SUPPORTED AQUEOUS PHASE CATALYSIS

by

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(ABSTRACT)

This work describes a novel family of catalysts denoted Supported Aqueous Phase Catalysts (S.A.P.C.). These catalysts consist of a water-soluble organometallic complex supported in a thin film of water residing on a high surface area hydrophilic solid; the reaction takes place at the water-organic interface where the organic contains the reactants and products.

This novel type of catalysis is demonstrated by liquid phase hydroformylation. The support chosen is CPG-240, a porous glass with a narrow pore volume distribution. The catalytic species, $HRh(CO)[m-P(PhSO_3Na)_3]_3$ was synthesized from $Rh(CO)_2(acac)$ by a new synthetic route and the complex was characterized by ^{31}P solution NMR, ^1H solid-state NMR, and FTIR. After dissolving the catalytic species in water, it was impregnated into CPG-240. The hydroformylation of oleyl alcohol (OLOH) was accomplished at 100°C and 725 psig of $H_2/CO = 1:1$ using 0.002g Rh/g OLOH. As an example, after 5.5 h of contact time, 96.6% conversion was achieved. Evidence of no leaching of Rh was obtained by filtering away the supported catalyst and attempting both the hydroformylation of additional OLOH and the hydrogenation of added 1-hexene. The absence of conversion in both cases indicated that Rh was not leached into the organic phase. Because: (1) OLOH is not water soluble, (2) its double bond is internal and (3) the Rh does not leach into the organic phase, the concept of SAPC, which is to perform catalysis at an interface, is proven.

To   ,   and   .

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And to my wife   who supported me so much in all the steps that led to this moment since I met her, I am specially grateful for her love and patience. And to my father and mother, for all the love, support and encouragement I received from them, I also give thanks.

Table of Contents

List of Illustrations

List of Tables

Chapter 1

INTRODUCTION

It would be difficult to understate the importance of catalysis in the chemical industry; there is hardly any process that does not make use of catalysis at one stage or another. Heterogeneous catalysis dominates the picture in terms of amount of products produced, but homogeneous catalysis has developed rapidly in the last few decades. Although soluble metal salts were used commercially as catalysts for acetylene reactions as early as 1910, broad use of soluble catalysts did not begin until the 1940s with the wartime restrictions on raw materials in Germany and the introduction of many new polymers between 1940 and 1960.

The growth of homogeneous catalysis, fostered by Nobel prize winners[1] and promoted by the industry, has as its major reasons of existence its selectivity[2] and activity. Those qualities are essential to current high efficiency processes which operate under relatively mild conditions with few by-products. Homogeneous transition metal species catalyze a wide spectrum of gas-liquid reactions such as hydrogenation, oxidation, and carbonylation, and have applications in specialty organic synthesis in the preparation of pharmaceuticals, dyes, and insecticides. As examples, Tennessee Eastman has undertaken the first major shift of feedstocks from petroleum to coal by

producing acetic anhydride from syn-gas[3] and Monsanto has, since 1968, developed and commercialized the catalytic hydrogenation of dehydroaminoacids[4].

It has been recognized for a long time that homogeneous processes suffer from the difficulties of separating the catalyst from products and it is for this reason that methods for immobilizing transition metal species have been studied in detail. Techniques used to immobilize the homogeneous catalysts have centered on the retention of its structure and properties, but in general the immobilized catalyst only approximates the catalytic properties of its homogeneous counterpart. Comprehensive reviews of immobilization techniques can be found elsewhere[5]. Heterogenation is generally achieved in one of three ways:

a) chemisorption of the metal complex on a solid support,

b) physical adsorption of the complex on a support, and

c) entrapment of metal complexes from in-situ synthesis within zeolites [6].

At present, none of the above methods has provided a commercially viable catalyst.

The chemisorption or heterogenation procedure through the formation of a chemical bond between the support and the catalyst has been performed using different techniques. The most studied one is the attachment of catalysts to polymeric matrices[5]. A number of techniques for the creation of polymer-anchored catalysts have been developed[7]. Surface hydroxyl groups have also been used as anchors for chemisorbed complexes[8] which are commonly called inorganic-anchored catalysts since the supports used are hydrated oxides (mostly silicas).

The physical adsorption of complexes onto solid supports' technique has made use of solids ranging from pumice to charcoal[9].

The entrapment of complexes into zeolites has received considerable attention because of the possibility of the added feature of the coupling of the selectivities achieved with normal homogeneous catalysis and shape-selective zeolites[10].

Unfortunately, the common feature of these methods has been heretofore the loss of activity or selectivity or the leaching of the catalyst from the support. Alternative multiphase methods, which in effect perform homogeneous catalysis, include partitioning the catalyst and the reactants/products between different phases, namely:

a) phase transfer catalysis,

b) dissolution of a complex in a non-volatile solvent (Rhone-Poulenc and Union Carbide hydroformylation processes), and

c) dissolution of a complex in a non-volatile solvent which is adsorbed on the surface of a support, i.e. supported liquid phase (SLP).

In phase transfer catalysis the reactants are often in two immiscible phases and it is the phase transfer catalyst that carries them from one phase to the other for the reaction to take place. Phase transfer catalysis has been used in the hydroxy-carbonylation of benzylic halides, oxidative carbonylation of phenols and reductive carbonylation of nitro compounds among others[11].

The Rhone-Poulenc and Union Carbide processes rely on the dissolution of the catalytic species into a suitable solvent and then contacting the catalytic phase with a gaseous phase containing the reactants. The reactants dissolve into the catalytic phase and are homogeneously converted. In the Union Carbide process, the catalytic species is an organic soluble one: $HRh(CO)(P(Ph_3))_3$, where $Ph = C_6H_5$, and in the Rhone-Poulenc process the catalytic species is its water soluble sulfonated phosphine counterpart. This only works when the product is volatile enough to "flash out" of the reactor.

In supported liquid phase catalysis, the catalyst is dissolved in a solid-supported liquid phase and then, it is contacted with reactants and products in a gaseous phase. It is the only industrially used method for the oxidation of SO_2 to SO_3 and the liquid

phase is the molten catalyst V_2O_5 without solvent. Supported liquid phase (SLP) organometallic Rh catalysts, dissolved in a molten phase, have also been extensively investigated[12] and the reaction itself has been shown to be homogeneously catalyzed. This method suffers from many disadvantages and some of them will be discussed in the next chapter.

It has been recognized for long that reactions taking place at an interface differ from those occurring in the bulk in the uniform and controlled accessibility and orientation of the reactant molecules[13]. This characteristic can lead to an alteration of the selectivity of the reaction. Examples of these kind of reactions are emulsion polymerization and hydrolysis of fats[13].

The purpose of this work is to study a novel immobilization technique. A water-soluble organometallic complex acts dissolved in a thin film of water which is supported on a high surface area hydrophilic solid. Reactions of liquid organic substrates will take place at the water-organic interface. See Figure 1 on page 5.

The system proposed differs significantly from traditional SLP catalysis. Firstly, SLP catalysis is designed for gas-phase reactants and suffers from extraction of the supported phase when liquids are used as substrates. Secondly, the supported liquid must have a low vapor pressure and be hydrophobic to dissolve traditional organometallic catalysts. Supported Aqueous Phase Catalysts (**SAPC**), as this new family of catalysts is named, is designed to work with liquid reactants and a low-boiling supported phase, i.e. water. which is maintained by using a hydrophilic support. Immobilization is accomplished via the insolubility of the organometallic complex in the organic media. An additional feature of this new family of catalysts is that, depending on concentrations of reactant/products, temperature, solvents and chemical structure of the substrate, the presence of the interface will ideally shift the selectivity of the reaction with respect to the homogeneous case.
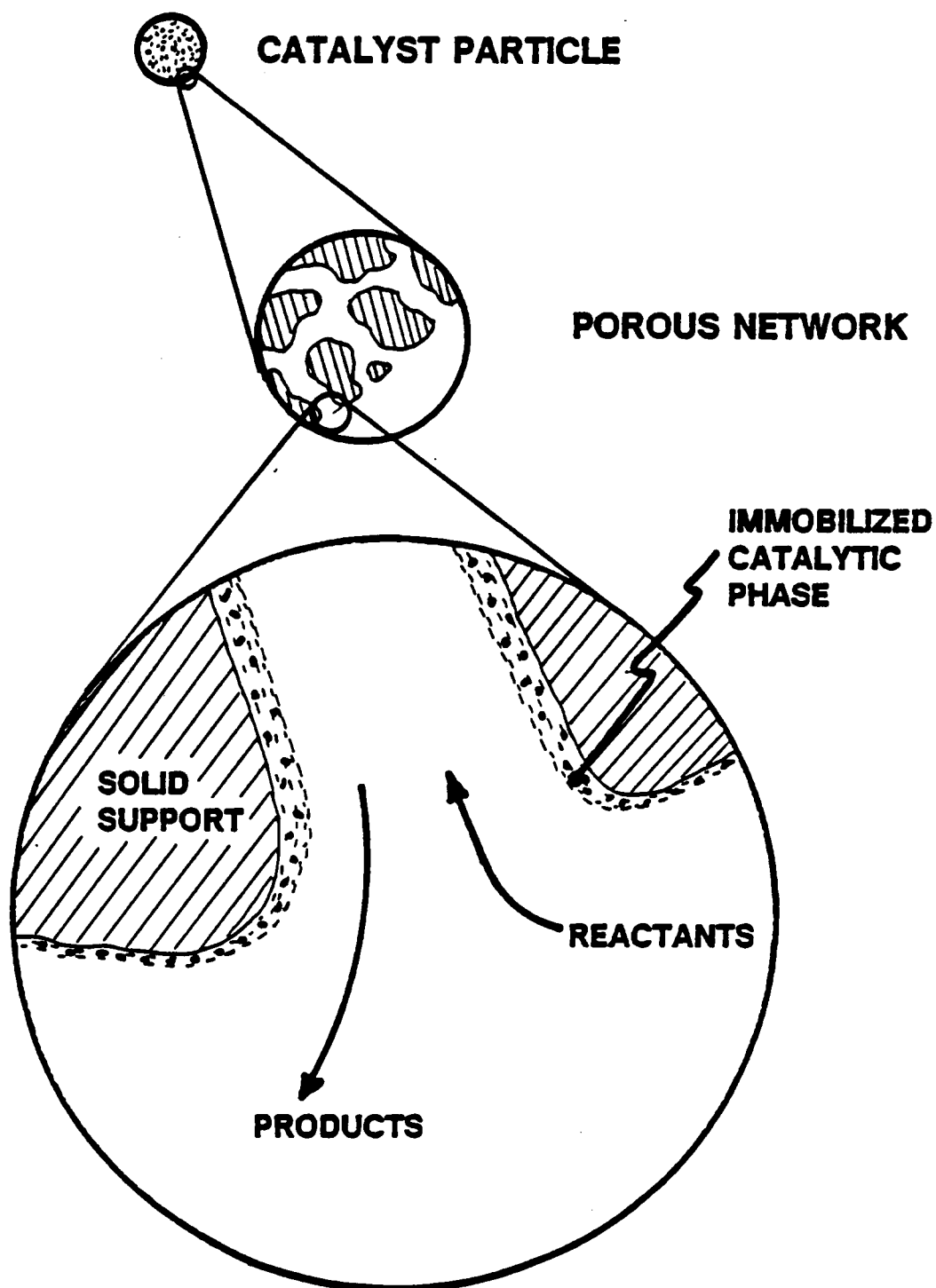
Figure 1. SUPPORTED AQUEOUS PHASE CATALYST

Chapter 2

LITERATURE REVIEW

2.1 Hydroformylation

The Oxo synthesis, or more properly called hydroformylation reaction was discovered by Otto Roelen in 1938[14] in the Ruhrchemie laboratories at Oberhausen-Holten, W. Germany. It is the oldest and largest homogeneous catalytic reaction of olefins[2]. Hydroformylation is the reaction of an olefin with carbon monoxide and hydrogen to form an aldehyde, and it does not proceed without a catalyst[15]; in general it may be illustrated by the following equation:
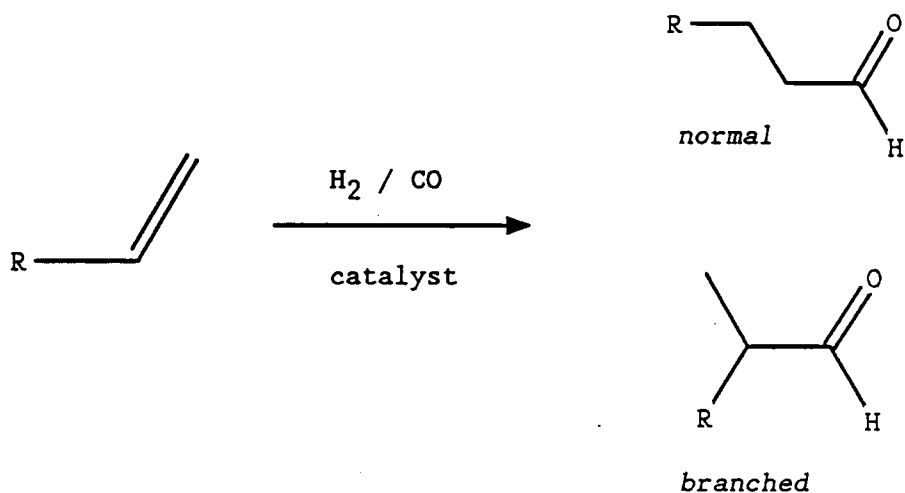
Hydroformylation may be accompanied by some degree of isomerization of the carbon-carbon double bond position, resulting in several other aldehyde structures in addition to those illustrated. In the above equation, R represents an organic radical, or other substituent e.g. a hydrogen or halogen atom, a hydroxyl group, a carbonyl group, etc. which does not interfere with the intended reaction at the double bond. The reaction is homogeneously catalyzed by a number of transition-metal carbonyl complexes.

Even though reactions such as hydroformylation of olefins have been used industrially since the early 1940s, these processes continue to grow in importance. This growth is expected to continue because carbon monoxide is available from many sources; like reforming of natural gas and naphta, or heavy petroleum fractions, or from coal. It is likely that coal-based synthesis gas will be a major source of chemicals in the future[2].

Cobalt is the most widely used catalytic element for this reaction, although the use of rhodium is becoming important. Rhodium catalysts increase both the reaction rate and the selectivity of the process. However, since rhodium is very expensive, the

problems of catalyst recovery are crucial to the economics of the process. The relative prices of rhodium to cobalt metal are on the order of 3500:1; an amount of rhodium equivalent to 1 part per billion of aldehyde product would be an unacceptable separation[16].

There have been a few but consistent reports about the use of water as the source of hydrogen in hydroformylation reactions[17]. These investigations stem mainly from research pointing towards performing the water-gas shift reaction at low temperature using transition metal complexes as catalysts. The appearance of water-soluble hydroformylation complexes has permitted the study of water as the hydrogen source in the hydroformylation of 1-hexene in a two-phase system. Heretofore the reaction has not gone beyond the bench scale.

2.2 Hydroformylation kinetics and mechanisms

Natta et al. studied the kinetics of the reaction and established the equation shown below for tetracarbonylhydridocobalt as a catalyst[18]:

$$\frac{d(aldehyde)}{dt} = k[olefin][Co]\frac{P_{H_2}}{P_{CO}}$$

Marko et al. have established a relationship, based on Natta's equation, which can be applied when $Rh_4(CO)_{12}$ is used for the hydroformylation of olefins. If 1-heptene is the substrate then the rate equation is[19]:

$$\frac{d(aldehyde)}{dt} = k[olefin][Rh]\frac{P_{H_2}}{P_{CO}}$$

The rate of reaction is strongly affected by the structure of the olefin; the more reactive one being styrene and the less reactive ones being branched olefins. There are other equations proposed and, despite the basic agreements, there are also discrepancies which may be partly caused by the somewhat different reaction conditions[20].

The product composition can be considered to arise from the formal addition of the elements of formaldehyde across the C-C double bond; however, formaldehyde is not an intermediate species in the reaction. Detailed discussions about the possible mechanisms operant at different conditions have been published[21], but a full description of the picture is still an open question.

In the case of unmodified rhodium catalysts, the mononuclear rhodium hydrido carbonyl $HRh(CO)_4$ is thought to be the active catalyst (probably in the form of coordinatively unsaturated intermediate, $HRh(CO)_3$).

With the catalysts $HM(CO)_m$, one or more CO ligands can be replaced by phosphines, phosphites, arsines etc., resulting in the new complex; the *modified* catalyst. In many cases this preferentially yields unbranched products. The bulkier, more sterically demanding ligands effect a preferential attack at the α-position of the olefin, producing more linear aldehydes. Besides this "steric" interpretation of the effect of ligand-modified oxo catalysts, electronic theories and explanations involving both effects have been proposed[22].

By substituting one or more CO ligands in $HRh(CO)_4$ with phosphines, phosphites, etc., complexes of the type $HRh(CO)_mL_n (n+m=4; L=PPh_3, PBu_3, etc.)$ can be obtained. The first complex of this type, $HRh(CO)(PPh_3)_3$, was introduced as a hydroformylation catalyst by Wilkinson in 1966[23]. This complex facilitated the Oxo synthesis to be conducted at low temperatures and pressures. Many mechanistic studies of the hydroformylation reaction with ligand modified complexes have been carried out with this catalyst[24]. According to these results[25] $HRh(CO)(PPh_3)_2$ is the active

catalytic species in the cycle. The attack of the alkene on this 16-electron species leads to the alkyl complex B as shown in Figure 2 on page 12. Subsequently, after the CO addition and insertion, the acyl derivative C undergoes oxidative addition of H_2 to give the dihydridoacyl complex D. The last step is the reductive elimination of the aldehyde taking place after the H transfer to the acyl carbon in D. A ratio H_2/CO smaller than 1 inhibits the hydroformylation reaction, probably through the formation of E which cannot react with hydrogen.

2.3   Industrial hydroformylation

The production of detergent-range alcohols is based on ethylene. An example of this is the SHOP process of Shell Oil Co., which uses a combination of ethylene oligomerization, olefin isomerization, and metathesis to produce C_{10}-C_{20} α-olefins and C_{11}-C_{14} internal olefins that are subsequently hydroformylated. This route produces alcohols of high linearity and subsequently formed detergents are easier to biodegrade than the corresponding branched aldehydes. The SHOP process uses ligand-modified cobalt catalysts.

Butanol and 2-ethyl hexanol, with U.S. capacities of 1,595 and 770 million lbs/year, respectively[26] are the largest volume single products from hydroformylation. Both butanol and 2-ethylhexanol are based on *propylene* as the base hydrocarbon feedstock, as shown in the scheme below:
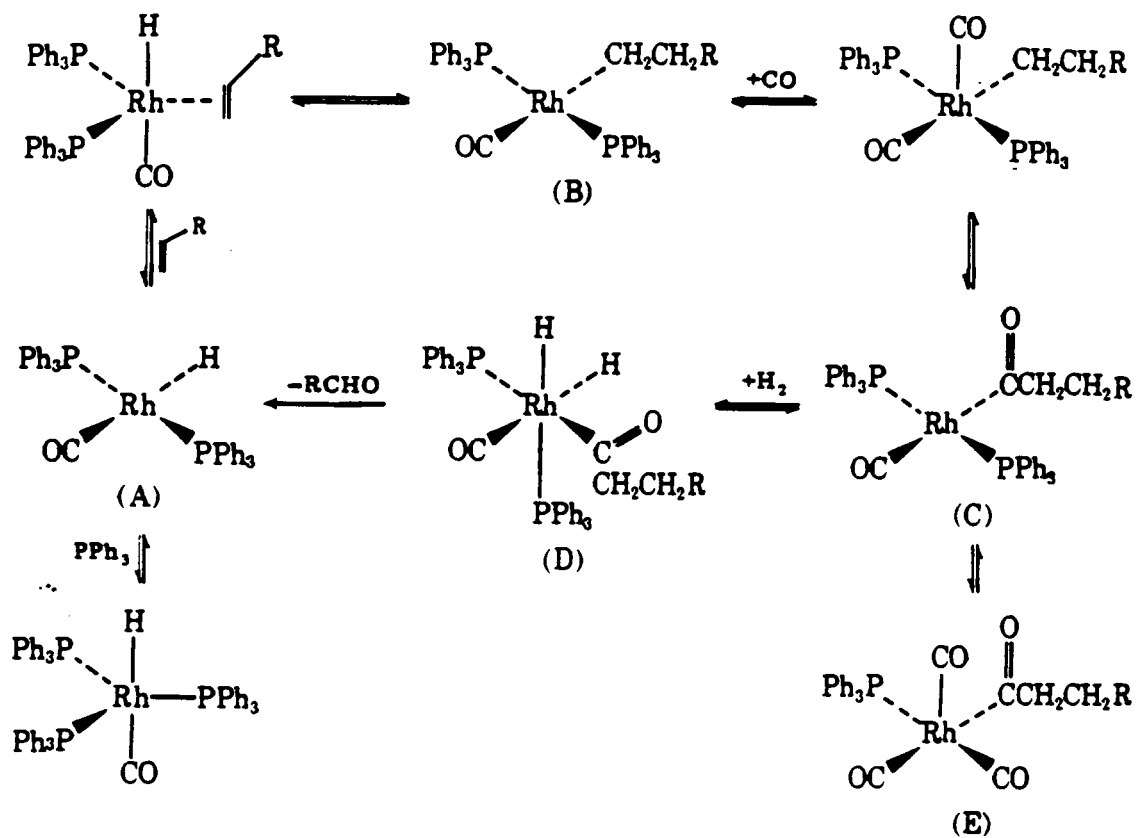
Figure 2. HYDROFORMYLATION MECHANISM. From ref. 25.
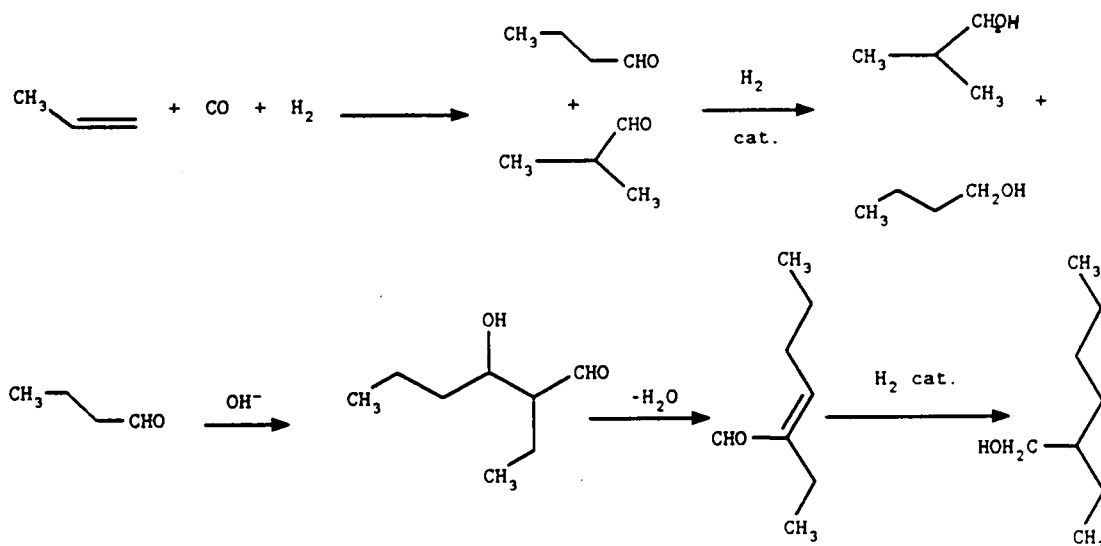
Table 1 on page 14 shows an overall picture of the main feedstocks and products in the hydroformylation industry.

Oxo processes involving ligand-modified *cobalt* catalysts have the following characteristic features compared to the unmodified ones:[9]

- Increased stability of Oxo catalysts.

- Reduced activity of ligand-modified catalysts.

- Marked increase in the hydrogenation activity (alcohols as products).

- High n/iso product ratio.

- Susceptibility towards poisoning due to phosphine oxide formation.

The catalyst recycle in the industrial Oxo processes is different in the case of unmodified from that of modified catalysts. With unmodified catalysts, the metalhydridocarbonyls should be removed from the reaction mixture before the

Table 1. HYDROFORMYLATION.

SUBSTRATE	INTERMEDIATE	PRODUCTS	APPLICATION
PROPYLENE	BUTYRALDEHYDE	BUTANOL	SOLVENT
		2-ETHYLHEXANOL	PLASTICIZERS
C_6-C_9 α-OLEFINS	—	C_7-C_{10} ALCOHOLS	PLASTICIZERS
C_{10}-C_{18} α-OLEFINS	—	C_{11}-C_{20} ALCOHOLS	DETERGENTS

distillation step because they would end up deposited in the distillation columns etc., during work-up and cause many processing and economical problems[9]. The separation is performed in many ways using chemical and thermal treatments and transformations of the complexes. The deposition, regeneration and recycling steps carried out with unmodified catalysts are impeded in the case of *modified* ones because of the presence of the readily decomposable ligand, which must be recycled along with the metal component. Therefore, the preferred method of recovery is to concentrate the modified catalyst via distillation, and if necessary in the presence of organic acids.

Ligand-modified *rhodium* catalysts can be characterized as follows:

- Increase in the stability of the catalyst allowing for its separation from the products (butanal and methyl propanal for the case of propylene as reactant) by distillation.

- Decrease in the activity of the catalyst necessitating higher concentrations in Rh.

- Fall in olefin conversion as a side effect leading sometimes to an additional stage with a Co catalyst to increase the conversion.

- Need for a H_2/CO ratio greater than 1 which in turn enhances the hydrogenation activity which must be opposed by limiting the reaction temperature.

