soluble asymmetric phosphines, which have one or more chiral centers, can be used as asymmetric catalyst when they coordinate with transition metals. Amrani, et al.[58] reported the synthesis of polyoxa-1,2- and 1,4-diphosphines. Its cationic Rh(I) complexes have been shown to be effective in catalytic asymmetric hydrogenation of pro-chiral substrates in water. Some other water soluble asymmetric phosphine such as sulfonated (S,S)-cyclobutanediop, PGE-17-DIOP, 2-[(diphenylphosphino)methyl]-4-(diphenylphosphine)pyrrolidine have been known.[58-62]

Stille and co-workers have made significant contributions towards the development of polymer supported transition metal asymmetric catalysts. In these complexes optically active species were covalently attached to polystyrene polymers, and relatively high ee's, 70~80 %, were obtained for the hydroformylation of styrene.[55,63,64]

2.6 Industrial Applications

The hydroformylation products prepared on the largest scale are butyraldehyde and ethylhexanol. Both of these are produced from propylene which is derived from natural gas. Either rhodium or cobalt phosphine complexes are employed as the catalyst.[30]

The second largest industrial application of hydroformylation is the production of C_8~C_{20} range alcohol which are the basic material of biodegradable detergents. This process starts with ethylene oligomerization, olefin isomerization and olefin metathesis, followed by hydroformylation. Collectively the olefin synthesis steps are refereed to SHOP for **S**hell **H**igher **O**lefin **P**rocess. Hydroformylation of SHOP olefins also uses modified cobalt catalysts.[31]

Union Carbide and Ruhrchemie developed hydroformylation processes which use $HRh(CO)(Ph_3)_3$, and $HRh(CO)(TPPTS)_3$ respectively. The modified rhodium catalyst has some advantages over cobalt as:

1. higher stability
2. higher activity
3. higher n/b ratio

Table 2.1 and 2.2 show the industrial applications of hydroformylation catalyst systems.[30,31]

Though a great effort has been put onto the development of (1) other transition metal complexes (other than Rh, Co); (2) supported catalyst systems; (3) asymmetric catalysts; these areas are still far from thoroughly studied. Rhodium complexes are generally considered to be the most effective catalyst for hydroformylation. However, studies on other metals are on going. Other noble transition metal complexes such as Pt, Pd, Ni, and Cr, etc. have been increasingly drawing attention.

Table 2.1 Commercial applications of hydroformylation of olefins[a]

Substrate	Products	Application
Propylene	Butanol	Solvent
	2-Ethylhexanol	Plasticizers
C_6~C_9 α-Olefins	C_7~C_{10} Alcohols	Plasticizers
C_{10}~C_{19} α-Olefins	C_{11}~C_{20} Alcohols	Detergents

a: Schrauzer, G.N. "Transition Metals in Homogeneous Catalysis", Marcel Dekker, 1971

Table 2.2 Commercial hydroformylation catalyst systems[a]

Company	Shell Oil	Union Carbide	Ruhrchemie
Catalyst system	$Co_2(CO)_6(PBu_3)_2$	$HRh(CO)(PPh_3)_3$	$HRh(CO)[P(PhSO_3Na)_3]_3$
Temperature °C	160 ~ 200	80 ~ 120	80 ~ 130
Pressure (atm.)	50 ~ 100	15 ~ 25	40 ~ 50
Selectivity %	80	96	99
n/b (1-alkene)	6~8/1	10~14/1	19/1
Metal/olefin %	0.5~1.0	0.01	0.2
Typical olefin	C_2 ~ C_{12}	C_2 ~ C_4	C_2 ~ C_4

a: Masters, C. "Homogeneous Transition Metal Catalysis", Chapman Hall, New York, 1977

CHAPTER 3. EXPERIMENTAL METHODS

3.1 Equipments and Chemical Pre-treatments

Since most of the catalysts involved in this work are oxygen sensitive, all manipulations including synthesis, characterization, and hydroformylation, were performed under nitrogen. A double manifold Schlenk line with vacuum pump and house nitrogen was employed. A glove box also was used to ensure the air-free handling of all compounds. All chemicals were pretreated in order to remove trace oxygen and other impurities except as noted. Hydrocarbon and ether solvents, such as toluene, pentane, THF, etc. were refluxed with metal Na, K, or Na/K under nitrogen before use. Methylene chloride was distilled from P_2O_5 under nitrogen. The asymmetric hydroformylation feedstock, styrene, was distilled immediately before use to remove trace polymers. Other olefins, e.g. 1-hexene, 1-heptene, and 1-octene were used as received.

High pressure reaction conditions are desirable for two reasons. First, P_{CO} has an influence on the dissociation of CO from cobalt carbonyl complexes. Relatively high P_{CO} is needed to keep the catalyst stable. The other reason is that in a batch reactor, the higher P_{CO} is, the more CO molecules are in a fixed volume reactor. A total pressure ranged between 800 to 1000 psi were chosen in this work. Therefore a reactor which can stand at least 1200 psi was used for safety reasons. Two autoclave reactors with different volume were employed. One has a volume of 300 mL and the other has 30 mL.

3.2 Analytical Methods

Several instruments were used for the characterization of catalyst synthesis. Chemical analysis were performed by Atlantic Microlab Inc. Infrared spectra were recorded on a Nicolet 5DXB FTIR machine. Solution ^{31}P, ^{13}C, and ^{1}H NMR were obtained on a Bruker WP-200 Spectrometer at 81.02, 50.33, and 200.16 MHz respectively. Solid state ^{31}P NMR spectra were recorded on a Bruker MSL-300 Spectrometer with Cross Polarization Magic Angle Spinning (CP MAS). All chemical shifts for ^{31}P spectra were reported relative to 85% H_3PO_4 and ^{13}C, ^{1}H were reported to tetramethylsilane (TMS). Single crystal XRD was performed on a Nicolet R3m/V X-ray Diffractometer. The water content of the glass supported complexes with different treatments was determined by thermogravimetric analysis. A Perkin-Elmer model TGS-2 machine under the following condition was used: gas flow rate 30 mL/min. dry N_2; temperature scan rate 20.0 deg./min.

Hydroformylation products were analyzed by a Gas Chromatography (model Varian 3000) with a fused silica capillary column (SPB-5, 0.32 mm ID, 30 M). The response factors for 1-hexene and 1-heptanal were calculated. The plots of GC response vs known standard concentration is shown in appendix A. The factors 1.12 and 0.91 were determined for 1-hexene and 1-heptanal respectively. Normal to branched ratios were confirmed by ^1H NMR. A temperature program was used in order to have the best separation. Enantiomeric excess was measured on a Perkin-Elemer 241 Polarimetry Spectrometer.

NMR shift reagents were also used to obtain the optical excess for some products as a calibration of the results from the polarimetry spectrometer. Figure 3.1 shows the ^1H NMR data for the procedure of shift reagent calibration. As shown in case 1 (Figure 3.1), two peaks at the downfield side (far left) are assigned as the aldehyde proton. n and b indicate the normal and branched aldehyde respectively. At room temperature, two optical isomers ***R*** and ***S*** form can not be identified under the NMR scale. They are overlapped within the branched aldehyde proton peak b. However, ***R*** and ***S*** formation were separated by gradually adding the shift reagent $Eu(hfc)_3$ ($Eu(hfc)_3$ = Tris[3-(heptafluoropropylhydroxymethylene)-(-)-camphorato]-Europium(III)). When the increasing amount of $Eu(hfc)_3$ was added (30 mg/mL and 50 mg/mL in case 2 and 3 respectively), the peak b is gradually split. Case 3b is an expanded plot of 3a. The *R* and *S* form of aldehyde are clearly separated. The ee's can be readily calculated by knowing the ratio of *R* and *S* peak area.

The evidence for catalyst leaching from aqueous or supported phase into organic phase was checked by either investigation of the catalytic activity of the filtered solution or by AA (Atomic Absorption) determination. Specifically, for the hydroformylation of 1-hexene, the second substrate, 1-heptene was added to the organic phase which was then charged into the reactor and subjected to hydroformylation under same condition as original reaction of 1-hexene. No conversion to octanals was taken to be a negative test for leaching.

3.3 Preparation of Water Soluble Cobalt and Platinum Monodentate Phosphine Complexes

The preparation of water soluble transition metal

Chiral NMR shift reagent Eu(hfc)$_3$ in (CD_3Cl)

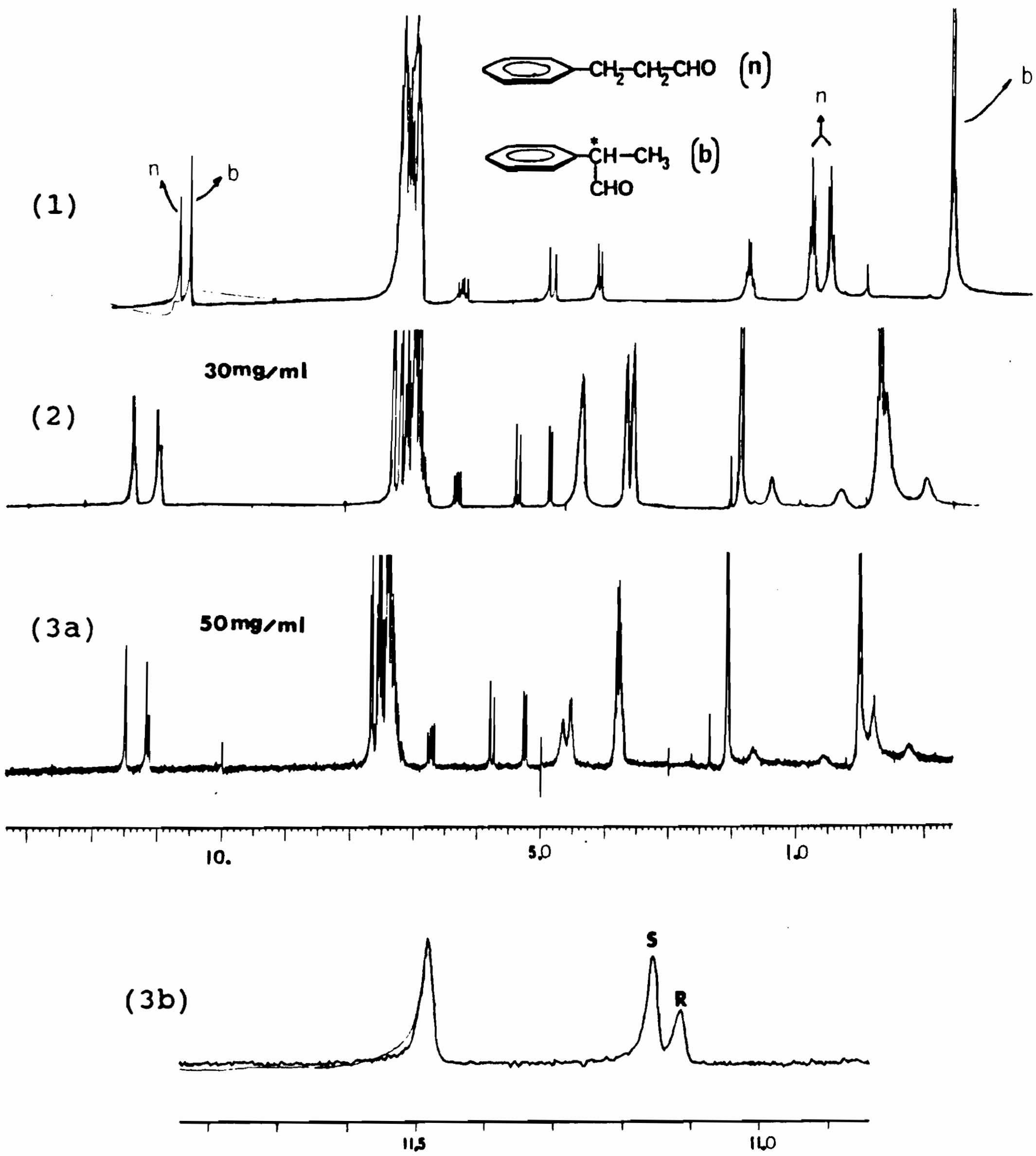


Figure 3.1 ^{1}H NMR analysis of R and S form of 2-phenylpropanal

complexes has recently attracted widespread attention.[66-71] The hope is that the water soluble complexes will give superior hybrid catalysts possessing the advantages of both homogeneous and heterogeneous catalyst system.

Several sulfonyl phosphines modified transition metal complexes has been successfully synthesized. Borowski, et al.[11] synthesized a number of Ru, Rh, Pd and Pt complexes with sodium diphenyl phosphine m-sulphonate (dpm) as ligands and applied them for catalytic hydrogenation and hydroformylation of alkenes in two phase systems. Toth, et al.[15-18] also reported the synthesis of $HRhCl(dpm)_3$, $HRh(OAC)(dpm)_3$, $HRhCl(CO)(dpm)_3$, and the catalysis for hydrogenation of 1-hexene and styrene. Tri-sulfonated phenyl phosphine (TPPTS) has higher solubility in aqueous phase and received more attention. A wide variety of organometallic and coordination compounds ware prepared with TPPTS as ligands. These include, $Ru_3(CO)_{11}(TPPTS)$, $PdCl_2(TPPTS)_2$, $Rh(COD)(TPPTS)_2$, and others.[72]

Recently, Herrmann[16] reported the synthesis of cobalt and platinum (TPPTS) complexes and ^{31}P NMR results. Furthermore, Co, Pt, Rh (TPPTS) complexes have been immobilized onto some high surface area hydrophilic support, such as glass, and used as supported aqueous phase catalyst (SAPC).[50,73,74]

In this subchapter, the synthesis and characterization of new family water soluble alkyl phosphine ligands $P[(CH_2)_m-C_6H_4-$

$SO_3Na]_3$ (m = 0 ~ 3) and their cobalt and platinum complexes are discussed.

3.3.1 Synthesis of Water Soluble Alkyl Phosphines

A three step reaction sequence was used to synthesize the water soluble alkyl phosphines, $P[(CH_2)_m-C_6H_4-SO_3Na]_3$ (m = 0, 1, 2, 3). An attempt to use traditional synthesis pathway through lithium reagents failed due to coupling reactions which produce unknown polymers. The compound TPPTS i.e. $P[m-C_6H_4-SO_3Na]_3$ has been made before.

The synthetic pathway developed in this work is fairly simple and easy to perform:

$$Br-(CH_2)_m-C_6H_5 + Mg \rightarrow Br-Mg-(CH_2)_m-C_6H_5 \quad (3.1)$$

$$3Br-Mg-(CH_2)_m-C_6H_5 + PCl_3 \rightarrow P[(CH_2)_m-C_6H_5]_3 \quad (3.2)$$

$$P[(CH_2)_m-C_6H_5]_3 + SO_3/H_2SO_4 \rightarrow P[(CH_2)_m-C_6H_4-SO_3H]_3 \quad (3.3a)$$

$$P[(CH_2)_m-C_6H_4-SO_3H]_3 + 3NaOH \rightarrow P[(CH_2)_m-C_6H_4-SO_3Na]_3 \quad (3.3b)$$

Reaction 3.1 is a simple Grignard reaction. Bromide alkyl benzene gives a higher activity than the chloride. The Grignard reagent from reaction 3.1 was used directly for reaction 3.2 without separation and purification. In reaction 3.2 excess Grignard was necessary to ensure the tri-substitution. The reaction temperature was -78°C to avoid oxidation. Sulfonation of alkyl phosphine was processed according to the literature.[75] Detailed procedures are given below.

3.3.1.1 Preparation of The Phenyl Alkyl Phosphines

One mole of the appropriate bromide alkyl phenyl, Br-$(CH_2)_m$-C_6H_5 ($BrCH_2C_6H_5$ = 124.2 mL; $BrC_2H_5C_6H_5$ = 136.5 mL; $BrC_3H_8C_6H_5$ = 153.2 mL), was added dropwise to a stoichiometric quantity of Mg chips (24.3 g) in 500 mL refluxing diethyl ether to form the corresponding Grignard reagents. The mixture was cooled down to -78° in a dry ice/acetone bath. One fifth mole ratio of PCl_3 (20.0 mL) diluted in 100 mL Et_2O was added dropwise into the Grignard with vigorous stirring. Excess Grignard was used to ensure tri-substitution. When the addition was finished, the mixture was hydrolyzed by the slow addition of 500 mL 1N NH_4Br/H_2O solution. The water phase was decanted and the ether layer was washed with 2 x 100 mL MeOH. The solvent was removed by vacuum and the phosphine, $P[(CH_2)_m-C_6H_5]_3$, was obtained as a white powder.

3.3.1.2 Sulfonation of Alkyl Phenyl Phosphine

Sulfonations of the alkyl phenyl phosphines were carried out under N_2 in SO_3/H_2SO_4 (20% SO_3) at 0°C for 48 hours. For example, 0.5 mol (185.0 g) $P[(CH_2)_3C_6H_5)]_3$ was dissolved in 10 mL 98% H_2SO_4. 50 mL 20% SO_3/H_2SO_4 was then added dropwise to the phosphine solution to form the acid, $P[(CH_2)_3C_6H_4-SO_3H]_3$. Then, the reaction mixture was neutralized by slowly pouring the mixture onto 100 g ice followed by the dropwise addition of a stoichiometric quantity of 1N NaOH solution until the pH was 7.0 (estimated by pH paper). The precipitate was removed by filtration. The solvent water was removed under vacuum distillation. The crude product was recrystallized two times from H_2O/MeOH (1/10) to remove mono- and bi-sulfonated by-products. The product was obtained as a white powder in 70% yield (245.3 g).

^{31}P NMR was used to characterize the products. The ^{31}P chemical shift data of alkyl phosphines and sulfonated alkyl phosphines are shown in Table 3.1.

