WATER SOLUBLE PHOSPHINES, THEIR TRANSITION METAL COMPLEXES, AND CATALYSTS

Jianxing Kang

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Brian E. Hanson, Ph.D., Chairman

Karen J. Brewer, Ph.D

Paul A. Deck, Ph.D

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ABSTRACT

In recent years two-phase catalysis has been established as a new field of catalyzed processes and has achieved industrial-scale importance in olefin hydroformylation. Two-phase reactions have a number of advantages, for example, ease of separation of catalyst and product, catalysts can be tailored to the particular problem, use of special properties and effects of water as a solvent, and low environmental impact. For higher olefins ($\geq C_6$), the reaction suffers low activity due to low water solubility of higher olefins.

Tricesium analog of TPPTS, m,m,m-trisulfonated triphenylphosphine, was synthesized and fully characterized. Two-phase olefin hydroformylation with $Rh(acac)(CO)_2$ was investigated. The results indicated that both activity and selectivity (linear to branch aldehyde ratio) are similar to Rh/TPPTS system. The salt effect showed that increase the solution ionic strength will increase the selectivity and decrease the activity in the olefin hydroformylation with TPPTS.

A new surface active phosphine, trisulfonated tris-m-(3-phenylpropyl)phenylphosphine, was synthesized and fully characterized. The results of biphasic olefin hydroformylation were consistent with aggregation of the ligand. The two phase 1-octene hydroformylation results showed that with only 3 methylene groups, there is no difference between the para and meta position of C_3 group.

A new chelating diphosphine, tetrasulfonated 2,2'-bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl, was prepared and fully characterized. Its application in two-phase hydroformylation of olefin showed enhanced activity and selectivity compared to the non-chelated phosphine analog.

Finally, homogeneous asymmetric hydrogenation was carried out in the presence of a chiral surfactant in an attempt to affect asymmetric induction. The catalytic results showed that at a surfactant/Rh ratio of 25, the asymmetric hydrogenation of AACA-Me (α-Acetamidocinnamic Acid Methyl Ester) in methanol has no effect on asymmetric induction with the introduction of this chiral surfactant.

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Dedication of this thesis is given with deepest appreciation to my wife, Yingwei Ma, and my family for their continued support morally and financially.

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Chapter 1. INTRODUCTION

The feedstocks for many common compounds derived from petroleum products are oxygenated hydrocarbons such as aldehydes, ketones, alcohols and carboxylic acids. These in turn may be obtained by cracking petroleum which yields ethylene and other alkenes or from synthesis-gas-derived methanol. The conversion of alkenes to oxygenated compounds utilizes transition metals as catalysts. The best catalysts are both active (producing high yields rapidly) and selective (producing mainly the desired product)[1]

Ever since the development of homogeneous catalysts, it has been recognized that one of its central problems is the separation of the catalyst from the product of the reaction.
Leaching of the catalyst and thermal decomposition lead to unacceptable losses in activity and selectivity. Immobilization of the catalyst is therefore very desirable. Various pathways with which to overcome this problem have recently been reported: (1) the catalyst and substrate are in immiscible phases; (2) the catalyst is bound to a solid support; and (3) the catalyst is entrapped within a microporous material.[2,3,4,5,6,7,8,9,10,11] Of these methods only water-soluble catalysts have proven to be commercially viable in the hydroformylation of olefins.

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[5] G. Jannes, Catalysis in Heterogeneous and Homogeneous, B. Delmon and G. Jannes, ed., New York, **1975.**
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[11] C. U. Pittman and G. O. Evans, Chemtech, **1973,** 3, 560

In industrial hydroformylation catalysis, rhodium is presently only useful for the hydroformylation of low-boiling alkenes such as propene.[12] Hydroformylation of higher alkenes is still performed with the less active and selective cobalt catalysts. Separation of the high-boiling aldehyde from the catalyst is generally done by distillation or extraction. The required vigorous distillation conditions can result in degradation of the cobalt catalyst. Since the cobalt catalysts are relatively inexpensive these processes are still commercially attractive. Commercial application of a faster but also more expensive rhodium catalyst in the hydroformylation of higher alkenes cannot tolerate a rhodium loss higher than 0.1 ppm in the reaction products.[13] The high boiling points of the products imply that a separation method other than distillation should be applied.

There are two promising methods for the separation of rhodium catalysts and high-boiling products. One approach involves anchoring the homogeneous catalyst to a support such as silica, resins or polymers. Until now, no industrial application has been reported; apparently the challenges (complicated synthesis, stability, leaching and selectivity) are too difficult.

Another approach comprises the use of water-soluble rhodium complexes which allows an easy separation of the catalyst and the organic reagents. To render rhodium catalysts water-soluble, many water-soluble ligands have been prepared and studied for their catalytic properties in the hydrogenation and hydroformylation reactions.[14] Most ligands are phosphines containing functional groups like sulphonate,[15] ammonium,[16] phosphonium,[17] and carboxyl[18] groups. Water-soluble derivatives of chiral phosphines like DIOP and Chiraphos, both cationic[19] and anionic[20] versions, have been reported. Fell et al. used phosphines which are not only water-soluble but also have phase transfer properties.[21]

These water-soluble catalysts, in principle, combine the virtues of conventional homogeneous and heterogeneous systems. Most of the research done in the field of water-soluble complexes is based on two-phase catalysis, in which an aqueous phase containing the catalyst and

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[13] P. Escaffre, A. Thorez and P. Kalck, J. Chem. Soc., Chem. Commun., **1987,** 146.
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[15] Z. Toth, F. Joo and M. T. Beck, Inorg. Chim. Acta., **1980,** 42, 153.
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[21] R. G. Nuzzo, D. Feitler and G. M. Whitesides, J. Am. Chem. Soc., **1979,** 101, 3683.

an organic phase containing the reagents are in contact during the reaction. The main disadvantage of two-phase catalysis is that the reaction rates may be low, primarily due to the low solubility of the substrate in water and/or phase-transfer limitations. The rhodium catalyzed hydroformylation process of propene using the water-soluble trisulfonated triphenylphosphine (TPPTS) may therefore not be applicable to higher alkenes.

A great deal of attention has been paid to the search for water-soluble transition metal complexes and related catalysts since water has a variety of properties that set it apart from most organic solvents. Water is not-toxic and available in most parts of the world in sufficient quality and quantity. In addition, the non-flammable nature of water is an important safety feature for large scale applications. In this thesis, immobilization of water soluble catalysts is achieved because the reactants and products are in the organic phase while the metal complex remains in the aqueous phase. Because most organometallic compounds have limited water solubility, the synthesis of novel water soluble transition metal complexes is central to the development of new immobilized homogeneous catalysts.

Much effort has been put into the development of more efficient water soluble ligands and immobilized catalysts which keep high activity and selectivity. 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. The catalytic results can then be correlated with the properties of the ligands.

Homogeneous asymmetric hydrogenation is slowly emerging as an useful tool in the production of enantiopure fine chemicals. Yet the number of industrial processes using asymmetric homogeneous hydrogenation are few compared to enormous effort in academic research. Selke et al investigated the enantioselectivity of asymmetric hydrogenation in water. In their work both the activity and selectivity were influenced by the addition of solubilizing agents that forms micelles.[22] Their studies into the hydrogenation of a large number of substrates with rhodium(1) biphosphines or biphosphinic acid ester as catalysts in water conclusively favor a real increase in selectivity, presumably by optimizing the conformation of the catalyst, which is concentrated on the micelle surface, in the transition state. Because of the expense of the ligand only reactions with extremely high turnover numbers have been commercialized.

Asymmetric catalysis potentially represents one of the most powerful and cost-effective methods for producing enantiomerically-enriched compounds. Despite obvious advantages, practical application of asymmetric catalysis remains limited, due in part to the fact that high enantiselectivities often can be achieved in only a restricted range of solvents, many of which are environmentally hazardous. That solvent type can so dramatically influence enantioselectivities is

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not surprising considering the small energy differences between diastereomeric transition states of stereoselective reaction ($\Delta\Delta G^{\neq}$ = 1.5 -3.4 kcal/mol for 85 - 99 % enantiomeric excess, ee). The significance of asymmetric reaction is that there is the potential for the synthesis of a wide variety of chiral compounds.[23]

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.[24] Roelen investigated the effect of added olefins to cobalt catalysts and identified aldehydes as one of the oxygen containing components.[25] Olefins can add H_2 and CO across the double bond to give aldehydes in the presence of a Co (or Rh) catalyst (eq. 2.1). The process is frequently referred to as the "Oxo" process, with Oxo being short for Oxonation, i.e. the addition of oxygen to a molecule. However, the term hydroformylation is descriptively more accurate and more useful in characterizing this type of reaction catalyzed by various transition metal complexes.[26]

$$RCH_2=CH_2 + CO + H_2 \rightarrow \underset{\text{"normal"}}{RCH_2CH_2CHO} + \underset{\text{"branched"}}{RCH(CH_3)CHO} \qquad \textbf{(2.1)}$$

The relative amounts of normal- and branched-chain aldehydes produced depend on the identity of R and other constituents of the reaction mixture. Normal-chain aldehydes, the more desirable products, usually are hydrogenated, affording straight-chain alcohols, or self-condensed, affording more complex aldehydes. With a terminal alkene as substrate, the normal/branched ratio is an important parameter in the industrial hydroformylation process; generally speaking, the higher the ratio the better, although significant markets have developed for the branched aldehydes. In

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[24] G. W. Parshall, Homogeneous Catalysis, Wiley, New York, **1980.**

[25] O. Roelen, German Patent, 849 548 **(1938).**

[26] G. N. Schrauzer, Transition Metals in Homogeneous Catalysis, Marcel Dekker, **1971.**

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.[27]

2.2 Hydroformylation Catalysts

One of the major problems associated with transition metal catalysis is the recovery and recycling of the catalyst, often the most expensive and environmentally toxic component of the system. One approach to the problem of the product/catalyst separation is to introduce a secondary liquid phase that contains the catalyst and is immiscible with products of the reaction. The separation of the products and complete recovery of the catalyst, in the immisicible phase, can then be accomplished by phase separation. The technical and commercial feasibility of the this scheme for catalyst recovery is demonstrated by the "Shell Higher Olefin Process" (SHOP).[28] In this process, ethylene is catalytically oligomerized over an organonickel complex in a polar phase of 1,4-butanediol, and the oligomers generated by the reaction from a secondary phase which is immiscible with 1,4-butanediol. The products are removed without distillation.

Homogeneous catalysts are transition metal complexes with various kind of ligands, such as phosphines. The ligands modify the coordination sphere of the metal electronically and sterically for better reactivity and selectivity. The water solubility of these complexes can be achieved by introducing polar functional groups to the ligand. Surveys of water soluble ligands and their application to catalysis can be found in several review articles.[29,30,31,32]

Catalytic reactions in the aqueous phase may show surprising changes of reaction reactivity and selectivity. The reactivity of a two phase catalysis is strongly dependent on the solubility of the organic reactants. For example, the two phase hydroformylation of propene, the Ruhrchemie/Rhone Poulenc process, has a comparable reaction rate to a homogeneous system due to the relatively high water solubility of propene. Mass transfer limitation causes a considerably lower activity for similar reactions with higher olefins, such as 1-hexene and 1-octene.[33]

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[27] J. Falbe, Carbon Monoxide in Organic Synthesis, Springer-Verlay, **1970.**

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[33] W. A. Herrmann, C. W. Kohlpaintner, Angew. Chem. Int. Ed. Engl., **1993,** 32, 1524.

The selectivity of a two phase catalyst is also profoundly influenced by water. Since most of the water soluble catalysts are ionic species, tuning the coordination sphere of the metal center by altering the ionic strength of the aqueous medium may result in a change of the reaction selectivity.

Herrmann and Kohlpaintner have written a comprehensive review on water soluble ligands, some of which are shown in Figure 2.1 and their metal complexes and related catalysis.[32] Although virtually all the available methods for introducing water soluble functionalities are discussed, most attention is given to the direct sulfonation of arylphosphines, which is the most widely used method to convert phosphines into water soluble derivatives. The preparation and purification of the sulfonated phosphines are described in detail. The use of water soluble phosphines in hydroformylation, asymmetric hydrogenation and other catalytic reactions, as well as supported aqueous phase catalysis is covered. Many new concepts and latest trends in the research of water soluble catalysis are included.

The most successful industrial application of the rhodium/m,m,m-trisulfonated triphenylphosphine (TPPTS) system is the hydroformylation of propylene in the Ruhrchemie/Rhone-Poulenc Process. The technical aspects of this process are described in detail by Cornils et al.[34]

Hanson and co-worker[35] described a new and more efficient process for the synthesis and purification of TPPTS. Monitoring the reaction by ^{1}H NMR spectroscopy to determine the extent of sulfonation and concurrent oxidation gives greater control over products. A facile method of purification is outlined, and data are reported for ^{1}H, ^{13}C, ^{31}P NMR parameters.

Hanson et al.[36] synthesized a new series of water soluble phosphines, tris(ω-phenyl)phosphines of the type $P[(CH_2)_x(C_6H_5)_3]$ x = 1, 2, 3 and 6 and tris[p-(ω-phenylalkyl)phenyl]phosphines. Sulfonation of these phosphines was successfully achieved under mild reaction conditions and without the formation of the corresponding phosphine oxide during the reaction.

The diphosphine 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBI), was sulfonated by Herrmann et al. using 60% oleum and resulted in a mixture of sulfonated products.[33] Although the direct sulfonation of biphosphines often yields a mixture with different degrees of sulfonation, these water soluble chelates give promising results in two phase catalysis. For

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[34] B. Cornils and E. Wiebus, Chemtech, **1995,** 33.

[35] T. Bartik, B. Bartik, B. E. Hanson, T. Glass and W. Bebout, Inorg. Chem., **1992,** 31, 2667.

[36] T. Bartik, B. Bartik, B. E. Hanson, I. Guo and I. Toth, Organometallics, **1993,**12,164.

example, BIBSI yields quite high n/b ratio (ca. 95% normal) with rhodium catalysis. Dependence upon condition, temperature and pressure were studied.