- Virtually isomerization-free hydroformylation with high ligand excess.

A great deal of interest in rhodium hydroformylation stems from the industrial significance of the process developed by Union Carbide and Ruhrchemie for the hydroformylation of propylene, based respectively in the use of $HRh(CO)(PPh_3)_3$ and $HRh(CO)(TPPTS)_3$ (where TPPTS = trisodium salt of the tri-meta-sulfonic acid of triphenyl phosphine), respectively, as catalysts. See Table 2 on page 16.

In general, for a given product distribution in the effluent (n/b ratio), a rhodium catalyst is much more active than a cobalt one. The reactivity of propylene is high due

Table 2. COMMERCIAL CATALYST SYSTEMS. * From ref. 27.

	$Co_2(CO)_8$*	$Co_2(CO)_4(PBu_3)_2$*	$HRh(CO)[P(Ph)_3]_3$*	$HRh(CO)[P(m-PhSO_3Na)_3]_3$
TEMPERATURE, °C	140-180	160-200	80-120	80-130
PRESSURE, ATM	250-350	50-100	15-25	40-50
SELECTIVITY, %	80	80 (as R-OH)	96	99
N/I (1-ALKENE)	3-4/1	6-8/1	10-14/1	19/1
METAL/OLEFIN, %	0.1-1.0	0.5-1.0	10^{-2}-10^{-3}	0.2
TYPICAL OLEFINS	C_2-C_{12}	C_2-C_{12}	C_2-C_4	C_2-C_4

to its solubility in the catalyst's solvent, and also because the double bond is terminal. The separation of the product from the catalyst is facilitated by the low boiling point of the aldehyde. With ligand modified rhodium catalysts, the regeneration methods serve to separate mainly phosphine oxide from the catalyst. Procedures employed include reverse osmosis or chemical treatment of the Rh-containing residue[9].

2.4   Hydroformylation in water

Since the beginnings of organometallic chemistry, water has been considered undesirable in the reaction mixture. Exceptions are oxidation and hydration reactions in which water acts as a reagent[28]. As early as 1958, a water soluble ligand, the sodium salt of (metasulfophenyl)diphenylphosphine (dpm) was prepared[29]. This ligand was used in 1974 for the hydrogenation of pyruvic acid to lactic acid by an aqueous solution of Ru- or Rh-dpm one-phase system[30]. Dpm is much less soluble in water than the trisulfonated equivalent which was prepared in 1974 by Kuntz[31]. The synthesis of the trisodium salt of tri(m-sulfophenyl phosphine) (TPPTS) has subsequently been improved[32]. The synthesis of TPPTS consists of the sulfonation of triphenylphosphine with SO_3 using H_2SO_4 as solvent. The reaction needs to be carried out at low temperature and controlled SO_3 concentration to prevent the competing reaction: the oxidation of the product to the oxide (OTPPTS) to dominate. The final step in the preparation of the ligand is the purification of the raw TPPTS. Also, other water soluble ligands have been synthesized featuring different functional groups, and their homogeneous rhodium catalysts have subsequently been prepared[33]. See Figure 3 on page 18.

Synthesis of Water-Soluble Diphosphines
(Tau = Sodium Taurinate, $NH_2CH_2CH_2SO_3^-Na^+$)
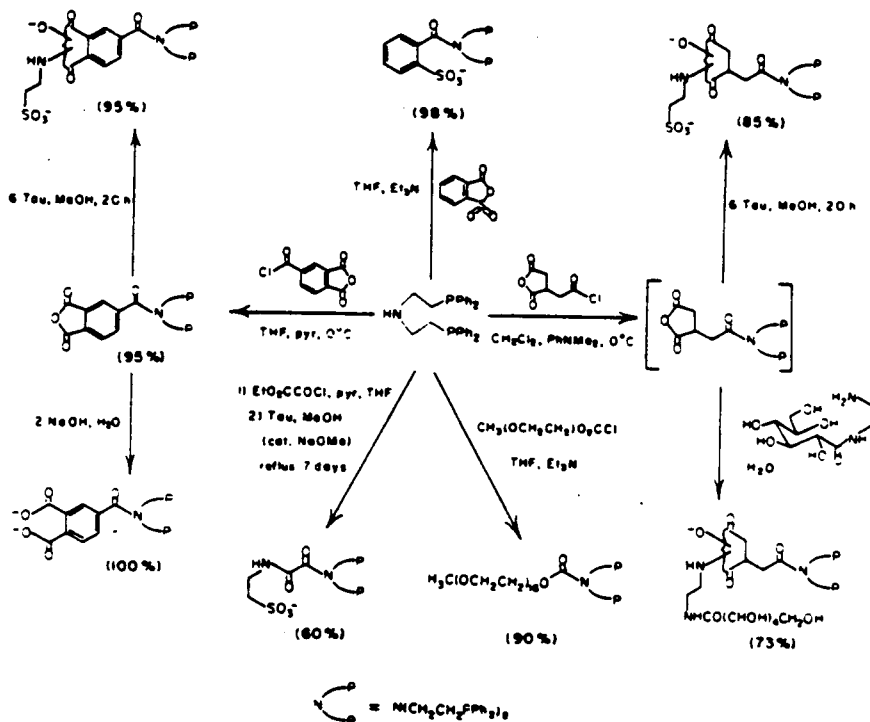
Figure 3. WATER SOLUBLE LIGANDS. From ref. 33.

The literature available on hydroformylation using rhodium water-soluble catalysts when this research was started consisted of a paper published by Wilkinson's group[34] and of patents[35]. Except for the case of Wilkinson's paper the catalytic species was always described as prepared in situ from diverse rhodium salts and the sulfonated ligand.

There have been a number of patents granted that use $HRh(CO)(TPPTS)_3$, but the publication of scientific work related to it has been null up to the publication of a very recent paper by Horvath et al.[36]. The publications by the group of Patin, in 1987, were the first to shed some light onto the chemistry of processes that use of TPPTS as ligand[37]. The work of Patin's group is mainly concerned with the chemistry of $ClRh(TPPTS)_3$, the water soluble equivalent of Wilkinson's complex. It is interesting to note the absence of catalytic activity of such complex in hydrogenation reactions. After our work was complete, a publication from Exxon laboratories detailed some of the chemistry about the synthesis, and characterization of $HRh(CO)(TPPTS)_3$ mainly by IR and high pressure NMR[36].

2.5 Hydroformylation of special substrates

There have been numerous reactivity studies on different substrates other than terminal olefins[38]. The reaction rates of various types of olefins follow much the same pattern with both cobalt- and rhodium-catalyzed systems[15]. Wender and co-workers[39] classified the nonfunctional substrates as straight-chain terminal, internal, branched terminal, branched internal and cyclic olefins. Some results are given in Table 3 on page 20.

Table 3. HYDROFORMYLATION OF VARIOUS OLEFINS. From ref. 15.

HYDROFORMYLATION OF VARIOUS OLEFINS,
RHODIUM[a]

Olefin	Rate constant ($10^3\ k\ min^{-1}$)
Styrene	124
(A) Linear olefins	
1-Hexene	55.8
1-Octene	50.1
1-Decene	40.5
cis/trans-2-Hexene	34.4
cis-2-Heptene	40.2
cis/trans-3-Heptene	41.9
(B) Branched olefins	
2-Methyl-1-pentene	25.7
2-Methyl-2-pentene	14.7
trans-4-Methyl-2-pentene	29.7
2,4,4-Trimethyl-2-pentene	3.0
2,3-Dimethyl-2-butene	0.7

[a] Reaction conditions: 0.5 mole olefin/liter; toluene solvent; 5.3×10^{-2} mmole $Rh_4(CO)_{12}$/liter; 75°C; 130 atm CO/H_2.

Significant observations can be made from these results. Straight-chain terminal olefins are the most reactive. There is little difference between 2- and 3-internal olefins. Branching is only important if present at one or more of the olefinic carbon atoms; the reactivity drops as branching increases. Cyclic olefins react in an irregular fashion, but are in general less reactive than terminal, linear olefins.

The hydroformylation of dicyclopentadiene has produced some interesting results[15]. With a rhodium catalyst at 115°C in tetrahydrofuran the dialdehyde was produced in good yield. With a rhodium catalyst modified by excess triphenylphosphite the unsaturated monoaldehyde was obtained in a rapid reaction under very mild conditions. The nonstrained 5-membered ring olefin required more strenuous conditions for hydroformylation (see following scheme).
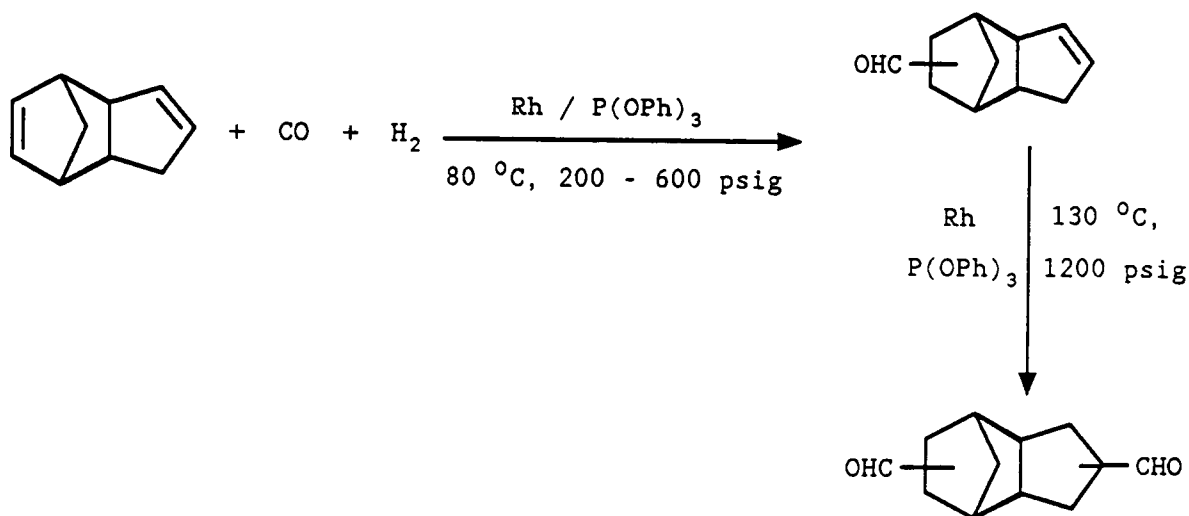
Many olefinic compounds containing various functional groups e.g. esters, nitriles, alcohols, ethers, acetals, etc., have been successfully hydroformylated. However, no commercial processes employing these substrates are operative to date. A variety of

these olefins are available in large amounts as typical petrochemical products; e.g., vinyl acetate, allyl acetate, allyl alcohol, acrolein acetals, acrylonitrile, methyl acrylate, methyl methacrylate, etc. There are some serious limitations to hydroformylation processes using olefins containing functional groups:

- chemoselectivities are often low,

- regioselectivities do not always favor the formation of the isomeric product with the highest commercial value,

- in general, reaction rates are lower than those found for hydrocarbon olefins[38].

The high cost of rhodium, mentioned before as a serious limiting factor, can be much easier to overcome with the hydroformylation of functionalized olefins, because of the much higher economic value of the aldehydes produced[38]. The sophisticated aldehydes produced often provide a substantial contribution to the answer to many synthetic problems not easily solved by the methods of classical organic chemistry.

High molecular weight polyols, useful as components for polymer formulations, are obtained through hydroformylation of oleyl alcohol catalyzed by rhodium derivatives followed by condensation in basic medium of formaldehyde with the formed formyloctadecanols. The bis(hydroxymethyl)octadecanols thus obtained find application in the manufacture of urethane polymers[38]. Such polyhydric alcohols are also employed for the preparation of acrylate ester and polyglycidyl ether derivatives.

It is a general feature of vinyl or alkenyl ethers to be preferentially formylated at the olefinic carbon atom nearest to the ether bridge, as outlined in the case of phenyl vinyl ether in the following scheme[38]:
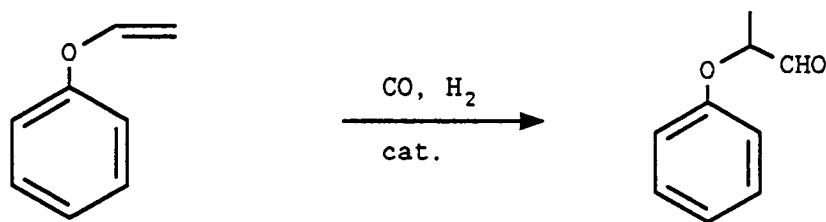
High pressure (60 - 70 MPa) and a temperature below 100°C allow very high selectivity to be achieved for 2-aryloxypropanal formation if rhodium carbonyls as catalytic precursors are employed. The tendency towards α-formylation is shown also by cobalt catalysis, but a logical explanation of such influence exerted by the oxygen atom on the isomer composition of the aldehyde products is far from being elucidated.

2.6 Hydroformylation with supported catalysts

The convenience of using heterogeneous catalysts arises from the difficulties found in separating the catalyst from the product if a homogeneous catalyst is used. The cost of the unrecovered catalyst adds to the problem of product contamination and becomes critical with noble metal catalysts and chemicals for human use. Heretofore, the solution has been elusive in most cases. In the case of hydroformylation, the driving force for obtaining a heterogenized complex has been strong and numerous attempts have been seen. With the exception of phase-transfer catalysis, all the methods outlined in the introduction for heterogenizing a homogeneous complex have been attempted, and reviews on the subject are available[9].

Various investigators[36] attempted to replace one or more CO groups of the

homogeneous complex catalyst $HM(CO)_mL_n$ not by monomolecular ligands but by polymeric complexing agents. In addition, precipitation of transition metal complexes onto supports of large surface area have been also attempted[9]. The object is always to attach the metal (M) to a carrier matrix. The underlying concept is to enable the hydroformylation to take place at fixed active sites thereby combining the advantages of homogeneous and heterogeneous catalysis.

The SLP catalyst suffers the same stability and deactivation problems as homogeneous catalysts, but additional difficulties arise due to the fact that liquid phase is distributed within the pore system of a solid. Since SLP catalysis occurs with a vapor phase reactant/product stream, product condensation is particularly troublesome. These problems are partly overcome by restricting partial pressures of condensables. Also, the use of low temperatures must be used in order to prevent the evaporation of the solvents in the catalytic phase. For example, in the hydroformylation of propene, the maximum conversion at 90°C, 1.57 MPa and equimolar reactant mixture is only 21.4%. If exceeded, the condensation of butyraldehyde eventually blocks the pores. An increase in the temperature to prevent the condensation leads to solvent evaporation and catalyst instability. Because the solid materials used as supports for SLP catalysis contain a distribution in pore sizes, the catalyst solution does not distribute in an even layer of liquid over the total surface. It has been shown[41] in that case that most of the catalyst solution was present in the small pores while the larger ones were only partially filled. The conversion is affected by two opposing effects; as more catalyst solution is loaded into the system the total amount of catalyst increases, but the gas-liquid interfacial area decreases.

It is evident from the problems found in SLP with respect to the distribution of the catalyst in the solid that, to avoid them in the development of Supported Aqueous Phase

Catalysis (SAPC), an appropriate support should be found. An ideal support should have a uniform pore size. Silicas with very narrow pore volume distributions are commercially available[42]. The materials are high silica glasses with mean pore sizes available in the range 70 to 3000 Å. For materials with a pore size greater than 105 Å at least 80% of the pore volume occurs in pores ± 10% from the mean.

Heretofore, the attempts for developing an effective heterogenized organometallic complex have not reached commercial success due to either problems with the activity, selectivity, metal discharge from the support or resistance to poisoning.

2.7   Interfacial reactions

There are many important reactions occurring at interfaces: oxidation of paints and varnishes, extraction of uranium from low-grade ores through complex formation of the uranyl ion at oil-water interfaces, emulsion reactions in general, etc.. As early as 1888 Thompson[13] suggested that chemical equilibria at interfaces might be different from those in bulk phases. The orientation of the molecules in interfacial films studied by Rideal, Raleigh, and others, is of fundamental importance in the analysis of the phenomena of reactions at liquid interfaces[13]. The first observation of a reaction in a monolayer was published by Adam[43] in 1926. It describes the oxidation of a film of oleic acid on water by acidic potassium permanganate. The reaction proceeds with expansion of the film since the double bond in the middle of the chain is converted into a dihydroxy group which is sufficiently hydrophillic to pull the hydrocarbon chain flat onto the surface of the water from its upright original position. Other similar substrates behaved in the same way. The rate of hydrolysis of ester molecules has been found to be a

function not only of the concentration of acid or alkali in the underlying aqueous solution, but also of the tightness of the packing of the molecules in the film[13].

The hydrogenation and hydroformylation of amphiphilic olefins packed into bilayers of phospholipds in the presence of water soluble homogeneous catalysts has provided a recent example[44] of the continued interest in the modification of reaction selectivities by the introduction of interfaces into the reaction system.

Chapter 3

OBJECTIVES

The overall goal of this dissertation is to describe a totally novel class of heterogeneous catalysts namely **SAPC**. The system will have the general features outlined in the introduction.

The development process is divided into six stages:

I.   Synthesis of a water-soluble homogeneous catalyst.

II.   Development of a procedure for an effective deposition of the previously synthesized organometallic complex in the chosen support.

III. Catalytic test of the heterogenized catalyst.

IV. Determination of whether the complex leaches or not from the support under the reaction conditions.

V.   Determination of whether the reaction is taking place at the interface of the aqueous/organic phase or whether it is a a homogeneous reaction.

VI. Comparison of selectivity patterns between the newly developed system and the homogeneous catalyst.

Chapter 4

EXPERIMENTAL METHODS

4.1   Analytical methods

Solution ^{31}P, ^{13}C, and ^{1}H Nuclear Magnetic Resonance (NMR) are recorded on a Bruker WP-200 SY spectrometer at 81.02, 50.33, and 200.16 MHz respectively. Solid state Cross Polarization Magic Angle Spinning (CP MAS) ^{31}P are obtained using a Nicolet NT-150 spectrometer at 60.7 MHz. ^{1}H Combined Rotation and Multiple Pulse Spectroscopy (CRAMPS) spectra and dephasing experiments are recorded at 187 Mz on a modified Nicolet NT-200 spectrometer. ^{31}P chemical shifts are reported relative to 85 % H_3PO_4 and ^{13}C and ^{1}H chemical shifts are reported relative to Tetramethylsylane (TMS). All NMR experiments are proton decoupled.

Thermogravimetric analysis (TGA) are performed in air on a Du Pont 951 thermogravimetric analyzer. N_2 adsorption isotherms are obtained using an Omnisorp 100 analyzer. Diffuse reflectance infrared measurements are recorded on an IBM IR/32 FTIR using a Spectra-Tech DRIFTS cell. Transmission infrared measurements are performed on a Nicolet 5DXB FTIR. Gas Cromatography (GC) analysis are obtained

using a HP 5790A chromatograph. High Performance Liquid Chromatography analysis was performed using a L-6200 Hitachi modular instrument equipped with an L-3000 photodiode array detector and a thermostatic oven. Electron microscopy analysis are performed using a Philips 420T STEM. Electron Microprobe analysis are recorded in an ARLSEMQ automated electron microprobe at 50 kV with 9 XRD channels.

4.2 Water-soluble catalyst

4.2.1 In search of a complex

A characteristic of a water-soluble organometallic complex is the presence of functional groups in the molecule that transform an otherwise organic-soluble complex into one soluble in water. The subject of transforming a molecule soluble in organic solvents (non polar) into one that is at least partially soluble in water (polar) is as old as soap. There is barely anything new in this subject in the sense of new functional groups. This is the reason why the experience that can be drawn from the field of surfactants and detergents is very useful. The functional groups are usually divided into anionic, cationic, non-ionic and amphoteric.

The *amphoteric* group is the most recently introduced, most chemically unstable, and less studied, and for these reasons it is not a good choice. In addition, the possibilities of interaction of this group (in the ligands) with the central atom in the complex may be important. The *non-ionic* and *cationic* groups generally introduce three or more methyl or methylene groups (except in the case of amonium salts). This requirement makes the ligand containing those methyl or methylene groups more soluble

in organic solvents, a quality that is detrimental in this case. To maintain the complex immobilized in the aqueous phase, the partition coefficient between the water and the organic phase should favor the water phase as much as possible.

The above discussion leaves the *anionic* group as the best candidate. In this group the choice should be made in terms of the ionization constants of the different functionalities; the most influential factor in the determination of the relative solubilities of the different functional groups in water. The sulfonate group, in addition to being the most used in surfactants, is the obvious choice. Additional advantages of this functional group are availability, versatility of substrates to be used on, relative inertness (less prone to hydrolysis) as a ligand (where a "soft" ligand is required), stability under a wide range of temperatures and pH conditions, and a large number of sulfonation techniques published. Probably, the most important advantage though, is the fact that it has already been used as a functional group to make water soluble ligands for organometallic complexes (see Introduction and Literature Review).

The choice of sulfonate group ($-SO_3^-Na^+$) as the functionality to make a ligand water-soluble requires ligands that can be sulfonated. Aromatics are easily sulfonated. Following the argument that the sulfonated ligand should be as water-soluble as possible, the size of the aromatic ring should be as small as possible. Hence, although naphthalene and larger aromatic groups can be easily sulfonated, the most appropriate one is benzene. At this point the choice of the heteroatom that will function as the Lewis base is straightforward. Triphenylphosphine is also a good π-acceptor and a widely used ligand with many transition metal atoms[44]. The fact that it has been used as a substrate for sulfonation is a powerful argument for its use as a ligand (see Introduction and Literature Review)..

The central atom in the organometallic complex can be almost any of the transition-elements because almost all of them act as catalysts in one reaction or

$Rh(acac)(C_2H_4)_2$

$[Rh_2Cl_2(SnCl_3)_4]^{4-}$

$Rh(acac)(CO)_2$ — $\xrightarrow[60°]{H_2, CO, 100 \text{ atm.}}$ — $\begin{cases} Rh_4(CO)_{12} \\ Rh_6(CO)_{16} \end{cases}$

$acac^-$

$SnCl_3^-$
$EtOH$

$acac^-$

$\eta^5\text{-}C_5H_5Rh(CO)_2$

C_5H_5Na

$[Rh_2Cl_2(C_2H_4)_2]$ — $\xleftarrow[EtOH]{C_2H_4}$ — $RhCl_3 \cdot 3H_2O$ — $\xrightarrow[100°]{CO, 1 \text{ atm}}$ — $[Rh(CO)_2Cl]_2$ — $\xrightarrow{RSH}$ — $Rh_2(SR)_2(CO)_4$

$Excess$
$PPh_3,$
$EtOH$

PPh_3

$RhH(PPh_3)_4$ — $\xleftarrow[PPh_3]{N_2H_4}$ — $RhCl(PPh_3)_3$ — $\xrightarrow[RCOCl, \text{ etc.}]{CO, RCHO}$ — $RhCl(CO)(PPh_3)_2$ — $\xrightarrow[EtOH]{CO, BH_4^-}$ — $RhH(CO)(PPh_3)_3$

C_2H_4

$CS_2,$
$PPh_3,$
$MeOH$

CH_3I

C_2F_4

$RhCl(C_2H_4)(PPh_3)_2$

$RhCl(CS)(PPh_3)_2$

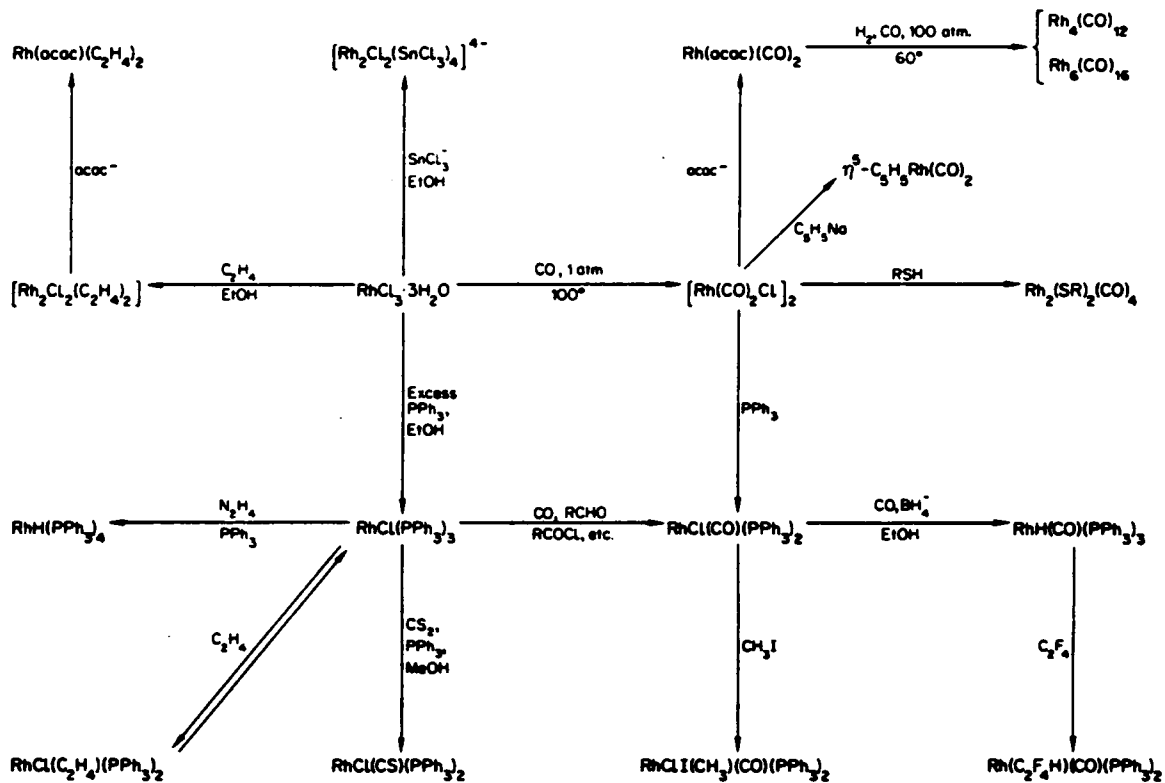$RhClI(CH_3)(CO)(PPh_3)_2$

$Rh(C_2F_4H)(CO)(PPh_3)_2$

Figure 4.   SOME PREPARATIONS AND REACTIONS OF RHODIUM. From ref. 25.

another. The most versatile ones though, are the ones in the group VIII. Rhodium is probably *the* most versatile transition metal in the periodic table[45]; it catalyzes many reactions, a large part of its consumption is related with its use as a catalyst[25]. Its complexes with PPh₃ have been studied intensively and, as it has been mentioned in the previous chapter, some organometallic complexes have been prepared in-situ with sulfonated PPh₃ (TPPTS and dpm), all of them with Rh in the +1 oxidation state. When this research was started no publication was available concerning the synthesis and isolation of the water-soluble compound formed in-situ and used for the hydroformylation of propylene[35]. From the preceding discussion and Figure 4 two complexes were found to be reasonable choices for this research; the sulfonated analogues of either RhCl(PPh₃)₃ or RhH(CO)(PPh₃)₃.