Table 3.1 ^{31}P NMR data of alkyl phenyl phosphines

Neutral Ligands	$\delta^{31}P$(ppm)	Sulfonated Ligands	$\delta^{31}P$(ppm)
$P[C_6H_5]_3$	-4.7	$P[C_6H_4-SO_3Na]_3$	-5.4
$P[CH_2-C_6H_5]_3$	-13.2	$P[CH_2-C_6H_4-SO_3Na]_3$	-7.7
$P[C_2H_4-C_6H_5]_3$	-27.5	$P[C_2H_4-C_6H_4-SO_3Na]_3$	-28.0
$P[C_3H_6-C_6H_5]_3$	-31.9	$P[C_3H_6-C_6H_4-SO_3Na]_3$	-32.9

Upfield shift of $\delta^{31}P$, as the increase of m from 0 to 3, is suggested due to the stronger electron donation (from the alkyl group) which results in more electron shielding to the phosphorus atom. The reason for the unexpectedly high value $\delta^{31}P$ of $P[CH_2-C_6H_4-SO_3Na]_3$ (-7.7 ppm) compared with other sulfonated and unsulfonated alkyl phosphine pairs is not clear.

3.3.2 Cobalt Complexes

Substitution of CO by phosphine in dicobalt octacarbonyl proceeds via the ionic complex, $[Co(CO)_4L_2]^+[Co(CO)_4]^-$, but ultimately yields the neutral dimeric product, $Co_2(CO)_6L_2$ as shown in Equation 3.4.

$$Co_2(CO)_8 + 2L \rightarrow Co_2(CO)_6L_2 + 2CO \qquad (3.4)$$

$$L = P[(CH_2)_m-C_6H_4-SO_3Na]_3 \quad (m = 0, 1, 2, 3)$$

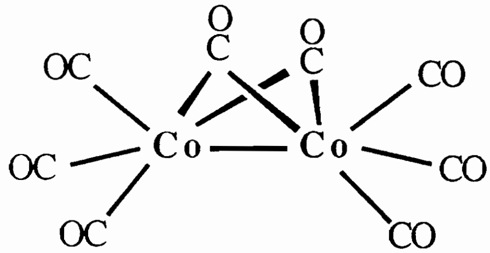
The specific procedure for the water soluble phosphines is as follows. Dicobalt octacarbonyl, 210 mg (0.61 mmol) was dissolved in 10 mL distilled toluene. Sulfonated alkyl phosphine (1.22 mmol) was added directly into the toluene solution followed by the addition of 10 mL degassed water. The phosphine dissolves in the aqueous layer while cobalt carbonyl remains in toluene. The mixture was stirred vigorously for 24 hours at room temperature. During this time the aqueous phase gradually became red-brown in color and the organic phase became nearly colorless. The aqueous phase was collected and the water removed under vacuum. The solid was recrystallized from water/methanol (1/10). Carbon and hydrogen analyses for the products are collected in Table 3.2.

A preliminary X-ray diffraction study shows that the two phosphines are axially located at the end of Co-Co axis as expected. The structure of $Co_2(CO)_8$ contains bridging CO ligands, see **1** in Figure 3.2, whereas the phosphine substituted dimmers contain no bridging CO ligands, see **2** in Figure 3.2.

Table 3.2 Elemental analysis for water soluble cobalt complex

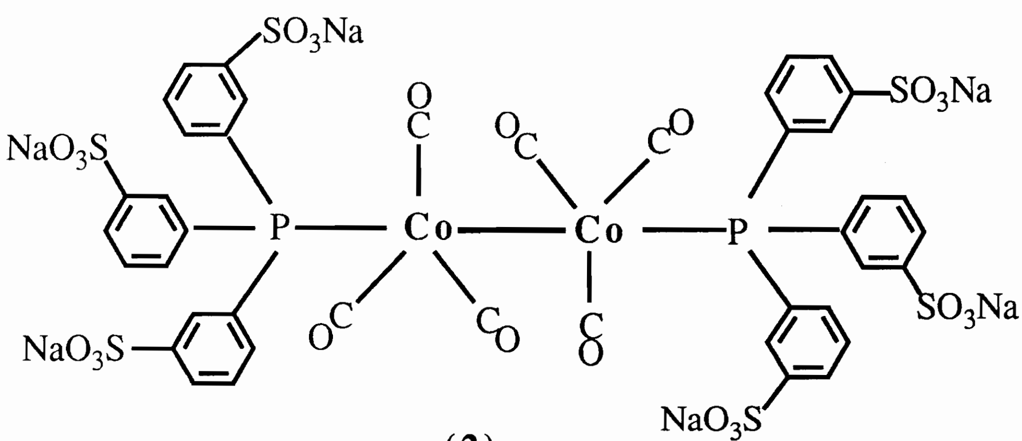
$Co_2(CO)_6[P((CH_2)_m-C_6H_4-SO_3Na)_3]_2\cdot 6H_2O$	Elemental Analysis			
	C %		H %	
	Found	Cal.	Found	Cal.
m = 0, $Co_2P_2C_{42}H_{36}O_{30}S_6Na_6$	34.0	33.1	2.7	2.4
m = 1, $Co_2P_2C_{48}H_{48}O_{30}S_6Na_6$	36.2	35.7	2.9	3.0
m = 2, $Co_2P_2C_{54}H_{60}O_{30}S_6Na_6$	38.3	38.2	3.4	3.5
m = 3, $Co_2P_2C_{60}H_{72}O_{30}S_6Na_6$	40.2	40.4	3.7	4.0

The ^{31}P NMR and FTIR data for $Co_2(CO)_6L_2$ are listed in Table 3.3. The ^{31}P NMR resonance of the phosphine shifts downfield compared to the free ligand (Table 3.1), and as expected from the free ligands, the signal moves upfield as the substituent changes from phenyl (m = 0) to propyl phenyl (m = 3). The IR frequency of the CO stretch also shows a trend to lower value while m increases. This suggests that



(1)

Dicobalt octacarbonyl



(2)

$Co_2(CO)_6(TPPTS)_2$

Figure 3.2 Structures of dicobalt octacarbonyl and $Co_2(CO)_6(TPPTS)_2$

the alkyl-phenyl phosphines are better electron donors than triphenyl phosphine as expected.

Table 3.3 ^{31}P NMR and IR data of $Co_2(CO)_6L_2$ complexes

$Co_2(CO)_6L_2$	$\delta^{31}P$(ppm)	v_{CO}(cm^{-1})	
L = $P[(CH_2)_0-C_6H_4-SO_3Na]_3$	66.9	2042	1955
L = $P[(CH_2)_1-C_6H_4-SO_3Na]_3$	63.7	2012	1951
L = $P[(CH_2)_2-C_6H_4-SO_3Na]_3$	54.5	2004	1948
L = $P[(CH_2)_3-C_6H_4-SO_3Na]_3$	52.7	1997	1946

Another cobalt phosphine complex, $Co_2(CO)_6(TRIMAPP)_2$ (TRIMAPP = tris(p-dimethylaminophenyl) phosphine) has been synthesized in this work as shown in Equation 3.5. In a typical reaction, 3.42 g (0.01 mol) of $Co_2(CO)_8$ was dissolved in 30 mL of toluene. 7.8 g (0.02 mol) of TRIMAPP was added in and the mixture was stirred at room temperature for 8 hours. The solvent was removed by vacuum and red-brown powder was obtained. ^{31}P NMR shows the phosphine peak at 47.6 ppm and IR frequency of CO at 1991 and 1888 cm^{-1}. The elemental analysis results consistent with the theoretical values: C (calculated 60.68%, found 58.92%); N (calculated 5.62%, found 5.51%); H (calculated 7.86%, found 7.54%).

$$Co_2(CO)_8 \quad + \quad 2TRIMAPP \quad \rightarrow \quad Co_2(CO)_6(TRIMAPP)_2 \quad + \quad 2CO \qquad (3.5)$$

$Co_2(CO)_6(TRIMAPP)_2$ has two triphenyl phosphine amino ligands and can be protonated or quaternized to become water soluble. More detailed information about the phase transfer catalysts recovery of this complex will be described in section 4.1.1.5.

3.3.3 Platinum Complexes

The platinum complex, $PtCl_2(NCPh)_2$ (235 mg, 0.5 mmol), was dissolved in 10 mL toluene and added to an aqueous solution of sulfonated phosphine ligands, e.g. TPPTS (568 mg, 1.0 mmol in 10 mL water). Iso-propanol (3 mL) was added into the reaction mixture to increase the mixing between the two phases. The mixture was stirred at 50°C for 10 hours. The light yellow color gradually transferred from the organic phase to the aqueous phase. The organic phase was decanted and the aqueous phase was washed with pentane (2 X 10 mL). The water was removed under vacuum to give the product $PtCl_2L_2$ (80 to 88% yield depending on the specific alkyl phosphines).

$$cis\text{-}PtCl_2(NCPh)_2 + 2L \rightarrow PtCl_2L_2 + 2NCPh \qquad (3.6)$$

$$L = P[(CH_2)_m\text{-}C_6H_4\text{-}SO_3Na]_3 \quad (m = 0, 1, 2, 3)$$

Preparation of sulfonated phosphine platinum complexes followed the same procedure as the cobalt complexes except (1) 50°C was used because of the lower reactivity of platinum; and (2) three ml of i-propanol was added in order to increase the solubility of $PtCl_2(NCPh)_2$ in the aqueous phase. Light yellow, crystalline samples of $PtCl_2[P((CH_2)_m\text{-}C_6H_4\text{-}SO_3Na)_3]_2$ were obtained. Carbon and hydrogen analyses for the products are collected in Table 3.4.

Surprisingly, the geometry of the product (cis vs. trans) was found to depend on the length of the methylene chain in the alkyl phosphine ligands. For example, when m = 0, only the cis product was obtained. When m = 1, the pure trans product was obtained, while for m = 2 and m = 3, mixtures of trans and cis product were observed. The cis product increases when m increases from 2 to 3. There is 30% cis product when m = 2, whereas, 35% cis product in m = 3 case. ^{31}P NMR results are shown in Figure 3.3 and Table 3.5. Assignment of the cis and trans isomers is straightforward based on ^{195}Pt-^{31}P coupling.[49]

3.4 Preparation of Water Soluble Platinum Bidentate Phosphine Complexes

Amino phosphines can be made water soluble by the quaternization at nitrogen.[76,77] The quaternized amino phosphine platinum complexes are water soluble and can be used for the asymmetric hydroformylation of pro-chiral phosphines.

Table 3.4 Elemental analysis of water soluble platinum phosphine

$PtCl_2[P((CH_2)_m-C_6H_4-SO_3Na)_3]_2 \cdot 6H_2O$	Elemental Analysis			
	C %		H %	
	Fnd.	Cal.	Fnd.	Cal.
m = 0, $PtP_2C_{36}H_{36}O_{24}S_6Na_6Cl_2$	29.7	28.6	2.5	2.4
m = 1, $PtP_2C_{42}H_{48}O_{24}S_6Na_6Cl_2$	33.2	31.6	2.9	3.0
m = 2, $PtP_2C_{48}H_{60}O_{24}S_6Na_6Cl_2$	35.6	34.3	3.5	3.6
m = 3, $PtP_2C_{54}H_{72}O_{24}S_6Na_6Cl_2$	37.6	36.8	3.9	4.1

Table 3.5 ^{31}P NMR data of $PtCl_2[P((CH_2)_m-C_6H_4-SO_3Na)_3]_2$

$PtCl_2L_2$	Trans-product		Cis-product		Cis- : Trans- (%)
	$\delta^{31}P$ (ppm)	J_{Pt-P} (Hz)	$\delta^{31}P$ (ppm)	J_{Pt-P} (Hz)	
$L=P[(CH_2)_0-C_6H_4-SO_3Na]_3$	----	----	13.8	3747	100:0
$L=P[(CH_2)_1-C_6H_4-SO_3Na]_3$	11.2	2497	----	----	0:100
$L=P[(CH_2)_2-C_6H_4-SO_3Na]_3$	10.3	2475	0.19	3493	30:70
$L=P[(CH_2)_3-C_6H_4-SO_3Na]_3$	9.8	2431	-0.11	3472	35:65

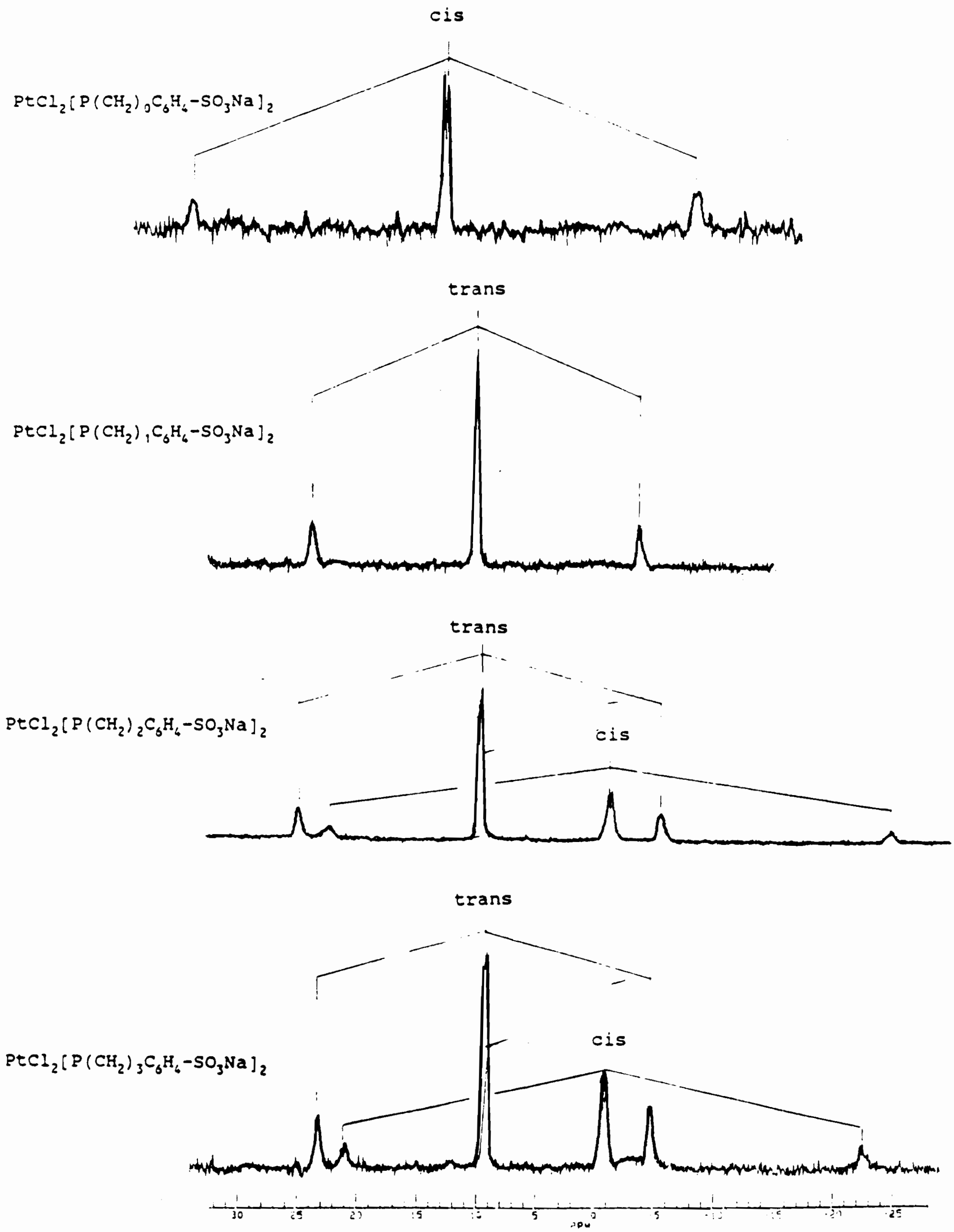


Figure 3.3 ^{31}P NMR spectra of $PtCl_2[P((CH_2)_m-C_6H_4-SO_3Na)_3]_2$

3.4.1 Bidentate Asymmetric Phosphine Platinum Complexes

Previous results[76] showed that tertiary phosphines containing the P-N,N-dimethyl-aminophenyl group are readily synthesized via the potassium phosphide, $KP(p\text{-}C_6H_4NMe_2)_2$. Substitution of chiral ditosylates, with $KP(p\text{-}C_6H_4\text{-}NMe_2)_2$ leads directly to chiral chelating amino phosphines. For example, $KP(p\text{-}C_6H_4\text{-}NMe_2)_2$ reacts with R,R-2,4-pentanediol-distosylate and to yield S,S-$CH_3CH(P(p\text{-}C_6H_4NMe_2)_2)\text{-}CH_2\text{-}CH(P(p\text{-}C_6H_4NMe_2)_2)CH_3$. This ligand has a polar functional group para to the phosphorus atom in contrast the sulfonation phenylphosphines which have the functional group in the meta position.[77,78,79] Since the orientation of the phenyl rings appears to be a necessary for good enantioselection, the introduction of substituents to the para position may be preferable for the modification of ligands. Figure 3.4 shows the synthetic pathway to the bidentate phosphines and their corresponding platinum bidentate phosphine complexes. The ligands were prepared as described by Toth et al.[77] In this work a series of bidentate phosphine platinum complexes was synthesized: $PtCl_2(CHIRAPHOS(NMe_2)_4)$, $PtCl_2(SKEWPHOS(NMe_2)_4)$, and $PtCl_2(DIOP(NMe_2)_4)$. These form chelate rings of 5, 6, and 7 members respectively. The elemental analyses of carbon, nitrogen, and hydrogen are in Table 3.6. Table 3.6 also shows the elemental analysis data of quaternized platinum bidentate phosphine complexes. The quaternization procedure will be discussed in the next section.