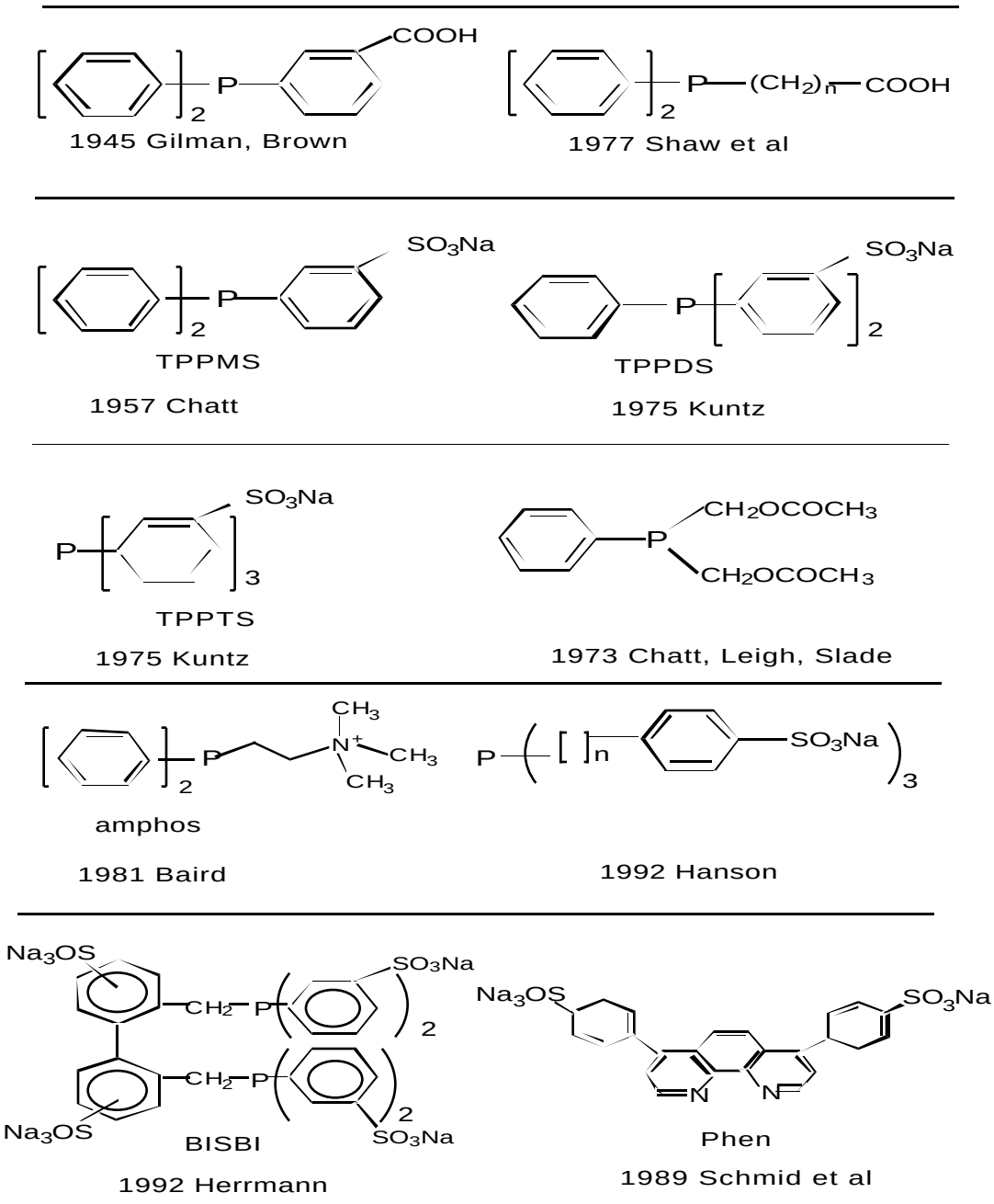

Figure 2.1 Some Water Soluble Phosphine Ligands[32]

2.3 Hydroformylation Mechanism

Although a better understanding of the hydroformylation mechanism led to only minor progress in the reaction control of the Oxo process or to advances in hydroformylation chemistry, the study of mechanistic aspects has always enjoyed priority among chemists working on the Roelen reaction. Nevertheless millions of tons of Oxo products were manufactured. Heck and Breslow in 1960 presented their currently accepted mechanism,[37] which is based on the postulated formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and hydrogen and its subsequent dissociation into $HCo(CO)_3$ and CO.

Natta et al's relationship established in 1955 and shown in Eq. (2.2) best represents all effects observed in the applied pressure and temperature range[38]

$$d\,[\text{aldehyde}]/d\,t = k \times [\text{olefin}] \times [\text{Co}] \times P_{H2} / P_{CO} \qquad \textbf{(2.2)}$$

Marko et al. have established a relationship, based on Natta's equation, which can be applied when using rhodium catalysts.[39]

$$d\,[\text{aldehyde}]/d\,t = k \times [\text{olefin}]^x \times [\text{Rh}]^y \times P_{H2} / P_{CO} \qquad \textbf{(2.3)}$$

$x = 0.1$ (depending on olefin), $y = 1.0 - 0.7$

Hydroformylation with rhodium catalysts was developed much later, and gained attention upon the publication by Evans, Osborn, and Wilkinson of their landmark work on the hydroformylation of alkenes with homogeneous rhodium catalysts modified by triphenylphosphine in 1968.[40,41]

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[37] R. F. Heck and D. S. Breslow, C. A. 55, 24 545 (**1961**); R. F. Heck, J. Amer. Chem. Soc., **1963**, 85, 651.

[38] G. Natta, R. Ercol and S. Castellano, Chin. Ind., **1952**, 34, 503.

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The mechanism of hydroformylation has been extensively studied and is reasonably well understood. Modern hydroformylation research focuses almost exclusively on the metals cobalt, rhodium, and platinum although considerable effort also went into ruthenium catalysts.[42] The general accepted order of hydroformylation activity with regard to the central atom clarifies this picture:[43]

$$Rh >> Co >> Ir, Ru > Os > Pt > Pd > Fe > Ni$$

Commercial hydroformylation plants are run exclusively with catalysts based on Rh or Co, namely $HCo(CO)_4$, $HCo(CO)_3PR_3$ and $HRh(CO)(PR_3)_3$.[44]

Under high pressure of hydrogen and carbon monoxide, olefins catalyzed by various metal oxides produce aldehydes which are one carbon heavier than the original olefins. Alcohols from the Oxo reaction sometimes are formed by the reduction of aldehyde.

The generally accepted mechanism for hydroformylation of α-olefin with $HRh(CO)(PPh_3)_3$ is shown in figure 2.2. Reaction paths for the side reactions, that lead to hydrogenation and isomerization, are also included schematicaly.[45]

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[43] F. P. Pruchnik, Organometallic Chemistry of Transition Elements, Plenum Press, New York, **1990,** 9, 691

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[45] B. E. Hanson and M. E. Davis, J. Chem. Ed., **1987,** 64, 928.

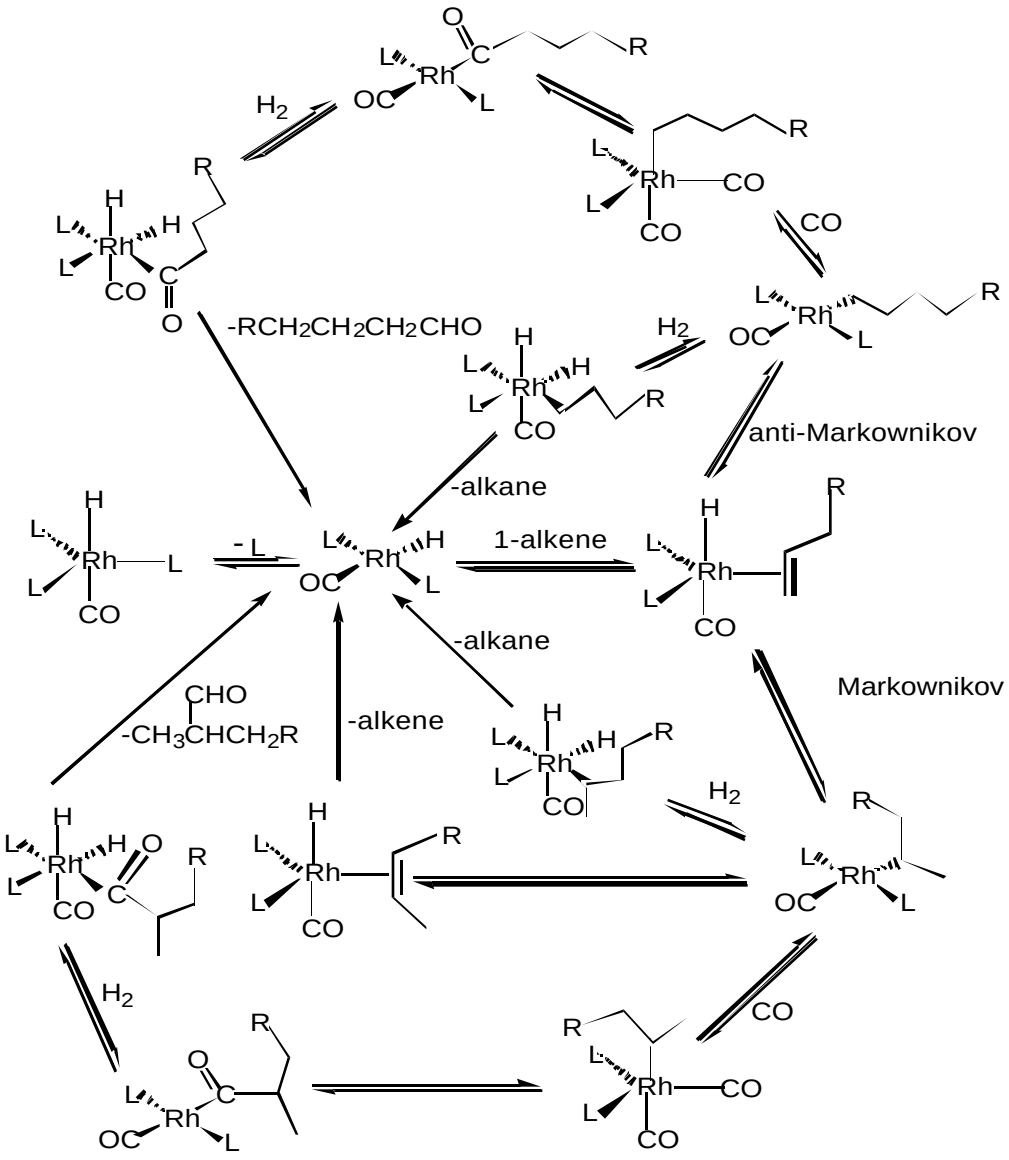

Figure 2.2 Schematic Representation of Possible Reaction Mechanisms for Hydroformylation, Isomerization and Hydrogenation of 1-alkene by $HRh(CO)(PPh_3)_3$ Catalysts ($L = PPh_3$)[45]

The mechanism for hydroformylation reveals that the selectivity to linear aldehyde is controlled by the way of metal hydride migration to π-bound olefin. Anti-Markownikov addition of hydride results in a linear aldehyde while Markownikov addition leads to branched aldehyde. Two factors, the acidity of the hydride and the steric constraints of the ligands, control the selectivity of the addition. Sterically demanding ligands such as triarylphosphines are expected to favor linear aldehyde formation by anti-Markownikov addition.

The isomerization and hydrogenation mechanisms share many intermediates with the hydroformylation reaction. Therefore careful control of reaction conditions is necessary to direct the catalytic reaction to the desired products. It has been shown that excess ligand such as triphenylphosphine can minimize the occurrence of isomerization and high partial pressure of CO prevents both isomerization and hydrogenation.[46,47]

Results from many studies[48,49,50,51,52,53,54,55] suggest that the equilibria represented by Figure 2.3 take place under hydroformylation conditions and that each of these species may act as the precursor to a catalytically active species that can operate in the catalytic cycle. Because the catalytic cycle starts at $HRh(CO)(PPh_3)_3$ (I) and the system is usually operated under large excess of PPh_3, the concentration of III and IV are minimized and the most predominated species are I and II. Both I and II can lose a PPh_3 to generate the 16 electron species, V and VI respectively, which are catalytically active towards hydroformylation.

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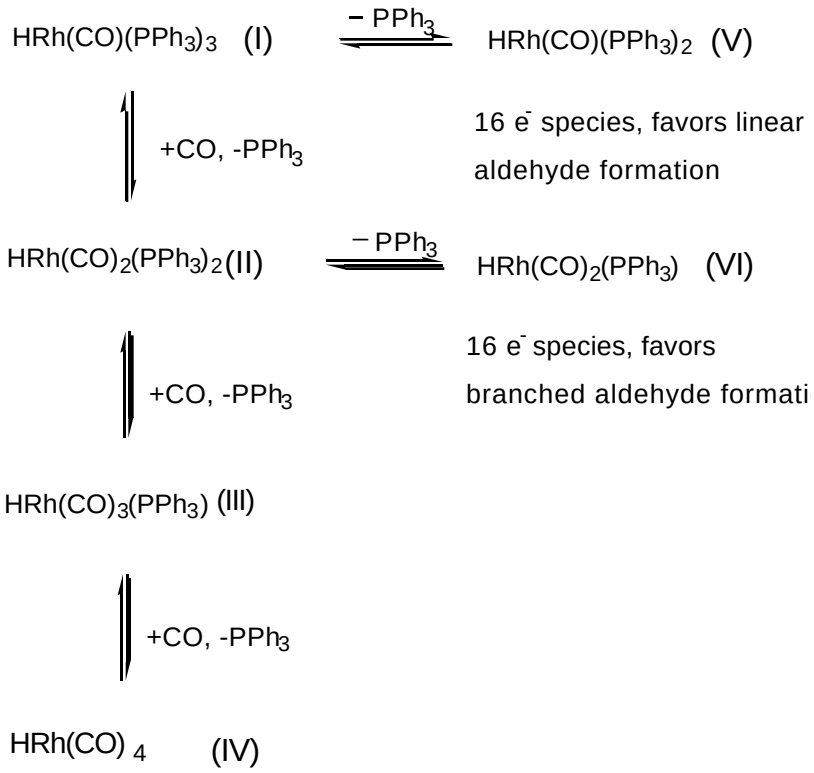

Fig 2.3 Possible Equilibria in Rh/PPh_3 System in the Presence of CO/H_2

The dissociative mechanism originally proposed by Wilkinson[40] is generally considered to be operative with oxidative addition of hydrogen as the rate determining step. A large excess of sterically demanding ligands, such as PPh_3, is required for good selectivity to linear aldehydes, however excess phosphine also reduces the reaction rate.

High concentrations of PPh_3 favor V over VI. If catalysis proceeds via the 16 e^- complexes V and VI, then excess phosphine forces the catalysis to go through the more sterically demanding intermediate V. This can explain the higher proportion of linear product obtained in the presence of excess phosphine. Therefore V is more selective compared to VI.

Today the main activities in hydroformylation research are in the field of new ligand design and synthesis and modified catalysts. Since the successful application of trisulfonated triphenylphosphine in 1975, the research activity in the area of two phase hydroformylation has been high. However fundamental understanding of the hydroformylation mechanism in aqueous solution is still lacking. This is partly due to the difficulties in gathering spectroscopic evidence, such as NMR and IR information, for ionic species in water.