The simplest synthesis pathway and the one that is first followed, is shown below:
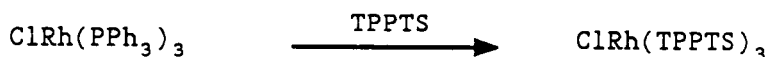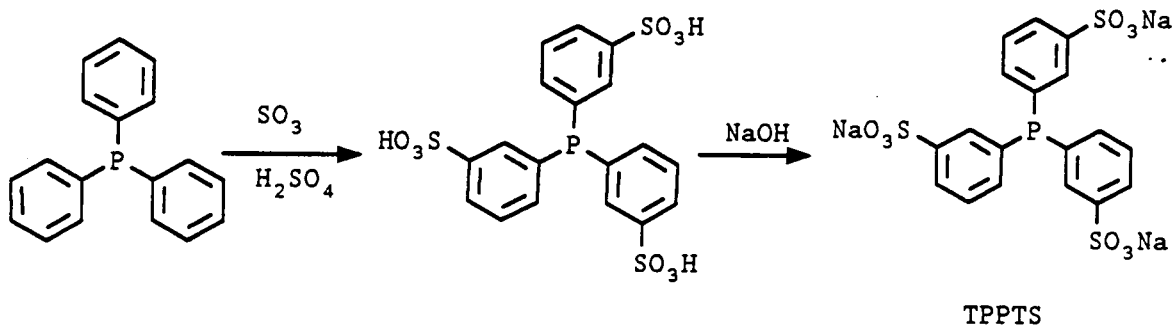
TPPTS

The first step is to prepare TPPTS.

4.2.2 Preparation of trisodium salt of tri-(m-sulfophenyl)phosphine (TPPTS).

A variation of the methods found in the patent literature is used[32,35]. The work-up procedure is illustrated in Figure 5 on page 34. The modifications to the published methods relate mostly with the work-up and purification procedures. The purification procedures of ref. 29 and ref. 31 are combined, even at the expense of lower yield, in order to obtain a purer product.

8 grams of triphenylphosphine (30.5 mmol) are vacuum deareated, and cooled in an Ar blanketed flask to 10°C by means of a water bath. 13.7 ml H_2SO_4 95 % are added dropwise with vigorous stirring. The stirring is continued until complete dissolution. A mixture of 10.8ml of SO_3 30 % (263 mmol) and 16.6 ml SO_3 99 % (382 mmol) is added slowly dropwise with stirring. The temperature of the bath is allowed to increase to 20.5°C over a 7-hour period. After 12 hours the reaction is quenched by cooling to 6°C followed by the dropwise addition of 200 ml deaerated cooled water. The aqueous solution is extracted two times with 50 g each of tributylphosphate. The tributylphosphate layer is neutralized by vigorous stirring with 50% NaOH in water (dropwise addition) in an ice bath, under Ar. The resultant sludge is washed 5 times with 100 ml of ethyl ether per washing and vacuum dried. The sludge is then dissolved in 75 ml of distilled water. Addition of 75 ml absolute methanol generates a brown precipitate. The solid is then removed by filtration. A ^{31}P NMR analysis of the solid revealed that it containes a large amount of TPPTS. The mother liquor is evaporated under vacuum to give TPPTS. 5.0 g of 99% TPPTS (1% water) are obtained (29% yield).

The sulfonation time necessary for the reaction to take place varies with the
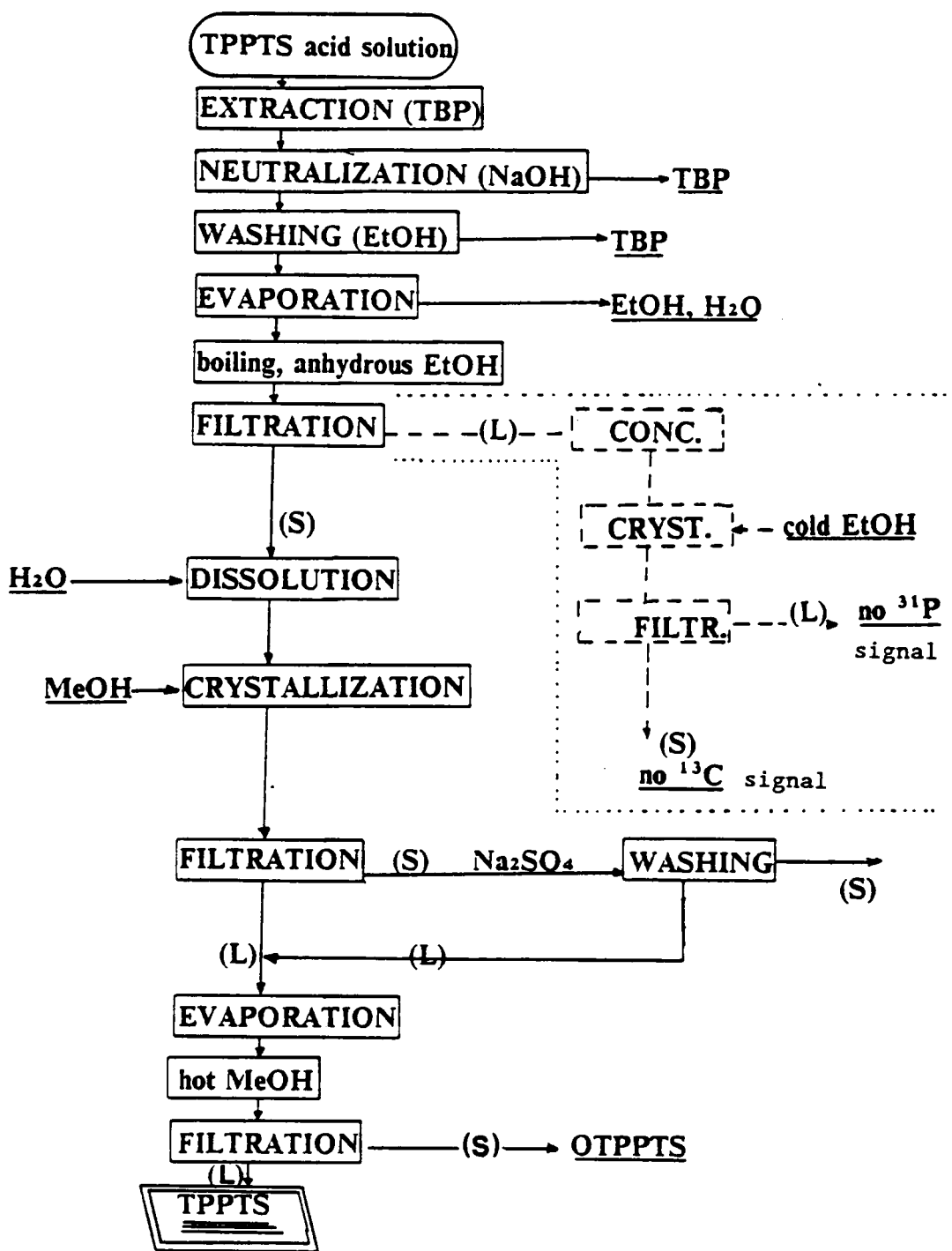
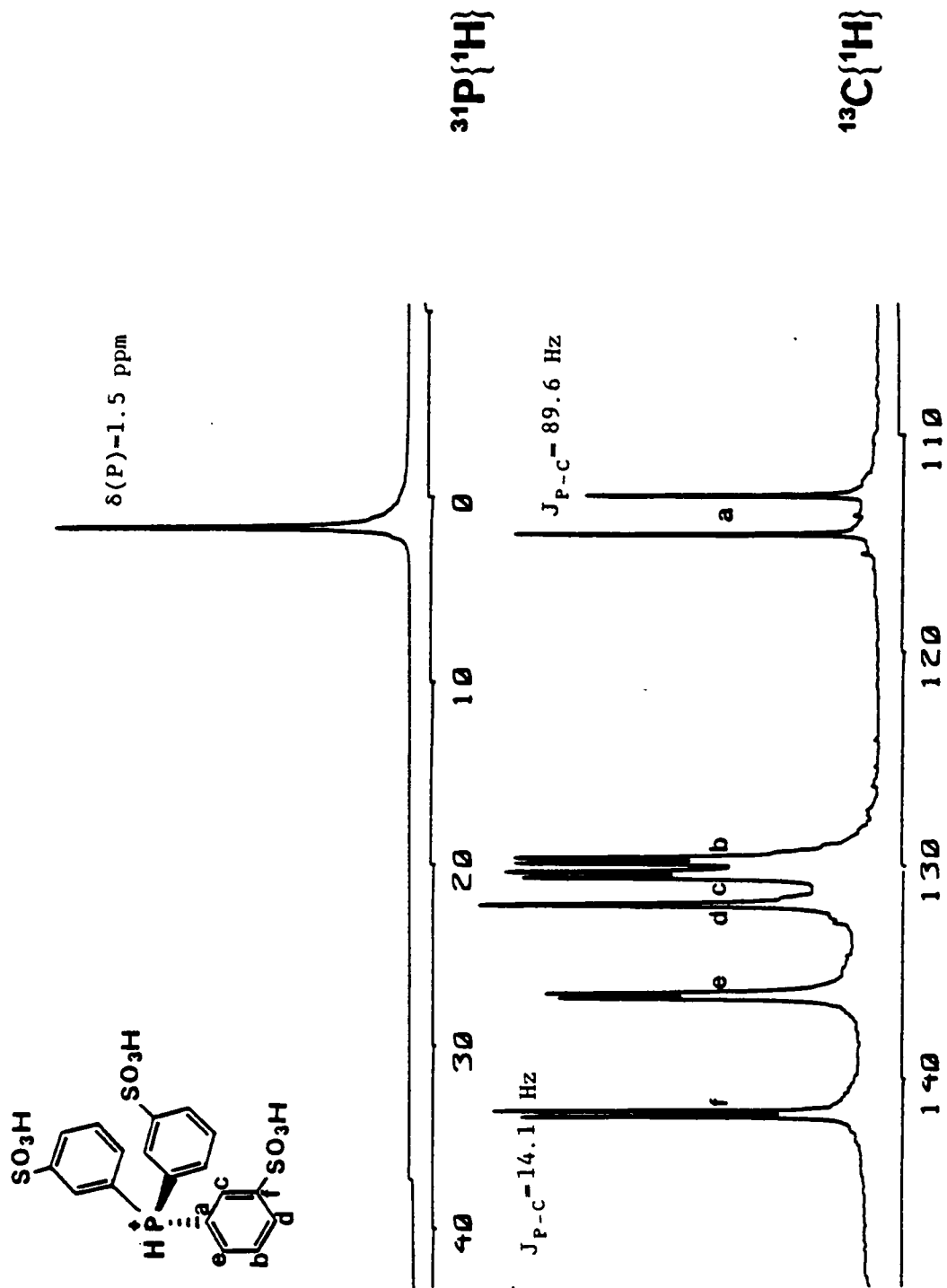**Figure 5.   PREPARATION   OF   TPPTS.**

$^{31}P\{^1H\}$

$\delta(P)=1.5$ ppm

$^{13}C\{^1H\}$

$J_{P-C}=89.6$ Hz

$J_{P-C}=14.1$ Hz

Figure 6.   NMR SPECTRA OF TPPTS BEFORE NEUTRALIZATION

reaction temperature, SO_3 concentration, and PPh_3 concentration. The reaction product is analyzed by 81.01 Mz ^{31}P and 50.32 Mz ^{13}C NMR in D_2O (see Figure 6 on page 35) The sulfonation has as the principal side-reaction the oxidation of TPPTS to OTPPTS[32]. The signal from the oxide appears at about 37 ppm.

After neutralization and purification a ^{31}P spectrum reveals only traces of oxide (OTPPTS) (signal at 34.6 ppm). The resonance of TPPTS appears at -5.1 ppm. The 270 Mz ^{1}H spectrum (see Figure 7 on page 37), shows two multiplets at 7.6 and 7.9 ppm characteristic of the aromatic ring coupled with ^{31}P.

An *approximate* determination of the purity of the ligand is carried out by integration of the signals in the ^{1}H NMR with the result given above; the synthesis and purification methods prove so to be very good, in spite of the low yields. The solubility of TPPTS is approximately determined in three solvents and is found to be extremely soluble in water, 0.52<s (g TPPTS/g H_2O)<0.85, but much less soluble in glycerine, 0.11<s (g TPPTS/g glycerine)<0.15, or ethylene glycol, 0.05<s (g TPPTS/g ethylene glycol)<0.08.

4.2.3 Preparation of ClRh(TPPTS)₃

4.2.3.1   ClRh(PPh₃)₃ as precursor.

The preparation of ClRh(TPPTS)₃ was attempted by a ligand exchange using Wilkinson's catalyst ClRh(PPh₃)₃ dissolved in an organic solvent and TPPTS dissolved in water.

0.90 grams of RhCl(PPh₃)₃ (0.97 mmol) are dissolved in 10 ml deaerated CH_2Cl_2. 1.56 grams of TPPTS (2.7 mmol) are dissolved in 20 ml deaerated H_2O. Both solutions
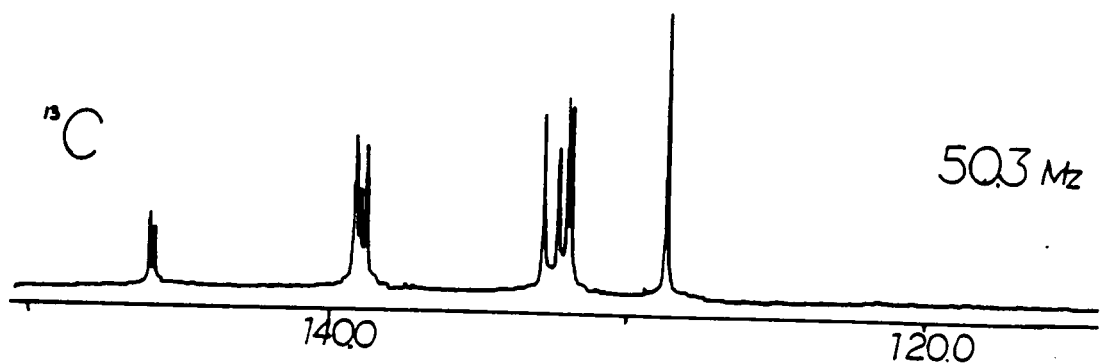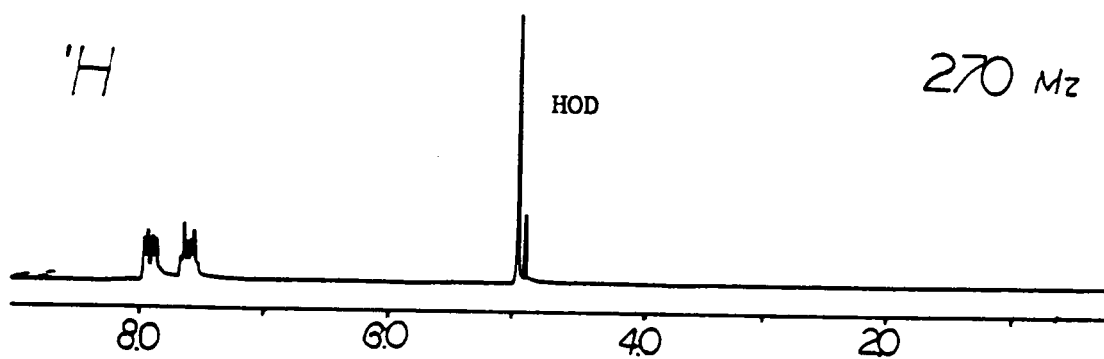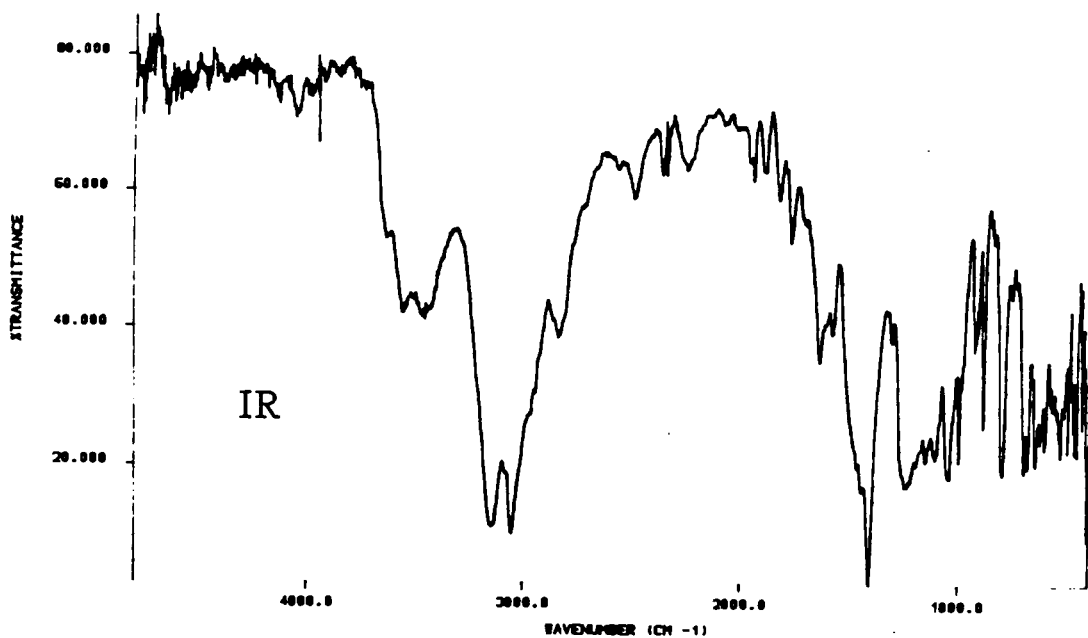
Figure 7. IR AND NMR SPECTRA OF TPPTS AFTER PURIFICATION

are vigorously stirred together under Ar and samples are periodically taken from the aqueous phase to monitor the conversion. The aqueous samples are analyzed by ^{31}P NMR. The concentrations of TPPTS, OTPPTS and ClRh(TPPTS)$_3$ are determined by integration of their NMR signals. The concentrations with respect to time along with a typical spectrum in the run are presented in Figure 8 on page 39.

The ^{31}P spectrum of ClRh(TPPTS)$_3$ consists of a doublet of doublets at 35.09 ppm with J(P-P) = 40 Hz and J(Rh-P) = 143 Hz and what appears to be a doublet of multiplets at 53.0 ppm. This last resonance has a very low signal to noise ratio. There appears to be an impurity at 27.07 ppm, a doublet with J = 100 Hz. As it can be seen in Figure 8 on page 39 the exchange does not take place satisfactorily, the oxidation reaction eventually dominates. The reaction is attempted at different conditions with similar results.

Due to the adverse results in the attempts to prepare ClRh(TPPTS)$_3$ a new route for the synthesis was explored.

4.2.3.2 [RhCl(C$_2$H$_4$)$_2$]$_2$ as precursor.

The preparation of ClRh(TPPTS)$_3$ was attempted by a ligand exchange using [RhCl(C$_2$H$_4$)$_2$]$_2$ without solvent and TPPTS dissolved in water.

112.5 mg of TPPTS (0.198 meq.) are dissolved in 0.5 ml deaerated H$_2$O. The solution is cooled until it solidifies. 11.5 mg of [RhCl(C$_2$H$_4$)$_2$]$_2$ (0.0594 meq. Rh) are added on top of the solid solution. The solid solution is allowed to slowly thaw while stirring vigorously under Ar. The ligand displacement takes place with effervescence; the C$_2$H$_4$ generated drives the reaction to completion. Gradually the solid [RhCl(C$_2$H$_4$)$_2$]$_2$ disappears and the solution turns orange-red. The aqueous solution is analyzed by ^{31}P NMR. The spectrum shows OTPPTS, ClRh(TPPTS)$_3$ and another unidentified

At time = 3 days

OTPPTS

$81 Mz \, ^{31}P$

ClRh(TPPTS)$_3$
J_{Rh-P}= 143 Hz, J_{P-P}= 40 Hz
$\delta(P)$=35.1 ppm

ClRh(TPPTS)$_3$
$\delta(P)$=53 ppm

TPPTS

60.0   40.0   20.0   0.0

SYNTHESIS OF ClRh(TPPTS)3

Ligand exchange: ClRh(PPh3)3--TPPTS

TPPTS

ClRh(TPPTS)$_3$

OTPPTS

CONCENTRATION (%)

TIME (days)

□ TPPTS   + OTPPTS   ◇ ClRh(TPPTS)3
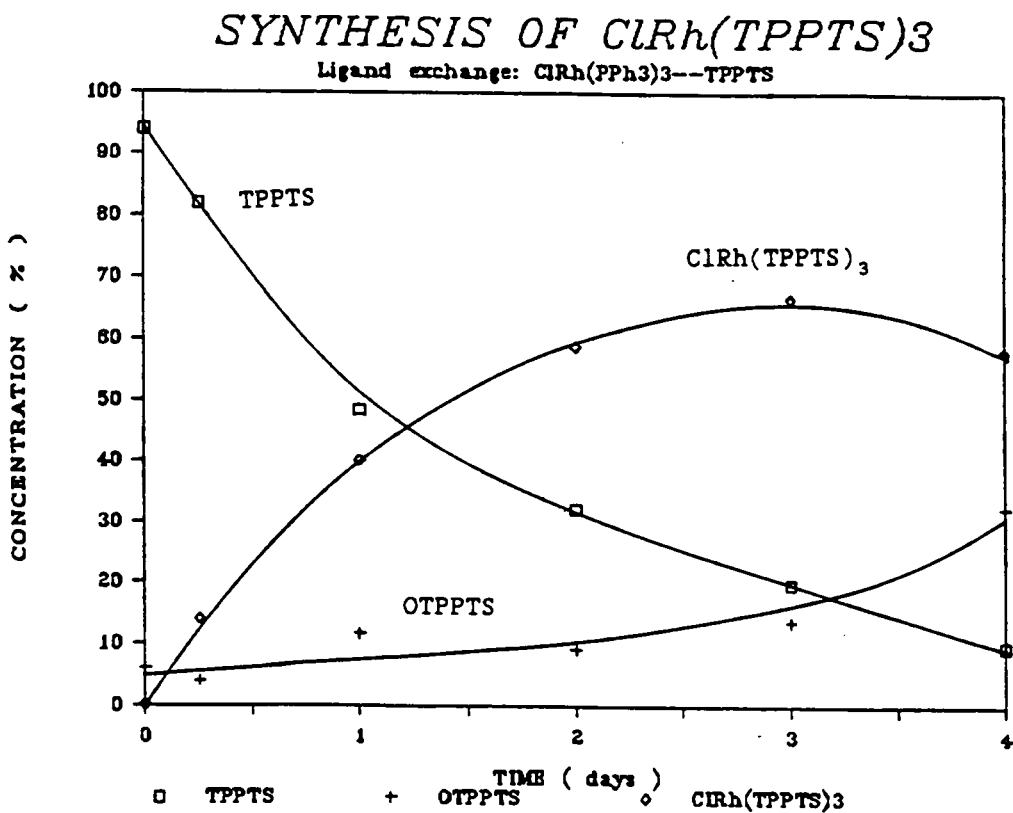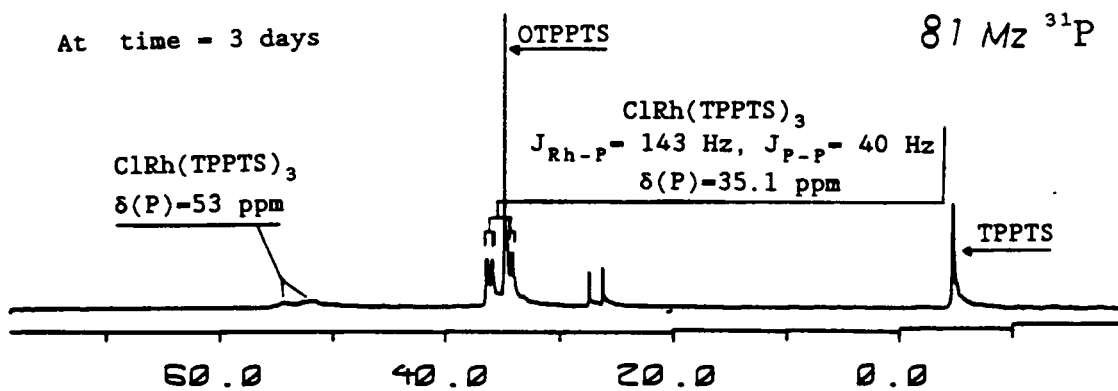
Figure 8. SYNTHESIS OF ClRh(TPPTS) BY LIGAND EXCHANGE

compound. ClRh(TPPTS)$_3$ appears as a doublet of doublets at 36.66 ppm with J(P-P) = 39 Hz and J(Rh-P) = 156 Hz; and a doublet of triplets at 51.15 ppm with J(P-P) = 40 Hz and J(Rh-P) = 170 Hz. OTPPTS's resonance is at 34.28 ppm. An unidentified compound appears as a broadened doublet at 57.51 ppm with J = 190 Hz. The relative amounts of the above mentioned P-compounds are 61% ClRh(TPPTS)$_3$, 13% OTPPTS, and 28% unknown. The above described procedure of freezing the aqueous TPPTS solution is the result of the trial and error optimization of many runs; it represents the best procedure tried. The unknown complex is present in all the preparations, sometimes in greater amounts than the desired product.