In a specific synthesis, 236 mg (0.5 mmol) $PtCl_2(NCPh)_2$ was mixed with 878 mg (1 mmol) of $SKEWPHOS(NMe_2)_4$ in 20 mL of hot benzene. The precipitate was filtered and washed with 10 mL x 2 of n-pentane. Figure 3.5 shows the ^{31}P NMR spectra of $PtCl_2(SKEWPOHS(NMe_2)_4)_2$. A singlet is obtained for the free bidentate phosphine since the two phosphorus are identical (case 1). When the bidentate phosphine coordinated with Pt, satellites due to ^{195}Pt-^{31}P coupling are observed (case 2). Generally speaking, a coupling constant of about 3000 Hz is expected for cis platinum phosphine compounds and 2000 Hz is expected for trans compounds. With chelating phosphines such as $SKEWPHOS(NMe_2)_4$ the complex must be cis and the coupling constant of 3477 Hz is consistent with a cis geometry. When the $PtCl_2(SKEWPHOS(NMe_2)_4)$ compound reacts with $SnCl_2$, the two phosphines are no longer identical. Two sets of ^{31}P signals are observed for the phosphines (case 3). One is located at -0.37 ppm; it is assigned to the phosphine which is cis to tin. The other is located at 8.92 ppm and is assigned to the phosphine trans to tin.

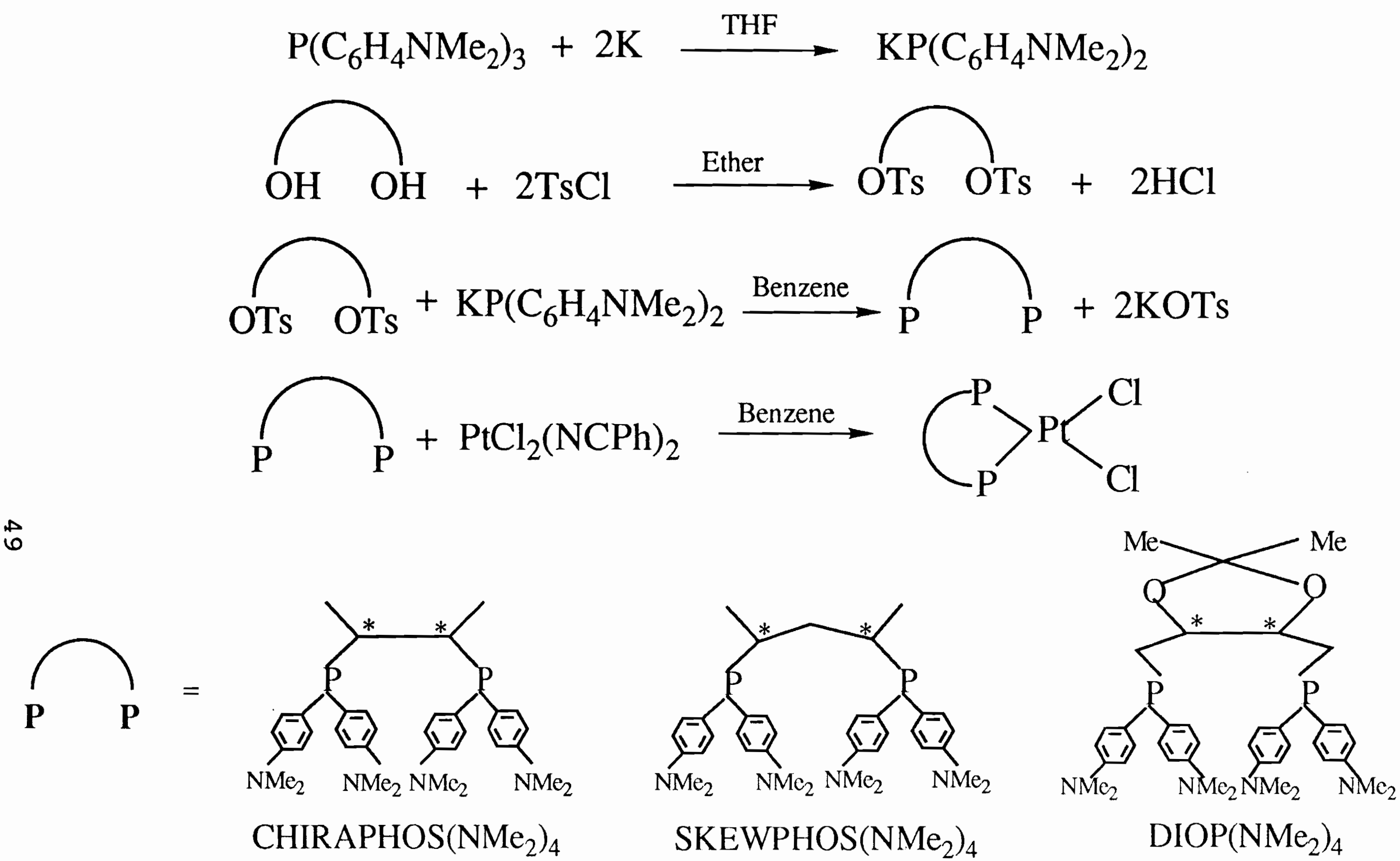


Figure 3.4 The synthetic pathways to Pt-biphosphine complexes

Table 3.6 Elemental analysis of platinum bidentate phosphine amino complexes

Pt Bidentate Phosphine Complexes		Elemental Analysis					
		C %		N %		H %	
		Fnd.	Cal.	Fnd.	Cal.	Fnd.	Cal.
Pt(CHIRAPHOS)	$PtP_2C_{36}N_4H_{48}Cl_2$	50.8	50.0	6.2	6.5	5.7	5.6
Pt(SKEWPHOS)	$PtP_2C_{37}N_4H_{50}Cl_2$	52.6	50.6	6.0	6.3	5.8	5.7
Pt(DIOP)	$PtP_2C_{39}N_4H_{52}O_2Cl_2$	50.2	50.0	5.8	6.0	5.6	5.6
Pt(CHIRA)(BF)	$PtP_2C_{40}N_4H_{60}B_4F_{16}Cl_2$	39.0	38.3	4.2	4.5	4.7	4.8
Pt(SKEW)(BF)	$PtP_2C_{41}N_4H_{62}B_4F_{16}Cl_2$	38.6	38.9	4.6	4.4	4.9	4.9
Pt(DIOP)(BF)	$PtP_2C_{43}N_4H_{64}O_2B_4F_{16}Cl_2$	38.4	38.9	4.2	4.2	4.7	4.8

^{31}P NMR Spectra of $PtCl[skewphos(NMe_2)_4]SnCl_3$

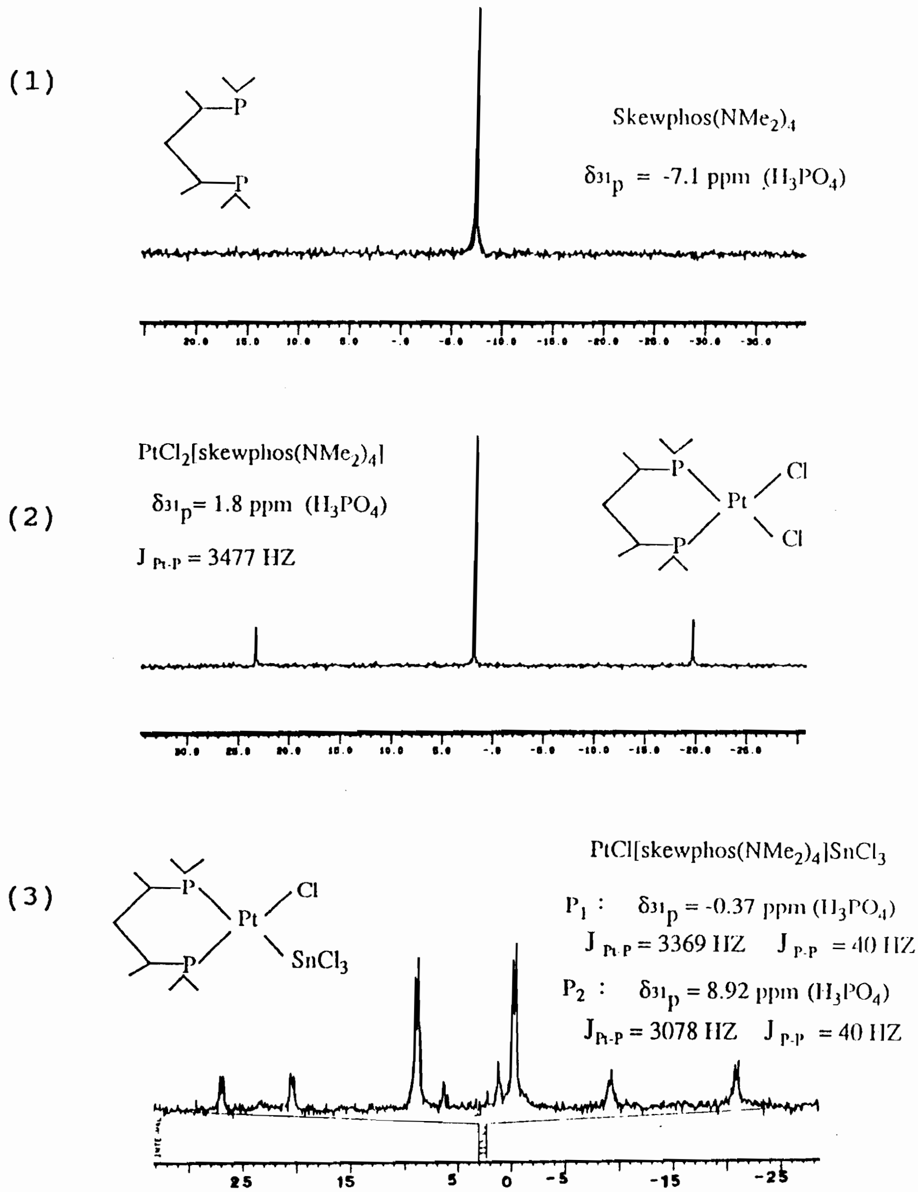


Figure 3.5 ^{31}P NMR spectra of $PtCl_2[SKEWPHOS(NMe_2)_4]_2$ complexes

3.4.2 Quaternization of Platinum Bidentate Phosphine Complexes

The quaternization of the free ligands cannot be achieved directly without oxidation of the phosphine to the corresponding phosphine oxide. However, phosphorus may be protected by coordination to a metal.[79,80] In the present case protection of phosphine was achieved by forming the platinum complexes. Then platinum bi-dentate phosphine complexes were quaternized by the addition of Me_3OBF_4 to a dry acetone solution of platinum complex. The synthetic reaction is given in Equation 3.7.

As an example, 878 mg (1 mmol) of [S,S-($CH_3CH(P(p\text{-}C_6H_5NMe_2)_2)CH_2CH(P(p\text{-}C_6H_4NMe_2)_2)CH_3$)]-$PtCl_2$ was dissolved in 20 mL of dry acetone. 147 mg Me_3OBF_4 was added to the solution with caution. Me_3OBF_4 is a very moisture sensitive reagent and decomposes in a few seconds when exposed to air. The extent of quaternization is readily monitored by NMR spectroscopy. Attempts to quaternize the free ligand give additional quaternization at phosphorus.

$$(S,S)\text{-}2,4\text{-}([P(p\text{-}C_6H_4NMe_2)_2]_2\text{-pentane})PtCl_2 + Me_3OBF_4$$

$$\rightarrow (S,S)\text{-}2,4\text{-}([P(p\text{-}C_6H_4NMe_3^{+}BF_4^{-})_2]_2\text{-pentane})PtCl_2 \qquad (3.7)$$

The resulting platinum complex with the methyl quaternized ligands has very high water solubility. For example, 100 mg of $PtCl_2[P(p\text{-}C_6H_4NMe_2)_2]_2$ dissolving in 1 mL water was achieved in this work.

3.5 Immobilization of Water Soluble Catalysts

Generally speaking, immobilization of water soluble cobalt and platinum complexes is achieved by dissolving the complexes in small amount of water and impregnating them onto the desired supports. However, attention has to be paid to the reaction sequence which plays an important role. Neglecting these steps, can lead to failure. For example, in the case of platinum complexes, too much water adsorbed on the support will lead the decomposition of Pt-Sn bonding. Specific reaction conditions are given in the following subsection.

3.5.1 Glass Supported Catalyst

The controlled pore glass, CPG-00350 from CPG Inc., was used in this work. The physical properties of the glass are as following:

Series No. CPG00350

Mean pore Dia. (Å):	343
Pore Dist. (±%):	5.0
Pore Vol. (cc/g):	0.97
Sur. Area (M^2/g):	67.5
Particle size (mesh):	120~200

3.5.1.1 Cobalt Complexes

The controlled pore glass was degassed by stirring in degassed deionized water for 5 hours. The water was removed by syringe and the glass was vacuum dried at room temperature. Sufficient water to dissolve 100 mg of $Co_2(CO)_6L_2$ ($L = P[(CH_2)_m$-C_6H_4-$SO_3Na]_3$, m = 0, 1, 2, 3) was used to prepare solutions of these complexes. For those catalyst systems with excess phosphine, the phosphine was dissolved together with the cobalt complex. The solution was then added to 3 g of degassed CPG-350 by the incipient wetness technique. Excess water removed under vacuum at room temperature to yield a "dry" catalyst. Thermogravimetric analysis showed that the dry glass contained 1.4% water by weight. The solid state ^{31}P NMR spectra for the supported cobalt catalysts were consistent with the solution NMR data.

3.5.1.2 Platinum Complexes

The same process was followed as described for the immobilization of cobalt complexes except the vacuum drying was 24 hours to remove the water. A water content which is too high will lead to the subsequent decomposition of Pt-Sn bond. To the "dry" $PtCl_2L_2$/glass was added a two-fold excess of $SnCl_2$ in CH_2Cl_2 solution. The slurry was stirred for 4 hours. The color of the solid changed from light yellow to orange consistent with the formation of a $PtClL_2$-$SnCl_3$ complex on the glass. The detailed scheme is shown in Figure 3.6a.

Immobilization of Pt-Sn Catalysts

$PtCl_2(TPPTS)_2$	$[PtCl_2(skewphos(NMe_3)_4)]^{+4}$
↓	↓
Supported on glass in water	Supported on resin in water
↓	↓
Vacuum dry 24 hrs	Vacuum dry 24 hrs
↓	↓
Add $SnCl_2$ in CH_2Cl_2	Add $SnCl_2$ in CH_2Cl_2
↓	↓
$PtCl(TPPTS)_2\text{-}SnCl_3$/glass	$[PtCl(skew)\text{-}SnCl_3]^{+4}$/resin
(3.6a)	(3.6b)

Figure 3.6 The procedure of immobilization of Pt-Sn complexes

3.5.2 Ion Exchange Resins Supported Catalysts

Both anion and cation exchange resins were used as supports in this work. The physical properties and functional groups of the materials are listed below:

Resin	Size (mesh)	Functional group	Stable pH
Amberlyst A-26(C)	16-50	$R-N(CH_3)_3^+$	0-14
Amberlite 200C(H)	16-50	$R-SO_3^-$	0-14

A typical process is as follows: 10 g of Amberlite was washed with 2 x 100 mL deionized water and stirred in 20 mL 1N NaOH for 24 hours. This neutralization step is necessary to avoid the polymerization of olefin which is catalyzed by the acidic sites of the cation exchange resin. The resin then was washed with methanol and water, and vacuum dried. Then 13.1 mg (0.015 mmol) quaternized $PtCl_2[SKEWPHOS(NMe_3BF_4)_4]$ was added with 10 mL of CH_2Cl_2 in which it is slightly soluble. The mixture was kept under N_2 for 48 hours to ensure exchange onto the resin. The organic phase gradually changed color from light yellow to colorless. The color of exchange resin turned yellow. The solvent was removed by syringe and the solid was washed with methanol. A two-fold excess of $SnCl_2$ in CH_2Cl_2 was added to the solid and the mixture was stirred for 8 hours. The solvent was then removed by syringe and the solid catalyst was washed three times with 20 mL pentane and vacuum dried. The dried supported catalyst was stored under N_2 in a Schlenk flask for further use. Figure 3.6b shows the detailed procedure.

3.6 Hydroformylation of Olefins

Cobalt or platinum complexes were charged into an autoclave under N_2. Olefin and solvent were pretreated as described in the section 3.1. The reactions were carried under H_2/CO (1:1 unless otherwise specified) at high pressure (for cobalt, 800 psi; for platinum, 1000 psi) and temperature (cobalt, 190°C; platinum, 100°C). The autoclave was equipped with a magnetic stirring bar. The autoclave was heated in an oil bath and the temperature was controlled by an omega unit during the entire reaction period. The gas uptake was monitored by a pressure gauge which was mounted on the autoclave. When the reaction was finished, the autoclave was cooled to room temperature and the pressure was released. The products were analyzed by GC and NMR (polarimetric analysis was also performed for asymmetric hydroformylation products). The average turnover frequency, tof (hr^{-1}), was used as a measurement of catalyst reactivity. tof (hr^{-1}) is defined as the moles of starting olefin which is converted to products per one mole of catalyst per hour.

All manipulations for catalyst recycling were carried out under nitrogen. In the cases of two-phase and supported aqueous phase catalytic runs, the organic phase was removed and the catalyst was recharged to the reactor for the next cycle. For the phase transfer catalyst recycling with $Co_2(CO)_6(TRIMAPP)_2$, water and HBF_4 were added until the color of organic phase was totally colorless. The organic phase was then removed for analysis. New substrate and solvent were then added. A schematic representation of the procedures used for catalyst recycling of $Co_2(CO)_6(TRIMAPP)_2$ is shown in Figure 3.7.