2.4 The Limitation of Two-Phase Reactions With Water-Soluble Catalysts

The reported X-ray structure of $[W(CO)_5P\{C_6H_5\text{-}m\text{-}SO_3\}_3]$ with [Na-Kryptofix-221] by Darensbourg et al.[56] showed that with regard to the M-P bond the sulfonated phosphine is quite electronically similar to that of its non-sulfonated analogue PPh_3. Nevertheless, the two ligands differ significantly in their steric influence. On the basis of a molecular model provided by the structure data, TPPTS appears to be approximately 20% larger than PPh_3. In terms of Tolman's cone angle, a value of 170° appears appropriate compared to 140° for PPh_3. In addition, when the metal center is multiply substituted with TPPTS ligands, the possibility exists for interligand interactions that can greatly affect the reactivity of such complexes.

The only reported crystal structure of a TPPTS complex in the absence of crown ethers was obtained by Hanson et al.[57] The structure of $Co_2(CO)_6(TPPTS)_2$ therefore provides valuable information about the interaction between sulfonate groups and counter ions. In the solid state, hydrophobic layers of $Co_2(CO)_6(TPPTS)_2$ are separated by hydrophilic planes of sodium cations and solvent.

The major limitation to further application of two phase hydroformylation catalysis is the solubility of higher olefins in water. Studies have shown that the hydroformylation of olefins under two phase conditions actually occurs in the aqueous phase.[58] Therefore the activity of the catalytic system is limited by the concentration of olefins in water.

A potential solution to enhance the solubility of an organic substrate in water may be the introduction of a surfactant. In fact, surfactants have been extensively studied as additives in two phase catalysis to increase the mixing of two phases. It has been shown that the addition of a surfactant to Rh/TPPTS two phase hydroformylation catalyst increases the reaction activity of two phase hydroformylation of 1-hexene.[59] Overuse of surfactants should be avoided since the formation of highly stable emulsions is in conflict with the goal of two phase systems, namely easy product-catalyst separation.

Another approach is to design a phosphine which has some characteristic features of a surfactant, but is not expected to stabilize emulsions. A surface-active phosphine is defined as a phosphine which bears a hydrophobic end and several hydrophilic ends. The molecule then serves not only as a phosphine ligand to satisfy the coordination chemistry of the central metal atom, but

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[56] D. J. Darensbourg, C. J. Bischoff and J. H. Reibenspies, Inorg. Chem., **1991,** 30, 1144.

[57] T. Bartik, B. Bartik, B. E. Hanson, K. H. Whitmire and I. Guo, Inorg. Chem., **1993,** 32, 5833.

[58] E. G. Kuntz, Chemtech, **1987,** 17, 570.

[59] H. Bahrman, B. Cornils, W. Konkol and W. Lipps, German Patent, 3 412 335 **(1985).**

as a surfactant as well. The surface activity of such a phosphine is shown by its ability to aggregate in aqueous solution. Aggregation of phosphines may improve the solubility of organic substrates in water. Since the surface activity of such phosphine does not arise from external additives, the activity and selectivity of such catalyst can be studied and understood mechanistically by simplifying two separate issues, namely the electronic and steric aspect of a phosphine and the surface active feature of an external additive, into a single issue of surface active phosphine. In other words, by introducing a surface active phosphine, the position of the hydrophilic functionality relatively to the metal center is well defined and potentially adjustable.

Many of the sulfonated phosphines reported in the literature are expected to be surface active. Even phosphine as simple as TPPMS shows surface-active character when used as a water-soluble ligand in 1-hexene hydroformylation.[12] More recently, Hanson et al synthesized a series of trisulfonated tris(ω-phenylalkyl)phosphines $P[(CH_2)_n(p\text{-}C_6H_4SO_3Na)_3]_3$ n=1, 2, 3, 6.[36] These sulfonated phosphines have a well-separated hydrophobic part and three hydrophilic ends. The two phase hydroformylation of 1-octene with these phosphines, especially with trisulfonated tris(6-phenylhexyl)phosphine, showed better activity and moderately enhanced selectivity at low ligand/rhodium ratios. Unfortunately, the activity of the catalyst dropped to almost zero at the high ligand to rhodium ratios necessary for the long term stability of the Wilkinson type catalysts.[36] This outcome is not surprising since these phosphines are electron donating and tend to block all the coordination sites of rhodium at high ligand : rhodium ratio. Because of the relatively small cone angle of these phosphines, the reaction selectivity showed no improvement compared to Rh/TPPTS system.

Based on the experimental observations with tris(ω-phenylalkyl)phosphines, it is obvious that a class of surface active phosphines which are electron-withdrawing and sterically demanding would be more suitable as ligands for Wilkinson type catalysts.

2.5 Influence of Salt on the Reactivity and Selectivity of Aqueous Hydroformylation

Several factors not encountered in nonaqueous homogeneous rhodium catalysis are now important in the two phase catalysis with water soluble catalysts derived from TPPTS. First, the stability of the substrate in water is significant in determining the reaction rates of a two phase hydroformylation reaction. Second, the catalyst and all proposed intermediates in the homogeneous system are neutral whereas all the rhodium-TPPTS complexes are inherently ionic due to the charge on the sulfonate groups. Third, although aqueous phase rhodium catalysts derived from TPPTS are generally considered to be similar to Rh/PPh_3 system mechanistically, dynamic NMR study of the exchange of water soluble rhodium hydroformylation catalyst $HRh(CO)(TPPTS)_3$ with free TPPTS indicated a special stability for water-soluble rhodium

complexes of TPPTS.[60] The high stability of $HRh(CO)(TPPTS)_3$ contributes to the observed high selectivity to linear aldehyde in aqueous hydroformylation system with rhodium-TPPTS catalyst.

In nearly all patented examples an additional salt is added to the aqueous phase.[59,61,62] Typically these are either ionic surfactants or sodium phosphates, e.g. Na_2HPO_4; the role of the added ionic components is apparently to either improve the mixing of the two phases, in the case of a surfactant, or to control the reaction pH. Examples with either propylene and hexene as the substrate show high selectivity for the linear aldehydes in the hydroformylation reactions is commonly observed. In contrast TPPTS catalysts without added salt, buffer or surfactant and low rhodium concentration give low selectivity; n/iso ratio usually in the range 2.5-5.0. The influence of solution ionic strength on selectivity may be due to the stability and the geometry of catalytic intermediates.

Ionic water soluble phosphines, such as sulfonated phosphines, and their metal complexes are strong electrolytes. Since addition of salt greatly changes the solution ionic strength, the presence of added salt is expected to influence the stability of catalytic intermediate. Thus the addition salt may be expected to have an effect on the activity and selectivity of water-soluble catalysis.

2.6 Industrial Applications

The hydroformylation products prepared on the largest scale are butyraldehyde and ethylhexanol.[26] Both of these are produced from propylene which is derived from natural gas. Either rhodium or cobalt phosphine complexes are employed as the catalyst.[26] The second largest industrial application of hydroformylation is the production of C_8-C_{20} range alcohols 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 referred to SHOP for Shell Higher Olefin Process.

Union Carbide and Ruhrchemie developed hydroformylation processes which use $HRh(CO)(PPh_3)_3$ and $HRh(CO)(TPPTS)_3$ respectively. The modified rhodium catalyst has some advantages over cobalt catalysts:

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[60] I. T. Horvath, R. V. Kastrup, A. A. Osward and E. J. Mozeleski, Catal. Letters., **1989,** 2, 85.

[61] a. E. Kuntz, French Patent, 2 314 910 **(1975).** b. E. Kuntz, German Patent, 2 627 354 **(1976).**

[62] a. J. Jenck, French Patent, 2 178 078 **(1981).** b. D. Morel and J. Jenck, French Patent, 2 550 202 **(1982).**

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

Table 2.1 and 2.2 show the industrial application of hydroformylation catalyst system.

Table 2.1 Commercial Application of Hydroformylation of Olefins[a]

Substrate	**Product**	**Application**
Propylene	Butanol 2-Ethylhexanol	Solvent Plasticizers
$C_6 \sim C_9$ α-Olefins	$C_7 \sim C_{10}$ Alcohols	Plasticizers
$C_{10} \sim C_{19}$ α-Olefins	$C_{11} \sim C_{20}$ Alcohols	Detergents

a: Schnauzer, G. N. “Transition Metals in Homogeneous Catalysis”, Marcel Dekker, 1971

Table 2.2 Commercial Hydroformylation Catalyst Systems[a]

Company	Shell	Union Carbide	Ruhrchemie
Catalyst System	**$Co_2(CO)(PBu_3)_2$**	**$HRh(CO)(PPh_3)_3$**	**$HRh(CO)(TPPTS)_3$**
Temerature (°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	$C_2 \sim C_{12}$	$C_2 \sim C_4$	$C_2 \sim C_4$

a: Master, C. “Homogeneous Transition Metal Catalysis”, Chapman Hall, New York, 1977

Though a great effort has been put onto the development of (1) 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 active catalysts for hydroformylation. However, studies on other metals continue.

Using these reactions among others as examples the early researchers found in comparison to the conversion of lower olefins very minor reaction rates apart from emulsifying surface active-active properties of the ligands. The decreasing miscibility of the aqueous catalyst solutions with increasing C number of the higher olefins is likely responsible for lowering the conversion rate. The following proposals should improve the solubilities and thus the conversion of biphasic processes:

1). Variation of the water-soluble ligands by means of surfactant or solubilizing properties
2). Addition of solvents and /or co-solvents

2.7 Objective of Research

One objective of this thesis is to further investigate water soluble rhodium catalysts by ligand modification. Specially the Cesium analog of TPPTS is prepared and its application in the two phase hydroformylation of higher olefins is investigated. A preliminary single crystal structure has been obtained on TPPTS-Cs_3. A related objective is to study the role of the size of the cation in determining reaction selectivity. Various transition metal complexes of TPPTS-Cs have been synthesized and characterized in order to elucidate their structure and catalytic properties in two phase hydroformylation of alkenes.

The synthesis and the two phase catalytic application of a novel surface active phosphine was pursued. Surface active phosphines are those phosphines which can potentially form aggregates in water to increase the solubility of organic substrate in water. Two phase hydroformylation of 1-hexene is also carried out for the purpose of demonstrating enhanced reaction rate and selectivity with this surface active phosphine compared to the two phase hydroformylation with rhodium-TPPTS under similar catalytic conditions.

A new water soluble chelating phosphine for aqueous phase catalysis also has been synthesized and characterized. Its application in hydroformylation of 1-octene shows that the rhodium catalyst with this sulfonated chelating BIBSI type phosphine offers both good activity and excellent selectivity under two phase conditions. Instead of a diphenylphosphino group, pendant diarylphosphino groups are introduced to biphosphines to generate a class of ligands which are easily sulfonated and have amphiphilic character.

Finally, asymmetric hydrogenation of a cinnamic acid derivative with (S,S-BDPP)Rhodium catalysts in methanol in the presence of a chiral surfactant is carried out to investigate the effect of the reaction medium in controlling the asymmetric induction.

Chapter 3. EXPERIMENTAL METHODS

General Considersions

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Deionized water was purged with argon gas for 15 min, heated at reflux for 12 hours, and then allowed to cool under nitrogen gas. Organic solvents were dried and degassed through activated alumina column for 12 h and stored under inert gas atmosphere. Reagents were used as provided by the suppliers without further purification unless stated otherwise.

NMR measurements were done on a Bruker WP 200 at 200.133 MHz for ^{1}H, 50.322 MHz for ^{13}C, and 81.015 MHz for ^{31}P. Some high field ^{1}H, ^{13}C, ^{31}P NMR data were obtained on a Varian RU 400 NMR spectrometer at 399.052, 100.577, 161.903 MHz, respectively.

Key to NMR data: s, singlet; d, doublet; t, triplet; quart, quartet; quint, quintet; m, multiplet; br, broad; asterisk, pseudo.

FAB Mass Spectra were recorded on a VG 7070E-HF spectrometer. Infrared spectra were recorded on a Nicolet 5DXB FTIR in either matched 0.1-mm CaF_2 cells (nonaqueous solvents) or matched 0.1-mm Irtran cells (aqueous solvents). The pH measurements were carried out on a Microcomputer pH-Vision, Cole/Parmer Model 05669-20.

3.1.1 Synthesis of Tricesium Salt of 3,3',3''-phosphinetriylbenzene-sulfonic Acid (TPPTS-Cs_3) (1)

$$P(C_6H_5)_3 + 3SO_3\,(H_2SO_4) \rightarrow P(C_6H_4SO_3H)_3 \quad \textbf{(3.1)}$$

$$P(C_6H_4SO_3H)_3 + 3N(C_8H_{17})_3 \rightarrow [HN(C_8H_{17})_3]_3[P(C_6H_4SO_3)_3] \quad \textbf{(3.2)}$$

$$[HN(C_8H_{17})_3]_3[P(C_6H_4SO_3)_3] + 3CsOH \rightarrow P(C_6H_4SO_3Cs)_3 + 3N(C_8H_{17})_3 \quad \textbf{(3.3)}$$

1

Oleum 96 g (30 wt.%) was placed in a 250-ml flask equipped with a stirrer, thermometer, dropping funnel, and cooler and cooled to an internal temperature of 15 °C. Over a period of one hour, 10.5 g (40 mmol) of triphenylphosphine and a further 32 g of 30 wt. % oleum was added with stirring. After the addition of oleum and triphenylphosphine had completed, the mixture was stirred for 150 h at 20 °C. Subsequently, the mixture was added to a 1-L flask containing 300 g of

water having a temperature of about 10 °C. During the addition the internal temperature was kept between 20 °C and 40 °C by external cooling.

The homogeneous sulfonation mixture was placed in a 1-L flask and stirred with a mixture of 47.7 ml (110 mmol) triisooctyl amine and 180 ml toluene. After the addition was completed, the reaction mixture was stirred for an additional 30 min and then left to separate for 30 min. The lower phase was separated and discarded.

Aaqueous cesium hydroxide solution (5 %) was added to the toluene solution with stirring until the mixture reached a pH of 5.5 (the aqueous solution which contains mainly tppms, tppds, minor amounts of oxide product). The aqueous solution was separated and discarded. The addition of base was continued until the mixture was reached to a pH of 6.0-6.5. The aqueous solution was separated. By concentration of the aqueous solution, the crude white solid of product **1** can be obtained.

Methanol and water (100 ml of a 10:1 mixture) was used to dissolve the Cesium salt of 3,3',3''-phosphinetriylbenzensulfonic acid. The reaction mixture was heated to reflux for 30 min, followed by filtration while the solution was hot.