Due to the low yields (max. 60%) in the attempts to prepare ClRh(TPPTS)$_3$ a new route for the synthesis was explored. At this point, the first publications by Patin's group about the synthesis and characterization of ClRh(TPPTS)$_3$ became available[37a,c] and their route was followed.

4.2.3.3   [RhCl(COD)]$_2$ [COD = cis-1,5-cyclooctadiene] as precursor.

The preparation of ClRh(TPPTS)$_3$ was attempted by a two-step ligand exchange using [RhCl(COD)]$_2$ dissolved in an organic solvent and TPPTS dissolved in water as shown in the scheme below:

Cl

Rh

Cl

Rh

2 TPPTS, HClO$_4$,

NaCl or HCl,

THF-H$_2$O

Cl

Rh

P(TPPTS)

Cl

P(TPPTS)$_3$

Rh

(TPPTS)$_3$P

P(TPPTS)$_3$
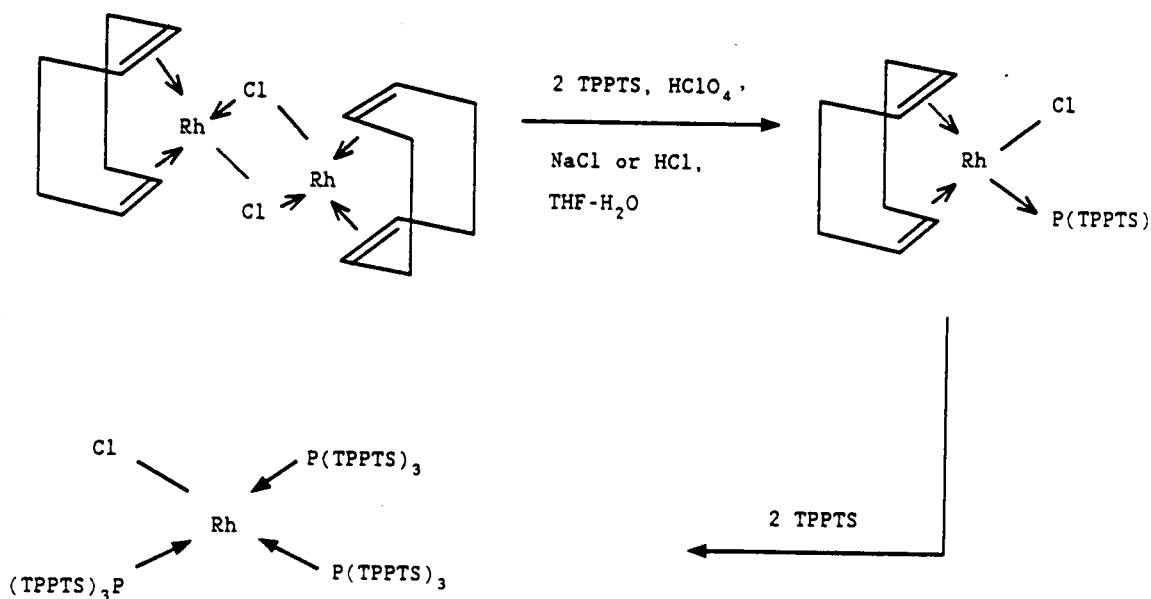
2 TPPTS

Patin describes the presence of chloride ion in the reaction mixture as strictly necessary for the reaction to take place.

9 mg of TPPTS (0.0158 meq.) and 29 mg of NaCl are dissolved in 0.5 ml deaerated H$_2$O. 4 mg of [RhCl(COD)]$_2$ (0.0162 meq) are dissolved into 0.5 ml deaerated THF. Both solutions are vigorously stirred together for 1/2 hour under Ar. Most of the THF is evaporated by pulling vacuum on the two-phase system and the aqueous solution was analyzed by ^{31}P. The spectrum consists of a doublet at 33.6 ppm with J(Rh-P) = 166 Hz. The analysis compares well with the published values for (COD)RhCl(TPPTS); δP = 31.9 ppm and J(Rh-P) = 151 Hz.

The second step in the synthesis is the displacement of COD in (COD)RhCl(TPPTS) by TPPTS. To the aqueous (COD)RhCl(TPPTS) solution obtained above 17.6 mg of TPPTS are added and the stirring is continued for three

hours. A subsequent ^{31}P NMR analysis reveals no better product than what it is obtained using [RhCl(C$_2$H$_4$)$_2$]$_2$ as precursor. The reaction is tried in different conditions with similar results.

4.2.4 Preparation of HRh(CO)(TPPTS)₃

From the attempts to synthesize ClRh(TPPTS)$_3$, ligand exchange between PPh$_3$ and TPPTS is very unlikely to succeed. However, starting from (CO)$_2$Rh(acac), Oswald et al. showed that the catalyst HRh(CO)(PPh$_3$)$_3$ is synthesized according to the following scheme[46]:

$$(CO)_2Rh(acac) \xrightarrow[\text{EtOH}]{\text{PPh}_3} (CO)Rh(PPh_3)_3(acac) \xrightarrow[\text{H}_2]{\text{PPh}_3} H(CO)Rh(PPh_3)_3$$

$$H(CO)Rh(PPh_3)_3 \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} H(CO)Rh(PPh_3)_3 \\ \text{precipitated} \\ \text{solid} \end{array}$$
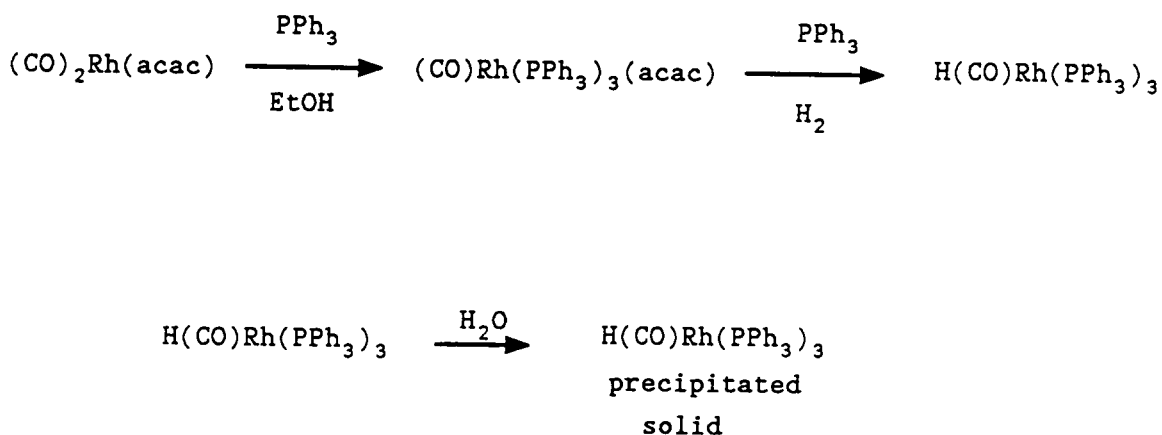
It was suggested that a similar route could be used to synthesize HRh(CO)(TPPTS)$_3$[47]. The synthetic route and purification procedure shown in Figure 9 on page 43 was developed.

50 mg acetylacetonate dicarbonyl Rh(I) (0.194 mmol) are stirred vigorously in a 1 ml H$_2$O deaerated solution containing 400 mg TPPTS (0.704 mmol) until complete dissolution of Rh(CO)$_2$(acac) under Ar. After the dissolution is complete, the agitation is continued under an atmosphere of H$_2$/CO (1:1) at room temperature and atmospheric

$H_2O + Rh(CO)_2(acac) + TPPTS$

| STIRRING
| 25°C
↓

$Rh(CO)(TPPTS)(acac)$ or $Rh(TPPTS)_2(acac)$ maroon sol.

| $H_2 / CO = 1:1$
| atm. press.
| 25°C
↓

$HRh(CO)(TPPTS)_3$ yellow sol.

| EtOH sat. with H_2 / CO
| PRECIPITATION
↓

$HRh(CO)(TPPTS)_3$ yellow solid

| CENTRIFUGATION
| &
| WASHING
↓

VACUUM DRYING

↓

$HRh(CO)(TPPTS)_3$

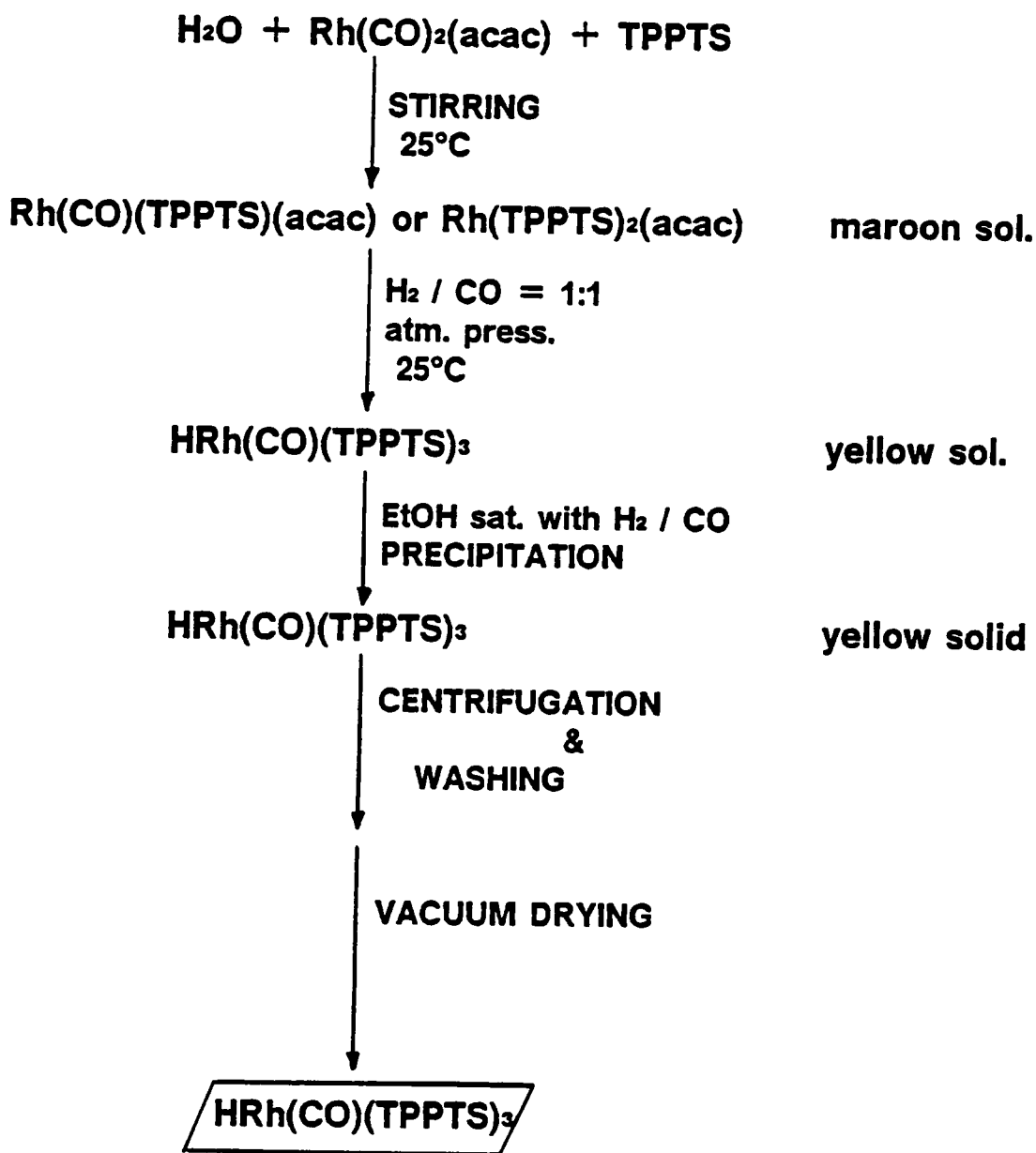**Figure 9. SYNTHESIS   OF $HRh(CO)(TPPTS)_3$**

.

pressure for 6 hours. Within 5 minutes, the color of the solution changes from maroon to yellow. The solution is filtered under nitrogen to remove small amounts of rhodium metal. 8 ml of absolute ethanol saturated with H_2/CO 1:1 are added and the precipitate is centrifuged, washed with absolute ethanol and vacuum dried. 380 mg 84% (16% H_2O) $HRh(CO)(TPPTS)_3$ are obtained (90% yield). A TGA analysis on the vacuum dried $HRh(CO)(TPPTS)_3$ shows 16% water (19.4 moles water/moles complex) (retention even after long periods under vacuum). A ^{31}P NMR analysis performed on the complex dissolved in D_2O reveals no traces of either OTPPTS or free TPPTS. The spectrum consists of a sharp doublet at 43.70 ppm with J(Rh-P) = 156 Hz. No other signal is present. See Figure 10 on page 45.

A FTIR spectrum of the solid complex after being vacuum dried shows two weak bands, at 1921 cm^{-1} and 2000 cm^{-1}, that are assigned to CO and H-Rh stretching respectively.

4.3   Immobilization of the catalyst on the solid support.

4.3.1   Choice of a solid support.

As it was discussed in the "Literature Review" the chosen support should have a narrow pore-volume-distribution (PVD), it should be hydrophilic and should have the appropriate mean pore-diameter with the maximum surface-area possible. The diameter of the pores needs to be such that the presence of the aqueous layer lining their internal surface does not close the opening so that the reactants dissolved in the organic solvent can penetrate them. A layer thickness of 50Å requires a pore diameter strictly larger
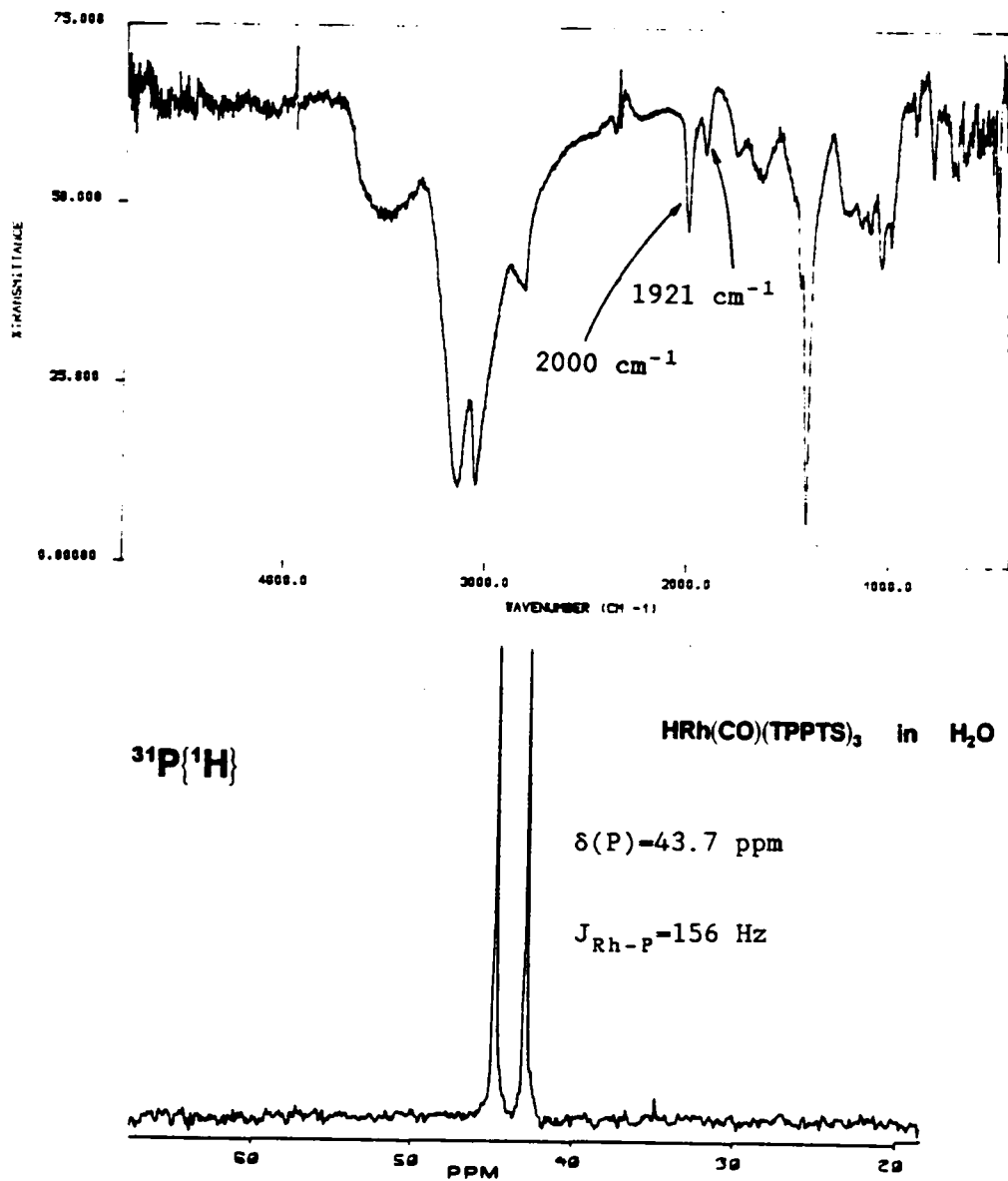
Figure 10. CHARACTERIZATION OF HRh(CO)(TPPTS)₃ by ³¹P NMR and FTIR .

than 100Å. CPG-240[42] with a nominal average pore diameter of 240Å is adequate for the purposes of this research. A larger pore diameter brings a smaller surface area, and a CPG with a larger surface area implies a smaller diameter increasing the diffusion problems.

The batch of CPG-240 bought has the following characteristcs:

Mesh size = -120/+200.

Mean pore diameter = 237Å

PVD = ±4.3 % around the mean.

Pore volume = 0.95 ml/g.

Surface area = 77.5 m²/g.

The homogeneity of the support's surface is a desired feature of CPGs. An inhomogeneous surface in the sense of having sites more active than others is disadvantageous; some molecules of the catalyst would behave different with the possibility of spreading the distribution of products. It has been reported that the surface hydroxyl groups of CPGs, in opposition to those of silica gel, are homoenergetic[48]. CPG-240 is used as received. From N$_2$ adsorption-desorption experiments on CPG-240 the values of surface area and dispersion around the mean of the PVD given by the supplier are confirmed. These experiments are discussed in the following section. CRAMPS experiments are also performed on CPG-240 and are discussed in the section treating the characterization of the supported catalyst.

4.3.2 Method for the deposition of a layer of catalytic phase on a support.

Independent of the nature of the catalyst or the support a method for the deposition of a liquid layer of catalyst solution lining the pores of the support was

EMPTY PORE

IMPREGNATION

LIQUID $\Big|$ HRh(CO)(TPPTS)$_3$ / TPPTS / H_2O

VAC. DRYING

H_2O VAPOR

VAC. DRYING

H_2O VAPOR
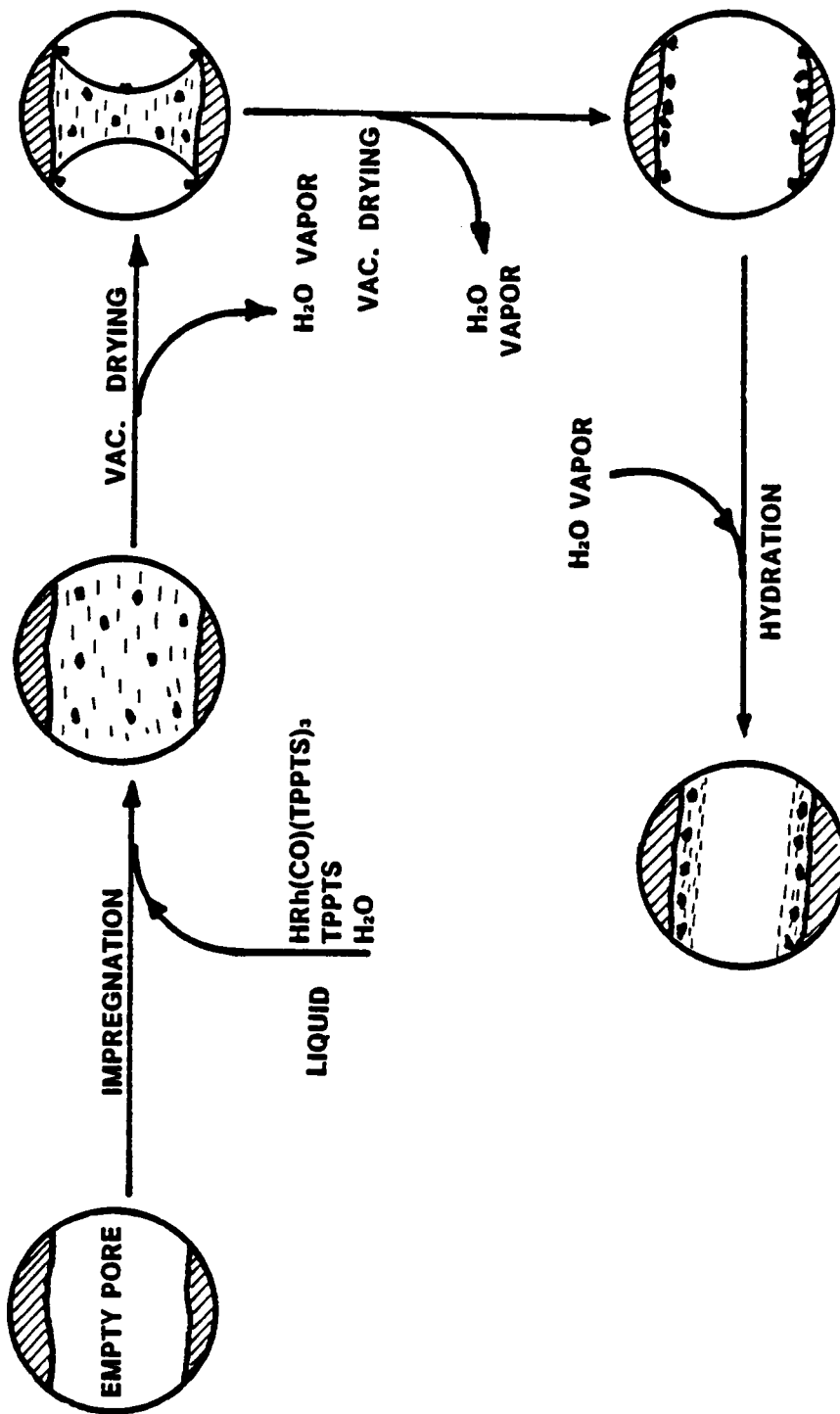
H_2O VAPOR

HYDRATION

Figure 11.   DEPOSITION OF A LAYER OF CATALYST IN A POROUS SUPPORT

developed. The liquid layer has to be as uniform in thickness as possible and the thickness has to be as controllable as possible. The method outlined in Figure 11 on page 47, illustrated for the case of HRh(CO)(TPPTS)₃, is the one devised for our purposes. The first step is the impregnation of the porous support with a solution of the catalyst; the pores are filled up with the desired amount of catalyst. The following step consists of evaporating the solvent in order to leave the catalyst adsorbed on the walls of the support and the pores open. In the next step water vapor is admitted into the system. A slow and controlled condensation takes place building-up a layer of liquid water that dissolves the catalyst previously adsorbed on the walls of the capillaries. By controlling the total pressure in the system, the vapor pressure of water, and the time of exposure, the thickness of the liquid layer can be controlled.

The amount of water to load in the system depends on the desired thickness of the layer and on the type of pores and their connectivity. To get a rough estimate in first instance, cylindrical, non-interconnected pores are assumed. Using 237Å as the diameter of the pore before loading, for a layer thickness of 50Å, the occupied volume is $\frac{237^2 - 137^2}{237^2} \times 100 = 67$ % of the total space. Using 0.95 ml/gram as the pore volume implies a water loading of 63 grams of water per 100 grams of dry CPG-240. That loading brings a decrease of $\frac{\pi 237 - \pi 137}{\pi 237} \times 100 = 42$ % of the initial surface area.

An analytical procedure to test the distribution of the liquid layer onto the porous support was devised. A comparison between a PVD of the support *before* the deposition and the PVD *after* the deposition procedure ideally should reflect the way the catalytic layer is spread. A slight change in the mean pore radius with a significant change in the pore volume indicates that the liquid layer is filling the pores in plugs. A shifting in the mean pore radius along with a reduction in the pore volume indicates that the liquid layer is lining the surface of the pores as a jacket and not as a plug.

A number of experiments were carried out on CPGs (70 Å, 240 Å, and 350 Å mean pore diameter) loaded and unloaded in order to test the proposed analytical method. The majority of the experiments were carried out on CPG-240. A typical experiment consists of:

1) Introduce a weighed amount of sample (loaded or not) into the instrument's holder and close the valve.

2) Immerse the holder into liquid nitrogen and connect it to the instrument.