Catalysis in organic phase during the reaction

Catalyst is extracted into water phase for recovery

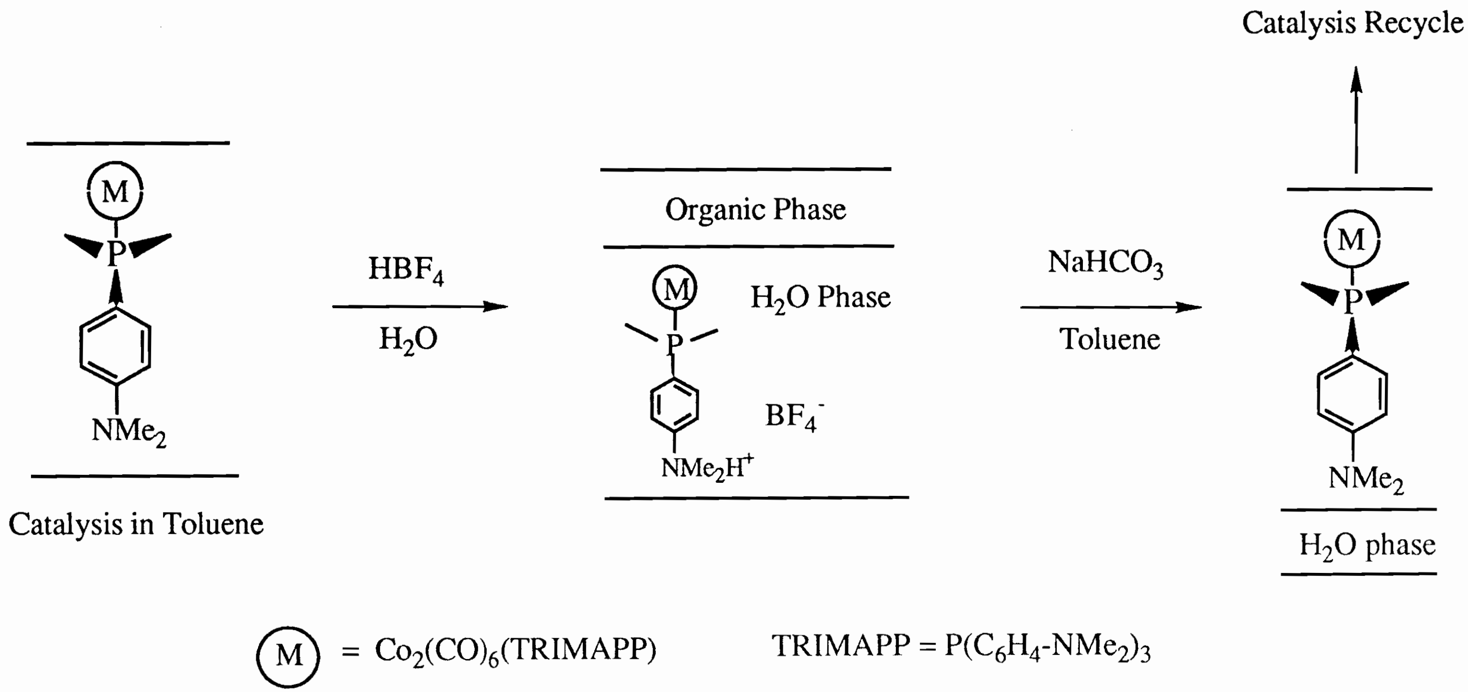


Figure 3.7 Procedure of phase transfer $Co_2(CO)_6(TRIMAPP)_2$ catalyst recovery

CHAPTER 4. RESULTS AND DISCUSSIONS

4.1 Hydroformylation of Linear Olefins

Recently, a large number of supported water soluble rhodium catalysts for the hydroformylation of olefins have been reported.[11,12,57,81-86] A supported version of the water soluble rhodium catalyst, $HRh(CO)(TPPTS)_3$, has also recently been developed.[57,81,85] The supported catalyst is generated by taking the aqueous phase which contains $HRh(CO)(TPPTS)_3$ onto the surface of a hydrophilic support such as a controlled pore glass.[81] This is referred to as a supported aqueous phase (SAP) catalyst. The key features of this catalyst system include no observable loss of transition metal to the substrate phase and enhanced activity towards high molecular weight olefins compared to a simple two-phase catalytic system.[57,81,85,86] The enhanced activity is expected from the increase in surface area between the supported phase containing the catalyst and the organic substrate phase. One major advantage of SAP catalysis is that the supported water layer is immiscible with hydrocarbons. This allows the SAP catalysts to be used with liquid hydrocarbon substrates in contrast with other supported liquid phase catalysts which can be used only with gas phase reactants.

Generally speaking, cobalt, rhodium, platinum water soluble complexes have been used in most catalytic applications for hydroformylation of olefins. In practice cobalt is often preferable to rhodium as a hydroformylation catalyst for liquid olefin substrates.[87] With higher molecular weight substrates the separation of catalyst and products is a difficult operation and the potential cost due to loss of rhodium in a liquid phase reaction is prohibitively high. Thus cobalt has an economic advantage over rhodium due to its lower cost. Rhodium however is orders of magnitude more active than cobalt which gives incentive to the development of immobilized rhodium catalysts such as the SAP catalyst mentioned above. Another advantage of cobalt carbonyl and its derivatives in the hydroformylation reaction is the high rate of isomerization that is achieved. Thus internal olefins can be used as the substrate and still yield a relatively high degree of linear aldehyde, or alcohol, as product. Although the recycling of phosphine modified cobalt carbonyls appears straightforward, the process could be simplified with a heterogeneous catalyst. For this reason immobilized phosphine cobalt carbonyl catalysts are also of interest. Cobalt carbonyls have previously been immobilized on polystyrene and on polyvinyl pyridine and used as hydroformylation catalysts.[88] In both cases significant quantities of cobalt are lost from the support.

Platinum phosphine complexes are also good candidates for the hydroformylation of different olefins. The most noticeable advantage of platinum complexes is the high optical selectivity towards to the aldehyde products when asymmetric diphosphines are used as the ligands. In addition, most platinum phosphine complexes are more stable in air than the corresponding cobalt and rhodium complexes.

Phosphines are well known as the most effective ligands which can be used in the modification of transition metal complexes. The influence is believed to be due to a combination of the electronic and steric effect. Detailed studies on these effects have been reported in the literature.[22,89]

In this work, a series of water soluble phenyl alkyl phosphine modified cobalt and platinum complexes were used under SAP catalysis conditions. Cobalt and platinum loss was significantly reduced compared to two-phase reaction conditions and the catalytic activity can be mostly attributed to the supported cobalt and platinum complexes rather than the cobalt and platinum in the organic phase. As the alkyl chain increases length, the activity and selectivity changes.

4.1.1 Hydroformylation by Cobalt Complexes

The emphasis of this section is placed on the investigation of virtues of $Co_2(CO)_6(TPPTS)_2$ catalysis. Then, the influence of alkyl groups in $Co_2(CO)_6(P((CH_2)_m-C_4H_6-SO_3Na)_3)_2$ (m = 0, 1, 2, 3); influence of H_2/CO ratio; influence of solvent pH are discussed. Finally, a special technique for catalyst recovery with $Co_2(CO)_6(TRIMAPP)_2$ is also reported.

4.1.1.1 By $Co_2(CO)_6(TPPTS)_2$

Results for the hydroformylation of 1-hexene by $Co_2(CO)_6(TPPTS)_2$ under "two phase" reaction conditions are shown in Table 4.1. The n/b ratios under these conditions are low and the degree of cobalt leaching to the organic phase is high. In examples 5 and 6 a liquid water phase is not present at the reaction temperature and pressure used. Not surprisingly the activity of the solid in the absence of a suitable solvent is virtually nil.

The corresponding results for the supported complex are given in Table 4.2. The water contents listed in Table 4.2 represent the total water present in the reactor during the

Table 4.1 Hydroformylation by $Co_2(CO)_6(TPPTS)_2$ under two phase reaction conditions

entry	@(mg)/H_2O(ml)/ toluene(ml)	P/Co	aldyd. conv.%	n/b of Aldyd.	alcol. conv.%	n/b of Alcol.	tof (hr^{-1})	cobalt leaching
1	100/50/20	1	26.7	1.25	0	---	19.0	10.9
2	100/50/20	2	27.1	1.85	4.8	1.46	19.3	5.7
3	100/5/5	1	32.6	1.33	3.0	0.99	25.4	3.6
4	100/2/5	1	19.0	1.37	1.4	0.91	14.5	3.1
5	100/0.5/5	1	3.96	1.07	0.2	1.14	3.0	1.7
6	100/0/5	1	0.73	1.48	0	---	0.5	0.5

@ = $Co_2(CO)_6(TPPTS)_2$, 190°C, 800 psi, H_2/CO = 1:1, 8 hours, 10 ml 1-hexene catalytic reaction. Cobalt leaching is reported as the percent of total cobalt in the reactor which is present in the organic phase after catalysis.

At high pressures of CO and H_2 the equilibria shown in the following scheme are likely for cobalt carbonyl phosphine complexes.[80]

Scheme 4.1

$$\begin{array}{ccc}
Co_2(CO)_6(TPPTS)_2 & \overset{H_2}{\rightleftharpoons} & 2HCo(CO)_3(TPPTS) \\
CO \downarrow\uparrow TPPTS & & TPPTS \uparrow\downarrow CO \\
Co_2(CO)_8 & \overset{-H_2}{\rightleftharpoons} & 2HCo(CO)_4
\end{array}$$

Dicobalt octacarbonyl and hydridotetracarbonyl cobalt are both more soluble in organic solvents than in water. Thus if these complexes are formed they are likely to be extracted into the organic phase under two-phase reaction conditions. The low n/b ratios obtained with $Co_2(CO)_6(TPPTS)_2$ are consistent with cobalt carbonyl in the organic phase as the dominant active species for hydroformylation. As the amount of water in the system is decreased the total amount of cobalt lost decreases. Also the activity as expressed by turnover frequency (tof) decreases. This suggests that less of the cobalt is active when the total water in the system is decreased. Given the large reactor volume and the high temperatures it is likely that much of $Co_2(CO)_6(TPPTS)_2$ precipitates during the reaction as water enters the gas phase and is thus unavailable for either decomposition to cobalt carbonyl or catalytic activity. The pure solid, entry 6 (Table 4.1), is virtually inactive for hydroformylation and also loses very little cobalt to the organic phase. The n/b ratios appear to be independent of water content.

More of the cobalt is kept in the water phase upon addition of excess phosphine (compare results from runs 1 and 2 in Table 4.1 and 4.2). However significant quantities of cobalt are still leaching into the organic phase. The relatively low n/b ratios are consistent with leached cobalt carbonyl as the dominant catalyst in the system.

The results shown in Table 4.2 demonstrate that immobilization of $Co_2(CO)_6(TPPTS)_2$ onto a controlled pore glass has a significant effect on its activity. Most noticeable are the improvement in n/b ratios and the decreased level of cobalt leaching. Because of the reactor volume and temperature only in examples 1 and 2 is a liquid water phase expected under reaction conditions. The total water content

Table 4.2 Hydroformylation by $Co_2(CO)_6(TPPTS)_2$ in a supported aqueous phase

entry	@ loading(mg)/ water(ml)	P/Co	aldyd. conv.%	n/b of aldyd.	alcol. conv.%	n/b of alcol.	tof (hr^{-1})	cobalt leaching
1	200/5.0[a]	1	50.6	2.02	20.4	1.39	25.3	1.1
2	200/5.0[a]	2	59.4	2.28	16.9	1.33	27.2	0.8
3	200/0.5[a]	2	66.3	2.20	5.6	1.12	25.6	0.4
4	200/0[a]	2	68.2	2.12	5.8	0.95	26.1	0.4
5	100/0.27[b]	1	34.0	2.06	10.3	1.20	31.6	0.5
6	50/0.27[b]	1	30.4	2.12	9.6	1.05	57.0	0.2
7	50/0.5[a]	2	32.0	2.37	4.2	1.36	51.4	0.1
8	30/0.27[b]	1	22.4	2.32	1.2	1.51	55.9	0.1
9	10/0.27[b]	1	5.9	2.50	2.9	1.73	59.7	0.1

190°C, 800 psi, H_2/CO = 1:1, 8 hours, 10 ml 1-hexene, 3.0 g glass

@ = $Co_2(CO)_6(TPPTS)_2$, a: 50 ml toluene, b: 10 ml toluene in the reactor does not significantly affect the activity of the supported catalyst; all catalysts behave similarly to the catalyst to which no water was added (entry 4, 1.4 wt% water). This is opposite to what was observed with rhodium SAP catalysts with octene and other high molecular weight substrates in cyclohexane solvent.[81] For the rhodium catalysts activity was maximized at about 8 wt% water and decreased rapidly as the water content increased. At elevated temperatures 1-hexene has appreciable water solubility which may account for the catalytic activity even in the presence of excess water which is expected to fill the pores of the glass (examples 1 and 2). Water, in turn, has an appreciable solubility in toluene; the substrate phase may in fact be homogeneous at these high temperatures. These aspects of the cobalt catalysts suggest that the surface composition has very little water content under reaction conditions.

Importantly, the activity of the supported catalysts does not correlate with cobalt leached to the organic phase. Both in absolute terms and when expressed as a percent of total cobalt, the amount of cobalt leached is much less when $Co_2(CO)_6(TPPTS)_2$ is supported on CPG-350 compare to the two-phase reaction. This suggests that the activity observed for the supported catalysts is due to the cobalt on the glass and not to the small quantities that have leached from the glass.

Further evidence for this conclusion comes from the observed n/b ratios which are higher for the supported catalysts than for $Co_2(CO)_6(TPPTS)_2$ at similar levels of conversion under two-phase conditions. The n/b ratios are similar to those obtained with triphenylphosphine modified cobalt carbonyl catalysts at similar temperatures and pressures.[87,90] Reaction selectivity is also a function of temperature and pressure and may be improved through modification of the reaction conditions.

The reaction rates, as expressed by the average turnover frequency per cobalt, improve as the cobalt loading of the catalysts is decreased. This suggests that at high cobalt loading much of the cobalt is not available for catalytic activity in the SAP catalyst.

The addition of excess phosphine to the cobalt SAP catalyst has little effect on the reaction selectivity and activity at 190°C and 800 psi. However cobalt loss from catalysts with P/Co ratios of 2 is further reduced under batch conditions (compare runs 1 and 2 in Table 4.1). Also a comparison of reactions 1 and 2 in Table 4.2 shows that even with an increase in the toluene volume less cobalt is leached in the presence of excess phosphine.

From studies of homogeneous phosphine modified cobalt catalysts it is well known that phosphine ligand dissociation is significant for triphenylphosphine and that the equilibria represented in Scheme 4.1 are shifted in favor of the phosphine substituted complexes in the presence of excess phosphine.[90] This is particularly true for large, less basic, phosphines such as triphenylphosphine. The role of excess phosphine in keeping the cobalt on the glass is most likely to lower the equilibrium concentration of $HCo(CO)_4$. Thus, the ultimate stability and lifetime of the cobalt SAP catalysts with TPPTS as the water solubilizing ligand is limited by this equilibrium. Also the catalysts darken with use which may indicate decomposition of some complex to cobalt metal on the glass.

4.1.1.2 Influence of Alkyl Chain

It is well known that the electronic and steric effects of phosphine ligands have an influence on the catalysis property of phosphine modified transition metal complexes.[22] In hydroformylation, it is believed that the presence of bulky phosphines is the key for the n/b selection. Phosphine modified rhodium catalysts give higher n/b ratio than similar cobalt systems. One explanation is that the rhodium hydrogen bond is less acidic than Co-H. Therefore, it is worth trying to adjust the basicity and bulkiness of cobalt complexes by changing the alkyl group in the phosphine. In this section, the influence of alkyl chain in phosphine ligands on the activity and selectivity of hydroformylation will be discussed.

Homogeneous phase system

Table 4.3 shows the results of hydroformylation of 1-hexene by $Co_2(CO)_6[P((CH_2)_m-C_6H_5)_3]_2$ (m = 0, 1, 2, 3) under homogeneous conditions. TP, BP, EP, and PP stand for triphenyl phosphine, benzyl phosphine, ethyl phenyl phosphine, and propyl phenyl phosphine respectively. While STP, SBP, SEP, and SPP stand for the corresponding sulfonated phosphines.

First, when P/Co is low (P/Co = 1), tof is high, comparing entries 1 ~ 4 with 5 ~ 8 in Table 4.3. Second, when P/Co = 5, n/b increases about two to three fold (compare 1 with 5 and 4 with 8) than that in P/Co = 1 case. The influence of excess phosphine is likely to increase the concentration of the active species $HCo(CO)_3L$.

Scheme 4.2

$$HCo(CO)_3L \underset{L}{\overset{CO}{\rightleftharpoons}} HCo(CO)_4$$

When P/Co = 1, the equilibrium expressed in scheme 4.2 is more likely to be generating more $HCo(CO)_4$. When cobalt carbonyl is used as a catalyst for hydroformylation of 1-hexene at 190°C and 800 psi ($H_2/CO = 1$), a n/b ratio of 3.8 is observed. When P/Co = 5, more $HCo(CO)_3L$ will be present resulting in the higher n/b ratios observed and giving lower activity. In entry 1 ~ 4, because of the dissociation of phosphine ligands from the complex, change in the alkyl group does not have much influence on the catalysis. n/b ratios are in the range of 1 to 2. However, in P/Co = 5 cases, the $HCo(CO)_3L$ species dominates. Thus, the n/b ratio reflects the change in alkyl phosphine ligands. For example, a n/b ratio as high as 9.4 is obtained in when $L = P((CH_2)_3{-}C_6H_5)_3$.