Upon cooling to room temperature, pure white crystalline solid of product **1** was obtained, 21.0 g (yield 60 %). Single crystals were obtained by redissolving the product **1** in warm MeOH/H_2O (6/1) and slowly cooling to the room temperature.

Analytical data for $P(C_6H_4SO_3Cs)_3$

White crystalline solid; ^{1}H NMR [δ in D_2O/MeOH(d_4)/THF(d_8) (2/3/5)]: 7.80 (m, 1H); 7.82 (m, 1H); 7.84 (m, 1H); 7.86 (m, 1H). ^{13}C NMR [δ in D_2O/MeOH(d_4)/THF(d_8) (2/3/5)]: 127.84 (s); 130.32 (d, J_{p-c} = 8 Hz); 131.50 (d, J_{p-c} = 32 Hz); 136.52 (d, J_{p-c} = 17.5 Hz); 137.76 (d, J_{p-c} = 18.5 Hz); 145.80 (d, J_{p-c} = 11.4 Hz). ^{31}P NMR (δ in D_2O): -5.21 (s). MS (FAB, Glycerol matrix): 767 (M-Cs^++2), 898 (M^+), 1031 (M+Cs^++1). Anal. Calc. $C_{18}H_{12}O_9S_3PCs_3$: C, 24.10; H, 1.35. Calc. as trihydrate $C_{18}H_{12}O_9S_3PCs_3$ $3H_2O$): C, 23.51; H, 1.50. Found: C, 23.48; H, 1.33.

3.1.2 Synthesis of Various Transition Metal Complexes With TPPTS-Cs_3

3.1.2.a Synthesis of Hexacesium Hexacarbonyl Bis[3,3',3"-phosphinetriylbenzenesulfonato] Dicobaltate [$Co_2(CO)_6$(TPPTS-$Cs_3)_2$]

$$Co_2(CO)_8 + 2TPPTS\text{-}Cs_3 \rightarrow Cs_6\{Co_2(CO)_6[P(C_6H_4SO_3)]_2\} + 2CO \quad \textbf{(3.4)}$$

In a 50 ml two neck flask, 100 mg (0.3 mmol) of octacarbonyl dicobalt, $Co_2(CO)_8$ was dissolved in 10 ml of toluene. TPPTS-Cs_3 (628 mg, 0.700 mmol) was dissolved in 10 ml water and added to the solution. The reaction mixture was stirred for 3 h at room temperature. During the reaction the organic phase was decolorized whereas the water phase turned brown. The mixture was transferred to a separatory funnel. After the phase have separated, the organic phase was extracted with water (2 x 5 ml), and the combined aqueous phases were washed with toluene (2 x 5 ml). The organic phases were discarded. The water phases were combined, and the solvent was removed under a vacuum. The crude product was purified by recrystallization from H_2O/MeOH (1/10) to afford 625 mg (90 %) of a brown solid.

Properties

$Co_2(CO)_6$(TPPTS-$Cs_3)_2$ was a brown colored solid which was moderately stable in air. The compound was very soluble in water and insoluble in organic solvents like toluene or hexene. ^{31}P NMR (D_2O) δ 66.8 (s). IR (KBr):1965cm^{-1} (CO). FAB (in Glycerol): 2082 (M^+), 2026 (M-2CO)$^+$, 1952 (M-Cs+1)$^+$.

3.1.2.b Synthesis of $Ni(CO)_3$(TPPTS-Cs_3)

$$Ni(CO)_4 + TPPTS\text{-}Cs_3 \rightarrow Ni(CO)_3(TPPTS\text{-}Cs_3) \quad \textbf{(3.5)}$$

The nickel complexes of the water-soluble phosphine (TPPTS-Cs_3) was prepared in 50 ml flask in 5:1 THF/H_2O mixture. $Ni(CO)_4$ in THF was transferred to the aqueous solution of TPPTS-Cs_3 and the reaction mixture was stirred for 10 h and the reaction was monitored by IR. After all the TPPTS-Cs_3 (detected by ^{31}P NMR) was consumed, the solvent was removed under reduced pressure and the product was characterized without further purification. ^{31}P NMR (D_2O) δ 32.0 ppm. IR (THF/H_2O) ν(CO): 2070 (w), 2000 (vs) cm^{-1}.

3.1.2.c Synthesis of $(TPPTS\text{-}Cs_3)_2MCl_2$ (M=Pd, Pt)

$$(PhCN)_2MCl_2 + 2TPPTS\text{-}Cs_3 \rightarrow (TPPTS\text{-}Cs_3)_2MCl_2 + 2PhCN \quad \textbf{(3.6)}$$

The L_2MCl_2 complexes of the water-soluble phosphine were prepared in a two phase reaction. For both M = Pd and M = Pt, 0.6 mmol of $(PhCN)_2MCl_2$ was dissolved in 15 ml of CH_2Cl_2 to give a yellow solution. 15 ml of aqueous solution of 1.1 g (1.2 mmol) TPPTS-Cs_3 was added. After the mixture was stirred for 30 min, the color had completely transferred to the aqueous layer. The yellow aqueous phase was separated and washed twice with 10 ml of CH_2Cl_2. The residual CH_2Cl_2 was removed under vacuum, and finally the pH was adjusted to 6 with addition of Hcl. For $(TPPTS\text{-}Cs_3)_2PdCl_2$, ^{31}P NMR (D_2O) δ 33.0 ppm (trans isomer 90 %), δ 28.9 ppm (cis isomer 10 %). FAB (glycerol): 1972 (M^+), 1770 (M-Cs-2Cl)$^+$, 1637 (M-2Cs-2Cl)$^+$. For $(TPPTS\text{-}Cs_3)_2PtCl_2$, ^{31}PNMR ($D_2O$) δ 22.0 ppm (trans isomer 95 %), δ 16.0 ppm (cis isomer 5 %). FAB (Glycerol) for Pt complex: 2062 $(M+1)^+$,1858 (M-Cs-2Cl)$^+$,1726 (M-2Cs-2Cl)$^+$.

3.1.2.d Synthesis of $HRh(CO)(TPPTS\text{-}Cs_3)_3$

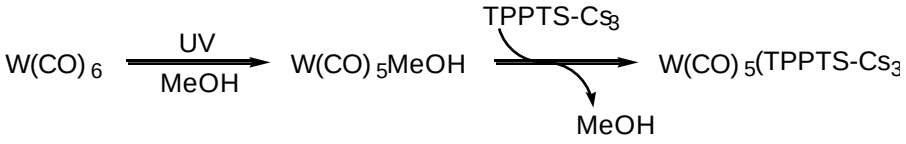
$$2Rh(acac)(CO)_2 + 6TPPTS\text{-}Cs_3 + H_2 \rightarrow 2HRh(CO)(TPPTS\text{-}Cs_3)_3 + 2CO + 2acac \quad \textbf{(3.7)}$$

$Rh(acac)(CO)_2$ (0.095 g, 0.370 mmol) was dissolved in 10 ml water and 0.99 g (1.1 mmol) of TPPTS-Cs_3 was added to the yellow solution. H_2 was bubbled through the reaction mixture and the reaction was monitored by ^{31}P NMR. After 6 h the solvent was removed under vacuum and the brown solid was purified by recrystallization from H_2O/acetone (1:10) to afford 0.83 g (80 %) of brown solid after pumping overnight.

Properties

Brown solid, ^{31}P NMR (D_2O): δ 44.0 ppm (d, $J_{P\text{-}Rh}$ = 160 Hz). ^1H NMR (D_2O): δ 7.1-7.8 (m, 36H), -9.5 (q, 1H). IR (D_2O): ν(CO) 2180 cm^{-1}, ν(H-Rh) 2098 cm^{-1}. FAB (Glycerol): 2826 (M^+), 2958 (M+Cs-1)$^+$, 2692 (M-Cs-1)$^+$, 2797 (M-CO-H)$^+$.

3.2.1.e Synthesis of $W(CO)_5(TPPTS\text{-}Cs_3)$

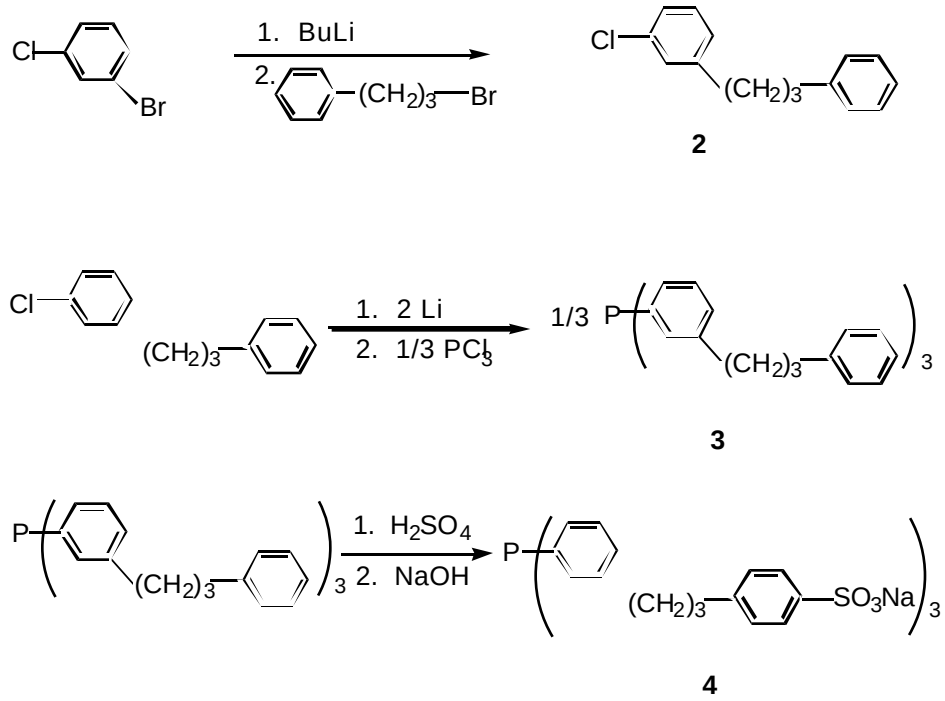


(3.8)

A solution of $W(CO)_6$ was prepared by dissolving 0.654 g (2.00 mmol) in 75 ml of MeOH. This solution was placed in a photolysis vessel and irradiated with a 400-W UV lamp for 30 min to yield the very substitutionally labile $W(CO)_5(MeOH)$ species, as identified by IR spectroscopy [ν(CO) 2075 w, 1932 s, and 1887 m cm^{-1}]. The methanol adduct was added by cannula to a flask containing 1 equiv (1.8 g, 0.002 mmol) of the solid TPPTS-Cs_3 ligand. The reaction was monitored by the disappearance of the ν(CO) infrared bands associated with the methanol adduct, with concomitant appearance of ν(CO) bands due to $W(CO)_5(TPPTS\text{-}Cs_3)$. The product was filtered through Celite and precipitated by the addition of isopropyl alcohol to yield a very flocculent pale yellow solid. The solid was centrifuged and the supernatant liquid decanted to yield a wet yellow paste. Final drying of the compound was accomplished under vacuum at ambient temperature over a 24-h period.

Data for $W(CO)_5(TPPTS\text{-}Cs_3)$ were as follows: ν(CO) in H_2O: 2070 (w), 1940 (s), and 1930 (m) cm^{-1}. δ (^{31}P) NMR in H_2O: 27.5 ppm [d, J(^{183}W-^{31}P) = 247.7]. FAB (Glycerol): 1223 $(M+1)^+$, 1355 $(M+Cs+1)^+$, 1083 $(M-5CO+1)^+$, 898 $(TPPTS\text{-}Cs_3+1)^+$.

3.2 Synthesis of Trisulfonated Tris-m-(3-phenylpropyl)phenylphosphine (4) [m-PC(3)]



Scheme 3.1 Trisulfonated Tris-m-(3-phenylpropyl)phenylphosphine

3.2.1.a Synthesis of m-(3-phenylpropyl)phenylchloride (2)

1-Bromo-3-Chlorobenzene (38.4 g, 0.2 mol) and 400 ml of diethyl ether were placed in a 1 L three-neck flask equipped with a reflux condenser, an pressure-equalizing dropping funnel, a gas inlet, and a magnetic stirrer. The solution was cooled to 0 °C. After the addition of 111 ml of 1.8 M butyllithium in cyclohexane/diethyl ether, the mixture was allowed to come to room temperature and stirred for an additional hour. A solution of 3-phenylpropylbromide (39.6 g, 0.200 mol) in 100 ml diethyl ether was added to the reaction flask dropwise and the mixture was heated at reflux temperature for five days. Lithium bromide was removed by filtration and the solvent was removed by distillation. The residue was distilled under reduced pressure (5 torr), and 29 g (64 %) of a colorless oil was collected at 152-156 °C.

Analytical data for m-(3-phenylpropyl)phenylchloride (**2)**

Colorless oil, bp. 152-156 °C (5mmHg), ^{1}H NMR (δ in $CDCl_3$): 2.06 (m, 2H); 2.74 (m, 4H); 7.23-7.44 (m, 9H, aromatic protons). ^{13}C NMR (δ in $CDCl_3$): 32.05 (s); 34.80 (s); 35.40 (s); 125.01 (s); 126.50 (s); 128.43 (s); 130.01 (s); 141.56 (s); 142.30 (s). GC-MS (in MeOH) [retention time 12.24 min, 230 (M^+)].

3.2.1.b Synthesis of Tris-m-(3-phenylpropyl)phenylphosphine (3)

Lithium metal (1.4 g, 0.20 mol) was chopped directly into 100 ml THF in a 500 ml three-neck flask equipped with an equal-pressure dropping funnel under an Argon atmosphere. m-(3-Phenylpropyl)phenylchloride (23.0 g, 0.1 mol) in 100 ml diethyl ether was added dropwise at 5 °C. The color of the reaction mixture slowly changed to deep red and a gray precipitate of LiCl formed. The mixture was stirred at room temperature for 3 hours until nearly all the lithium metal was consumed. The flask with the resulting deep red solution was chilled to 5 °C by ice-water bath and 4.6 g (0.033 mol) PCl_3 in 50 ml diethyl ether was added over a period of 1 hour. The ice-water bath was removed, and the reaction mixture was stirred further for 10 hours at 20 °C. Dry ice (10 g) was added slowly to the mixture, and the solution was filtered under Ar. The filtrate was pumped to dryness and redissolved in 100 ml diethyl ether. The solution was washed with 3×50 ml degassed water and dried over $MgSO_4$. The diethyl ether was removed under reduced pressure to give 15.8 g (77 %) tris-m-(3-phenylpropyl)phenylphosphine **(3)** as a pale yellow oil.

Analytical data for tris-m-(3- phenylpropyl)phenylphosphine **(3)**.