3) Wait a few minutes until all the loaded water is frozen.

4) Open the valve connecting the holder with the instrument, pull vacuum into the sample and begin the adsorption experiment.

5) Run the instrument's software that process the information collected by the instrument.

Table 4 on page 50 shows the analytical information that the described procedure gives on a representative set of some of the experiments performed.

The first column in the table is the identification number of the run. The second column is the sample weight. The third column shows the amount of water loaded into CPG-240 using the method already described. The fourth is the mean pore diameter read from the PVD plot. The three subsequent columns describe the shape of the PVD curve; the fifth column is the ordinate of the PVD curve at $r = r_{av}$, the sixth column states the broadness of the curve (width at half height), and the seventh one shows how much the curve deviates from zero at $r = 100$ Å. The two subsequent columns show the pore volume calculated by the instrument; the eighth column the total pore volume and the ninth one the pore volume comprising the radii around $r = r_{av}$. The tenth column shows the value for the surface area calculated using the B.E.T. equation. The last column provides additional information concerning the experimental conditions.

Experiment 00 is the only one not done by the described procedure; the data are

Table 4. PHYSICAL CHARACTERIZATION OF SAPC's WITH THE OMNISORP 100

ID	Weight (g)	% H$_2$O	Mean R (Å)	(dPV/dRP) max	W ½ (Å)	(dPV/dRP) @ 100 Å	Pore Volume (cc/g) Total	Pore Volume 100-200 Å	S.Area (m²/g)	Additional Information
00	-	0	119 †	-	5 †	-	.95 †	-	77.5	Values reported by manufacturer
05	.1575	0	170	7	20	0.2	.289	.211	-	8 hours vac. dried
06	.1575	0	165	13	5	0.3	.276	.196	-	Rep. of 05
07	.1575	0	170	7	15	0.3	.298	.216	-	Rep. of 05
08	.322	0	160	120	20	-	.844	.836	-	Double weight, a lot of noise
09	.0772	0	170	550	?	<<10	-	.567	89	Half weight, large spike
11	.117	0	165	35	5	0.5	-	.323	75	3/4 weight
18	.1975	0	165	5	15	0.3	-	.158	-	5/4 weight
30	.0732	0	165	25	15	<0.1	.631	.584	84	+ Water, vac. impregnated & dried
32	.0732	0	165	28	?	<<1	-	.451	-	Rep. of 30, only half of curve
15	.1424	?	161	8	15	0.2	-	.234	76	+ Water vapor adsorbed (air)
17	.139	?	162	35	?	<1	-	.156	-	+ Water vapor adsorbed (vac.)
19	.1332	53	150	12	15	<0.1	-	.338	-	+ Water vac. loaded & desorbed
20	.1145	31	159	10	15?	0.1	.268	.265	-	Idem 19; only half of curve
21	.1517	66	160	8	10	<0.1	.288	.268	20	Idem 19; bimodal distribution
22	.1517	66	159	10	10	0.1	.279	.272	25	Rep. of 21; no bimodal distr.
24	.1217	33	150	11	20	0.2	-	.385	44	Idem 19
26	.099	35	152	11	?	0.2	.143	.109	-	Idem 19, only half of curve
27	.099	35	155	17	10	0.3	-	.404	31	Rep. of 26
29	.1447	?	-	-	-	-	-	-	12	+ Water/TPPTS vac. loaded & des.‡
33	.117	42	157	7	?	0.1	.158	.136	24	Idem 29
36	.1066	30	154	12	15	<0.1	.425	.404	39	+ Water/RhCl(TPPTS), vac. load & des.
38	.1126	57	165	22	10	0	.35	.32	25	ID 29 dried & water vapor ads.(vac.)
40	.1192	45	165	28	14	0	.367	.345	29	ID 36 dried & water vapor ads.(vac.)
42	.0825	15	160	90	?	0	.912	.834	-	Idem 38

† Mercury porosimetry.
‡ PVD did not start.

provided by the manufacturer of CPG-240: except for the surface area, the remainder data are from mercury porosimetry . Experiments with IDs 05 to 18 are performed on the unloaded sample and are devoted to determine the reproductibility of the technique and the experimental conditions under which the run should be conducted. From those runs it is evident that the flow rate of adsorbate (N_2) and the sample weight are related for the shape of the curve to be "well behaved". The comparison between a "well behaved" PVD and one from an experiment with too much sample for the given flow rate is shown in Figure 12 on page 52.

The experiments in the table with IDs from 30 to 27 are performed on samples that have been loaded with only water following the procedure outlined above. From them it can be seen that the results are essentially the same as the ones above. Additional experiments are carried out on samples that have been loaded not only with water but also with TPPTS or $ClRh(TPPTS)_3$ (see section on deposition of the catalyst on the support). It is very reasonable to assume that TPPTS and an organometallic having it as a ligand have very similar properties as surface active agents. This similarity between them constitutes a good reason for using TPPTS in experiments of this kind.

4.3.3   The first example of the SAPC family.

4.3.3.1   ClRh(TPPTS)₃

After the synthesis of $ClRh(TPPTS)_3$, although being less than perfect purity, a deposition onto CPG-240 according to the proposed method was performed.

The $ClRh(TPPTS)_3$ solution previously obtained (see section about the preparation of $ClRh(TPPTS)_3$) containing 0.0594 meq of Rh is added to 1.1 grams of CPG-240
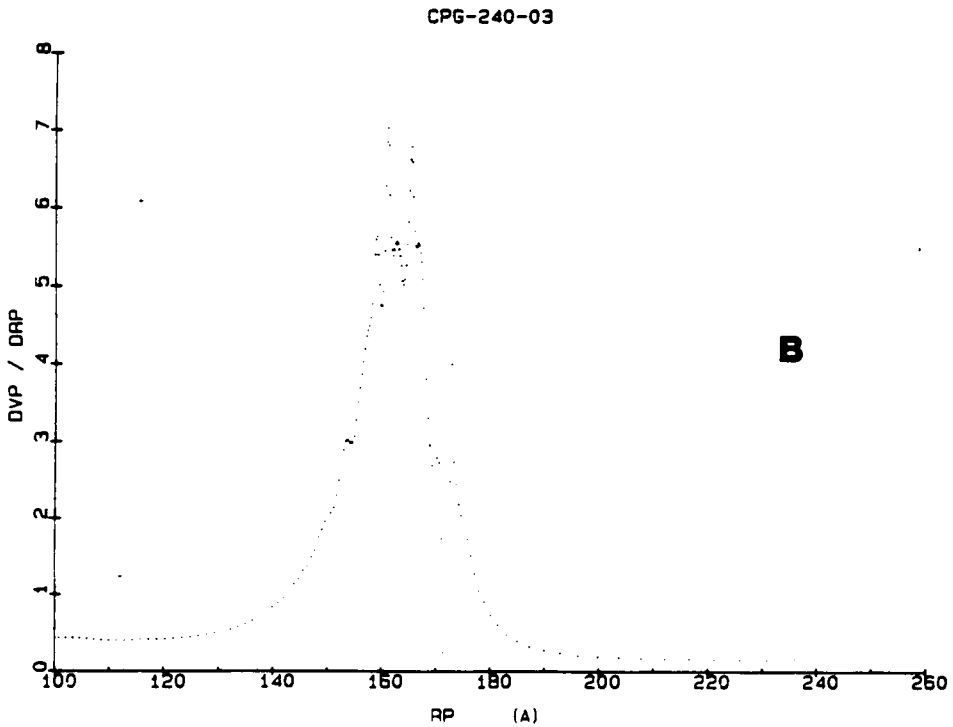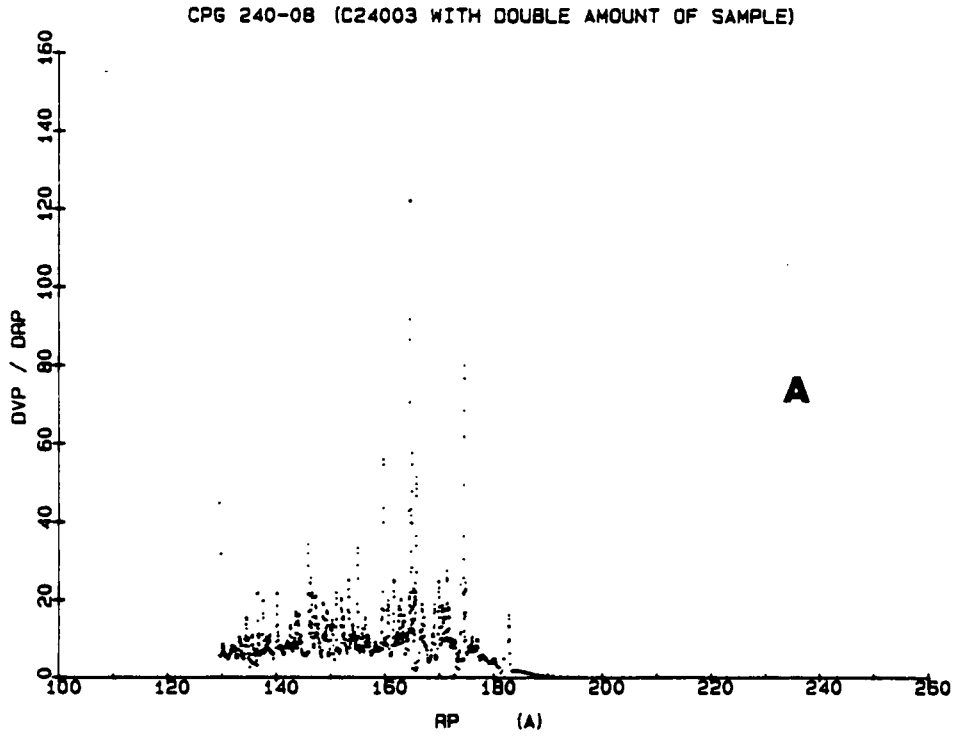
Figure 12. PORE VOLUME DISTRIBUTIONS FOR THE SAME
SAMPLE. A) too much sample B) adequate amount of sample.

(about 10% solids loading). After the solution impregnates the support it is vacuum dried and then backfilled with Ar. The color of the slurry before drying is red. The color of the solid after drying is orange. The vapor-phase water-adsorption on the impregnated solid is done under Ar at atmospheric pressure and 1°C (ice bath). The solid is exposed to the vapors coming from a vial containing water connected to the holder containing the CPG. The low-temperature exposure is followed by exposure at room temperature for three more days. The amount of water absorbed by the solid amounts to about 60% by weight and the sample is a yellow free-flowing powder. A ^{31}P NMR analysis is done on the sample and it reveals a very broad but distinctly visible single peak at about the same position as the OTPPTS appears in the normal liquid-state ^{31}P NMR. The catalyst appears to completely decompose.

4.3.3.2   HRh(CO)(TPPTS)₃

The deposition of HRh(CO)(TPPTS)₃ on CPG-240 is performed according with the procedure described below:

340 mg HRh(CO)(TPPTS)₃ are dissolved in 25 ml deaerated water along with 410 mg TPPTS (pH of the solution is 10.5) (moles P / moles Rh = 6.9) and poured onto 8.8 g CPG-240 previously deaerated and Ar blanketed. After degassing the slurry by exposure to vacuum, it is blanketed with Ar at 1 atm. The slurry is vacuum dried and left at atmospheric pressure and room temperature under an atmosphere of H_2/CO 1:1. The impregnated support is yellow.

Characterization.: Electron microprobe analysis[49] on the small SAPC particles before hydration shows that the Rh/P ratio is constant across the particles.

FTIR analysis performed on the sample before hydration reveal very weak bands in the 1900-2100 cm⁻¹ region. The assignment of those bands is uncertain even after analysis where CO is exchanged by ^{13}CO.

Water is adsorbed using a similar procedure as in the case of ClRh(TPPTS)₃ in the preceding section. A ^{31}P NMR on the sample reveals some degradation of the complex to OTTTPS. The presence of what is probably undegraded complex is also detected along with an unidentified new resonance. The spectrum is shown in Figure 13 on page 55. There are four peaks at 46 ppm, 36 ppm, 29 ppm, and -2 ppm in relative amounts 18%, 40%, 15%, and 29% respectively and are assigned to HRh(CO)(TPPTS)₃, OTPPTS, unknown, and TPPTS respectively. The peaks are broad but distinct. This piece of information indicates the much greater stability of HRh(CO)(TPPTS)₃ than ClRh(TPPTS)₃ upon impregnation.

CP MAS ^{31}P analysis on the unrehydrated SAPC[50] reveals broad bands at 45, 30, -3, and -18 ppm. Figure 14 on page 56 shows a typical spectrum at 4.8 kHz spinning frequency and its deconvolution. The relative amounts of P in each environment in an unrehydrated sample of SAPC can be approximately quantified as: 30% at 45 ppm, 26% at 30 ppm, 15% at -3 ppm, and 29% at -18 ppm. The tentative assignments are respectively HRh(CO)(TPPTS)₃, OTPPTS, TPPTS, and probably an adsorbed form of TPPTS. The spectrum at lower spinning frequencies is complicated by the very large anisotropy; the spinning sidebands obscure the whole spectrum as it can be seen in Figure 15 on page 57 where the spinning frequency is varied.

^{1}H CRAMPS (Combined Rotation and Multiple Pulse Spectroscopy) experiments[51] were performed on the unrehydrated sample along with experiments on HRh(CO)(TPPTS)₃ and on CPG-240 to compare and help in the interpretation of the spectra on SAPC[50]. Figure 16 on page 59 shows three spectra representative of those taken. To assign the signals with greater precision and to get more information about
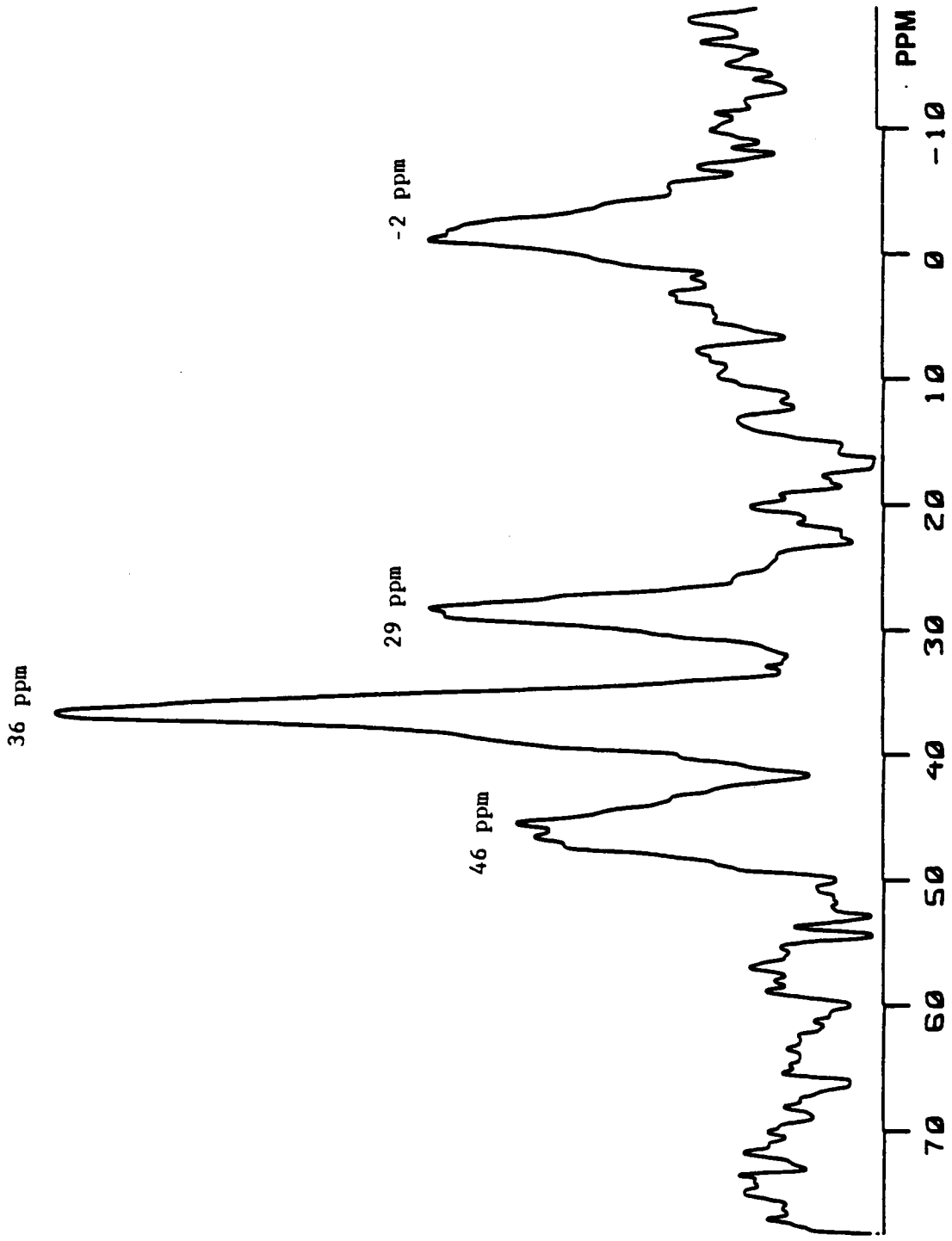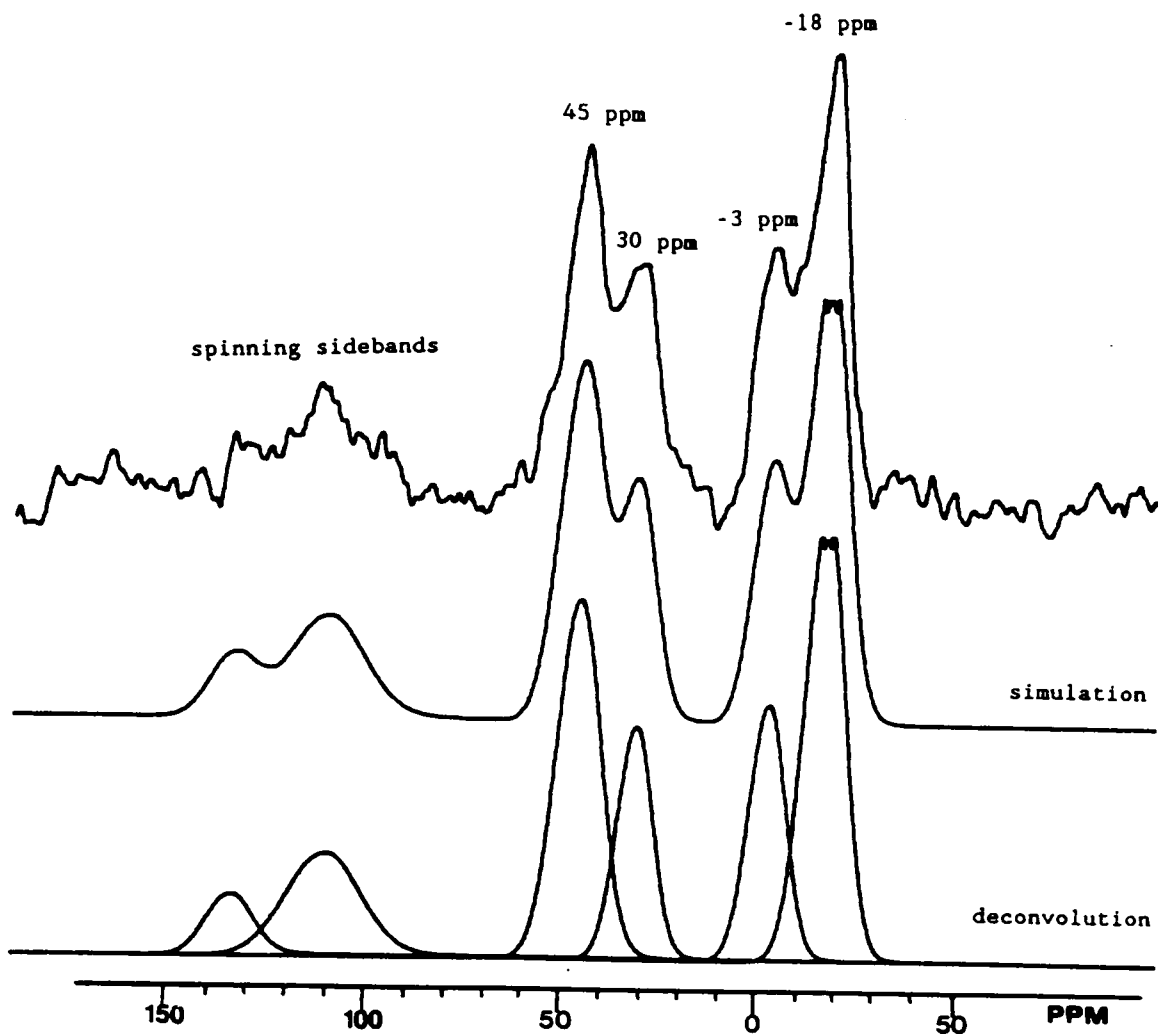
Figure 13. LIQUID STATE ^{31}P NMR ON SAPC (40% H_2O)

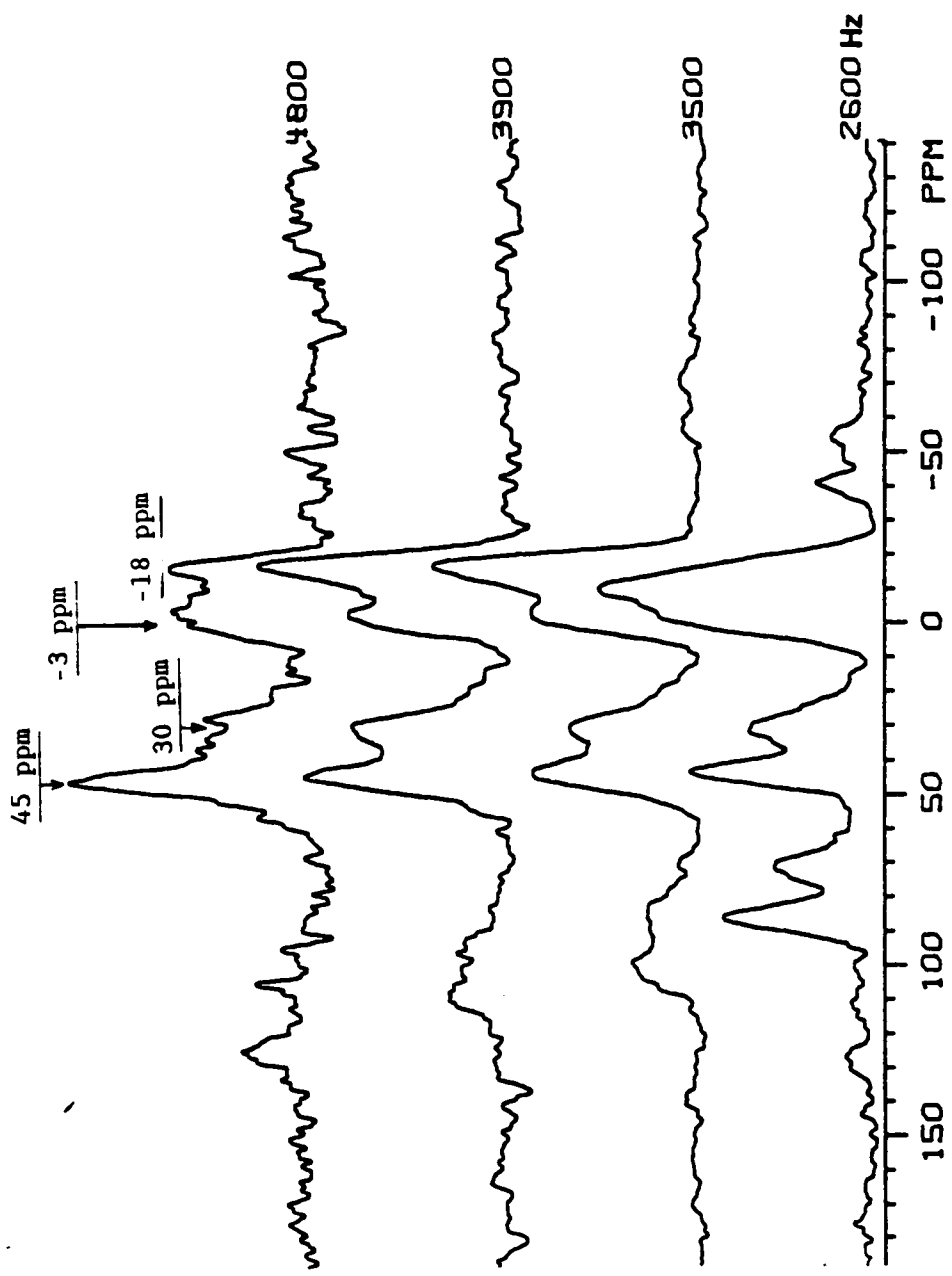**Figure 14.** CP MAS ^{31}P NMR AND ITS DECONVOLUTION ON UNHYDRATED SAPC

Figure 15. CP MAS ^{31}P NMR AT VARIED SPINNING FREQUENCIES ON UNHYDRATED SAPC

the motion of the different species on the surface, a series of dipolar dephasing experiments are performed[50,51]. The results of those experiments are shown on Figure 17 on page 60. The assignments are as following: 1.5 ppm isolated silanols, 3.7 ppm physically adsorbed water, 7.5 ppm aromatic protons. The assignment of the broad signal in the 4.5-5.5 ppm range is more uncertain and is discussed in the next chapter. The signal that appears in the $HRh(CO)(TPPTS)_3$ spectrum at -8 ppm is assigned to the hydride.