Table 4.3 Hydroformylation by homogeneous phase $Co_2(CO)_6L_2$

catalyst system	P/Co	aldyd. conv. %	n/b	alcol. conv. %	tof(hr^{-1})	Co leaching
$Co_2(CO)_6(TP)_2$	1	39.1	1.09	8.9	50.2	-----
$Co_2(CO)_6(BP)_2$	1	68.2	1.05	11.7	99.8	-----
$Co_2(CO)_6(EP)_2$	1	58.7	1.03	6.1	81.0	-----
$Co_2(CO)_6(PP)_2$	1	43.5	3.10	21.0	80.6	-----
$Co_2(CO)_6(TP)_2$	5	27.1	2.55	12.5	49.5	-----
$Co_2(CO)_6(BP)_2$	5	38.6	3.05	13.3	64.9	-----
$Co_2(CO)_6(EP)_2$	5	23.9	5.27	8.7	40.8	-----
$Co_2(CO)_6(PP)_2$	5	20.6	9.40	29.5	62.6	-----

Co/1-hexene = 1/500, 190°C, 800 psi, 4 hours, solvent = toluene

Two phase system

One of the most serious problems with water soluble catalysts is the loss of metal into the organic phase. This degrades the catalyst system constantly and results in loss of activity and perhaps selectivity. Much effort has been made to reduce the leaching of active species from immobilized. The results of two phase system catalysis by $Co_2(CO)_6L_2$ in Table 4.4 show that the cobalt leaching can be reduced by adjusting the alkyl phosphine ligands in the complex. As shown in entry 1, when m = 0, there is 5.7% of cobalt metal leaches to the organic phase after a batch reaction. However, when m = 1, 2, 3, the cobalt loss becomes nil. Stronger Co-P bonding is expected because of stronger electron donation from the alkyl phosphines. The cobalt complexes are more firmly held in the aqueous phase by these water soluble phosphine ligands.

Unfortunately, while the cobalt gave relative good n/b ratios in toluene, the sulfonated analogues gave low n/b ratios in water. n/b ratios are in the range of 1 to 1.8 even in the P/Co = 5 cases. The low selectivity suggests that water is a poor solvent for hydroformylation. The high polarity of water may lead to different preferred orientation of the olefin when coordinated to the metal.

Table 4.4 Hydroformylation by two phase $Co_2(CO)_6L_2$

catalyst system	P/Co	aldyd. conv. %	n/b	alcol. conv. %	tof(hr^{-1})	Co leaching
$Co_2(CO)_6(STP)_2$	1	27.1	1.85	4.8	19.9	5.7%
$Co_2(CO)_6(SBP)_2$	1	34.3	1.20	1.2	22.2	No
$Co_2(CO)_6(SEP)_2$	1	31.8	1.07	3.6	22.1	No
$Co_2(CO)_6(SPP)_2$	1	38.0	1.18	2.6	25.4	No
$Co_2(CO)_6(STP)_2$	5	26.8	1.52	0.8	17.3	0.4%
$Co_2(CO)_6(SBP)_2$	5	24.6	1.35	1.3	16.2	No
$Co_2(CO)_6(SEP)_2$	5	28.7	1.30	1.2	18.7	No
$Co_2(CO)_6(SPP)_2$	5	34.5	1.34	0.7	22.0	No

Co/1-hexene = 1/500, 190°C, 800 psi, 8 hours, solvent = toluene/water

Supported aqueous phase

In supported aqueous phase catalysis, water soluble complexes adhere to the surface of the hydrophilic support. The metal may have access to the organic phase if there is insufficient surface water to cover the entire metal complex. Therefore, similar results may be obtained for SAP catalysts compared to homogeneous phase catalysts in nonaqueous solvents, except perhaps that lower activity may be observed due to mass transfer. For example, m = 3 a n/b ratio of 3.1 to 3.7 (Table 4.5) is obtained in the supported case. This is intermediate between the values obtained for $Co_2(CO)_6(PP)_2$ in toluene and $Co_2(CO)_6(SPP)_2$ in water. Summarizing the results of Table 4.3, 4.4, and 4.5, some interesting features can be seen:

System	CHO conv.%	n/b	COH conv.%
Homogeneous	H	H	H
Two phase	M	L	M
SAP	L	M	L

(H = high, M = medium, L = low)

Not surprisingly, the homogeneous system yields the highest conversion in both hydroformylation and hydrogenation. This means that mass transfer is still a problem for the two phase and supported aqueous phase systems. Intermediate n/b ratios are obtained in the supported phase. This may be explained by a relatively non polar environment at the metal in the supported system since insufficient water is present to cover the metal complex. A value of n/b = 3.58 is obtained in the P/Co = 5 case (entry 5 in Table 4.5). Even though this number is not as good as the commercial process (n/b = 4~6), the supported system does have the advantage of catalyst/product separation and does not show the cobalt leaching.

No conversion to alcohol is observed in the supported aqueous phase cases.

4.1.1.3 Influence of H_2/CO Partial Pressure Ratio

Hydrogen plays three roles in hydroformylation reaction: (1) initiation of the Co-H bond; (2) hydrogenation of olefin double bond; (3) hydrogenolysis of the Co-acyl intermediate to an aldehyde or alcohol. The results in Tables 4.3, 4.4, and 4.5

Table 4.5 Hydroformylation by supported phase $Co_2(CO)_6L_2$

catalyst system	P/Co	aldyd. conv. %	n/b	alcol. conv. %	tof(hr^{-1})	Co leaching
$Co_2(CO)_6(STP)_2$	5	29.7	2.28	1.69	19.6	No
$Co_2(CO)_6(SBP)_2$	5	20.2	1.97	0.43	12.9	No
$Co_2(CO)_6(SEP)_2$	5	13.7	2.01	0.41	8.8	No
$Co_2(CO)_6(SPP)_2$	1	16.7	1.45	0	10.4	No
$Co_2(CO)_6(SPP)_2$	5	15.3	3.58	0	9.6	No
$Co_2(CO)_6(SPP)_2$[a]	5	12.4	3.71	0	7.8	No
$Co_2(CO)_6(SPP)_2$[b]	5	10.1	3.15	0	6.3	No

Co/1-hexene = 1/500, 190°C, 800 psi, 8 hours, solvent = toluene

a: 150°C, b: without water

show that in two phase and supported aqueous phase catalysis, low conversion to alcohol was obtained. It was suspected that H_2, which has a low solubility in water may be in low concentration at the active center. A set of experiments was carried out in order to study the role of H_2 partial pressure. The H_2/CO ratio was set at three different values: (1) $H_2/CO = 1/9$; (2) $H_2/CO = 1/1$; (3) $H_2/CO = 9/1$. The different H_2/CO ratio was adjusted by controlling the partial pressure of these two gases. For example, in $H_2/CO = 1/9$ case, 80 psi H_2 was introduced to the reactor first. Then 720 psi of CO was quickly introduced to the reactor in order to avoid the hydrogen back feeding. The hydroformylation reactions were performed under same condition except the H_2/CO partial pressure ratio. As shown in Table 4.6, there is no strong evidence shows that H_2 solubility is the reason for low conversion to alcohol in water. First, the conversion of alcohol does not change when H_2/CO ratio changes in two-phase and supported aqueous phase cases (entries 5 and 6, 8 and 9). Second, hexene hydrogenation conversion changes when the H_2/CO ratio changes. For example, conversion to hexane is 14.0% when $H_2/CO = 1/9$; it increases to 48.0% when H_2/CO ratio increases to 9/1 (entries 5 and 6). Hydrogenation to alkane also requires a high concentration of hydrogen. Third, as suggested

Table 4.6 Influence of H_2/CO ratio on hydroformylation with catalysis of $Co_2(CO)_6L_2$

system	H_2/CO	reaction time(hr.)	aldyd. conv. %	n/b	alcol. conv. %	n/b	alkane conv. %
L=PP	1:1	4	20.6	9.40	29.5	31.5	15.5
Homog.	9:1	4	0	---	52.5	8.8	18.9
phase	1:9	4	24.6	10.6	12.8	*	13.1
L=SPP	1:1	8	34.5	1.34	0.7	1.2	18.4
Two	9:1	8	10.5	0.71	0	---	48.0
phase	1:9	8	38.2	2.32	0	---	14.0
L=SPP	1:1	8	15.3	3.58	0	---	30.6
Heteg.	9:1	8	8.7	3.55	0	---	44.2
phase	1:9	8	27.3	3.71	0	---	19.8

Co/1-hexene = 1/500, 190°C, 800 psi, 4 hours, solvent = toluene, P/Co = 5

* pure normal aldehyde was observed

previously, the supported metal complex was in the same situation as in the homogeneous phase except the water soluble phosphine is anchored on the surface of support. However, unlike that in the homogeneous phase, there is no alcohol conversion in the supported case. This fact can be explained by possibility of interaction between the cobalt complex and support. The surface interaction may change the selectivity of supported cobalt catalyst.

Similar conclusions can be drawn from the n/b ratio. The supported aqueous phase system yields intermediate n/b ratios which are higher than obtained under two-phase conditions and lower than obtained for homogeneous catalysts. These differences are likely due to the different environments at the metal complexes in the three reaction conditions. In the homogeneous phase, the metal center does the catalysis under the influence of the organic solvent (toluene in this case). In the two phase-system, the active complex is in the water layer. This environment somehow destroys the orientation of coordination of olefins. In the supported phase, the metal mostly in the organic phase. However the bonding to the surface does affect the n/b ratio and selectivity to alcohol to some extent.

4.1.1.4 Influence of Solvent pH

Influence of pH of solvent has been studied in order to learn that best pH for the reaction of hydroformylation by cobalt complexes. Tables 4.7, 4.8 show the results of influence of pH on the hydroformylation catalyzed by $Co_2(CO)_6(TPPTS)_2$ and $Co_2(CO)_6(SPP)_2$ (SPP = sulfonated propyl phenyl phosphine) respectively. Different pH values in these reactions were controlled by the buffer solution of dibasic and monobasic sodium phosphate (Na_2HPO_4, pH = 9.0; NaH_2PO_4, pH = 4.0). The same reaction conditions were kept except the change of pH.

As shown in Table 4.7 and 4.8, the maximum n/b appears at the pH = 7.0 and the activity reduces as the pH increases in both $Co_2(CO)_6(TPPTS)_2$ and $Co_2(CO)_6(SPP)_2$ case. As the pH increases higher concentrations of $[Co(CO)_3(SPP)]^-$ should be present. The cobalt carbonyl anions are relatively inactive for hydroformylation.

Table 4.7 Influence of pH on hydroformylation by $Co_2(CO)_6(TPPTS)_2$

pH	conv. to aldyd.%	n/b	conv. to alcol.%	n/b	Co leaching
5.5	26.8	1.5	0.8	1.3	No
6.0	21.1	1.8	0	---	No
7.0	15.5	2.3	0	---	No
8.0	14.3	1.8	0	---	No
9.0	13.5	1.6	0	---	No

190°C, 800 psi, 8 hours, P/Co = 5, Co/1-hexene = 1/500, solvent = H_2O/toluene

Table 4.8 Influence of pH on hydroformylation by $Co_2(CO)_6(SPP)_2$

pH	conv. to aldyd.%	n/b	conv. to alcol.%	n/b	Co leaching
5.5	34.5	1.3	0.7	1.1	No
6.0	23.3	1.6	0	---	No
7.0	9.6	2.2	0	---	No
8.0	6.8	1.5	0	---	No
9.0	6.0	1.5	0	---	No

190°C, 800 psi, 8 hours, P/Co = 5, Co/1-hexene = 1/500, solvent = H_2O/toluene

4.1.1.5 $Co_2(CO)_6(TRIMAPP)_2$

$Co_2(CO)_6(TRIMAPP)_2$ (TRIMAPP = tri-methyl-amino-phenyl-phosphine) is known for its potential water solubility upon protonation or quaternization. An interesting catalyst recovery process was used for the hydroformylation of 1-octene by $Co_2(CO)_6(TRIMAPP)_2$. The key point here is that $Co_2(CO)_6(TRIMAPP)_2$ does the catalysis in organic phase and is extracted into water phase by protonation after the reaction is finished. The procedure is described in Figure 4.1 as the follows: (1) first, a batch reaction is catalyzed by fresh $Co_2(CO)_6(TRIMAPP)_2$; (2) when the reaction is complete, the cobalt complex is protonated by HBF_4 and extracted into the water phase; (3) the organic phase is removed and the catalyst stays in the water phase; (4) new substrate and solvent then are added; (5) the protonated cobalt complex is neutralized by $NaHCO_3$ and returns to the organic phase; (6) the water phase is removed and the organic phase is ready to go another catalytic cycle. The important feature of this process is that the catalyst does the catalysis in homogeneous phase. Higher selectivity and activity is received.

Catalysts Recovery of $Co_2(CO)_6(TRIMAPP)_2$ by $HBF_4/NaHCO_3$

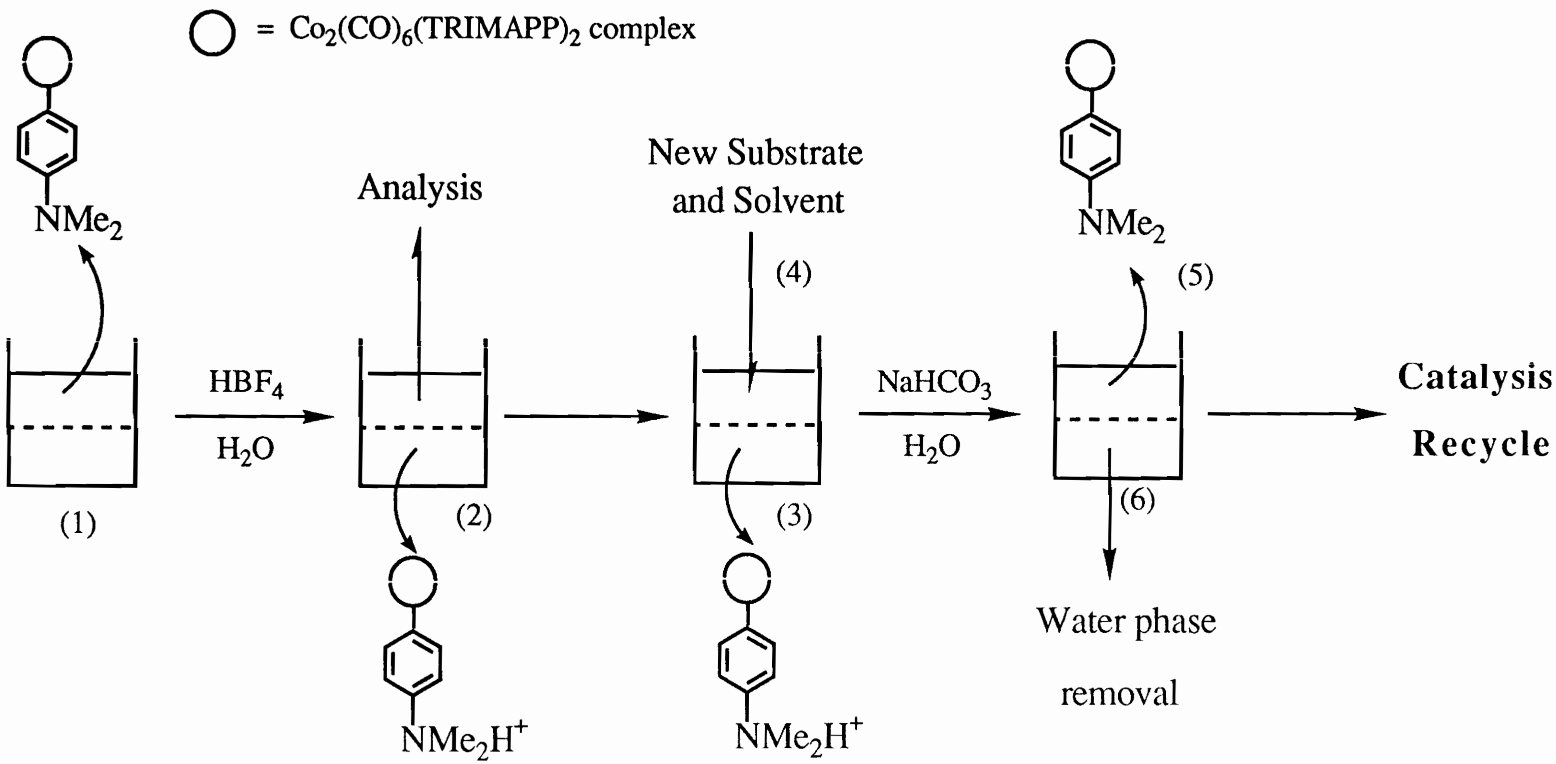


Figure 4.1 Catalyst recovery of $Co_2(CO)_6(TRIMAPP)_2$

Table 4.9 shows the results of catalyst cycle of $Co_2(CO)_6(TRIMAPP)_2$. After four cycles, tof decreases from 14.9 to 11.3 and n/b decreases from 5.6 to 4.0. Considering the factor that certain amount catalyst was lost during the phase transfer because of the small amount of catalyst used (100 mg), these results are promising.

4.1.2 Hydroformylation by Platinum Complexes

The most effective platinum hydroformylation catalysts contain tin(II) chloride as a co-catalyst as, for example, in $Pt(PPh_3)_2Cl-SnCl_3$. The presence of tin not only increases the rate of hydroformylation but also improves the reaction selectivity toward linear aldehyde products. Although the role of tin chloride in the hydroformylation reaction has not been unambiguously established,[91] it is essential in obtaining the most active platinum based hydroformylation catalysts.