^{1}H NMR (δ in $CDCl_3$): 1.97 (quint, $^{3}J_{H-H}$ =7.5 Hz, 6H); 2.65 (t, $^{3}J_{H-H}$ = 7.5 Hz, 12H); 6.64-7.32 (m, 27H, aromatic protons). ^{31}P NMR (δ in $CDCl_3$): -7.34 (s).

3.2.1.c Synthesis of Trisulfonated Tris-m-(3-phenylpropyl)phenylphosphine (4) [m-PC(3)]

Tris-m-(3-phenylpropyl)phenylphosphine 5 g (0.0081mol) was placed into a 1000- ml flask under Ar at -78°C, and 20 ml 96 % H_2SO_4 was added. The mixture was then warmed to room temperature with stirring. After 6 hours the brown reaction mixture was neutralized by slow addition of 20 % NaOH. The final pH was 9 and the final volume was about 120 ml. 720 ml methanol was added and the mixture was heated to reflux for 30 min. The mixture was then filtered

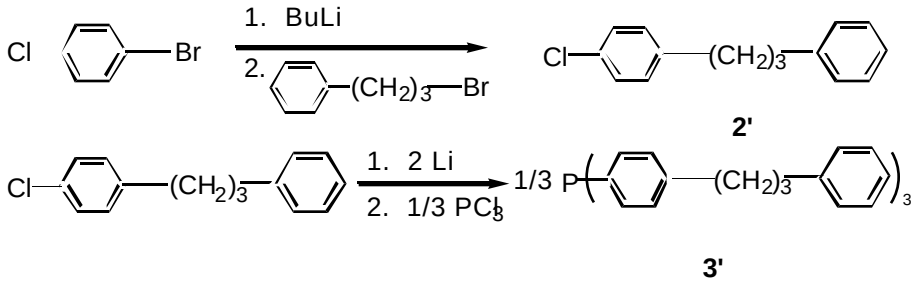
and the precipitate was extracted with 200 ml hot methanol. The methanol extracts were combined and the volume was reduced to about 45 ml. Acetone (270 ml) was then added to precipitate the crude product. This precipitate was collected and dried to afford 6.8 g (90 %) of pure **4** as a white solid.

Analytical data for Trisulfonated Tris-m-(3-phenylpropyl)phenylphosphine (**4)**

White solid, ^{1}H NMR (δ in D_2O): 1.40 (m, 6H); 2.10 (m, 12H); 6.80-7.50 (m, 27H). ^{13}C NMR (δ in D_2O): 34.29 (s); 36.75 (s); 126.10 (s); 127.90 (s); 129.50 (s); 131.20 (s); 131.47 (s); 133.65 (s); 142.72 (s); 143.04 (s); 144.81 (s); 147.72 (s); 148.96 (s). ^{31}P NMR (δ in D_2O): -6.27 (90 %) + -6.20 (10 %). MS (in Glycerol matrix) 901 ($M-Na^+$+1); 923 (M^++1); 945 ($M+Na^+$+1); A small peak is observed at 1026 (M^++SO_3Na), this suggests some oversulfonation. Elemental analysis is consistent with over-sulfonated product. Calc. ($C_{45}H_{42}S_3O_9Na_3P$) C 58.60, H 4.55. Found: C 53.42, H 4.54.

3.3 Synthesis of Tetrasulfonated 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl [BIBSI-PC(3)-Na_3] (6)

3.3.1 Synthesis of Tris-p-(3-phenylpropyl)phenylphosphine (3')

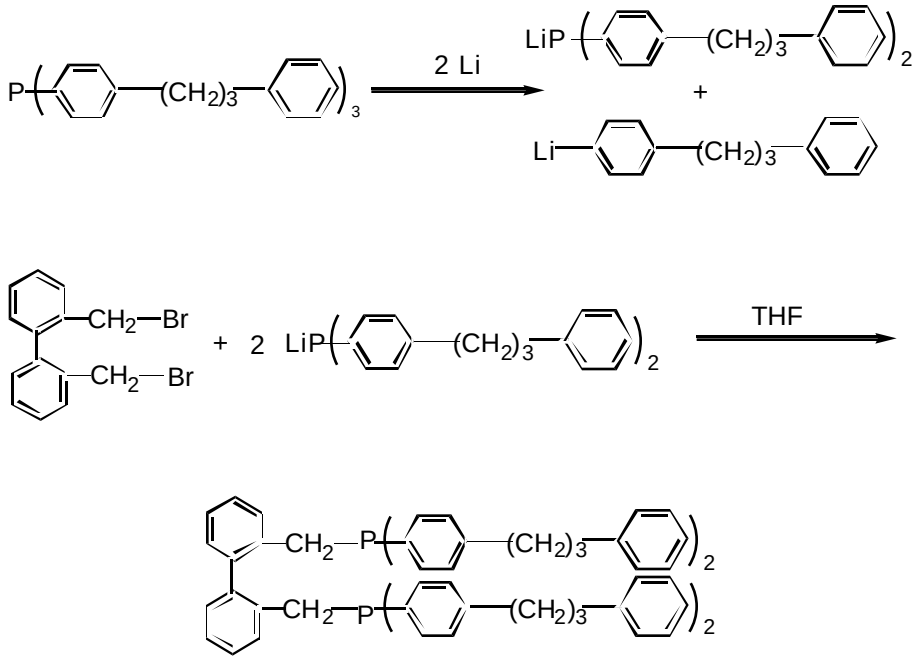


Scheme 3.2 Synthesis of Tris-p-(3-phenylpropyl)phenylphosphine

The synthesis of p-(3-phenylpropyl)phenylchloride **2'** and tris-p-(3-phenylpropyl)phenylphosphine **3'** followed the same procedure as Tris-m-(3-

phenylpropyl)phenylphosphine **3**. The properties of this phosphine [P(C_3)] have been published.[63]

3.3.1.a Synthesis of 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl (5)



5

Scheme 3.3 Synthesis of BISBI-PC(3)

Finely chopped lithium metal (0.14 g, 0.02 mol) was suspended in 10 ml dry THF, and tris-p-(3-phenylpropyl)phenylphosphine (6.2 g, 0.01 mol) in 100 ml THF was added from a dropping funnel over a period of about 10 minutes with vigorous stirring. The resulting deep red solution was stirred at room temperature for an additional 2 hours. tert-Butylchloride (0.93 g, 0.01 mol) was added and the reaction mixture was brought to reflux for 15 minutes. The volume of the solution was reduced to about 10 ml and 80 ml dry degassed pentane was added. The flask was then cooled to -78 °C to yield a dark red viscous residue and a colorless ligand. After decanting the colorless ligand, the residue was redissolved in 50 ml THF {^{31}P NMR (THF): -25.97}. To this

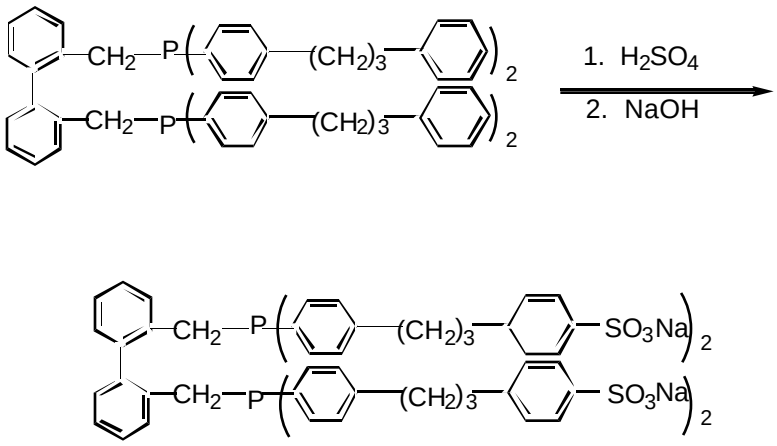
[63] H. Ding, B. B. Bunn and B. E. Hanson Inorganic Synthesis, **Accepted**

solution, 2,2'-dibromomethyl-1,1'-biphenyl (1.7 g, 0.005 mol) in 10 ml THF was added dropwise at the temperature of an ice-water bath. The color of the solution slowly changed to pale yellow. The mixture was stirred for additional 10 hours and then the solvent was removed under vacuum. Diethyl ether (50 ml) was added and was washed with water (3x10 ml). The ether phase was separated and dried over $MgSO_4$. The solvent was then removed under vacuum. The resulting pale yellow viscous oil was purified over silica gel column. After eluted with Et_2O:hexane (1:10) to afford 3.57 g (70 %) of pure product.

Analytical data of 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl **(5)**

Pale yellow viscous oil, ^1H NMR (δ in $CDCl_3$): 1.83 (m, 8H); 2.51 (m, 16H); 3.06(quart, 4H); 6.9-7.2 (m, 44H). ^{13}C NMR (δ in $CDCl_3$): 32.72 (d, $^7J_{C-P}$ = 3.7 Hz); 33.65 (d, $^1J_{C-P}$ = 16.1 Hz); 35.12 (d, $^6J_{C-P}$ = 2.3 Hz); 35.31 (d, $^5J_{C-P}$ = 13.0 Hz); 125.71 (s); 128.26 (s); 128.33 (s); 128.36 (s); 129.65 (s); 129.75 (s); 132.64 (d, $^3J_{C-P}$ = 18.3 Hz); 133.25 (d, $^2J_{C-P}$ = 319.1 Hz); 135.18 (d, $^1J_{C-P}$ = 14.5 Hz); 135.88 (d, $^3J_{C-P}$ = 9.2 Hz); 140.82 (d, $^2J_{C-P}$ = 4.5 Hz,); 142.09 (s); 142.44 (s). ^{31}P NMR (δ in $CDCl_3$): -11.8 (s). MS (FAB, from a glycerol matrix yielded only the phosphine oxide); 1055 (M^+ +1).

3.3.1.b Synthesis of Tetrasulfonated 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl [BIBSI-PC(3)-Na_3] (6)



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Scheme 3.4 Synthesis of BIBSI-PC(3)-Na_3

A sample of 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl (2.2 g, 2.2 mmol) was dissolved in 8 ml H_2SO_4 (96 %) with an ice-water bath. The brown solution was stirred at room temperature for 7 hours. The mixture was then neutralized by 20 % (w/w) aqueous NaOH. The final pH was 8.5. Methanol (320 ml) was added and the mixture was brought to reflux for 30 min. The precipitate, Na_2SO_4, was then filtered, and the salt was washed with 100 ml of hot methanol. Two portions of the filtrates were combined and the volume was reduced to 50 ml under vacuum, and then aceton (270 ml) was added to generate a white precipitate. The precipitate, tetrasulfonated 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl, was collected by filtration and dried under vacuum (2.8 g, 93 %).

Analytical data of Tetrasulfonated 2,2'-Bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl (**6**)

^{1}H NMR (δ in CD_3OD): 1.91 (m, 8H); 2.57 (m, 8H); 2.63 (m, 8H); 3.10 (quart, 4H); 6.8-7.8 (m, 40H). ^{13}C NMR (δ in CD_3OD): 34.12 (d, $^1J_{C-P}$ = 13.1 Hz); 34.15 (s); 36.13 (s); 36.20 (s); 127.08 (s); 129.36 (s); 129.77 (s); 130.70 (s); 130.75 (s); 133.75 (d, $^3J_{C-P}$ = 18.3 Hz); 134.51 (d, $^2J_{C-P}$ = 19.8 Hz); 143.92 (s); 146.15 (s). ^{31}P (δ in CD_3OD): -10.7 (s). MS (FAB, in glycerol matrix): 1453 ($M + Na^+$). Phosphorus analysis calc. 4.33 %, found 4.12 %.

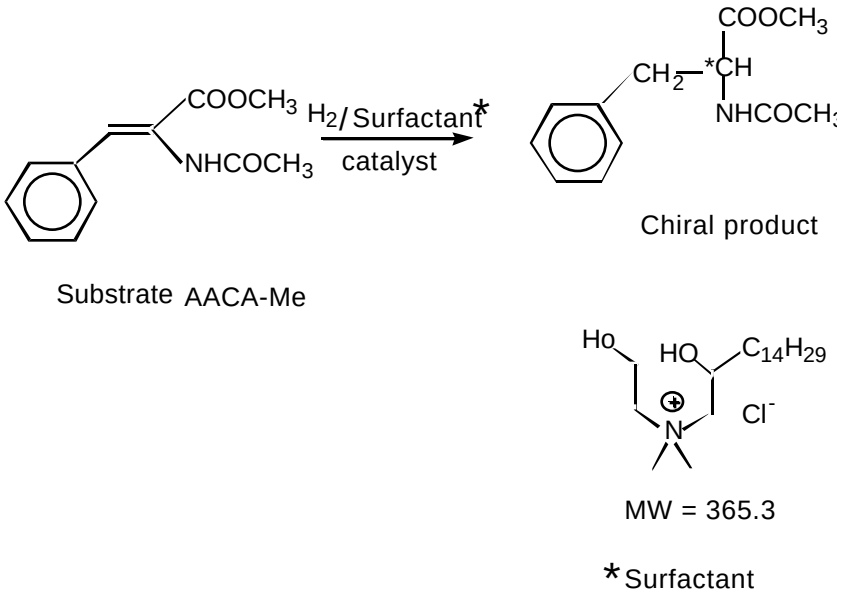
3.3.2 Aqueous Phase Hydroformylation Reactions

Two phase hydroformylation reactions of 1-octene, 1-hexene and 1-tetradecene with rhodium complexes of TPPTS-Cs_3 [M(C_3) and BIBSI-PC(3)-Na_3] were carried out in a 30 ml stainless steel reaction vessel. The catalyst was made in situ by mixing 0.76 ml 0.01 M $Rh(acac)(CO)_2$ in methanol and the required amount of 0.1 M aqueous solution of ligand. Water was added to adjust the total aqueous methanol volume to 1.56 ml. The substrate, 0.60 ml of 1-octene, was then transferred into the reaction vessel under positive pressure of CO. Nonane, 0.40 ml, was added as an internal standard for gas chromatography analysis. The octene/Rh ratio was 500/1 in all catalytic runs. In case of addition of salt, the salt was added directly under an atmosphere of CO/H_2. After the reaction vessel was loaded and pressurized with CO/H_2 to 210 psi, the reaction was initiated by placing the reaction vessel into a temperature bath preheated to 120 °C. The temperature of the oil bath was controlled by an Omega CN 2000 temperature process controller. The reaction mixture was constantly stirred with a magentic stir bar at 350 rpm. Catalytic reactions were terminated by removing the vessel from the oil bath and depressurizing after cooling in an ice-water bath. In all cases the organic layer was colorless and readily separated from aqueous layer after the reaction.