CP MAS ^{13}C NMR were performed on the same unrehydrated sample. The signal obtained, at 120-140 ppm, was featureless; the signal to noise ratio was very low most probably due to the very low concentration of ^{13}C (natural abundance). A ^{13}C analysis of the complex on the CPG after ^{13}CO exchange is under way.

4.4   Catalysis with SAPC

4.4.1   Choice of a reaction

SAPC represents a new type of heterogenation and it is also designed to catalyze reactions at an interface. The methods to test the particular orientation of the reactants at the polar/non-polar interface can be divided into analytical- and reactivity-based. Analytical methods that can be used rely on the use of NMR or ESR techniques. Intermolecular selective polarization transfer from the protons of the H_2O to the ones of the substrate that are more likely to be towards the interface because of the presence of polar groups in the molecule may be possible. However, the large average intermolecular distance is very likely to be a disturbing effect since the efficiency of the
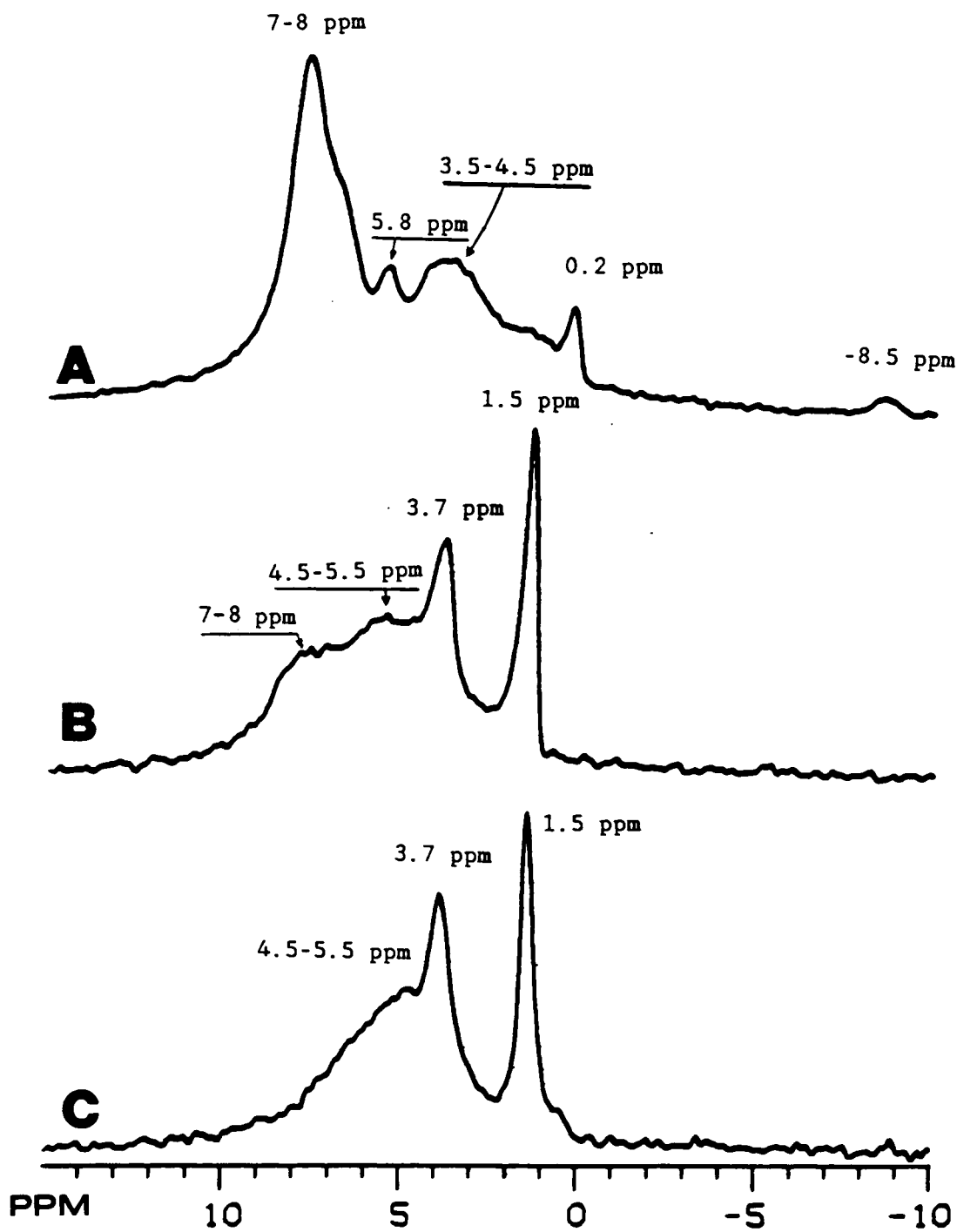
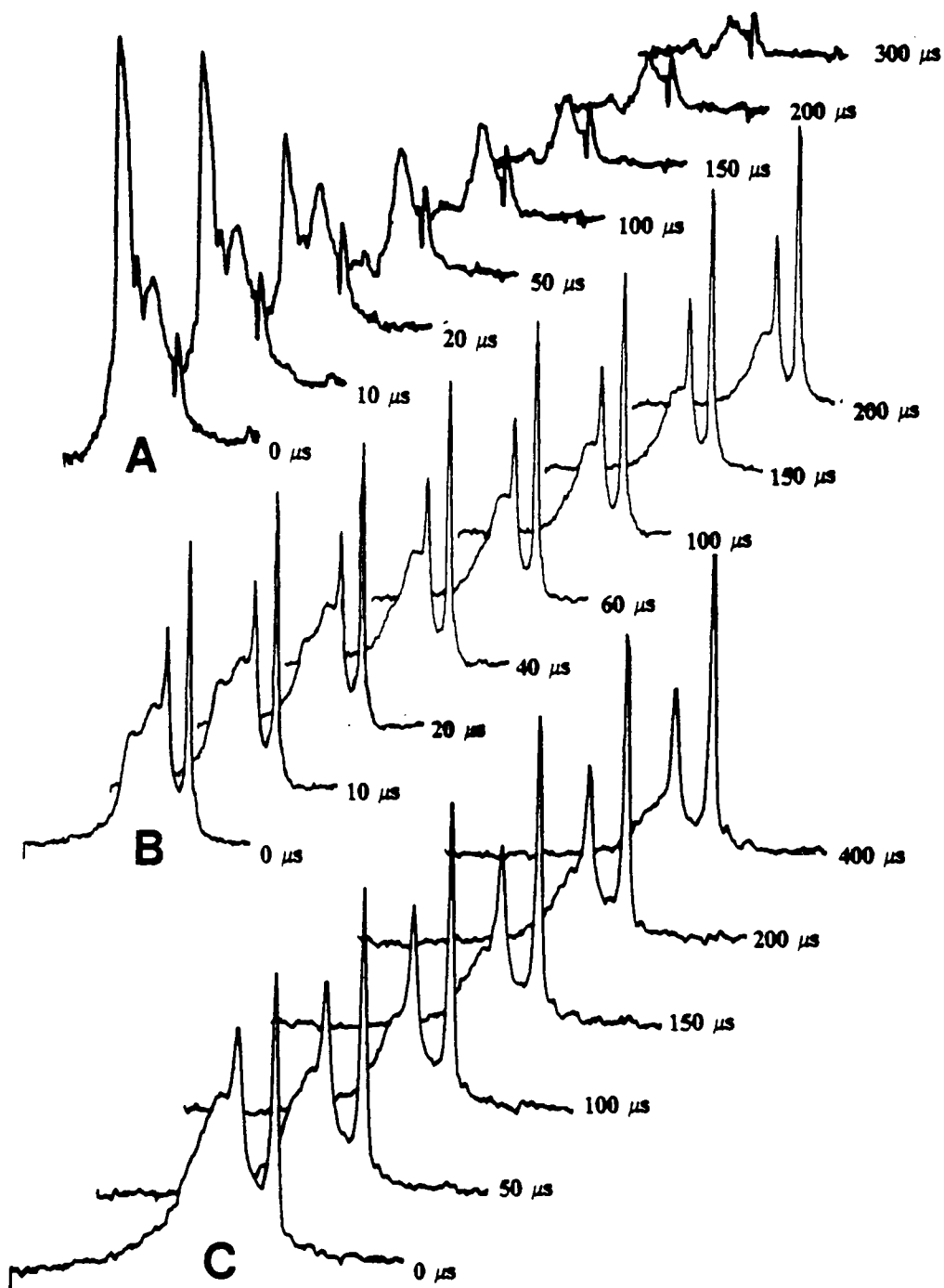Figure 16. ^{1}H CRAMPS EXPERIMENTS: A) HRh(CO)(TPPTS)$_3$, B)
SAPC, and C) CPG-240.

Figure 17. ¹H CRAMPS DIPOLAR DIPHASING EXPERIMENTS: A) HRh(CO)(TPPTS)₃, B) SAPC, and C) CPG-240.

process is directely proportional the sixth power of the inverse of the distance. There are no immediate precedents of this technique applied to molecules so weakly bound, but there is a recent precedent with molecules bound by weak interactions like hydrogen bonding.[52]. Another method is the T_1 and/or chemical shift measurement of the different [1]H's and [13]C's of the substrates when adding a water soluble paramagnetic impurity. The proximity to the interface is to be revealed by the change in the T_1 and/or the chemical shifts[53]. These measurements are very difficult to perform under reaction conditions and they would actually constitute an indirect evidence of the main objective which is to change the selectivity of the reaction. These facts added to the fact that they are very involved procedures leave them out of the scope of the current research.

The reactivity-based methods to test the orientation of the molecules at the interface consist of using a reactive molecule as a probe. Variations in selectivity with respect to the homogeneously catalyzed reaction would constitute a positive result. The reverse, that is the absence of selectivity variations, constitute no proof; it can be due to the choice of nonadequate reaction or reaction conditions. Although this constitutes a disadvantage, the relative simplicity of this approach compared to the one previously exposed tilts the balance in favor of using reactivity as the probe.

4.4.1.1 Isomerization.

The first step is to test the influence of the interface in simple systems. The homogeneous isomerization of 1-octene and 1,7-octadiene is likely to proceed at different relative rates if the reaction is catalyzed by a water-soluble catalyst in a heterogeneous reaction instead of a homogeneous one. The rationale is that the different orientations with respect to the interface of the two substrates will affect the reaction activity and selectivity. The higher electron density about a double bond causes

the double bonds to preferentially orient towards the interface[43]. Because of that, and provided the concentrations are low enough to prevent the packing of the molecules at the interface, the 1-octene should orient perpendicular to the interface while the 1,7-octadiene lie parallel to it. Thus, the coordination of the catalyst with the third carbon of the chain should be easier with 1,7-octadiene than with 1-octene as shown in the following scheme:
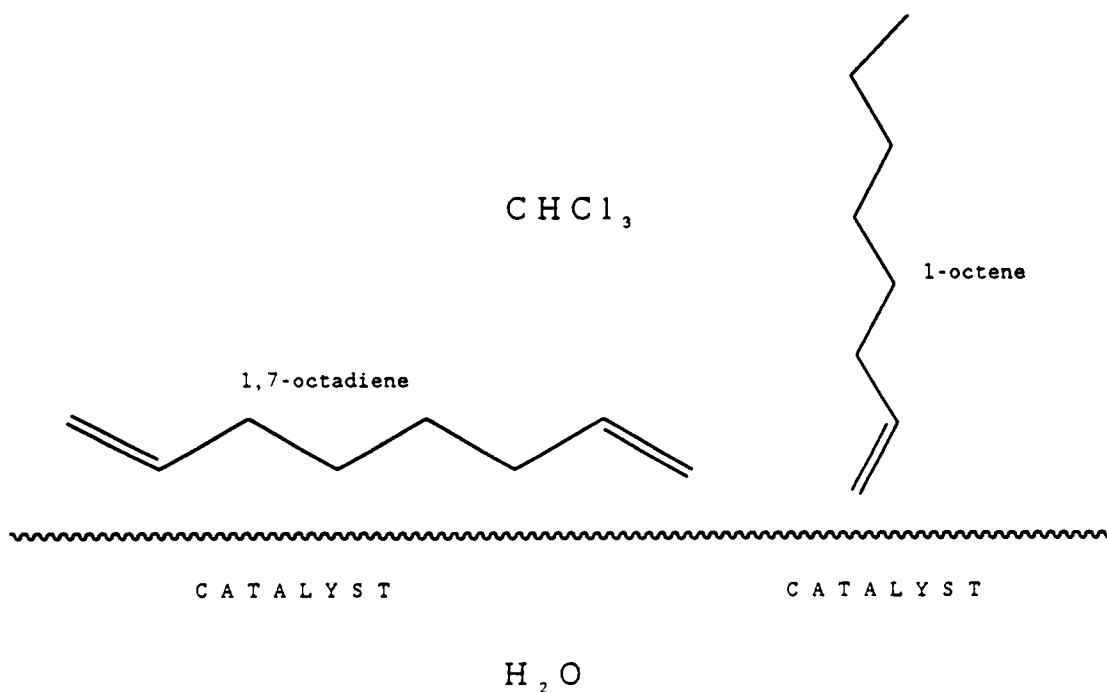
The isomerization reaction is first carried out homogeneously using ClRh(PPh₃)₃ as catalyst and CHCl₃ as a solvent. In first instance 1-hexene is used instead of 1-octene ; the reaction is monitored by Gas Chromatography (GC) and the isomerization products

of 1-octene are not easily separated from the isomerization products of 1,7-octadiene.

1.0 gram of 1-hexene (11.9 mmol) and 0.658 grams of 1,7-octadiene (5.95 mmol, 11.9 mmol of double bonds) are dissolved in 40 grams $CHCl_3$ (335 mmol). The solution is equilibrated at 50°C under Ar and then 0.2 grams $ClRh(PPh_3)$ (0.216 mmol) are added while stirring. The progress of the reaction is monitored by GC. The results are shown in the plot in Figure 18 on page 64. It can be seen from the plot that the isomerization reaction is extremely slow considering the huge amount of catalyst used. The temperature is already fairly high. The use of $HRh(CO)(PPh_3)_3$ as catalyst produces similar results.

The isomerization reaction is also attempted using $ClRh(TPPTS)_3$ as catalyst, prepared in-situ, in a two-phase system:

40.2 grams deaerated $CHCl_3$ are used to dissolve 0.20 grams of a mixture of 0.98 g 1-heptene and 1.1 g 1,7-octadiene. The solution is equilibrated at 50°C. 40 mg of $[RhCl(C_2H_4)_2]_2$ are used to prepare the water-soluble catalyst $ClRh(TPPTS)_3$ as described before. An excess of TPPTS of 50% is used, 20 ml degassed water is used as solvent. The aqueous and non-aqueous solutions are vigorously stirred together for two days under N_2 without any noticeable conversion. A ^{31}P NMR on the aqueous phase reveals only OTPPTS; the catalyst decomposes completely.

The isomerization reaction is attempted using SAPC with $ClRh(TPPTS)_3$ as the active species prepared as described before with the same result; the complete decomposition of the catalytic species. At this point it is evident that the stability of $ClRh(TPPTS)_3$ is a severe restriction to the development of SAPC and it is completely abandoned as a catalyst.
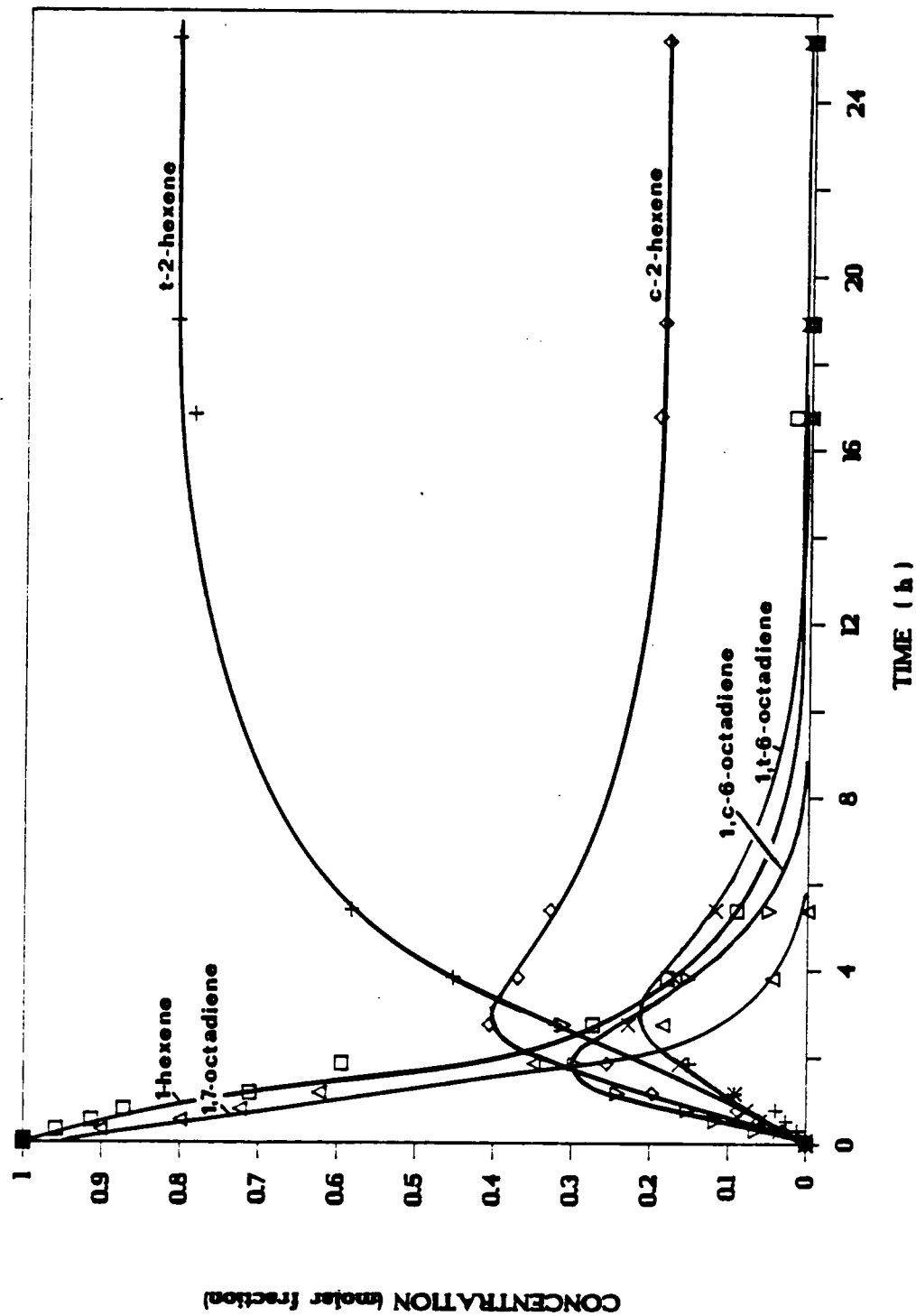
Figure 18. HOMOGENEOUS ISOMERIZATION OF 1-HEXENE AND 1,7-OCTADIENE.

4.4.1.2 Hydroformylation.

Hydroformylation is the reaction adopted to test SAPC due to:

a) the impossibility to use the water-soluble analog of the Wilkinson's catalyst because of its lack of stability,

b) the lack of activity of ClRh(PPh₃)₃ and HRh(CO)(PPh₃)₃ towards isomerization, and

c) the success obtained with the use of HRh(CO)(TPTS)₃, a hydroformylation catalyst, on its synthesis and deposition procedure.

The catalytic species used in SAPC for the hydroformylation is HRh(CO)(TPPTS)₃. It is extremely insoluble in non-polar solvents; barely soluble in polar solvents like glycerine and ethylene glycol. Hence, if it proves to be active for hydroformylation the places where the catalysis can take place are restricted to either the aqueous phase or the interface (it would be very unlikely that being so unsoluble in organic solvents it can migrate into it to catalyze the reaction). To assure that if the hydroformylation proceeds the catalysis is taking place at the interface and not at the aqueous phase the substrate has to comply with some requirements. It has to be organic-soluble, insoluble in water, and preferably its double bond has to be non-terminal. The non-terminality of the double bond makes much more unlikely the hypothesis that the molecule is introducing just its double bond into the aqueous phase while still being in the organic phase. Oleyl alcohol complies with all the aforementioned requirements and it has been successfully hydroformylated using a closely related catalyst, HRh(CO)[P(m-PhSO₃NR₄)₃]₃, as a homogeneous organic-soluble catalyst[54]. Because of all the aforementioned reasons oleyl alcohol is chosen as the first hydroformylation substrate for testing SAPC as a catalyst.

Reactor design: Hydroformylation reactions usually use reaction temperatures between 100 and 200°C and pressures between 200 and 5000 psig. The reactor should be made of an inert material able to resist those stresses. The principal obstacle in the choice of a reactor that this research faces is size. The procedure chosen to prepare the ligand is long, involved, and with low yields. Hence, the convenience of running low-volume reactions is obvious. A rough estimate of the free-volume that the reactor should have gives something in between 0.5 to 1.5 ml. It should be stirred and safe because of working with a highly flammable and toxic gas. The reactors comercially available are all too big. The final design of the reactor is the one presented in Figure 19 on page 67. The advantages of this reactor are its low price, low catalyst usage, simplicity of operation and availability. The disadvantages are low capacity, impossibility to take samples without stopping the reaction, and impossibility to monitor the stirrer's rotation speed.

In all the hydroformylation reactions the ratio H_2/CO is always 1:1. The stirring rate and the solvent in which the substrate is dissolved are also maintained the same in all the experiments. Cyclohexane is the solvent used, the sole exception being in the hydroformylation of both stigmasterol and cis-1,2,3,6-tetrahydrophtalic anhydride where $CHCl_3$ is used instead because of solubility problems. The temperature, pressure, substrate and its concentration, and the hydroformylation time were varied. Special care is taken in order to avoid the presence of oxygen at all times.

2-phase catalysis: Oleyl alcohol (OLOH) is loaded as a 26 weight % solution in cyclohexane into the hydroformylation reactor along with an aqueous solution of $HRh(CO)(TPPTS)_3$ and TPPTS. The hydroformylation conditions are the following:

weight (aqueous phase) / weight (organic phase) = 0.26,

moles P / moles Rh = 7.8,
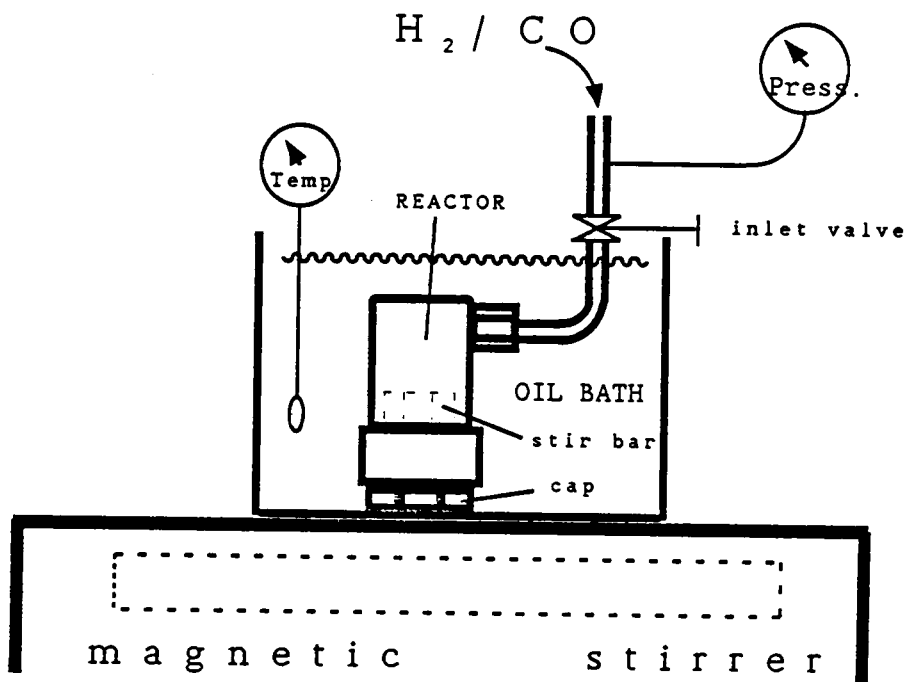
Figure 19. HYDROFORMYLATION APPARATUS.

weight Rh / weight OLOH = 0.0033,

temperature = 100°C,

H_2/CO pressure = 850 psig,

reaction time = 13 hours.

The conversion after the hydroformylation attempt is below the detection limit (0.1%). The aqueous phase, yellow at the beginning of the reaction, is black at the end indicating the decomposition of the catalyst.

Supported Aqueous Phase Catalysis (SAPC): Oleyl alcohol is loaded as a 26 weight % solution in cyclohexane into the hydroformylation reactor along with the *unrehydrated* SAPC. The reaction conditions are the following:

weight Rh / weight OLOH = 0.002,

temperature = 100°C,;

H_2/CO pressure = 725 psig,

reaction time = 5.5 hours.
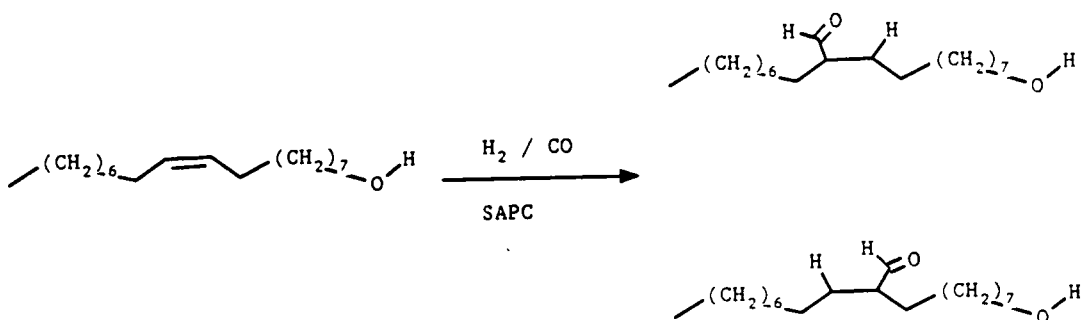
The conversion after the hydroformylation is 96.6% by GC. The SAPC, yellow at the begining of the reaction, remains yellow. The product of hydroformylation of oleyl alcohol is characterized by transmission FTIR and ^{1}H and ^{13}C NMR; the spectra are

consistent with the hydroformylation of the internal double bond of OLOH and are shown in Figure 20 on page 70. Although not detected, it is not possible to rule out some degree of isomerization; the GC peaks are broad because of the tailing caused by the alcohol group. However, the final product is a carbonyl attached to a secondary carbon (the ^{1}H on the carbonyl is a doublet in the NMR spectrum).