It was noted that Pt-Sn bonds are subject to hydrolysis and for this reason water soluble platinum hydroformylation catalysts are not likely to give either good activity or selectivity. Development of supported aqueous phase rhodium hydroformylation catalysts showed that active supported catalysts could be generated with $HRh(CO)(TPPTS)_3$ on

Table 4.9 Hydroformylation of 1-octene by $Co_2(CO)_6(TRIMAPP)_2$

cycle No.	conv. to aldyd.%	n/b	tof(hr^{-1})
1	23.9	5.6	14.9
2	19.9	4.9	12.4
3	18.4	4.2	11.5
4	18.1	4.0	11.3

Co/substrate = 1/500, P/Co = 5, 800 psi, 8 hours, solvent = toluenecontrolled

controlled pore glasses which contain as little as 3 wt% water.[57] At this level of water content it is likely that most of the adsorbed water serves to hydrate the strongly ionic sodium sulfonate groups. In this section, evidence is given that it is possible to support $PtCl[P((CH_2)_m-C_6H_4-SO_3Na)_3]_2-SnCl_3$ (m = 0, 1, 2, 3) on a controlled pore glass in the presence of a small amount of water. These conditions are essentially those of supported aqueous phase catalysis described in the previous section.

4.1.2.1 Supported Aqueous Phase $PtCl(TPPTS)_2-SnCl_3$

The results from the hydroformylation of 1-hexene with Pt supported on glass under a variety of conditions are summarized in Table 4.10. The effect of added water on the reaction with Pt-Sn supported on glass as the catalysts is shown in Figure 4.2.

Complex $PtCl_2(TPPTS)_2$ functions as a catalyst for the hydroformylation of 1-hexene under two phase reaction conditions. Without the addition of excess phosphine there is evidence that some platinum is lost to the nonaqueous phase. The normal to branch ratios obtained, *ca* 2.8, is similar to the results obtained with $Pt(PPh_3)_2Cl_2$ in nonaqueous solvents.[93] Also, the rates are low which is expected for platinum complexes without tin as a co-catalyst.

Virtually identical results are obtained with $PtCl_2(TPPTS)_2$ supported on CPG-350. For the supported catalysts the normal to branch ratio varies from 2.35 to 3.01 depending on whether excess phosphene is present. Unlike the cobalt catalyst, the selectivity of the platinum phosphine tin catalysts does not improve in the presence of excess phosphine. Actually the reactivities and n/b ratios decrease when excess phosphine is added. Importantly, the qualitative test for platinum leaching (see experimental section) is negative for the glass supported catalysts.

Since the glass supported catalysts contain so little water, 1.4%, the in situ preparation of Pt-Sn on the glass is possible. The direct immobilization of Pt-Sn onto the glass is not viable since, as noted above, since the Pt-Sn bond is readily hydrolyzed.

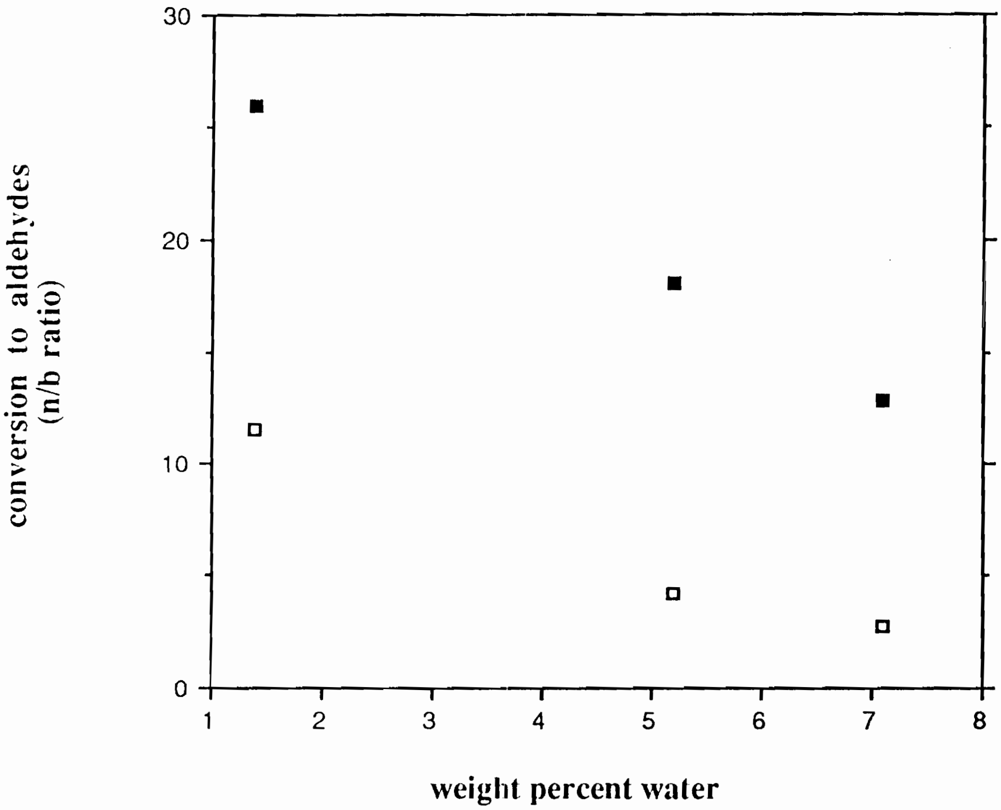
Table 4.10 Hydroformylation by $PtCl_2(TPPTS)_2$

catalyst System	P/Pt	aldyd. %	n/b	tof(hr^{-1})	Pt leaching
$PtCl_2(TPPTS)_2$ (Solid)	2	19.1	2.83	1.59	positive
$PtCl_2(TPPTS)_2$ (Two phase)	2	31.6	2.84	2.63	positive
$PtCl_2(TPPTS)_2$ (Two phase)	5	9.0	2.79	0.75	negative
$PtCl_2(TPPTS)_2$/glass	2	20.1	3.01	1.68	negative
$PtCl_2(TPPTS)_2$/glass	5	18.7	2.35	1.56	negative
$PtCl(TPPTS)_2$-$SnCl_3$/glass	2	26.0	11.5	2.17	negative
$PtCl(TPPTS)_2$-$SnCl_3$/glass	5	14.4	5.58	1.20	negative

100°C, 1000 psi, solvent = toluene, Pt/1-hexene = 1/1000, reaction time = 120 hours

Evidence that Pt-Sn complex is formed on glass is obtained from the catalytic results. Although the rate of hydroformylation is unchanged the reaction selectivity dramatically improves. Normal to branch ratios of up to 11.5 are observed. This is consistent with the high n/b ratios observed with $PtCl(PPh_3)_2$-$SnCl_3$ as a catalyst in toluene.[92,93]

The rates for hydroformylation with Pt-Sn as a catalyst however are still slow. Since it is known that the rate of hydroformylation with supported aqueous phase rhodium catalysts is highly dependent on water content the effect of water on the supported platinum catalysts was investigated. Maximum activity for the rhodium catalysts was observed at ca 6 to 8 wt% water.[81] It was hoped that the addition of water to the extent of 5 to 10 wt% for the platinum catalysts would also yield an increase in the reaction rate. For this to be effective however the platinum-tin bond must not be hydrolyzed in the adsorbed complex. As seen in Figure 4.2 the addition of water to the extent of 7.4 wt% results in a slight decrease in conversion while the n/b ratio drops to 2.5, a value similar to the two phase reactions with $PtCl_2(TPPTS)_2$ as the catalyst. The lower reaction selectivity suggests that 7.4 wt% water in the catalysts is sufficient to hydrolyze the platinum-tin bond. Tests of platinum leaching to organic phase were negative.



□ conversion to aldehyde; ■ n/b ratio

Figure 4.2 Conversion and n/b ratio as a function of water content

4.1.2.2 Influence of Alkyl Chain

The results for the hydroformylation of 1-hexene with $PtCl_2L_2$, L = $P[(CH_2)_mC_6H_5]_3$, $P[(CH_2)_mC_6H_4SO_3Na]_3$, m = 0, 1, 2, 3 under homogeneous and supported aqueous phase conditions are shown in Table 4.11.

The variation in n/b ratio as a function of phosphine for the homogeneous catalysts is most likely due to a combination of steric and electronic effects. The bulkiest phosphine triphenylphosphine (TP) gives the highest n/b ratio. For the phenyl alkyl phosphine n/b increases as the number of methylene groups increases. The results for the supported aqueous phase catalysts paroled these obtained under homogeneous conditions. The sulfonated triphenylphosphine, STP, gives the best n/b ratio and n/b increases as the number of methylene groups increase for the sulfonated phenyl alkyl phosphines. Overall the activity of the supported catalysts is much less than the homogeneous catalysts.

Table 4.11 Influence of alkyl chain on hydroformylation by $PtClL_2-SnCl_3$

catalyst system	P/Co	aldyd. conv. %	n/b	alcol. conv. %	tof(hr^{-1})	Pt leaching
(Homogeneous phase catalysis)						
$PtCl(TP)_2-SnCl_3$	2	83.7	18.5	0	104	-----
$PtCl(BP)_2-SnCl_3$	2	16.7	3.48	0	70.9	-----
$PtCl(EP)_2-SnCl_3$	2	49.4	5.61	0	61.8	-----
$PtCl(PP)_2-SnCl_3$	2	42.4	7.19	0	53.0	-----
(Supported aqueous phase catalysis)						
$PtCl(STP)_2-SnCl_3$	2	4.6	10.3	0	5.7	No
$PtCl(SBP)_2-SnCl_3$	2	3.6	3.72	0	4.5	No
$PtCl(SEP)_2-SnCl_3$	2	2.4	5.82	0	3.0	No
$PtCl(SPP)_2-SnCl_3$	2	2.1	8.71	0	2.6	No

Pt/1-hexene = 1/1000, 100°C, 1000 psi, 8 hours, solvent = toluene

4.2 Asymmetric Hydroformylation

At the present time, all commercial hydroformylation process use either rhodium or cobalt complexes as catalysts.[94] In the area of asymmetric hydroformylation, however, platinum complexes hold promise for future application since modified platinum-tin catalysts have provided the highest degree of enantioselection to date for asymmetric hydroformylation.[55]

Comparatively little is known of the mechanism of hydroformylation by platinum phosphine tin chloride complexes. Although recent studies with $Pt(PPh_3)_2Cl-SnCl_3$ have revealed many important details,[91,95] much remains to be discovered. For example, it is not known whether the addition of CO takes place before or after the formation of a Pt-alkyl. At low temperature (-80°C) the formation of Pt-alkyl complexes was found to be faster than their reaction with CO,[96] however it is difficult to predict whether this is true at the higher temperatures typical of catalytic reactions.[93] Also the comparative rate of Pt-acyl complex formation, hydrogen activation, and the role of Pt-Sn bond in the hydrogen activation has not been determined.[95,97]

For asymmetric hydroformylation it has been suggested that the initial coordination of the olefin controls the ultimate enantioselectivity.[23] It has been shown that the alkyl groups in Pt-alkyl complexes already have chirality,[29,87] but it is not certain if the overall optical purity of aldehydes corresponds to the diastereomeric ratio of Pt-alkyl complexes or if this, in turn, corresponds to the diastereomeric ratio of Pt-olefin complexes.[98,99] It is possible that the overall enantioselectivity is kinetically controlled as observed in asymmetric hydrogenation.

The hydroformylation of styrene with PtCl[(S,S)-SKEWPHOS]-$SnCl_3$ (SKEWPHOS = 2,4-bis(diphenylphosphino)-pentane) leads to the enantioselective formation of 2-phenylpropanal.[25,52] The optical yields in this case are strongly influenced by the reaction temperature. At 40°C the (S) product enantiomer predominates in excesses up to 75%, while at 120°C the (R) product with enantiomeric excesses up to 19%. The prevalence of the opposite product enantiomers at higher temperatures was suggested to be due either to a change of the Pt-SKEWPHOS chelate ring conformation or to a kinetic effects.[52] A change in ring conformation of δ-SKEW to the less stable λ-SKEW conformation could, in principle, lead to the predominance of the opposite product configuration.[100] A similar reversal of product configuration as a function of temperature was reported earlier in the hydroformylation of 1-

butene with PtCl(DIOP)-$SnCl_3$ (DIOP = 2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane).[99] In this case, isomerization of the α-olefin and decomposition of a catalyst was considered to be responsible for the switch in product enantiomer. Other systems with different substrates or ligands, do not show such a strong influence on the reaction temperature, although the enantioselectivities typically improve at low temperature.[23,25,55,81] For example, the enantiomeric excess (ee) for the asymmetric hydroformylation of styrene with PtCl(BPPM)-$SnCl_3$ (BPPM = N-t-butoxycarbonyl-4-(diphenylphosphino)-2-diphenylphosphine)methylpyrrolidine,[102] increased from 57% to 96% upon decreasing the reaction temperature from 95°C to 25°C.[55,100]

For this dissertation, a series of bidentate chiral phosphine platinum complexes has been synthesized: PtCl(CHIRAPHOS$(NMe_2)_4$)-$SnCl_3$, PtCl(SKEWPHOS$(NMe_2)_4$)-$SnCl_3$, and PtCl(DIOP$(NMe_2)_4$)-$SnCl_3$. The chelate ring size in these compounds is 5, 6, and 7 member respectively. The preparation of tetra amino functionalized platinum bidentate complexes, was undertaken based on the success of PtCl(SKEWPHOS)-$SnCl_3$ in homogeneous enantioselective hydroformylation,[25,52] and the ease of catalyst handling provided by the amino groups in Rh(diene)BDPP-$(p\text{-}NMe_2)_4$ for asymmetric hydrogenation.[102] Detailed studies of the influence of solvent, temperature on hydroformylation activity and selectivity have been carried on. The purpose of this part of the work was to: (1) learn the influence of chelate ring in platinum bidentate phosphine on the enantioselectivity of asymmetric hydroformylation; (2) understand the temperature dependence of these catalyst systems; (3) shed light on the mechanism of the reaction; (4) search and examine possible applications of supported aqueous phase Pt-Sn catalyst systems.

It was found that the catalytic systems $PtCl(CHIRAPHOS(NMe_2)_4)-SnCl_3$, $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$, and $PtCl(DIOP(NMe_2)_4)-SnCl_3$ have different temperature dependence on enantioselectivity. For instance, a maximum 56.7% (R) form was observed at 100°C and 60.6% (S) form at 25°C in $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$ case. The optical selectivity switched sign at about 57°C from (S) to (R). At higher temperature (>100°C), the ee's declined very sharply. No enantioselectivity was observed when a reaction was carried on at 140°C for 1 hour. Since hydroformylation of styrene by supported Pt-Sn-bidentate complexes requires longer reaction times and higher temperature, low ee's are observed for all supported catalyst cases. Racemization of product aldehyde is responsible for the low enantiomeric excess at high temperature.

4.2.1 Homogeneous Phase Catalysis

4.2.1.1 Influence of Solvents

Several solvents which are different in polarity were used in order to examine the influence of solvents on the activity and selectivity of hydroformylation.

The results are given in Table 4.12. Toluene which has intermediate polarity among these solvents examined gave the best result for catalyst activity and optical selectivity. Stille and et al.[55] reported that the use of triethyl orthoformate as solvent could increase the enantioselectivity by trapping the product aldehyde as shown in Equation 4.1. The resulting acetal is not susceptible to racemization. The acetal can be converted to aldehyde by reaction with pyridinium p-toluene sulfonate. The ee's has been reported to increase from 60% to 80% by the protection.

$$R^{*}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H \quad + \quad CH(OC_2H_5)_3 \quad \rightarrow \quad R^{*}\text{-}\underset{\underset{\displaystyle OC_2H_5}{|}}{\overset{\overset{\displaystyle OC_2H_5}{|}}{C}}\text{-}H \qquad (4.1)$$

Disappointingly, no improvement was found in PtCl(SKEWPHOS$(NMe_2)_4$)-$SnCl_3$ case in this work. Only 70% of aldehyde was converted to acetal and low optical purity was observed.

4.2.1.2 Influence of Bidentate Phosphine Frame

Data for the hydroformylation of styrene with PtCl(S,S-CHIRAPHOS$(NMe_2)_4$)-$SnCl_3$, PtCl(S,S-SKEWPHOS$(NMe_2)_4$)-$SnCl_3$, and PtCl(S,S-DIOP$(NMe_2)_4$)-$SnCl_3$ are listed in Table 4.13, 4.14, 4.15 respectively. The styrene conversion values were intentionally kept low in order to minimize racemization of the product which occurs at high conversion of olefin.[55]
There are some interesting points: (1) $PtCl_2$(DIOP$(NMe_2)_4$) complex which has 7 member ring system gives the highest tof; (2) no hydrogenation was observed in all three systems when the reaction temperature was lower than 60°C; (3) the regioselectivity (n/b) to 2-phenylpropanal decreases as temperature increases.