The reaction product distribution was analyzed by gas chromatography on a Varian 3300 gas chromatography equipped with a HP-1 column (25m×0.32mm×0.52μm), and FID detector, He was the carrier gas, the temperature program was from 35 °C (4 min) to 220 °C (1 min), at a heating rate of 10°/min. A injection port sleeve was installed to facilitate the separation of analytes. The produced aldehydes have no appreciable solubility in aqueous methanol; no aldehydes were detected by NMR or GC analysis of the aqueous layer; in all catalytic reactions the organic phase was colorless, that means these phosphines have enough water solubility in order to keep the catalysts in aqueous phase; in a recycling test the organic phase recovered from a catalytic run showed no activity for hydroformylation of 1-heptene.

3.4 Asymmetric Hydrogenation of α-Acetamidocinnamic Acid Methyl Ester (AACA-Me)

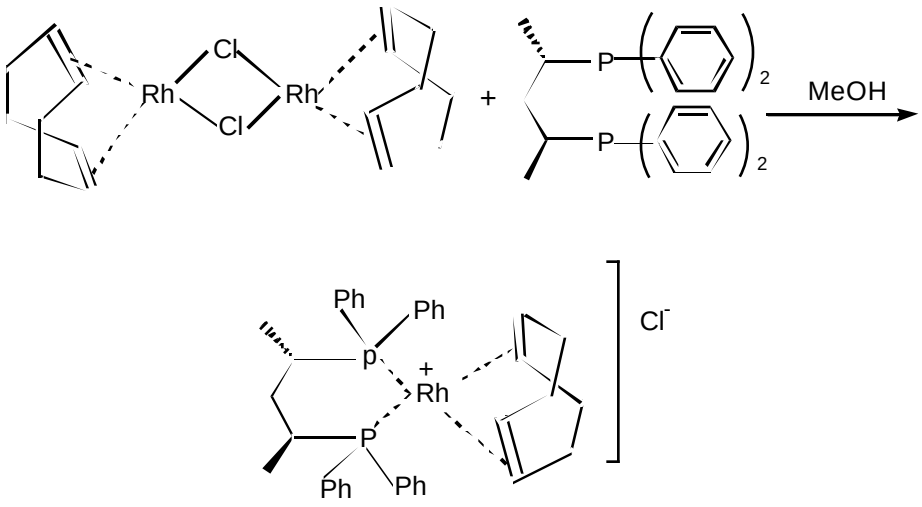
α-Acetamidocinnamic Acid Methyl Ester (AACA-Me) is common substrate for testing chiral ligands, including many chair biphosphines which are structually similar to BDPP [Bis-(diphenylphosphino)pentane]. Hydrogenation of AACA-Me is shown as Scheme 3.5.



Scheme 3.5 Asymmetric Hydrogenation of AACA-Me

Methanol was dried by standard methods and distilled under nitrogen prior to use. The chemicals, such as Bis-(diphenylphosphino)propane, (BPPP), S,S-Bis-(diphenylphosphino)pentane, (S,S-BDPP), $[(COD)RhCl]_2$ were purchased from Strem. Both chiral and racemic surfactant ($C_{20}H_{44}O_2NCl$) were provided by R. D. Gandour.

3.4.1.a Preparation of the Hydrogenation Catalysts



Scheme 3.6 Synthesis of [(S,S-BDPP)Rh(COD)]Cl

The catalysts were made as the Scheme 3.6: 0.18 g (0.42 mmol) of $[Rh(COD)Cl]_2$ was dissolved in 10 ml MeOH, and 0.35 g (0.84 mmol) S,S-BDPP in 10 ml MeOH was added from a dropping funnel over a period of 10 minutes with vigorous stirring. The resulting orange solution was stirred at room temperature for additional 1 hour. The reaction was monitored by ^{31}P NMR [δ in MeOH, 25.5 (d, $J_{P\text{-}Rh}$ = 140 Hz)]. After all the S,S-BDPP was consumed, the methanol was removed under reduced pressure to afford 0.55 g (91 %) orange solid.

3.4.1.b Asymmetric Hydrogenation Reactions

Hydrogenations were performed in glass reactors connected to gas burettes at atmospheric pressure of H_2. In 25 ml 2-neck flask equipped with a stirrer, AACA-Me 0.55 g (2.5 mmol) was dissolved in 5 ml dry methanol and the surfactant 0.23 g (0.63 mmol) was added under positive pressure of H_2. Catalysts in methanol 5 ml (2.5×10^{-5} M) was transfered to the flask using a syringe. Reaction products from the hydrogenations in methanol were worked up as follows: the methanol was removed under vacuum and the residue was dissolved in 10 ml of ethyl acetate. The solution was then extracted with Et_2O (3 × 10 ml). The ether extracts were washed with water and dried over $MgSO_4$. Removal of the solvent resulted in nearly surfactant free products. The

product was then dissolved in methanol to run silica gel column to separated the rhodium catalysis. The product was

checked ^{1}H NMR and optical yield was determined in methanol by polarimetry.[64] The conversion of the reaction was determined by H_2 uptake and NMR spectroscopy.

Chapter 4. RESULTS AND DISCUSSION

4.1.1 Synthesis of TPPTS-Cs_3 Complexes

To date only two X-ray structures of transition metal complexes of the TPPTS [trisodium tris(m-sulfonatophenyl)phosphine] ligand have been obtained; these are $Co_2(CO)_6$(TPPTS-Na_3) by Hanson et al.[57] and [Na-Kryptofix-221]$_3$[$W(CO)_5P\{C_6H_4$-m-$SO_3\}_3$] by Darensbourg et al.[56] (Kryptofix-221 = 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane). Since the cesium anolog of TPPTS was easily crystallized from methanol/water, the goal here was to synthesize various water-soluble transition metal complexes of TPPTS-Cs_3 and to obtain crystals and to further investigate the electronic and steric properties of these water soluble complexes without the benefit of crown ether. To date, however the quality of the crystals obtained is insufficient for X-ray structure determination.

Conventional sulfonation of TPPTS-Na_3 suffers low yield and time consuming purification due to the harsh reaction condition. Using triisooctyl amine in toluene to extract the acidic form of TPPTS, [$P(C_6H_4SO_3H)_3$], into organic phase hence leave large amount of sulfuric acid in aqueous phase and therefore to avoid the tedious purification. Another advantage of this method is that the analytically pure product can be easily obtained by just control the pH of the reaction mixture in the step of neutralization with CsOH.

The preliminary structure provided by Rheingold and Yap shows the sulfonate groups directed away from the phosphorus lone pair of electrons. The three meta sulfite groups are in close proximity probably due to the intramolecular hydrogen bonding between the sulfite group and water or methanol. A representation of the structure is shown in Figure 4.1.

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[64] I. Toth and B. E. Hanson, Tetrahedron: Asymmetry, **1992,** 3, 235.

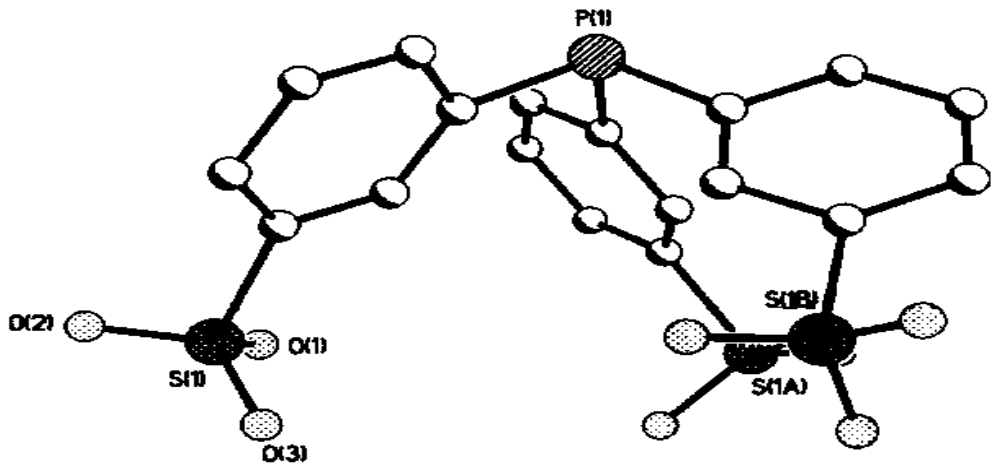

Fig 4.1. The Crystal Structure of TPPTS-Cs_3

4.1.2 Two Phase Hydroformylation of 1-Octene With Rhodium Complexes of TPPTS-Cs_3 (1)

Experiments were carried out here to test the so-called cation effect observed by H. Ding at ligand/rhodium = 3. Ding's work showed that in the two phase hydroformylation of 1-octene with TPPTS-Na_3 both the activity and the selectivity are slightly different in the case of addition of Cs_2SO_4 and Na_2SO_4. In order to further investigate the cation effect at various L/Rh, the two phase hydroformylation of 1-octene has been done using TPPTS-Na_3 and TPPTS-Cs_3.

Catalytic results for the two phase hydroformylation of 1-octene with methanol as cosolvent are summarized in Tables 4.1 and 4.2 at ligand/Rh ratios of 3 and 9, respectively. Significant activity for alcohol formation is seen at high conversion for all catalysts, as it has been observed elsewhere.[40,52,65] The reaction yield refers to total products of aldehyde plus alcohols.

[65] M. E. Brossavol, B. Juma, S. G. Train, W. -J. Peng, S. A. Laneman and C. G. Stanley, Science, **1993,** 260, 1784.

The yield of nonanols represents up to 8 % of the total products at conversions greater than 80 %. Reaction selectivity at highest conversions, as normal to branched product ratios and the percentage of linear aldehyde (1-nonanal), is given in Tables 4.1 - 4.4. Results for selectivity were obtained with the reaction yield from the same catalytic run.

Table 4.1 Reaction Yield as a Function of Time for the Ligands TPPTS-Na_3, TPPTS-Cs_3 in the Rhodium Catalyzed Hydroformylation of 1-Octene at L/Rh(acac)$(CO)_2$ Ratio of 3.[a]

reaction time (h)	yield (%)	
	with TPPTS-Na_3	with TPPTS-Cs_3
1	16 ± 2	14 ± 2
3	22 ± 2	21 ± 2
5	26 ± 2	24 ± 2
10	30 ± 2	.....
20	39 ± 2	36 ± 2
44	.....	51 ± 2

[a] [Rh] = 0.005 M; 1-octene/Rh = 500/1; the volume of aqueous phase is 1.5 ml and the volume of organic phase is 1.0 ml; the pressure of CO/H_2 is 19.5 atm; the reaction temperature is 120 °C; the stirring rate is 350 rpm.

Table 4.2 Reaction Yield as a Function of Time for the Ligands TPPTS-Na_3, TPPTS-Cs_3 in the Rhodium Catalyzed Hydroformylation of 1-Octene at L/Rh(acac)$(CO)_2$ Ratio of 9.[a]

reaction time (h)	yield (%)	
	with TPPTS-Na_3	with TPPTS-Cs_3
1	44 ± 2	44 ± 2
3	62 ± 2	60 ± 2
5	70 ± 2	71 ± 2
20	75 ± 2	75 ± 2

[a] [Rh] = 0.005 M; 1-octene/Rh = 500/1; the volume of aqueous phase is 1.5 ml and the volume of organic phase is 1.0 ml; the pressure of CO/H_2 is 19.5 atm; the reaction temperature is 120 °C; the stirring rate is 350 rpm.

Fig 4.2. 1-Octene Hydroformylation In Aqueous Methanol (Reaction Yield Vs. Time At L/Rh = 9)

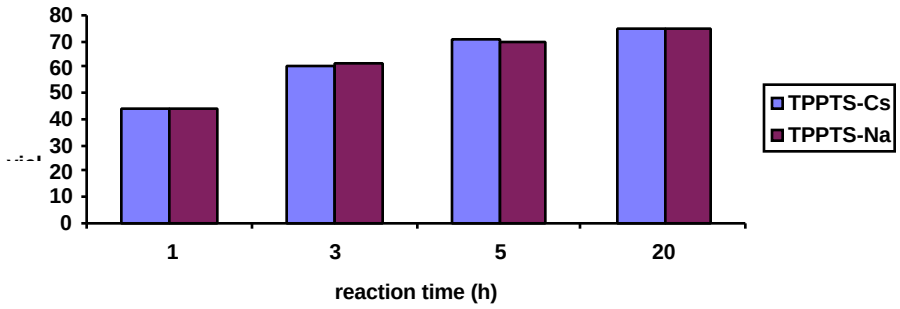

Table 4.3 Reactivity Selectivity (N/B) At 20 Hours Conversion In Hydroformylation Of 1-Octene In Two-Phase System 1-Octene/Aqueous Methanol[a]

	L/Rh = 3		L/Rh = 9	
	yield (%)	n/b (% of 1-nonanal)	yield	n/b (% of 1-nonanal)
TPPTS-Na_3	39 ± 2	1.8 64 ± 2	75 ± 2	3.0 75 ± 2
TPPTS-Cs_3	36 ± 2	2.2 69 ± 2	76 ± 2	3.0 76 ± 2

[a] Conditions: the reaction temperature, 120 °C; the initial pressure, 19.5 atm; [Rh] = 0.005 M; the stirring rate, 350 rpm.

Table 4.4 Reaction Yield as a Function of L/Rh(acac)$(CO)_2$ Ratio for the Ligands TPPTS-Na_3, TPPTS-Cs_3 in the Rhodium Catalyzed Hydroformylation of 1-Octene [a]

ligand/rhodium	yield (%)	
	TPPTS-Na_3	TPPTS-Cs_3
3	16 ± 2	14 ± 2
5	26 ± 2	27 ± 2
7	38 ± 2	39 ± 2
9	44 ± 2	44 ± 2

[a] [Rh] = 0.005 M; 1-octene/Rh = 500/1; the reaction time is 1 h; the volume of aqueous phase is 1.5 ml and the volume of organic phase is 1.0 ml; the pressure of CO/H_2 is 19.5 atm; the reaction temperature is 120 °C; the stirring rate is 350 rpm.

For a given ligand the turnover frequency in the first 1 h of reaction is faster at L/Rh = 9 than L/Rh = 3. This is true for both TPPTS-Na_3 and TPPTS-Cs_3. The fact that the rates improve at higher ligand/Rhodium ratio is in contrast to the case for Rh/PPh_3 homogeneous catalysts, in which reaction rate drops at high ligand concentration.[52,66] It has been suggested that catalysis under biphasic conditions with water soluble catalysts and water immiscible organic substrate is mass-transfer limited.[32] Therefore it appears that the water-soluble phosphines not only serve to complex the rhodium but also facilitate the mixing of the immiscible phases.