Reactions using SAPC hydrated by the procedure outlined before (60 - 70% water) were carried out. The activity of the catalyst is lower. A noticeable feature is the change in the catalyst's color after reaction at 100°C; the catalyst turns brownish if water is loaded into it before the reaction. If SAPC is used unrehydrated there is no noticeable change in its color when the reaction is performed at temperatures under 140°C. The reaction temperature is varied when using the unrehydrated catalyst from 70°C to 140°C and found that the catalyst is active in that temperature range. At 140°C, after 5 hours reaction under the specified pressure (400 psig CO, 400 psig H$_2$), the SAPC used (moles P / moles Rh = 6.9) starts to darken in color.

Both the water loaded and the unrehydrated SAPC were tested to determine if the catalytic phase is "blown out" of the support when suddenly decompressing them from the operating pressure to atmospheric pressure. A qualitative test after 3 decompression cycles reveals that SAPC is still active for hydroformylation. No accurate determinations on activity loss were performed. More detailed and controlled reactions aimed at determining the influence of water in the activity and selectivity of the hydroformylation are shown in the next sections.

Testing for leaching of catalyst from SAPC: A direct method of testing for leaching of the organometallic catalyst from SAPC under reaction conditions is to analyze the solution with the products for presence of rhodium. There is though an important problem with that approach; sensitivity. As it is mentioned in the introduction, the
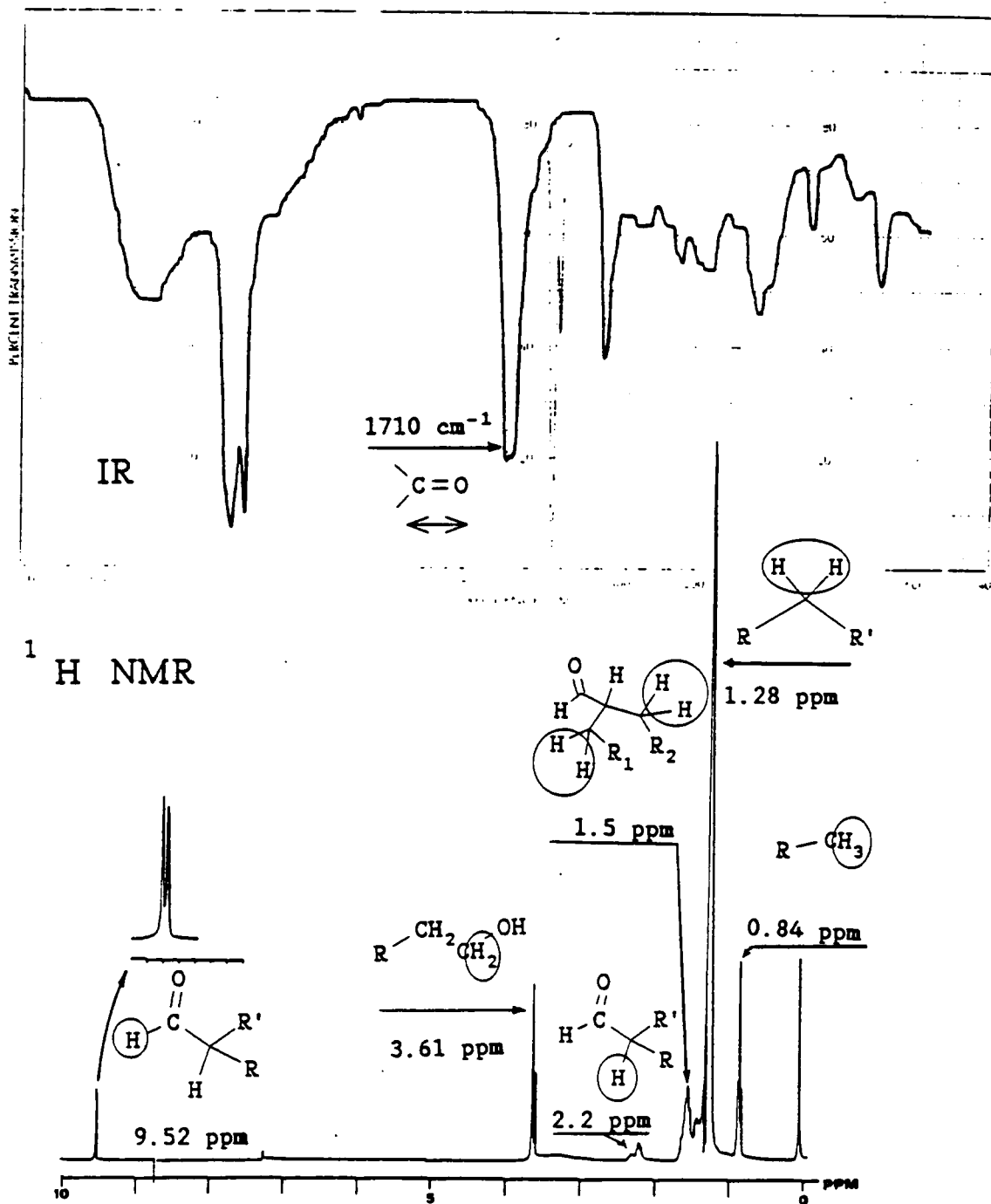
Figure 20. CHARACTERIZATION OF HYDROFORMYLATION PRODUCT OF OLEYL ALCOHOL.

amounts of rhodium lost into the effluent stream that would invalidate its use as a catalyst are extremely small. The analytical methods for testing rhodium at ppb levels are difficult and hard to reproduce. Fortunately rhodium is a very active catalyst for both hydroformylation and hydrogenation. Its ability to catalyze those reactions in parts per billion concentrations is used to detect it in the effluent after reaction.

The slurry after the hydroformylation reaction in the preceding section is filtered under N_2 to separate the solid catalyst. To the liquid, pure oleyl alcohol is added to raise its concentration from 3.4% to 46%. The solution, without the SAPC, is again subjected to the same temperature, H_2/CO pressure and stirring conditions as before for 9 hours. By GC analysis, no increase in the concentration of aldehydes is observed. The cyclohexane is vacuum evaporated away from the solution. To the oleyl alcohol with its hydroformylation products remaining after the evaporation of the cyclohexane, 0.10 ml 1-hexene is added. The reactor is flushed with H_2 and pressurized at 60 psig with H_2. The temperature is raised to 100°C and stirring under H_2 is maintained for 2 hours. No hydrogenation of the 1-hexene is detected indicating no Rh^0 in the system.

Another run filtering the catalyst off after reaction and adding more OLOH is performed in a very similar way as it is described above. This time the attempt of hydroformylation is carried at an increased temperature, 140°C, and during longer time, 13 hours, with the same result which is no increase in the concentration of aldehydes indicating no hydroformylation activity.

Another run is carried out using 1-octene as substrate. The reaction is taken to 98.3% conversion and after filtering SAPC off under N_2 more substrate is added. The reaction is attempted again as before but no conversion is detected.

The evidence accumulated indicates that there is no Rh leaching from SAPC (as an estimation, no more than on the order of 25 ppb).

The tests performed to prove that rhodium does not leach from the support did

reveal a side reaction with OLOH (it is not observed whth 1-octene). An unidentified product with a retention time slightly lower than OLOH increases in concentration during the hydroformylation process. The reaction takes place either with SAPC or after it is filtered off. It is more noticeable when there are comparable amounts of OLOH and its hydroformylation products. By the shape of the peak (no tailing), it is not an alcohol. It has the same peak shape and retention time on the CG as *cis*-13-octadecenal. Blank reactions are performed with OLOH and all the ingredients of SAPC excepting the active complex without the reaction taking place. In another blank a long chain aldehyde is mixed with OLOH and subjected to the same hydroformylation conditions as before but without SAPC and the reaction does not take place. It is very likely that the unidentified product comes from the reaction of OLOH and one or more of its hydroformylation products[47,55].

Influence of water in SAPC: Some aspects concerning the influence of water in SAPC have already been exposed in the preceding section. They are mainly related with the stability of the active species and are mostly qualitative. The influence of the amount of water on the activity and selectivity of the reaction are tested using 1-octene as the substrate for hydroformylation.

20 mg of unrehydrated SAPC is loaded into the reactor, immersed into a thermostatic bath at 30°C and exposed to vacuum. The evacuated catalyst is allowed to adsorb water by exposing the reactor to water vapor from a communicating flask filled with degassed water and immersed also into the 30°C thermostatic bath as shown in the following scheme.
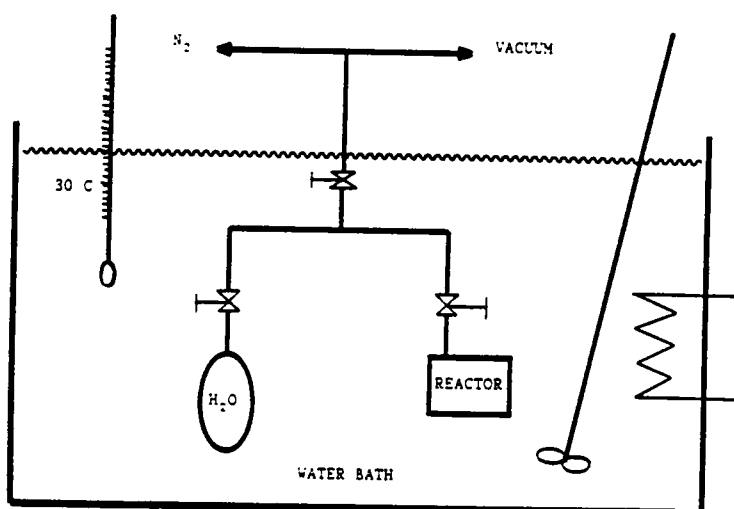
Since both vessels have been previously evacuated the total pressure is equal to the vapor pressure of water at 30°C. The contact with water vapor is held for a period of time t after which Ar is admitted into the system and the reactor immediately closed. The amount of water present in the catalyst is determined by thermogravimetric analysis run on a parallel experiment. Varying the hydration time t, different amounts of water are loaded into the catalyst. Subsequent samples of SAPC with differents amounts of water are used to hydroformylate 1-octene always at the same conditions. The water content of the finished SAPC is analyzed at three different hydration times t = 0 h, t = 2 h, and t = 6 h; the % H_2O is found to be 2.8, 7.5, and 31 respectively. The reaction conditions are the following:

concentration of 1-octene in cyclohexane = 25%,

weight Rh / weight 1-octene = 0.0005,

temperature = 70°C,

H_2/CO pressure = 750 psig,

reaction time = 5 hours.

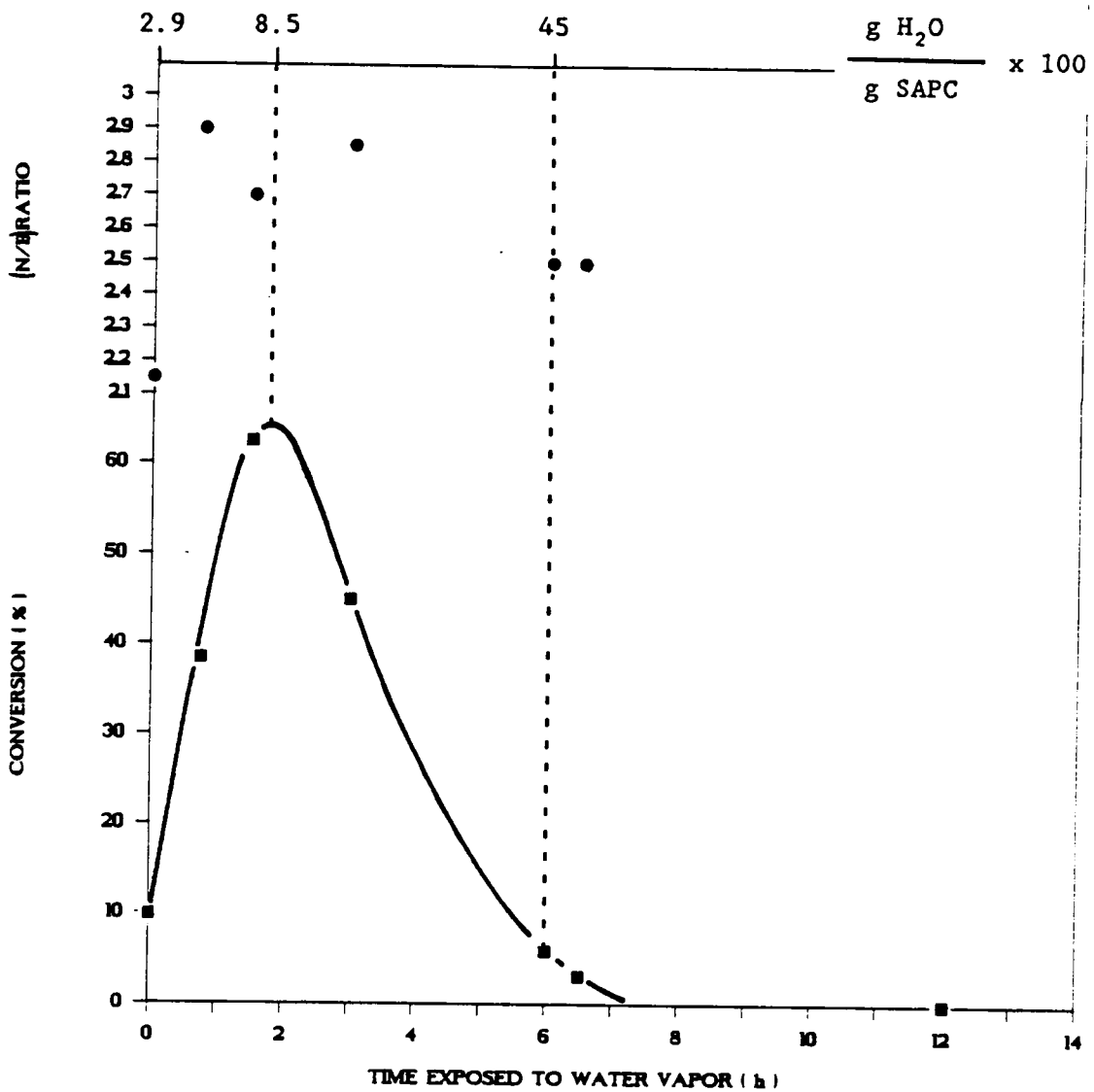The results of the various experiments can be seen in Figure 21 on page 74. It is

Figure 21. INFLUENCE OF WATER IN SAPC. HYDROFORMYLATION OF 1-OCTENE.: One monolayer of water onto the glass support is equivalent to 0.019 $gH_2O/gSAPC$.

evident the dramatic influence of the moisture content in the SAPC on its activity. These effects are disscussed further in the next chapter.

Use of HRh(CO)(TPPTS)₃ without support as a catalyst: The fact that SAPC is active as hydroformylation catalyst even with as little water as 2.9% poses an interesting question to address; does the catalytic species behave as a solid phase catalyst. To address this question and to get another piece of information about the mechanism of reaction, a hydroformylation reaction is set up with just the solid organometallic as catalyst, i.e., no support.

5 mg Rh(CO)₂(acac) (0.0194 meq) and 49.5 mg TPPTS are used to prepare the solid catalyst HRh(CO)(TPPTS)₃ using the procedure outlined before. The precipitation procedure from the water solution using absolute EtOH yields a **very** finely divided solid. A SEM analysis[56] reveals almost spherical particles with a diameter of about 180Å. From this value, assuming spherical particles, a rough estimate of the surface area is calculated; about 100 m²/g.

20 mg of the vacuum-dried complex HRh(CO)(TPPTS)₃ prepared as described above are loaded into the reactor along with 0.40 ml of 20% 1-octene in cyclohexane. The substrate is hydroformylated at 750 psig and 100°C for 5.25 hours.

The conversion is 98.7% with 89.7% aldehydes and a n/b ratio of 1.86. A crude comparison of catalyst activity on an interfacial area basis gives similar results for SAPC and HRh(CO)(TPPTS)₃ without support. The n/b ratio is also comparable. The comparison is further discussed in the next chapter.

Influence of molar P/Rh ratio: A new batch of SAPC is prepared with the same Rh loading as before but with P/Rh $\simeq$ 33 instead of 6.9. The deposition procedure used is

the same. The sample is not hydrated.

20 mg SAPC prepared as described above are loaded into the reactor along with 0.40 ml 20% 1-octene in cyclohexane. The substrate is hydroformylated at 750 psig and 100°C for 5 hours.

The conversion is 65.7% with 61.4% aldehydes and a n/b ratio of 2.3 compared with n/b ratio of 1.8 when P/Rh = 6.9.

Influence of pore radius on activity: To test the pore radius influence on the activity of SAPC a solution of the catalyst is used to impregnate two samples of CPG, one with $r_{av} = 237$Å and another one with $r_{av} = 343$Å. The characteristics of the first CPG have already been exposed, the characteristics of CPG-350 are the following:

Mesh size = -120/+200.

Mean pore diameter = 343Å

PVD = ±5.0 % around the mean.

Pore volume = 0.97 ml/g.

Surface area = 67.5 m²/g.

6 mg of $HRh(CO)(TPPTS)_3$ along with 6 mg of TPPTS are dissolved into 1.2 ml H_2O. 0.4 ml of the solution are used to impregnate 200 mg of CPG-240 and another 0.4 ml are used to impregnate 230 mg of CPG-350. Both amounts of support have 15.5 m² surface area. Thus the same amount of Rh is spread on the same total surface area. There seems to be a difference in the surface chemistry of the CPGs. After the rhodium deposition the SAPC with CPG-240 is yellow while the one with CPG-350 is almost completely white.

After having performed both hydroformylation reactions in the same conditions, the results are the following:

For CPG-240, the conversion is 83.0% with 69.2% aldehydes and a n/b ratio of

2.60.

For CPG-350, the conversion is 97.9% with 69.5% aldehydes and a n/b ratio of 1.84.

Hydroformylation of other substrates: The scope of SAPC using $HRh(CO)(TPPTS)_3$ as catalyst is explored further by attempting to hydroformylate different substrates.

Dicyclopentadiene (DCPD) has been used as a substrate for hydroformylation an was described in Chapter 2. It has also been hydroformylated in a homogeneous reaction[57] using a complex closely related to the one used in SAPC; $HRh(CO)[P(m-PhSO_3NR_4)_3]_3$.

The reaction conditions are the following:

concentration of DCPD in cyclohexane = 50%,

weight Rh / weight DCPD = 0.0002,

temperature = 100°C,

H_2/CO pressure = 750 psig,

reaction time = 5 hours.

The conversion is 74.4%. Only 0.7% dialdehydes are detected. The reaction is carried out for 5 more hours and the conversion is 100% with 9.2% dialdehydes.

t,t-2,4-hexadien-1-ol and 2-acetyl-5-methylfuran were attempted to be hydroformylated under similar conditions to dicyclopentadiene without success,i.e., no conversion was detected.

4.5 Attempts to find a selectivity change by the influence of the interface

4.5.1 Development of a selectivity model.

The feature that makes SAPC different than organic, homogeneous catalysis in terms of possible selectivity variations is the presence of a polar phase in the immediate vicinity of the active site. To exploit that feature the substrate has to align differently or behave differently than in organic, homogeneous catalysis at a critical stage of the catalytic cycle. For the substrate to be influenced by the presence of the adjacent aqueous phase it has to have polar and non-polar groups; the polar group atracting the molecule towards the interface and the non-polar one repulsing it away from the interface. A double bond ajacent to a polar group would be attracted to the interface with more intensity than one adjacent to a non-polar one. Hence, the first double bond would be, on average, closer to the catalyst than the second one. A difference in reactivity towards hydroformylation would be expected if those conditions are satisfied. To test the model, a set of reactants complying with the following condition has to be hydroformylated and the relative reactivities of each of the two double bonds in the molecule has to be determined:

The molecule should have two double bonds equivalent in everyway but in the polarity of at least one group nearby, see following scheme:

DOUBLE BOND 1 (non-polar)   DOUBLE BOND 2 (polar)
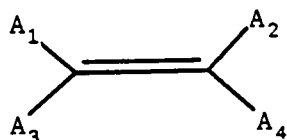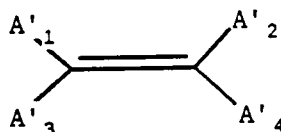
$$A_1 \diagdown \diagup A_2$$
$$A_3 \diagup \diagdown A_4$$

$$A'_1 \diagdown \diagup A'_2$$
$$A'_3 \diagup \diagdown A'_4$$

$$A_i \neq A'_i$$

Where A_1, A_2, A_3 and A_4 are either H or C (with hybridization sp^3, i.e. no double or triple bond). The difference between double bond 1 and double bond 2 is that in double bond 1 there are only H or C attached to *atoms* A_1, A_2, A_3, and A_4; and in double bond 2 there is at least one heteroatom (not being Si) attached to any of the atoms A_1, A_2, A_3, or A_4. The following is the drawing of a possible molecule complying with the aforementioned requirements.

$$H H H H$$

$$H_3C CH_2-CH_2-CH_2-CH_2 CH_2OH$$
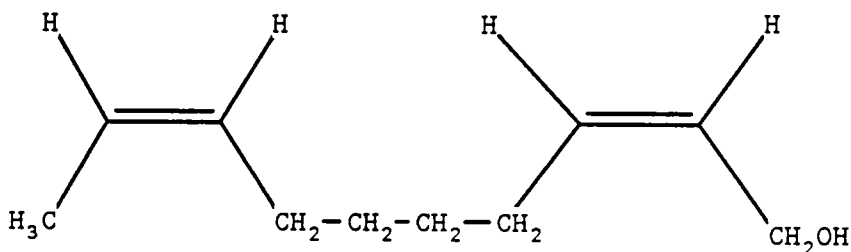
Another type of test, more sophisticated and difficult to perform, can be done using only one double bond with diasterotopic faces. If there is one of the faces that has a polar environment and the other one does not, the interface-catalyst could ideally recognize it.

The requirements are restrictive; there are few molecules commercially available that comply.

4.5.2 Molecules selected

Because of the absolute scarcity of substrates complying with the requirements there are some that are close that have been tried anyway.

cis-1,2,3,6-Tetrahydrophthalic anhydride (THPA)
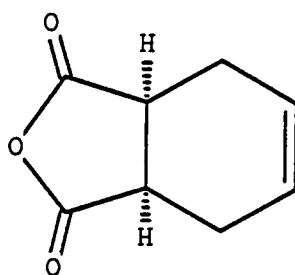
20 mg SAPC, 0.32 ml CHCl₃, and 50 mg THPA are introduced into the reactor and hydroformylated for 5 hours at 100°C and 725 psig. After reaction the filtered slurry is analyzed by HPLC and found no conversion. The reaction is repeated with an even larger catalyst/substrate ratio for a longer time with similar results. In all attempts performed the catalyst after reaction conserves its yellow color likely indicating no decomposition.

cis-Jasmone
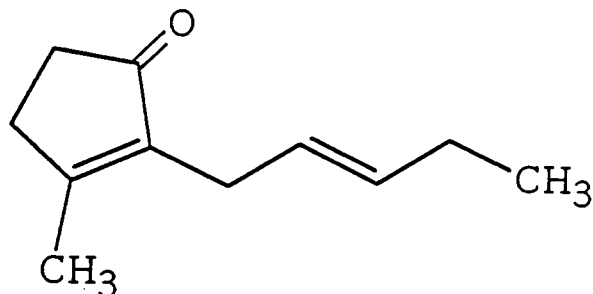
20 mg SAPC, 0.20 ml of *c*-jasmone and 0.20 ml cyclohexane are loaded into the reactor and hydroformylated for 5 hours at 100°C and 750 psig. The substrate is isomerized, partly monohydroformylated, and partly dihydroformylated. The total conversion is 87%, aldehydes represent only 53%, the number of monohydroformylated products is at least one (18% of the total of aldehydes), the number of dihydroformylated products is at least four. The selectivity, if any, is obviously poor.

Stigmasterol (STS)
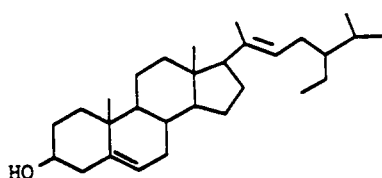
21 mg SAPC, 52 mg STS, and 0.60 ml $CHCl_3$ are loaded into the reactor and hydroformylated for 24 hours at 97°C and 720 psig. After reaction the catalyst has not changed color. The effluent is analyzed by HPLC revealing the partial conversion of the reactant into two products. The products are separated by preparative HPLC and one

of them is analyzed by ^{1}H NMR. It is an isomerization product of STS. The other one is another isomerization product. The double bonds in the lateral chain are not hydroformylated but isomerized. When the reaction is carried out in cyclohexane the conversion decreases substantially. An explanation of the facts is given in the next chapter.