Table 4.12 Influence of solvents on asymmetric hydroformylation

solvents	reaction time (hr)	total conv. %	aldyd. conv. %	n/b	ee's	alcol. conv. %	tof(hr^{-1})
Hexene	20.0	46.3	31.7	3.4	23.6	4.6	23.2
Benzene	5.0	45.6	43.3	4.1	27.1	2.6	91.8
Toluene	3.0	32.6	28.6	3.2	37.4	4.0	108.6
C_6H_5Cl	6.0	26.0	22.5	3.7	36.4	3.5	43.3
MEK	28.0	8.4	7.9	3.4	27.2	0.5	3.0
THF	22.0	28.6	22.7	4.3	32.9	5.9	13.0
TOF	21.0	37.6	37.6	3.3	2.9	---	17.9

MEK = methylethylketone, TOF = triethyl orthoformate, 100°C, 1000 psi

catalyst = PtCl[SKEWPHOS$(NMe_2)_4$]-$SnCl_3$, substrate = styrene

Table 4.13 Asymmetric hydroformylation by $PtCl(CHIRAPHOS(NMe_2)_4)-SnCl_3$

temp. (°C)	reaction time(hr)	conversion to aldyd. (%)	n/b	ee's	conversion to alcol. (%)	tof(hr^{-1})
25	300	12.4	0.62	46.0(R)	0.1	0.41
50	96	12.6	0.64	37.0(R)	0.2	1.31
70	70	18.2	0.71	32.9(R)	0.6	2.60
80	30	16.3	0.79	30.4(R)	0.8	5.43
90	19	23.3	1.19	22.1(R)	1.3	12.3
100	12	19.6	1.46	12.4(R)	2.4	16.3
120	6	13.1	1.35	7.4(R)	3.0	21.8
140	2	10.5	1.94	6.0(R)	3.5	70.0

1000 psi, Pt/styrene = 1/1000, solvent = toluene

Table 4.14 Asymmetric hydroformylation by $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$

temp. (°C)	reaction time(hr)	conversion to aldyd.(%)	n/b	ee's	conversion to alcol.(%)	tof(hr^{-1})
30	550	17.1	1.52	60.6(S)	0	0.3
40	120	45.2	1.65	39.1(S)	0	1.7
50	48	18.2	1.71	7.3(S)	0	3.7
60	48	34.0	1.80	9.4(R)	0	7.1
70	40	67.2	2.17	17.2(R)	0.8	18.7
80	14	71.3	3.00	26.4(R)	1.1	50.7
100	3	32.1	3.32	37.4(R)	4.0	108.0
100[a]	0.3	23.6	3.60	56.7(R)	2.1	71.6
120	3	57.2	3.62	12.7(R)	12.7	115.0

1000 psi, solvent = toluene, Pt/styrene = 1/1000, a: Pt/styrene = 1/100

Table 4.15 Asymmetric hydroformylation by $PtCl(DIOP(NMe_2)_4)$-$SnCl_3$

temp. (°C)	reaction time (hr)	conversion to aldyd. (%)	n/b	ee's	conversion to alcol. (%)	tof (hr^{-1})
25	480	20.2	1.30	20.0(R)	0	0.4
35	17	28.6	1.40	16.6(R)	0	1.7
45	46	34.5	1.38	8.3(R)	0	7.5
60	20	18.0	1.37	5.6(R)	0	9.2
80	6	39.0	1.38	3.6(S)	0	65.0
90	4	37.2	1.78	4.7(S)	3.2	101
100	2	17.6	1.84	6.4(S)	5.1	113
120	1	22.8	2.18	4.2(S)	10.0	238

1000 psi, Pt/styrene = 1/1000, solvent = toluene

4.2.1.3 Influence of Reaction Temperature on ee's

The dependence of enantiomeric excess on reaction temperature is plotted in Figure 4.3. It should be noted that with $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$ as the catalyst, a maximum span of ee's i.e. 60.6% (S) and 37.0% (R) at temperature range of 25 to 100°C was observed (case 2 in Figure 4.3). With $PtCl(CHIRAPHOS(NMe_2)_4)-SnCl_3$ (case 1 in Figure 4.3), the conformation does not change sign within the temperature range of 25 to 120°C. Whereas $PtCl(DIOP(NMe_2)_4)-SnCl_3$ (case 3 in Figure 4.3) has a flat ee's curve i.e. at 25°C, ee = 20% (R); 120°C, ee = 7% (S). More detailed discussion is undertaken in following for $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$ because of its higher ee's and reaction rate compared to other two.

As shown in case 2 in Figure 4.3, after the switch in sign of the optical rotation of the product at about 57°C, the enantioselectivity continues to increase with increasing temperature. An optical yield of 37.4% for the product of (R) configuration was observed at 100°C. Further increase in temperature results in a drop in enantioselectivity. The use of excess $SnCl_2$ does not result in a significant change compared to the performance of $PtCl_2(SKEWPHOS(NMe_2)_4)$ alone.

Racemization of the 2-phenylpropanal is rapid at temperature greater than 100°C. For example, a sample of pure aldehyde with 60% ee (S), was completely racemized in 24 hours at 120°C in the presence of 0.001 equivalent of $PtCl(SKEWPHOS(NMe_2)_4)$-$SnCl_3$. Another indirect evidence for the racemization is that the optical yields are significantly improved when the time of exposure to heat is decreased. For example, as high as 56.7% (R) ee was obtained when the reaction time was reduced to 20 minutes by increasing the Pt/substrate ratio from 1/1000 to 1/100 (Table 4.14, a).

4.2.1.4 Proposed Asymmetric Hydroformylation Mechanism

The mechanism of asymmetric hydrogenation is far better established mainly through the work of Halpern et al.[98,103] than that of asymmetric hydroformylation. In spite of this, there is still an uncertainty about the influence of reaction temperature on the enantioselection.[48] Two possible mechanisms have been proposed in order to explain the dependence of optical selectivity on the reaction temperature. The first is that two different active chelate conformations were assumed which lead different optical products. These two chelates are temperature dependent. The second suggestion is

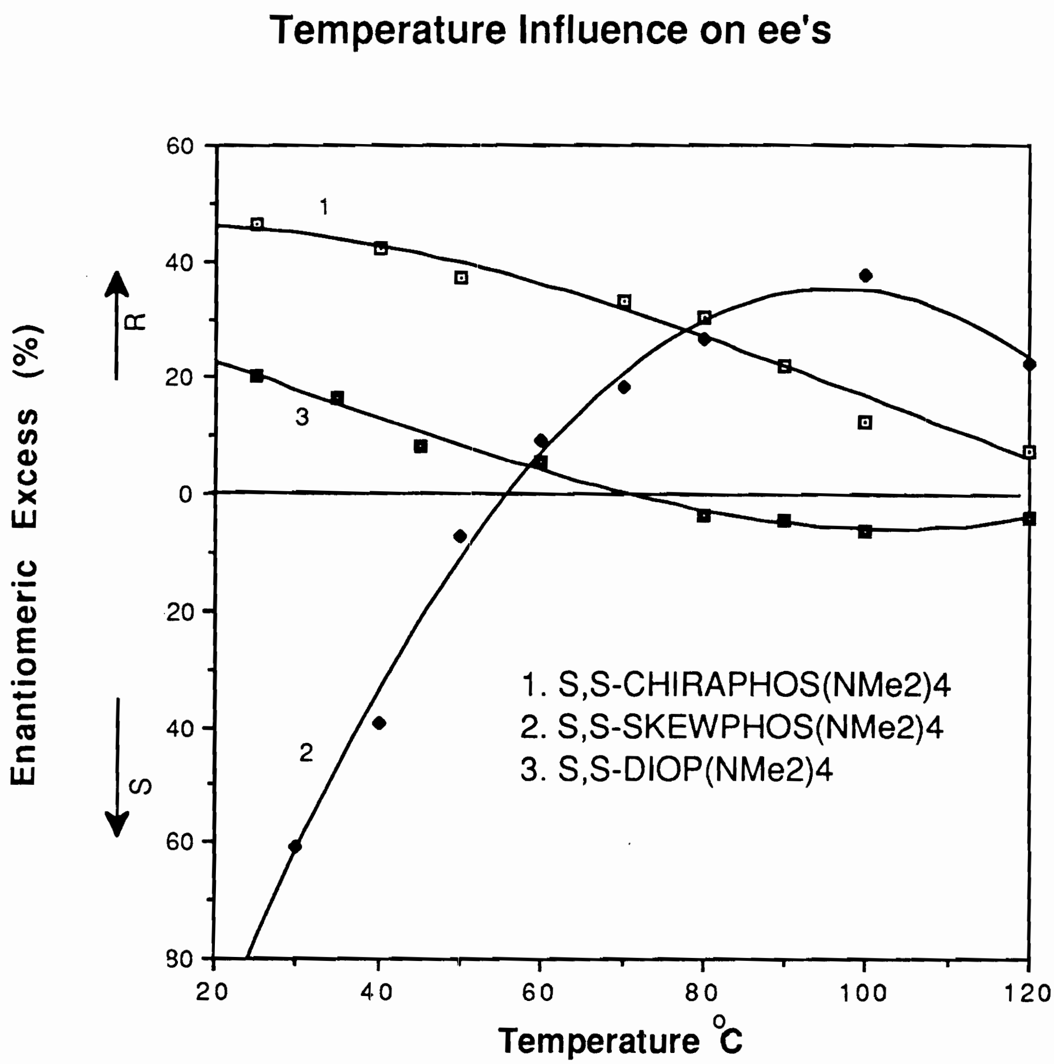


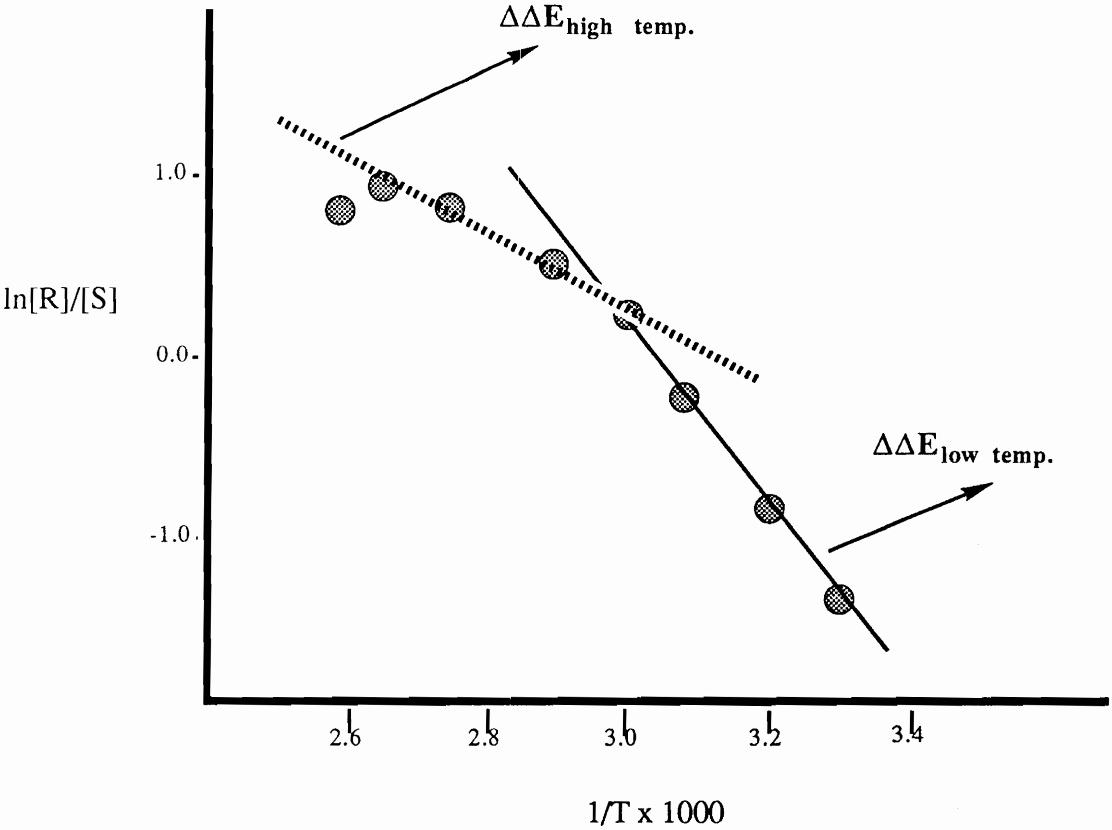
Figure 4.3 Influence of temperature on enantioselectivity

that the coordination of olefin in asymmetric hydroformylation has been considered as the main reason for the enantioselection. This suggestion appears to be proved by the fact that in the hydroformylation of α-deuterostyrene catalyzed by Rh(DIOP) complex, the branched and normal products had the same optical purity.[51] Recent studies, however, revealed that Rh-secondary alkyl complexes undergo ß-elimination, which is responsible for the increasing normal/branched ratio by increasing temperature.[104,105]

The ^{31}P, ^{13}C, ^{1}H NMR spectra for $PtCl_2(SKEWPHOS(NMe_2)_4)$ did not show noticeable change in the temperature range of 177K - 373K and the chelate ring of $SKEWPHOS(NMe_2)_4$ seems to be stable in other complexes too.[106] On the other hand the change in the prevalence of the opposite product antipode occurs at relatively low temperature, which would be unfavorable for thermodynamically unstable conformation.[78] The conformation change also can be excluded by the results of $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$ in the discussed temperature range for substrates different than styrene, which did not show change in sign of the product configuration.[100]

Activation energy difference $\Delta\Delta E$ ($\Delta\Delta E = -(\Delta E_r - \Delta E_s)$) was estimated by plotting ln[R]/[S] vs 1/T in Figure 4.4. The plot is based on several assumptions. First, the reactions toward S and R product are in same order. Second, no significant racemization occurs at temperatures below 80°C. Third, enantioselectivity is independent to the conversion at low temperature. This determination of activation energy difference is a rough estimation and can only be used for qualitative purpose. In figure 4.4 it shows that there is a change in slope at about 60°C. Again, the activation energy difference at high temperature, which is plotted in dotted line, could have a large error because of the racemization of product aldehyde. The activation energy difference at low temperature is larger than the one at high temperature.

Thus, a kinetic mechanism is a better fit for the asymmetric hydroformylation of olefin. A mechanism is proposed in this work which based on Halpern's hydrogenation mechanism.[98] As shown in Figure 4.5, two different coordination forms of olefin are in a fast equilibrium. Each form then, goes through Pt-alkyl and Pt-acyl intermediate and gives the final (S) or (R) product. The rate constants for (S) route and (R) route are defined as k_s and k_r respectively. Both of them are temperature dependent, i.e:



$\Delta\Delta E_{high\ temp.}$ = **the activition energy difference at high temperature**

$\Delta\Delta E_{low\ temp.}$ = **the activition energy difference at low temperature**

Figure 4.4 The plot of activition energy determination

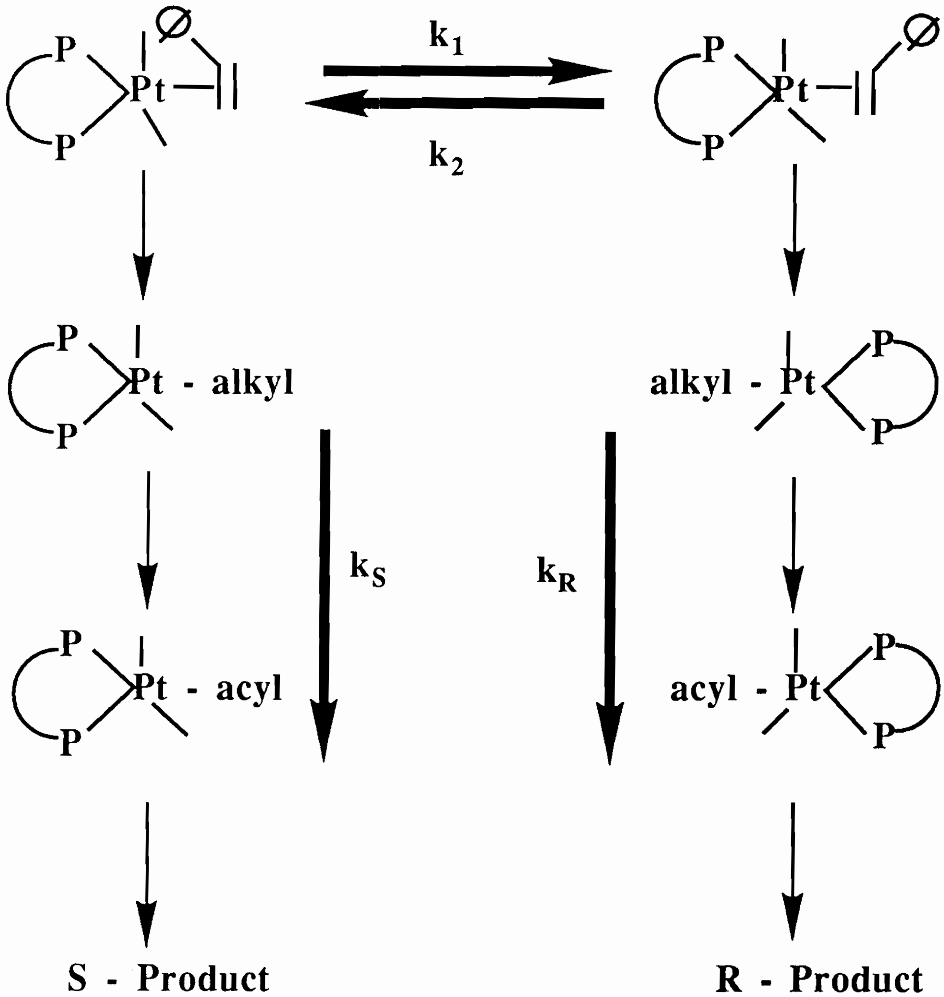


Figure 4.5 The proposed mechanism of asymmetric hydroformylation

$$k_s = A_s\, e^{-\Delta Es/RT} \qquad \text{and} \qquad k_r = A_r\, e^{-\Delta Er/RT}$$

The concentration of [S] and [R] product depends the ratio of k_s/k_r at certain temperature. In PtCl(SKEWPHOS$(NMe_2)_4$)-$SnCl_3$ case, k_s is dominant at low temperature (large $\Delta\Delta E$ means either large ΔE_r or small ΔE_s). Therefore, more (S) product is produced. As the temperature increases, k_r increases. When temperature is about 57°C, k_s is almost equal to k_r. No optical selectivity is obtained. With a further increase in temperature, k_r becomes dominant (small $\Delta\Delta E$ means either small ΔE_r or large ΔE_s) and the (R) product is in excess. If the temperature is high enough to let the racemization occur, the optical selectivity is destroyed. This mechanism can successfully explain the rise, fall or change sign of enantioselectivity by increasing the temperature in asymmetric hydroformylation of styrene.