4.1.3 Hydroformylation of 1-Hexene with Water Only as the Solvent

The methanol in the previous study originated from the stock solution of Rh(acac)$(CO)_2$. Methanol as a co-solvent greatly enhances the activity of a two phase system.[66] However, both the presence of methanol and the phosphines may contribute to the water solubility of the olefin substrate. Since the solution ionic strength plays an important role in determining the reaction rate and selectivity of aqueous hydroformylation, it is necessary to investigate a system without methanol as a co-solvent. The salt addition may also have an influence on hydroformylation activity and selectivity. These effects are best studied in water alone as a solvent.

Catalytic results for the hydroformylation 1-hexene with H_2O only are summarized in Tables 4.5 and 4.6.

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[66] F. Monteil, R. Queau and P. Kalck, J. Organomet. Chem., **1994,** 480, 177-184.

Table 4.5 Reaction Yield as a Function of Ligand/Rhodium Ratio for the Ligands TPPTS-Na_3, TPPTS-Cs_3 in the Rhodium Catalyzed Hydroformylation of 1-Hexene in H_2O Only[a]

ligand/rhodium	yield (%)	
	TPPTS-Na_3	TPPTS-Cs_3
3	45 ± 2	44 ± 2
5	55 ± 2	56 ± 2
7	68 ± 2	68 ± 2
9	75 ± 2	75 ± 2

[a] [Rh] = 0.005 M; 1-hexene/Rh = 500/1; the reaction time is 24 h; the volume of aqueous phase is 1.5 ml and the volume of 1-hexene 0.47 ml; the pressure of CO/H_2 is 210 psi; the reaction temperature is 120 °C; the stirring rate is 350 rpm.

Table 4.6 Reaction Selectivity (n/b) at 24 hours Conversion in Hydroformylation of 1-Hexene in Aqueous Phase[a]

ligand/rhodium	TPPTS-Na_3		TPPTS-Cs_3	
	yield (%)	n/b (%.1-heptanal)	yield (%)	n/b (%.-heptanal)
3/1	45 ± 2	4.0 (80 ± 2)	44 ± 2	4.0 (80 ± 2)
7/1	68 ± 2	5.2 (84 ± 2)	68 ± 2	5.2 (83 ± 2)

[a] Conditions: the reaction temperature, 120 °C; the initial pressure, 210 psi; [Rh] = 0.005 M; the stirring rate, 350 rpm.

4.1.4 The Effect of Salt on the Activity and Selectivity of Hydroformylation of 1-Hexene in H_2O Only

Hydroformylation of 1-hexene in water both activity and selectivity were dependent on the solution inoic strength.[67] Addition salts will change the solution ionic strength therefore can affect the catalytic results.

The results of hydroformylation of 1-hexene in H_2O with or without added salts (Na_2SO_4, Cs_2SO_4) are summarized in Table 4.7.

Table 4.7 The Effects of Salts on the Activity and Selectivity of Hydroformylation of 1-Hexene With (TPPTS-Na_3, TPPTS-Cs_3)/$Rh(acac)(CO)_2$ [a]

conc. of salt	(TPPTS-Na_3/Rh = 7) + Na_2SO_4			(TPPTS-Cs_3/Rh = 7) + Cs_2SO_4		
	μ[b]	yield (%)	n/b (%.1-heptanal)	μ[b]	yield (%)	n/b (%.1-heptanal)
0 (M)	0.35	68 ± 2	5.2 (84 ± 2)	0.35	68 ± 2	5.2 (83 ± 2)
0.1 (M)	0.65	50 ± 2	7.3 (88 ± 2)	0.65	50 ± 2	7.2 (87 ± 2)
0.5 (M)	1.85	38 ± 2	9.0 (90 ± 2)	1.85	40 ± 2	9.0 (90 ± 2)

[a] the Reaction temperature, 120 °C, the Pressure at RT = 210 psi, the Reaction time = 24 h, [Rh]/[1-hexene] = 500, [Rh] = 0.005 M
[b] Solution Ionic Strength

High ionic strength is anticipated to decrease the solubility of 1-hexene in water. For this reason alone, rates are expected to be lower in the catalytic reactions at high salt concentration. This is indeed observed with $HRh(CO)(TPPTS)_3$ as the catalyst. Even with excess TPPTS (TPPTS/Rh = 7) the catalytic activity drops as Na_2SO_4 or Cs_3SO_4 is added.

The fact that high solution ionic strength tends to stabilize the catalytic intemediates with relative high charge suggests that the high selectivity of aqueous hydroformylation is expected when the solution is of high ionic strength. This is indeed observed as seen from the data reported in Table 4.3. the lower activity of the Rh/TPPTS catalyst in the presence of salt is consistent with decreased solubility of 1-hexene in water solution of high ionic strength. The selectivity however

[67] H. Ding, B.E.Hanson and T. E. Glass, Inorganic Chimica Acta, **1995**, 229, 329-333.

increases as the salt concentration increases. At a TPPTS/Rh ratio of 7/1 the selectivity to linear aldehyde is 90 % (n/b = 9) in the presence of Na_2SO_4, compared to 84 % (n/b = 5.2) in the absence of Na_2SO_4.

4.1.5 Hydroformylation of 1-Tetradecene in Ethylene Glycol/Methanol

Compared to TPPTS-Na_3, the solubility of TPPTS-Cs_3 in methanol and ethylene glycol is relatively large. Based on this fact, ethylene glycol was chosen as the solvent in hydroformylation of 1-tetradecene instead of water, because 1-tetradecene has no solublity in water alone. The system here is still biphasic and the solvents separated into a 1-tetradecene rich phase and a ethylene glycol rich phase. After the reaction, the products are obtained as solids, the catalyst remains exclusively in the glycol phase. TPPTS-Na_3 has limit solubility in glycol and added as slurry. Rh(acac)$(CO)_2$ was prepared in methanol, so the hydroformylation of 1-tetradecene was done in ethylene/methanol mixture (1/1, v/v). The catalytic results are summarized in Tables 4.8 and Table 4.9.

Table 4.8 Hydroformylation of 1-tetradecene in ethylene glycol/methanol[a]

ligand/rhodium	time (h)	yield (%)	n %	note (acetals/ald)
3	24	60 ± 2	67 ± 2	56/5
5	24	69 ± 2	70 ± 2	66/4
7	24	73 ± 2	73 ± 2	70/3
9	24	76 ± 2	73 ± 2	74/2
5	2	46 ± 2	68 ± 2	29/17
5	5	57 ± 2	70 ± 2	44/13
5	70	68 ± 2	70 ± 2	59/9

[a] Reaction conditions: the reaction temperature, 120 °C; the initial pressure, 210 psi; [Rh] = 0.005 M; the stirring rate, 350 rpm; 0.76 ml methanol solution of Rh(acac)$(CO)_2$, 0.6 ml 1-tetradecene and 0.4 ml nonane was introduced to reactor, the volume of ethylene glycol was to adjust the right concentration for catalysts.

Fig. 4.3. Reaction Yield (%) vs. L/Rh at Reaction Time 24 (h)

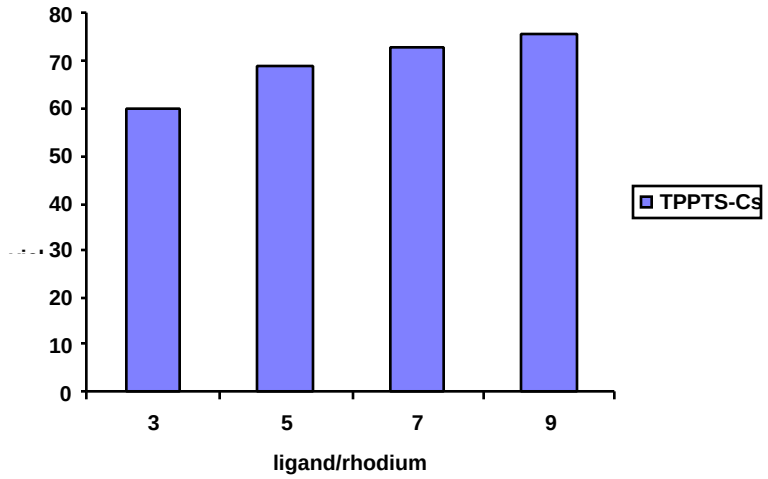


Table 4.9 Hydroformylation of 1-Tetradecene in Ethylene Glycol[a]

ligand/rhodium	TPPTS-Cs_3		TPPTS-Na_3	
	yield (%)	n/b (aldehyde)	yield (%)	n/b (aldehyde)
3/1	14 ± 2	70 ± 2	12 ± 2	70 ± 2
80/1	32 ± 2	86 ± 2	24 ± 2	85 ± 2

[a] Reaction conditions: the reaction temperature, 120 °C; the initial pressure, 210 psi; [Rh] = 0.005 M; the stirring rate, 350 rpm; the reaction time, 20 h, selectivity was determined by ^{1}H NMR.

From the results obtained with TPPTS-Cs_3 it is concluded: (1) The synthetic route to TPPTS-Cs_3 is simpler than the route to TPPTS-Na_3. The purification of the water-soluble phosphine required just a single crystallization from aqueous methanol; (2) The solubility in alcohol was higher for cesium analog compared to sodium salt of TPPTS thus extends the potential operating condition for TPPTS based catalysts; (3) No significant cation effect was observed at L/Rh ≥ 3 in the two phase hydroformylation of higher alkene; (4) The two-phase catalytic activity is decreased as increase the solution ionic strength and the selectivity is increased as increase the solution ionic strength.

4.2 Effect of Amphiphilic Water-Soluble Phosphines on two Phase Hydroformylation of 1-Octene

The synthesis of m-PC(3) is straightforward and followed Ding's procedure for PC(3) except starting with reagent 1-bromo-3-chlorobenzene. The goal here is to investigate the geometry effect (para vs. meta position of C_3 group) on the two phase hydroformylation of 1-octene.

Catalytic results for the two phase hydroformylation of 1-octene with trisulfonated tris-m-(3-phenylpropyl)phenylphosphine **4** [m-PC(3)] with methanol as a co-solvent are summarized in Tables 4.10 and 4.11.

Table 4.10 Reaction Yield as a Function of Time for the Ligands TPPTS-Na_3, m-PC(3) in the Rhodium Catalyzed Hydroformylation of 1-Octene at L/Rh(acac)$(CO)_2$ Ratio of 3.[b]

reaction time (h)	yield(%)		
	TPPTS-Na_3	m-P(C_3)	***P(C_3)***[a]
1	16 ± 2	32 ± 2	***40 ± 2***
3	22 ± 2	40 ± 2	***45 ± 2***
5	26 ± 2	46 ± 2	***50 ± 2***
10	30 ± 2	51 ± 2	***60 ± 2***
20	39 ± 2	75 ± 2	***80 ± 2***

[a] P(C_3) data from H. Ding Ph.D thesis

[b] [Rh] = 0.005 M; 1-octene/Rh = 500/1; the volume of aqueous phase is 1.5 ml and the volume of organic phase is 1.0 ml; the pressure of CO/H_2 is 19.5 atm; the reaction temperature is 120 °C; the stirring rate is 350 rpm.

Fig. 4.4 Reaction Yield vs. Time at L/Rh = 3 for 1-Octene

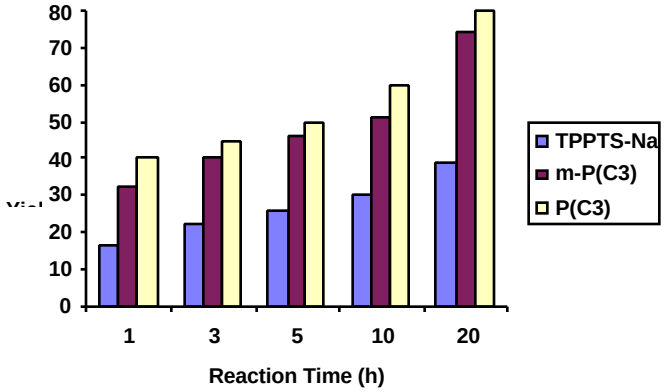


Table 4.11 Reaction Yield as a Function of L/Rh(acac)$(CO)_2$ Ratio for the Ligands TPPTS-Na_3, m-PC(3) in the Rhodium Catalyzed Hydroformylation of 1-Octene [a]

ligand/rhodium	yield(%)		
	TPPTS-Na_3	m-P(C_3)	***P(C_3)***
3	22 ± 2	40 ± 2	***50 ± 2***
5	45 ± 2	60 ± 2	***62 ± 2***
7	70 ± 2	80 ± 2	***78 ± 2***
9	75 ± 2	87 ± 2	***88 ± 2***

[a] [Rh] = 0.005 M; 1-octene/Rh = 500/1; the reaction time 5 h; the initial pressure is 19.5 atm; the reaction temperature is 120 °C; the stirring rate is 350 rpm.

Fig. 4.5 Reaction Yield vs. L/Rh at reaction time 5 (h)

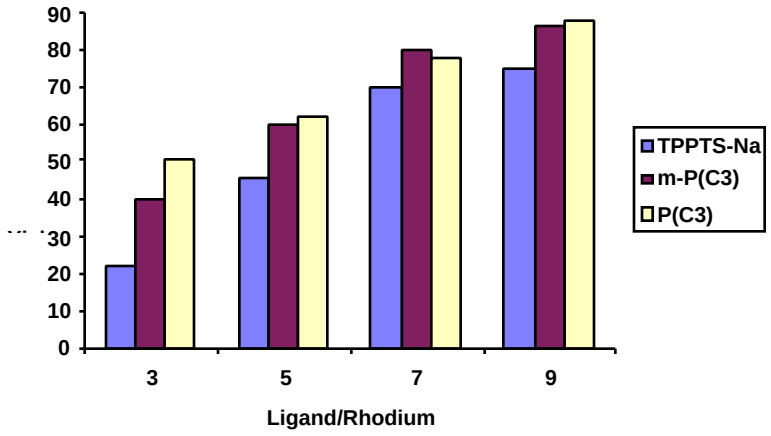


Table 4.12 Reactivity Selectivity (n/b) at 20 hours Conversion in Hydroformylation of 1-Octene in Two Phase (methanol/water)[a]

	ligand/rhodium = 3		ligand/rhodium = 9	
	yield (%)	n/b (%.1-nonanal)	yield (%)	n/b (%.1-nonanal)
TPPTS-Na_3	39 ± 2	1.8 (64 ± 2)	75 ± 2	3.0 (75 ± 2)
m-PC(3)	80 ± 2	4.0 (80 ± 2)	89 ± 2	9.0 (90 ± 2)
PC(3)	***81 ± 2***	***3.7 (78 ± 2)***	***90 ± 2***	***8.0 (89 ± 2)***

[a] Conditions: the reaction temperature, 120 °C; the initial pressure, 210 psi; [Rh] = 0.005 M; the stirring rate, 350 rpm.

Compared to TPPTS-Na_3, the surface active phosphine, $P[C_6H_4\text{-}m\text{-}(CH_2)_3\text{-}C_6H_4SO_3Na]_3$, is significantly larger in the sense that the sulfonate groups are linked to the ends of three long aryl groups in the phosphine at the meta position. The steric size of these surface active phosphine, as estimated by the Tolman cone angle, should be larger than PPh_3, and similar to TPPTS-Na_3. It has been suggested that catalysis under biphasic conditions with water soluble catalysts and water immiscible organic substrates is mass transfer limited.[32] Therefore in the solution of low ionic strength the key catalytic intermediate for linear aldehyde formation, $HRh(CO)L_2$, when L is surface active phosphine, may still be the predominant catalytic species compared to $HRh(CO)_2L$, especially when ligand concentration is high. On the other hand, the same catalytically active species with TPPTS may not be present as the most available intermediate for catalytic hydroformylation in such a low ionic strength solution due to electrostatic repulsion between six sulfonate groups in close proximity. Therefore the catalytic cycle may be more likely to proceed via $HRh(CO)_2$TPPTS which in turn leads to a higher percentage of branched aldehyde products. This rationale can count for the higher n/b ratio observed with surface active phosphine, especially at high L/Rh ratio, compare to rhodium/TPPTS system in aqueous methanol solution which has low ionic strength.

From results above, it is concluded: (1) the new surface-active phosphine was synthesized and can be sulfonated under mild condition with well defined sulfonation site (on ^1H NMR the sulfonated phenyl group showed AABB pattern which demonstrated the para-sulfonation site); (2) the two phase olefin hydroformylation showed enhanced activity and selectivity compared to TPPTS/Rh system; (3) with only 3 methylene groups, there is no difference between the para and meta position of C_3 group.

4.3 Amphiphilic Chelating Phosphine and its use in the Hydroformylation of 1-Octene

Tris-p-(3-phenylpropyl)phenylphosphine was cleaved under Li/THF to give the lithium phosphine complex after poison the side product with tertiary butylchloride, the dark red viscous residue was redissolved in THF followed by addition of 2,2'-dibromomethyl-1,1'-biphenyl to give BISBI type organo-soluble phosphine, the water soluble phosphine BISBI-PC(3) can be obtained by direct sulfonation with 98 % sulfuric acid within 7 h.

Hydroformylation results of 1- octene with BIBSI-PC(3)-Na_3 are summarized in Table 4.13. For comparison, results from the two phase hydroformylation of 1-octene with TPPTS under the same reactions are also listed.

Table 4.13 Two Phase Hydroformylation of 1-Octene With TPPTS-Na_3 and BISBI-PC(3)-Na_3[a]

Rh/P	TPPTS-Na_3		BIBSI-PC(3)-Na_3	
ratio	yield (%)	n/b (%/%)	yield (%)	n/b (%/%)
1/2	20 ± 2	65/35	45 ± 2	68/32
1/3	28 ± 2	68/22	57 ± 2	76/24
1/5	50 ± 2	73/27	69 ± 2	88/12
1/7	54 ± 2	75/25	73 ± 2	94/6
1/9	70 ± 2	76/24	67 ± 2	97/3
1/14	.....	.....	30 ± 2	98/2

[a] Reaction conditions: the reaction time, 5 h; the reaction temperature, 120 °C; the initial pressure, 210 psi (at 25 °C); the stirring rate is 350 rpm; [Rh] = 0.005 M.

Fig 4.6 Yield vs. L/Rh at Reaction Time 5 (h)

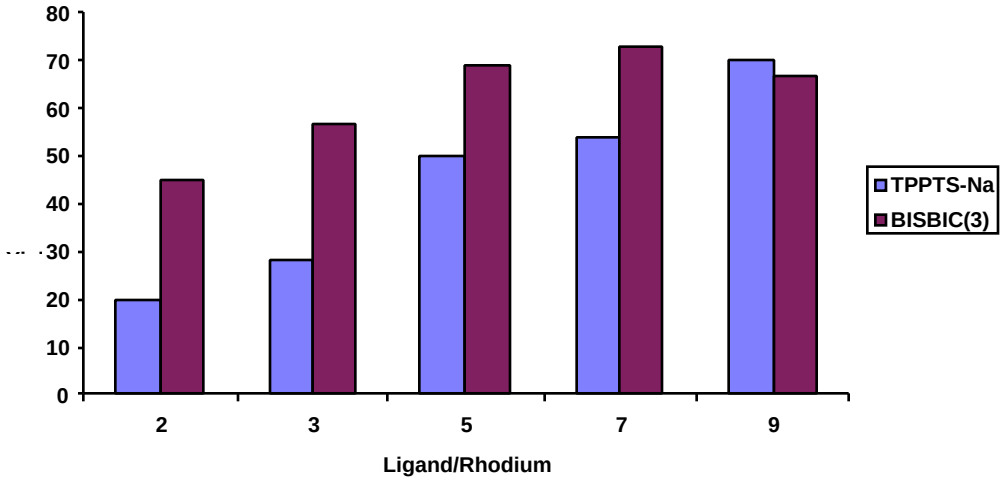
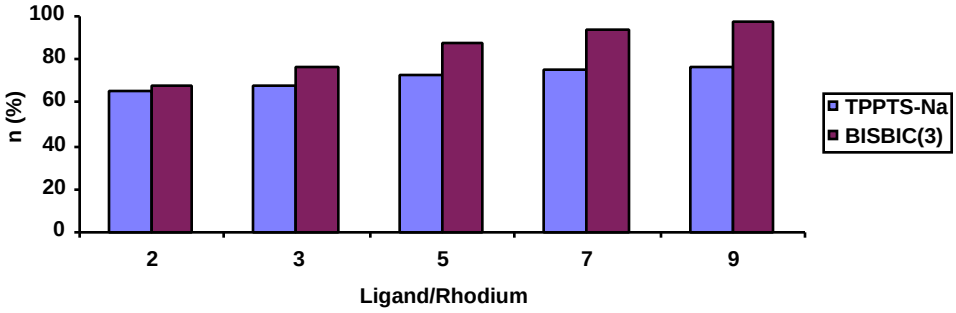


Fig 4.7 Selectivity (n %) vs. L/Rh at reaction Time 5 (h)



The concentration of rhodium in both the organic and aqueous phase after catalysis was checked by ICP analysis of the different phases. The results along with a more detailed analysis of the reaction products are summarized in Table 4.14. The organic phase is colorless in all reactions suggesting that the sulfonated phosphine; like TPPTS, is very efficient at keeping rhodium in the aqueous phase.

Table 4.14 Results from two phase hydroformylation of 1-Octene at Rh/P = 1/7[a]

	TPPTS-Na_3	BISBI-PC(3)-Na_3
yield of C_9 aldehyde	58	74
selectivity (%. 1-nonanal)	74	93
C_8 hydrocarbons (%)	34	23
1-octene (%)	5	14
C_9 alcohols (%)	7.1	2.5
heavy ends (%)	0.8	0.2
Rh in org. phase (ppm)	not detected	not detected
Rh in aq. phase (ppm)	508	514

[a] Reaction conditions: [Rh] = 502 ppm, Rh/1-Octene = 1/500, the reaction temperature = 120 °C, the pressure = 210 psi at room temperature, the reaction time = 5 h, the stirring rate = 350 rpm. The [Rh] is determined by ICP method. Both standard and samples are prepared in MeOH.

The tetrasulfonated BIBSI-PC(3)-Na_3 ligand, is the best ligand prepared in this study for the two phase hydroformylation of 1-octene. At a ligand/Rh ratio of 7-9, the rhodium catalyst with this ligand offers good reactivity and selectivity towards 1-nonanal. Increased activity, compared to the Rh/TPPTS system, may be explained in part by the surface activity of the ligand. At high ligand to rhodium ratios the TPPTS ligand shows similar activity. In agreement with previous results the selectivity of TPPTS catalysts suffers in aqueous methanol as the reaction solvent. In conclusion, excellent selectivity (n % = 98 %) is observed with this chelating ligand. This result was attributed to reduced electrostatic repulsion in BIBSI-PC(3)-Na_3 which is much larger than TPPTS. The high selectivity may also be attributed to the special steric effect of the nine membered chelating ring in the catalysts.

The reasons for the special effectiveness of BIBSI-PC(3)-Na_3 are not yet obvious, a study concerning the influence of diphosphines of the type Ph_2P-$(CH_2)_n$-PPh_2 on the hydroformylation activity[68] showed that especially for n = 1 and n = 6, the effects of high conversion rates are small in comparison to those for n = 2, 3, and 4. In contrast, BIBSI-PC(3)-Na_3 (n = 3) shows very high activities. This may be due to electronic effects and the more rigid structure of BIBSI-PC(3)-Na_3 compared with these alkyl-chain diphosphines. The precursor BIBSI-PC(3)-Na_3 was shown to adapte to steric requirements of the metal(s) in a very flexible way as shown by molecular modeling, crystal structures.[69] Both the cis and trans geometries are possible. At the same time, the bidentate nature of BIBSI-PC(3)-Na_3 prevents the ligand from leaving the metal. The medium-size ring system (nine atoms) does not put significant steric and kinetic constraints upon the intermediates that operate in hydroformylation.

The new water-soluble diphosphine, BIBSI-PC(3)-Na_3, yields outstanding results when employed as a ligand in the rhodium-catalyzed hydroformylation of 1-octene, particularly in view of the low ligand-to-rhodium ratio of only 7-9/1. It is not usually appreciated that the industrial process depend on large amounts of phosphines to be used for suffeciently long operating times of catalysts, the ligand-to-rhodium ratios normally being 50/1 to 100/1 in hydroformylation.

From the results above, it is concluded: (1) the water-soluble version of BISBI type diphophine showed both higher activity and excellent selectivity compare to TPPTS; (2) the best ratio of L/Rh was 7 ~ 9 in two-phase 1-octene hydroformylation reaction for BISBI-PC(3)-Na_3.

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[68] N. Yoshimura and M. Tamura, Successful Design of Catalysis, Stud. Surf. Sci. Catal., 1**989,** 44, 307.

[69] W. A. Herrmann, C. W. Kohlpaintner, E. Herdtweck and P. Kiprof, Inorg. Chem., **1991,** 30, 4271.

4.4 Asymmetric Hydrogenation of AACA-Me in Methanol with Chiral Surfactant

The hydrogenation catalysts were made in methanol and then transferred to glass reactors containing substrate and surfactant at atmospheric pressure of H_2. The reaction was monitored by H_2 uptake and the product was determined by NMR spectroscopy. The optical yield was determined in methanol by polarimetry.

The results from asymmetric hydroformylation in methanol are summarized in Table 4.15.

Table 4.15 Asymmetric Hydroformylation of AACA-Me in Methanol[a]

exp #	L+Surfactant	solvent	P(H_2)(atm)	time (h)	yield	ee (%)
1	BPPP	methanol	1	0.13	100	0
2	BPPP + chiral surfactant	methanol	1	0.3	100	0.1
3	BPPP + achiral surfactant	methanol	1	0.2	100	0
4	S,S-BDPP	methanol	1	0.83	100	61 ± 2
5	S,S-BDPP + chiral surfactant	methanol	1	1.7	100	62 ± 2
6	S,S-BDPP + achiral surfactant	methanol	1	1.3	100	60 ± 2

[a] Reaction conditions: the temperature, 20 °C; [Rh] = [Ligand] = 0.0025 M; [AACA-Me]/[Rh] = 100; [Surfactant]/[Rh] = 25; ee(%) was determined by polarimetry method [62]; the conversion was checked by ^{31}P NMR and H_2 uptakes.

Although the results from Selke and co-workers suggest that the addition of surfactants can induce a modest increase in enantioselectivity as well as reaction activity in the hydrogenation of cinnamic acid derivative with the diphosphine derivatives of methyl-α-d-glucopyranosides (glup) ligands in water.[70,71,72,73] Our results, at surfactant/Rh ratio as low as 25, unfounately showed that

[70] A. Kumar, G. Oehme, P. P. Roque, M. Schwarze and R. Selke, Angew. Chem. Int. Ed. Engl., **1994,** 33, 2197.

[71] R. Selke, C. Fackiam, H. Foken and D. Heller, Tetrahedron: Asymmetry**, 1993,** 4, 369.

[72] G. Oehme, E. Paetzold and R. Selke, J. Mol. Catal., **1992,** 71, L1.

[73] Alyea & Meek, Catalytic Aspects of Metal Phosphine Complexes, **1982.**

nearly identical hydrogenation results are observed with rhodium complexes of BDPP and BPPP with or without this particular surfactant, when the reactions are done homogeneously in methanol.

This indicates that the attempt to improve the asymmetric induction by adding chiral surfactants failed. In general, the reaction follows a pathway in which the original cationic rhodium diolefin complex first is hydrogenated to give a solvate, which then reacts rapidly with the dehydroaminoacid substrate to give an enamide complex existing in two diastereomeric forms. These then traverse the rate-determining step by cis-specific addition of hydrogen, the difference in the free energy of the diastereomeric transition states being related to the optical yield. This is because the equilibrium between the two enamide complexes which represent the resting state of the catalyst is fast relative to their hydrogenation. In the final post-rate-determining step of the reaction the rhodium alkyl decompose rapidly by a cis-specific mechanism giving a product and the solvate complex. So far, the concerted addition of hydrogen to the enamide complex may be considered as a possible mechanism.[69] It has the attraction of offering a simple explanation of the origin of asymmetric induction.

From the results above, it is conclude: (1) at surfactant/Rh ratio of 25, the asymmetric hydrogenation of AACA-Me in methanol has no effect on asymmetric induction with the introduction of this chiral surfactant; (2) since both of the species (catalyst and surfactant) are cationic in the solution, the repulsion between them may be responsible for the negative result.

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VITA

Jianxing (Jim) Kang

Personal Data:	Date of Birth: November 23, 1965 Place of Birth: Shanghai, P. R. China
Education:	Shanghai University of Science and Technology, Shanghai, P. R. China: Chemistry, B.S., 1986 East Tennessee State University, Johnson City, Tennessee: Chemistry, M.S., 1994 Virginia Polytechnic Institute and State University, Blacksburg, Virginia: Chemistry, M.S., 1997
Professional Experience:	Teacher, Dept. of Chem. Shanghai University of Science and Technology. 1986-1992 Graduate Assistantship, East Tennessee State University, College of Art and Science, Dept. of Chem. 1992-1994 Graduate Assistantship, Virginia Polytechnic Institute and State University, Dept. of Chem. 1994-1997