4.2.2 Supported Asymmetric Pt-Sn Catalyst

PtCl[SKEWPHOS$(NMe_3)_4$][BF_4]$_4$ is chosen as the catalyst to be immobilized on the different supports because PtCl(SKEWPHOS$(NMe_2)_4$)-$SnCl_3$ has relatively higher optical selectivity comparing with $PtCl(CHIRAPHOS(NMe_2)_4)-SnCl_3$ and $PtCl(DIOP(NMe_2)_4)-SnCl_3$. The technique for immobilization has been described in section 3.5. The reaction catalyzed by immobilized $PtCl(SKEWPHOS(NMe_2)_4)-SnCl_3$ is much slower than that of homogeneous phase catalysis (compare entries in Table 14 with entry 3 in Table 4.16). Longer reaction times were needed to give the minimum conversion for product separation and analysis. In the case of Pt/substrate = 1/1000, at 100°C, only 4.3% of ee was obtained which is much lower than that of homogeneous case (45.0% ee). It has been discussed in section 4.2.1.3 that long period reaction time and high reaction temperature could cost the racemization of aldehyde. Several experiments have been tried with the hope that lower temperatures and shorter reaction times will reduce the racemization. As shown in Table 4.16, when Pt/substrate ratio increases from 1/1000 to 1/100, and the reaction time is reduced from 488 to 24 hours and the ee increases from 4.3% to 10.7%. Also the temperature is lowered from 100 to 60°C, the ee increases further to 14.1% (entry 3). Though these changes improve the selectivity much more progress is clearly needed. Specifically supported catalysts of higher activity are required.

Table 4.16 Asymmetric hydroformylation by supported PtCl[SKEWPHOS(NMe_3BF_4)$_4$]-$SnCl_3$

catalyst system	reaction time (hours)	total conv. %	aldyd. conv. %	n/b	ee's	alcol. conv. %	tof (hr^{-1})
Glass supported							
Pt/substrate=1/1000	288	37.6	22.0	1.7	4.3	15.6	1.3
Pt/substrate=1/100	24	39.5	27.8	1.4	10.7	11.6	16.4
Pt/subs.=1/100, 60°C	48	39.2	36.4	1.9	14.1	2.8	8.2
Amberlyst supported							
Pt/substrate=1/1000	264	37.4	25.0	1.1	2.4	12.4	1.4

100°C, 1000 psi, P/Pt = 1, substrate = styrene, solvent = toluene

CHAPTER 5. CONCLUSIONS

The main conclusions of this dissertation fall into four categories: (1). synthesis and characterization of new families of water soluble phosphine modified cobalt and platinum complexes; (2). immobilization of these complexes onto different supports using different techniques; (3). hydroformylation of linear olefins by these immobilized cobalt and platinum catalyst systems; (4). asymmetric hydroformylation of styrene by platinum bidentate phosphine complexes in homogeneous phase and immobilized phase.

(1) Synthesis and characterization of a new family water soluble alkyl phosphine modified cobalt and platinum complexes

A series of water soluble alkyl phosphine were synthesized. Metal complexes of these ligands have extensive solubility in water. In the cobalt case, ^{31}P NMR shows an upfield shift and IR shifts to lower frequency as the alkyl chain increases. This is proposed to be due to stronger electron donation from the alkyl substituents to the phosphorus atom. Water soluble platinum complexes also show some interesting results. It was found that the distribution of geometric isomers of platinum complexes depends on the length of alkyl chain. When m = 0, pure cis isomer of $PtCl_2L_2$ was received. When m = 1, pure trans isomer was obtained. When m = 2 and 3, mixtures of cis and trans isomer were observed. The cis/trans ratio increases when m increases from 2 to 3.

(2) Immobilization of water soluble cobalt and platinum complexes

The cobalt and platinum complexes were immobilized on several supports by different techniques. It was found that when m increases from 0 to 3, the metal leaching from water phase to organic phase was significantly reduced. A process, named as phase transfer catalyst recovery in this work, shows that it is possible for cobalt amino phosphine complexes to do the catalysis in an organic phase and then be extracted into a water phase for catalyst recovery.

(3) Hydroformylation of linear olefins

These newly synthesized water soluble cobalt and platinum complexes have been used for hydroformylation of 1-hexene and 1-octene. Systematic investigation was done in order to learn the influence of temperature, pressure, P_{CO}/P_{H2} ratio, P/metal ratio, metal/substrate ratio, solvent, pH etc. on the catalytic activity and selectivity. Supported aqueous phase cobalt catalysts recover some of the activity observed under homogeneous conditions compared to the two-phase catalysts.

Supported $PtCl[P((CH_2)_m-C_6H_4-SO_3Na)_3]_2-SnCl_3$ could be generated in the presence of small quantities of water. Although these showed similar selectivity to the corresponding homogeneous catalysts the activity of the supported catalysts is much reduced.

(4) Asymmetric hydroformylation of styrene by platinum bidentate phosphine complexes

A series of platinum bidentate phosphine amino complexes: $PtCl(CHIRAPHOS(NMe_2)_4)$, $PtCl(SKEWPHOS(NMe_2)_4)$, and

$PtCl(DIOP(NMe_2)_4)$ were synthesized. These complexes can be quaternized and made water soluble. The hydroformylation of styrene by these complexes shows a very strong temperature dependence. For example, the enantiomeric excess of 60% (S) was obtained at 25°C, in $PtCl(SKEWPHOS(NMe_2)_4)\text{-}SnCl_3$ case. This changes to (R) form at 57°C, and reaches 37% ee(R) at 100°C.

Immobilization of these asymmetric platinum bidentate phosphine complexes on different supports results in a loss of optical selectivity. It is suggested that the high reaction temperatures and long reaction times needed because of the low activity of the supported catalysts leads to the racemization of aldehyde.

CHAPTER 6. FUTURE WORK

In this dissertation, the general features of water soluble phosphine modified cobalt and platinum complexes, as the catalysts for hydroformylation of olefins, have been investigated. The basic understanding of these two systems has been established. Asymmetric hydroformylation of styrene by platinum bidentate phosphine complexes has also been studied. However, more detailed work still needs to be done in terms of catalyst characterization. Some recommendations for future work in the area follow:

(1) Cobalt system

Other olefins, such as high molecular weight olefins, should be used under two-phase catalysis conditions in order to examine the influence of water solubility of the olefins. The high molecular weight olefins, which have little or no solubility in water, will test if the reaction occurs in the water phase or in the organic phase. Other solvents of different polarity should be investigated to try to understand the solvent effects. Also the influence of different polar co-solvents such as methanol, glycol etc. should be employed to increase the solubility of substrate in the water phase where the catalyst is. Sometimes a slight increase in solubility of reactant will greatly affect a reaction.

(2) Platinum system

First, solid state ^{31}P, ^{129}Sn, ^{195}Pt NMR should be applied to the supported Pt-Sn catalyst systems. The characterization of the formation of Pt-Sn complexes on the surface of support has been done only by the color change and by the catalytic activity. This is not sufficient for the characterization of the surface species.

Second, sulfonated bidentate phosphine modified asymmetric platinum complexes will be good candidates for the water soluble asymmetric hydroformylation.

Third, mixed phosphine platinum complexes should be synthesized, e.g. $PtCl_2LL'$ (L = TPPTS, L' = other water soluble phosphines). The result of hydroformylation of olefins by mixed phosphine platinum complex could be different than that of simple phosphine platinum compound.

(3) Others

a. X-ray diffraction structure study

Single x-ray diffraction structures of these water soluble cobalt and platinum complexes have not been done so far. The difficulty is to locate the cation Na^+, or H_2O which surround the sulfonate ligands. A rough structure of $Co_2(CO)_6(TPPTS)_2$ was made in this work. Unfortunately, the R value (standard error) was too high to be published (R = 17). Further effort is strongly recommended in order to determine the structures of these water soluble transition metal complexes.

b. Water soluble metal cluster

Many multistep reactions occur readily with heterogeneous catalyst but not with homogeneous one. The usual explanation is that several catalytic active sites are necessary for these complexes transformations. Such multiple sites are available on the surface of metal crystallite but not in a conventional soluble catalyst centered on a single metal. In principle, a metal cluster compound could provide several active sites or could act as a reservoir for electrons in a multielectron redox process.

c. Polymer supported water soluble transition metal complexes

As mentioned in Chapter 2, Stille and co-workers successfully synthesized polymer supported transition metal complexes by using phosphinated polyester. This system is hydrophobic and can be used for the organic phase reaction, if there is no metal leaching. The inversive method could be developed if the metal has one or more water soluble phosphine ligands as shown in Figure 6.1.

This type of catalyst system could be used for hydrophilic solvents and for perhaps in waste water treatment. The reactant can easily contact with the metal center because of the water soluble ligands. The catalyst recovery is simple.

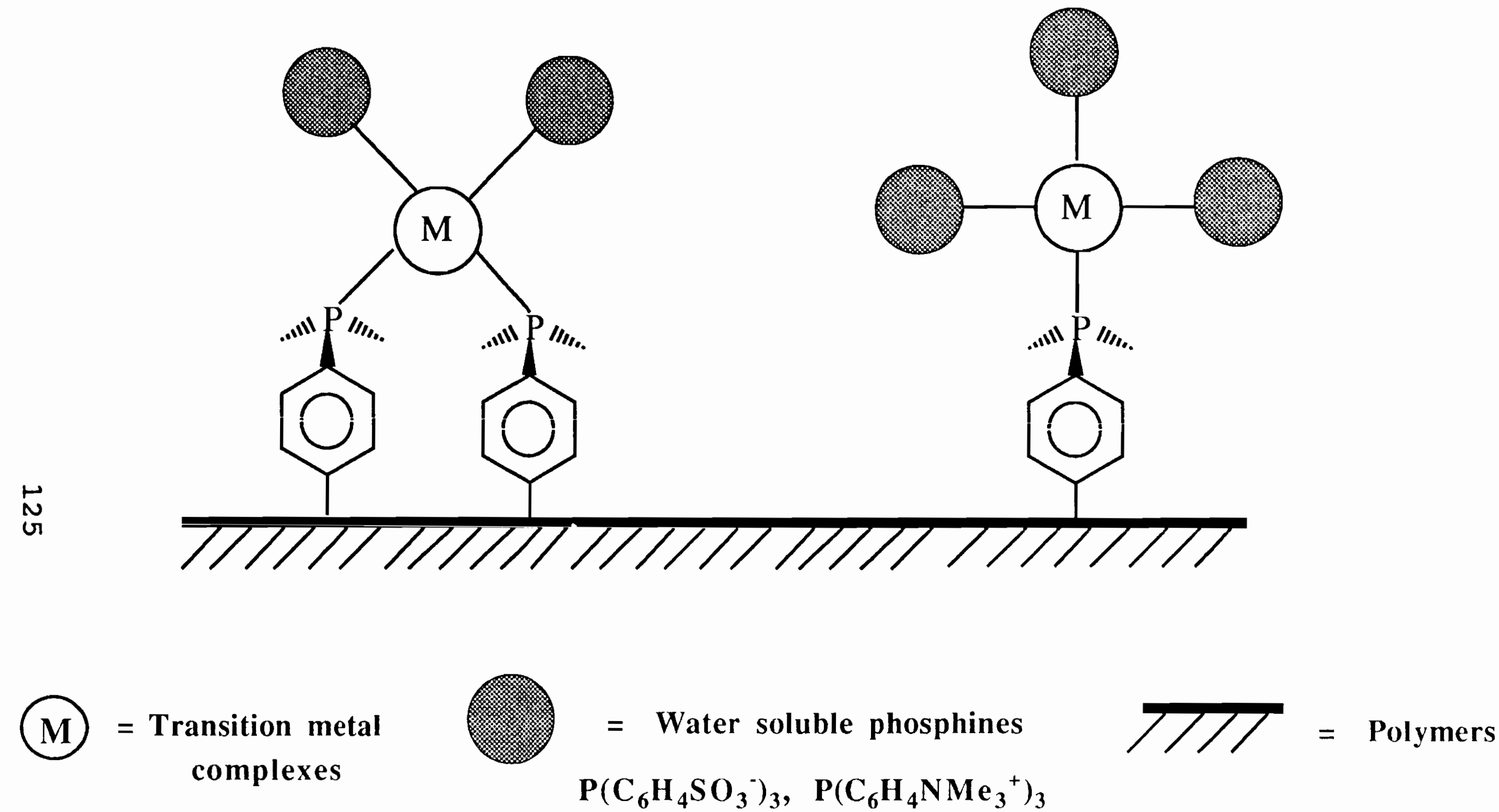


Figure 6.1 Polymer supported water soluble transition metal complexes

CHAPTER 7. REFERENCES

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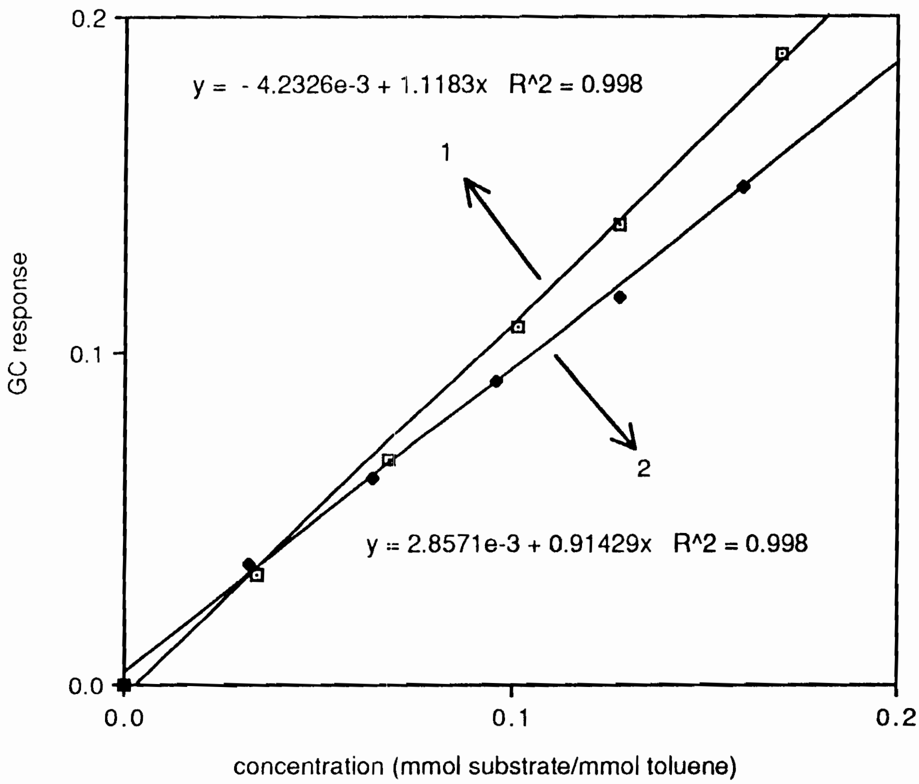
APPENDIX



column 1: 1-hexene, column 2: 1-heptanal

Calbiration of GC response factors

VITA

The author, son of Dr. Juan Liang and Dr. Xiexian Guo, was born on December 4, 1954 in Dalian, Liaoning, China. He graduated from Dalian Polytechnic Institute with a Bachelor degree in chemistry in 1982. He then worked at Dalian Institute of Physics and Chemistry as a research assistant for three years. He entered the University of Alberta, Canada, in 1985 and received his M.Sc. in Chemical Engineering in 1987. In that fall, he enrolled in the Department of chemistry, Virginia Polytechnic Institute and State University to pursue a Ph.D. degree. He will start working for Alberta Research Council, Canada, in April 1991. Following is a list of publications and presentations by this author and his colleagues during his Ph.D. program.

SELECTED PUBLICATION

1. "Bis-[Tris(m-sodium-sulfonato)phenylphosphine] Hexacarbonyl Dicobalt, $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$, in a Supported Aqueous

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3. "Hydroformylation of 1-Hexene with $Pt[P(m\text{-}C_6H_4SO_3Na)_3]_2Cl_2$ and Its Tin Chloride Analogue on a Controlled Pore Glass", I. Guo, B.E. Hanson, I. Toth, and M.E. Davis, J. Organomet. Chem. *submitted*

4. "Synthesis of New Families of Water Soluble Alkyl Phosphine Cobalt and Platinum Complexes", I. Guo, B.E. Hanson, and I. Toth, Organometallics, *submitted*

5. "Influence of the Reaction Temperature on the Enantioselective Hydroformylation of Styrene Catalyzed by $PtCl(SnCl_3)$(-)(2s,4s)-2,4 bis[bis(-P(-N,N-dimethylamino)phenyl)phosphinenol]pentane", I. Toth, I. Guo,

B.E. Hanson, and M.E. Davis, *in preparation*

6. "Hydroformylation of 1-Hexene by Water Soluble Cobalt Complexes, $Co_2(CO)_6[P((CH_2)_n-C_6H_4-SO_3Na)_3]_2$ (n = 0, 1, 2, 3)", I. Guo and B.E. Hanson, *in preparation*

7. "Influence of Carbon Chain Length in $PtCl[P((CH_2)_n-C_6H_4-SO_3Na)_3]_2-SnCl_3$ (n = 0, 1, 2, 3) as Catalysts on Hydroformylation of Olefins", I. Guo and B.E. Hanson, *in preparation*

8. "Polymer Supported Platinum Bi-dentate Phosphine Catalysts for the Asymmetric Hydroformylation of Styrene", I. Guo, I. Toth, and B.E. Hanson, *in preparation*

PRESENTATIONS

1. "Immobilization of Pt-Sn Hydroformylation Catalysts on Ion Exchange Resins", <u>200th National ACS Meeting</u>, Washington D.C., Aug., **1990**

2. "Synthesis and Computer Modelling of Molybdenum Polyether Complexes", <u>41th Southeast Regional ACS Meeting</u>, Winston-Salem, North Carolina, Oct., **1989**

3. "Polymers as Ligands for Mo, W Carbonyl Complexes and Their Use in Olefin Metathesis and Isomerization", <u>11th North American Meeting of the Catalysis Society</u>, Dearborn, Michigan, May, **1989**

Lpin Guo