Allyl 9-Decenyl ether: Because of the scarcity of substrates complying with the mentioned requirements the synthesis of one is performed (see following scheme).
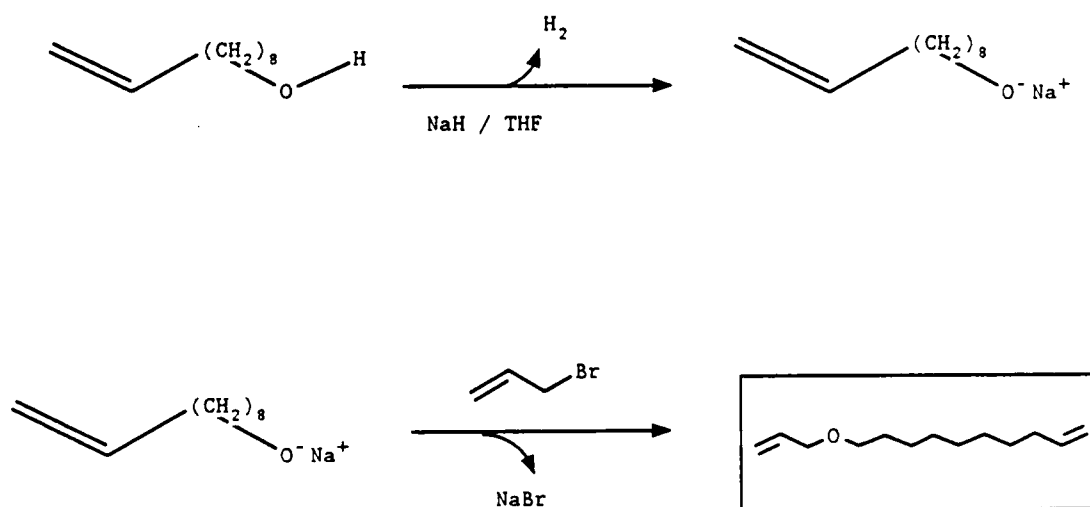
9-Decen-1-ol from Aldrich is analized by GC and HPLC and since its purity is good it is used as received. A technique for the synthesis of allyl ethers is used as reported in the literature[58]

0.65 g dry 97% NaH (0.0263 mol) are suspended in 35 ml dry THF under Ar with vigorous stirring. A solution of 4 g of 9-Decen-1-ol 99% (0.0253 mol) in 25 ml dry THF

is slowly added on the NaH suspension (5 min) and it is refluxed under Ar for about one hour. The mixture turns yellow. It is then cooled down to room temperature. A dissolution of 3.1 g 99% allyl bromide (0.0254 mol) in 5 ml dry THF is added slowly (5 min) while stirring. The mixture forms a white solid in suspension (NaBr) and it is refluxed for approximately 2 hours. The solution is cooled down to room temperature and filtered through a fritted glass under N_2 pressure. Most of the THF is evaporated under vacuum and approx. 30 ml Et_2O are added. The solution is extracted four times with 50 ml deionized water each time. The organic layer is dried with Na_2SO_4 and after filtration the Et_2O is vacuum evaporated. The mixture obtained is analyzed by GC and found that conversion is only 13%. The separation of the product from the unreacted alcohol is performed by column chromatography[59]. The stationary phase is silica gel (230-400 mesh ASTM) deactivated with 10% water, the mobile phase is hexane/ethyl acetate, 9:1. After the separation, CG and ^1H NMR analysis confirm a 95% pure allyl 9-decenyl ether (A9DE).

20 mg SAPC and 0.50 ml of a solution of 0.12 g A9DE in 2.5 ml cyclohexane are loaded into the reactor and hydroformylated for 24 hours at 97°C and 710 psig. After reaction the catalyst is filtered off and analyzed by GC. The conversion is 45%. There is 21% of a monoaldehyde and no dialdehydes, the rest is mainly isomerization products (if the reaction is allowed to proceed further, the dialdehydes start to appear).

The homogeneous reaction is performed in order to compare the product distribution with the one obtained using SAPC.

1 mg of $HRh(CO)(PPh_3)_3/PPh_3$, 1:9 is loaded into the reaction with 0.5 ml of the same A9DE solution as before. The hydroformylation is carried out for 4.25 hours at 97°C and 710 psig. The conversion is 61%. There is 51% of a monoaldehyde and no dialdehydes, the rest is mainly isomerization products. The monoaldehyde produced is the same in both cases. A ^1H NMR analysis reveals that the double bond

hydroformylated is the allylic one.

Chapter 5

DISCUSSION OF RESULTS

5.1 TPPTS

The position of the TPPTS NMR signals in the acid solution before neutralization depend strongly on its concentration. Being an acid solution, the P in the sulfonated phosphine is protonated, as $[HP(m\text{-}Ph_3SO_3H)]^+[HSO_4]^-$, and the extent of the protonation depends on the pH. The resonance position of $[HP(m\text{-}Ph_3SO_3H)]^+$ in the ^{31}P spectrum in Figure 6 on page 35 is, because of the reasons given previously, variable around 1.5 ppm. After neutralization the signal shifts upfield to -5.1 ppm as it can be seen in Figure 7 on page 37 The shift in the OTPPTS's signal from before to after neutralization is, because of the presence of the oxygen, less drastic; it goes from 37 to 34.6 ppm.

The pH changes drastically the position of the peaks and the coupling constants in the ^{13}C spectrum. The changes in the carbon α to the P are the most pronounced as it can be appreciated by a comparison between Figure 6 on page 35 before neutralization, and Figure 7 on page 37 after neutralization and purification.

Table 5.   PREDICTION OF ^{13}C NMR CHEMICAL SHIFTS FOR TPPTS AND OTPPTS

	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8
δa	128.4	125.7	117.9	128.5	130.7	128.4	128.5	125.7
Δ	+0.0	−2.7	−10.5	+0.1	+2.3	+0.0	+0.1	−2.7
δb	128.6	128.5	130.6	127.7	134.2	131.6	130.7	132.9
Δ	+0.2	+0.1	+2.2	−0.7	+5.8	+3.2	+2.3	+4.5
δc	133.6	130.6	133.6	135.8	135.8	131.9	134.1	135.9
Δ	+5.2	+2.2	+5.2	+7.4	+7.4	+3.5	+5.7	+7.5
δd	137.2	144.1	135.1	130.9	130.9	133.7	129.2	147.3
Δ	+8.6	+15.1	+6.7	+2.5	+2.5	+5.3	+0.8	+18.9
δe				137.1	117.8		133.6	
Δ				+8.7	−10.6		+5.2	
δf				144.1	146.3		144.1	
Δ				+15.7	+17.9		+15.7	

BENZENE: 128.4 ppm w.r.t. TMS

δi......chemical shift of carbon i
Δ ....δi−δ(*BENZENE*)

In the ^{13}C NMR *before* neutralization, the carbon bonded to the P (at 113.27 ppm) has a large P-C coupling constant (89.6 Hz) characteristic of protonated phosphines[60]. The other five carbons give smaller coupling constants. The analysis of the spectra and assignment of the peaks are done by analogy with compounds having similar functional groups. Those compounds, found in ref. 59, are the following: $PhSO_3H$, PPh_3, $OPPh_3$, and $[EtPPh_3]^+Br^-$. The review by Gorenstein[61] is also useful. Table 5 depicts the available data and the procedure used. Additivity of displacements is assumed and the Δ values are the shifts with respect to benzene (128.9 ppm w.r.t. TMS). The chemical shifts for TPPTS and OTTPS shown in the table are the predicted ones which compare well with the experimental ones. The resonances at 129.48 ppm (J = 13.1 Hz), 129.78 ppm (J = 13.1 Hz), 131.50 ppm (singlet), 135.78 ppm (J = 10.6 Hz) and 141.06 ppm (J = 14.1 Hz) are assigned to the carbons B, C, D, E, and F (see Figure 6 on page 35) respectively. The assignment of the signals in the spectrum after neutralization is more difficult because the resonances are much closer together.

Although the purification procedure proves to be very good in terms of the purity of the product obtained, the yield is low. The synthesis of the organometallic complex using TPPTS produces OTPPTS and the deposition procedure also produces OTPPTS. Since the work-up procedure for $HRh(CO)(TPPTS)_3$ eliminates OTPPTS, a so thorough purification procedure for TPPTS is probably not necessary in this case. A purification based only on the extraction of TPPTS with tributylphosphate is probably adequate for this synthesis.

5.2 ClRh(TPPTS)₃

This complex has been thoroughly studied by Patin's group along with its preparation procedure. They also found that TPPTS and PPh₃ have approximately the same basicity[37a]. Patin and coworkers report that they attempted the ligand exchange between ClRh(PPh₃)₃ and TPPTS using a very similar method as the one used in this research. They found the same lack of driving force towards the exchange and they attribute it to the fact of both ligands having the same basicity. Another common feature with this research is the fact that they could not avoid the oxidation of TPPTS to OTPPTS during the exchange. There are, though, differences. Patin reports that they could not synthesize ClRh(TPPTS)₃ in absence of either NaCl, HCl or HClO₄. Performing the synthesis at low temperature the desired complex is formed in 60% yield in this research. However, Patin et al. report a quantitative conversion when a NaCl solution is used; a result that was not achieved by following a similar procedure here (although an optimization was not attempted). It is interesting to note that the synthesis of the intermediate (COD)RhCl(TPPTS) was achieved without any oxidation of TPPTS; the degradation comes in the second step of the synthesis in this work.

The interpretation of the ³¹P NMR spectrum is reported in ref. 37c. The doublet of triplets downfield represent the phosphorus atom trans to the halogen and the doublet of doublets upfield represents two phosphorus atoms trans to one another. The coupling constants reported; J(P-P) = 39 Hz, J(P₁-Rh) = 144 Hz and J(P₂-Rh) = 193 Hz compare fairly well with the values in this research (J(P-P) = 39 Hz, J(P₁-Rh) = 156 Hz and J(P₂-Rh) = 170 Hz). The values for the chemical shifts differ somewhat probably because of very different Cl⁻ concentrations; δP_1 = 34.4 ppm and δP_2 = 50.8 ppm reported vs. δP_1 = 36.7 ppm and δP_2 = 51.1 ppm from this research.

5.3 HRh(CO)(TPPTS)₃

It is noticeable in the synthesis developed for HRh(CO)(TPPTS)₃ the need of CO in the hydrogenation step (see Figure 9 on page 43). If no CO is added to the H_2 after the first ligand exchange in the synthesis, (acac)Rh(CO)₂ with TPPTS, the conversion to HRh(CO)(TPPTS)₃ is unlikely to occur. The presence of CO assures the completion and reproducibility of the reaction. This **may** indicate that the intermediate is not (acac)Rh(CO)(TPPTS) but (acac)Rh(TPPTS)₂ instead; the CO would be needed to complete the reaction[62]. In the purification procedure the lower solubility of HRh(CO)(TPPTS)₃ in EtOH enables its separation from TPPTS and OTPPTS. This is very useful since the separation of OTPPTS from TPPTS is by itself a very difficult task. The separation of OTPPTS and TPPTS by such a fractional crystallization is very poor. However, it works very well when the total charge in the molecule is multiplied by three, i.e., in HRh(CO)(TPPTS)₃.

The ³¹P NMR spectrum of HRh(CO)(TPPTS)₃ in D_2O compares very well with the one lately reported by investigators at Exxon[36], after our work was complete; δP = 43.7 ppm and J(Rh-P) = 156 Hz found vs. δP = 42.8 ppm[36] and J(Rh-P) = 156 Hz[36]. The interpretation of the doublet in the ³¹P as indicating a trigonal bipyramid is also shared by the Exxon group. The similarity to the ³¹P spectrum of HRh(CO)(PPh₃)₃ is good; δP = 39.8 ppm and J(Rh-P) = 155 Hz.

The FTIR absorptions for Rh-H and CO obtained with the solid HRh(CO)(TPPTS)₃ and the ones reported for the solids HRh(CO)(PPh₃)₃ and HRh(CO)(dpm)₃, and HRh(CO)(TPPTS)₃ dissolved in water are shown in Table 6 on page 90.

The CRAMPS experiments performed on the solid HRh(CO)(TPPTS)₃ (see

Table 6.   IR ABSORPTIONS OF COMPLEXES RELATED TO HRh(CO)(TPPTS)$_3$

	H-Rh (cm^{-1})	CO (cm^{-1})
HRh(CO)(PPh$_3$)$_3$ [*]	2041	1923
HRh(CO)(dpm)$_3$ [*]	2000	1910
HRh(CO)(TPPTS)$_3$ [**]	2017	1933
HRh(CO)(TPPTS)$_3$ [***]	2000	1921

[*]   Solid. From ref. 34

[**]   Aqueous solution. From ref. 36

[***]   Solid. This work.

Figure 16 on page 59) show the presence of the hydride signal at -8.5 ppm, the aromatic protons at 7-8 ppm, a broad signal in the region 3.5-4.5 ppm assigned to water and two more small sharp peaks at 0.2 and 5.8 ppm probably from occluded ethanol. The deconvolution also shows two more small peaks at 1.5 ppm and 7 ppm the assignments of which is uncertain at the moment. The hydride signal is the first one reported by CRAMPS[63]. The dipolar diphasing experiments are discussed along with the ones performed on CPG and SAPC. Taking into account the trigonal bipyramid structure of HRh(CO)(TPPTS)$_3$ a rough estimation of the size of the molecule is calculated using CHEMX[64]. The three bulky phosphines surround the Rh atom forming a platform approximately 15Å in diameter (about 170Å^2 in surface) and 8Å in height. The following is a sketch of the organometallic complex.
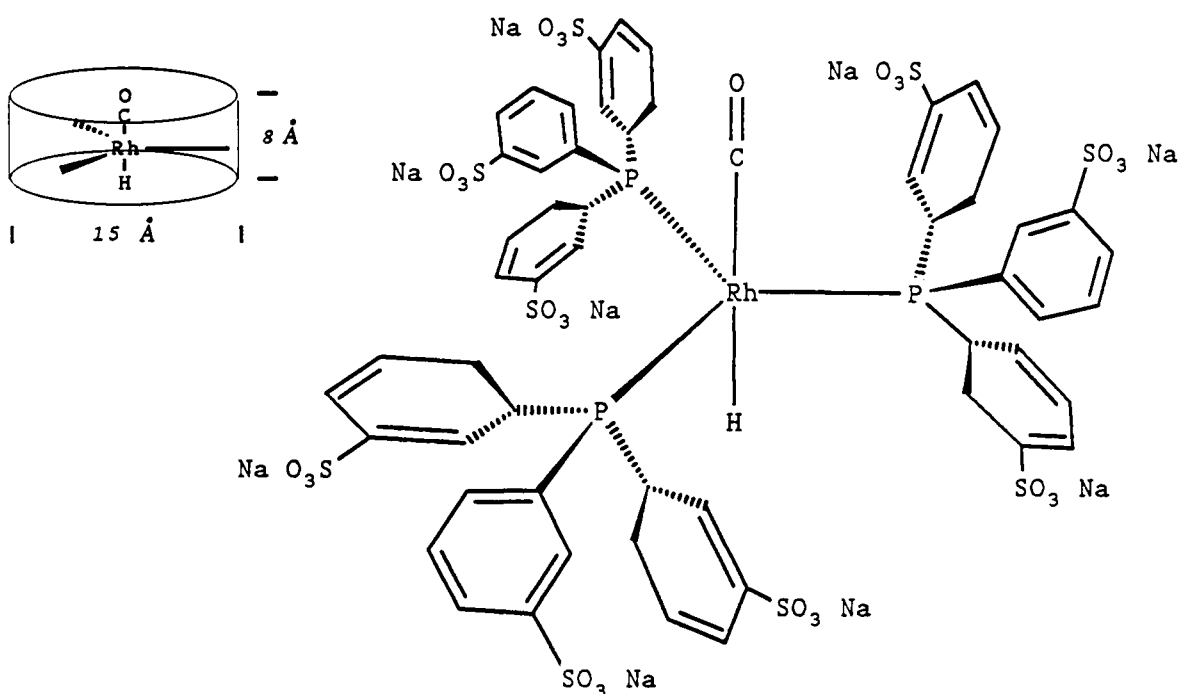
5.4 Solid Support

The calculations about the amount of water needed to get a layer thickness of 50Å lining the pores of CPG-240 have been done assuming a network of non-interconnected pores. To relax this assumption is a difficult task that requires knowledge of the type of connectivity in the network. However, although the change in surface area is not the same if the pores are in fact interconnected, it is not a dramatic change. As an example, a quick calculation using square channels with and without interconnections is done. When there is one intersection of three mutually perpendicular channels (3-D network) every three channel diameters (actually channel sides since they are assumed square) the error committed assuming non-interconnected channels is less than 7%.

With respect to the PVD analysis, from the data given in experiments with IDs 05 to 18 shown in Table 4 on page 50 it can be concluded that if the amount of sample is too large for the N_2's intake flow rate, the pressure changes per unit time in the holder are too small. Under those conditions, since the curve pressure vs.time is almost completely horizontal in the capillary condensation region, the noise produces very large variations in the inverse of the slope of the digitized curve. The software calculates the PVD essentially by calculating the inverse of the derivative of the curve pressure vs. time. See following scheme:

P | | t

W | | r

$\frac{dW}{dr}$ | | r
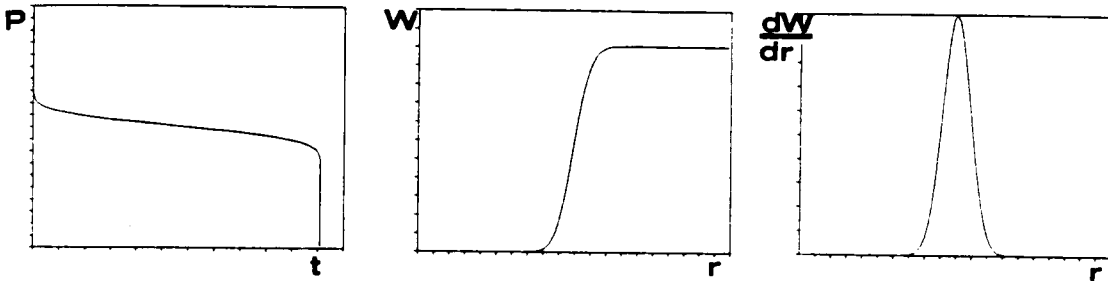
After converting the raw data from:

1)*time* to *amount* of N_2 adsorbed using the flow rate and other parameters that previously measures, and

2)*pressure* to capillary *radii* using the Kelvin equation, the instrument gets the curve capillary radii vs. amount of N_2 adsorbed. To get the derivative of the curve the software apparently calculates the quotient of the differences between two adjacent ordinates and their correspondent abscissas.

From the Theory of Propagation of Errors,

$$E(PVD) = \partial \frac{(\frac{\Delta W}{\Delta r})}{\partial W} \Delta W + \partial \frac{(\frac{\Delta W}{\Delta r})}{\partial r} \Delta r$$

Where E(PVD) is the error in the PVD.

Since the first term in the right hand side of the equation is much smaller than the second:

$$E(PVD) \simeq \partial \frac{(\frac{\Delta W}{\Delta r})}{\partial r} \Delta r$$

For a flat curve, at the inflexion point: $\quad \partial \dfrac{(\frac{\Delta P}{\Delta t})}{\partial t} \to \pm \infty$

so $\quad \partial \dfrac{(\frac{\Delta r}{\Delta W})}{\partial r} \to \pm \infty \quad$ which in turn implies that

$$\partial \frac{(\frac{\Delta W}{\Delta r})}{\partial r} \Delta r \to \pm \infty \quad \text{so} \quad E(PVD) \to \pm \infty$$

For a given error bar in the ordinates, the error bar in the inverse of the derivative is inversely proportional to its value. Since its value approaches zero (flat curve), the absolute value of the error in the ordinate of the PVD curve goes to very large values. The fact that the software does not fit the experimental values by any numerical method makes things worse since the random variations in pressure (noise) dominate. This behaviour is reflected in the experiments shown in Figure 12 on page 52.

The next feature noticeable from runs 05 to 18 is the reproducibility of the r_{av}, they are all around ± 5 Å from the mean. In spite of that it is also very noticeable the large discrepancy between the value from mercury porosimetry provided by the manufacturer (ID = 00) and the values given by N_2 adsorption using this instrument.

The main conclusion from these experiments is that the support loaded with water loses it in the course of the experiment. It is very likely that when the holder with the loaded CPG is immersed in the liquid N_2 to start the experiment, before the water can freeze in the pores and get immobilized, it evaporates from them and condenses on the cold wall of the holder. That behaviour has been seen in other similar situations and has also been suggested to happen under these circumstances[65]. This behaviour invalidates the proposed analytical method. There is an alternative method that could be used with some modifications to determine the way the aqueous layer is deposited on the support[66]. It is a recent development based on low-field NMR experiments performed on water-loaded solid supports that could probably be adapted to serve the needs of this research. The NMR technique should be explored in the future.

5.5 SAPC

From the solid-state NMR experiments performed on $HRh(CO)(TPPTS)_3$-based SAPC some conclusions can be drawn about the catalytic species on the surface of the support[50]. The ^{13}C CP/MAS NMR performed on the sample do not yield a high enough signal to noise ratio to obtain a good spectrum. However, from the improvements in signal to noise by varying the contact time, it can be concluded that the proton relaxation time is on the order of a couple of seconds. The only signal visible is the one coming from the phenyl groups, no signal from the carbonyl is noticeable.

From the ^{31}P spectra (see Figure 14 on page 56 and Figure 15 on page 57). it can be inferred that the complex is rather immobile on the tens of kHz time scale; the spinning sideband array is fairly intense; the chemical shift anisotropy is large. The

phosphine is not undergoing large-amplitude motion that would partially average the chemical shift anisotropy.

[1]H CRAMPS spectra and dipolar diphasing experiments shown in Figure 16 on page 59 and Figure 17 on page 60 reveal some interesting features of this SAPC. In previous publications using silica-gel the broad resonance at 4-5 ppm has been assigned to hydrogen-bonded silanols[51]. The dephasing experiments performed in this case reveal a different behaviour; the decay rate of the signal is slower than in a typical silica-gel. Instead this resonance could be water associated with the complex; it has been noted that the ligand is extremely hygroscopic so it is very likely that part of the water present on the surface is strongly associated with it with restricted movement. It is interesting to note the absence of the hydride signal in the supported complex; that signal is present at -8 ppm in the unsupported HRh(CO)(TPPTS)$_3$. This absence could be due to the abstraction of the hydride itself as it has been noted before[67], or to other complex-support interactions affecting the behaviour of the hydride in the NMR experiment[63].

5.6 SAPC hydroformylation

The hydroformylation of heavy molecules like OLOH by traditional methods carries an already discussed problem; the separation of the catalyst from the product. The fact that it can be hydroformylated using SAPC indicates the first success of the new immobilization technique. OLOH cannot be hydroformylated using a two-phase system. Its hydroformylation is not a simple task; the same company that developed the water-soluble hydroformylation system had to resort to a cumbersome procedure like the

one depicted in ref. 54. The procedure essentially performs a homogeneous hydroformylation using HRh(CO)[P(m-PhSO$_3$NR$_4$)$_3$]$_3$ as a homogeneous organic-soluble catalyst. After reaction the separation of the catalyst is achieved by hydrolyzing the catalyst to the sodium salt with NaOH and separating it into the aqueous layer. The catalyst suffers ostensible decomposition (about 4% of it remains in the organic phase after one extraction) and some problems arise due to the presence of a strong alkali with an aldehyde. A schematic comparison between the two processes is shown in Figure 22 on page 98

It is also noticeable the enhancement in stability of the catalytic species achieved by its heterogenation as SAPC with respect to the aqueous unsupported species. The restricted mobility of the complex on the surface of the support detected by solid-state NMR may be attributed as the cause for the increase in stability. It may be blocking an intramolecular deactivation mechanism requiring greater mobility to occur[68]. That would also explain the decrease in activity with large water contents as seen in Figure 21 on page 74. It also seems evident from the same plot that an increase in activity is achieved with an increase in mobility; the first part of the plot, with increasing water concentrations, indicates that type of behaviour. Hence, there are two opposing effects taking place. At the position where the two effects compensate each other, a maximum is observed in the activity of SAPC. There is a strong analogy between unhydrated SAPC and a non-mobile solid-like catalytic complex manifested in the solid-state NMR experiments. That analogy is reinforced by the similarity with the results obtained in the hydroformylation of 1-octene using unsupported HRh(CO)(TPPTS)$_3$. It has to be noted, however, that the use of such unsupported catalyst is not only disadvantageous because of using about 20 times more Rh but also because of the extremely small particle size.

It has been noted that the for a given *ligand to Rh* ratio the *normal to branched* ratio

REACTION CONDITIONS

	SAPC	RUHRCHEMIE
g Rh / g substrate	0.2×10^{-2}	0.76×10^{-4}
% substrate conc. in sol.	25	63
CO/H_2	1	1
P (psig)	725	4000
T (°C)	100	130
time (h)	5.5	6
Conversion (%)	96.6	99.5
Approach	HETEROGENEOUS	HOMOGENEOUS

Figure 22. HYDROFORMYLATION CONDITIONS IN REF.54 AND USING SAPC

for the aqueous hydroformylation of propylene is higher than for the non-aqueous one[62], i.e., HRh(CO)(TPPTS)$_3$ is more selective than HRh(CO)(PPh$_3$)$_3$. Nevertheless, the n/b ratios obtained using SAPC suggest a similarity between the catalytic species in SAPC and HRh(CO)(PPh$_3$)$_3$. A 10-fold excess of PPh$_3$ using HRh(CO)(PPh$_3$)$_3$ as the catalyst gives a n/b ratio of 2.3[24]. The n/b ratio obtained when using SAPC with moles P / moles Rh = 33 is also about 2.3 (altough all things considered, n/b is not dependent on P/Rh but on the ligand concentration). The apparent regression in selectivity for a given ligand / Rh ratio can be rationalized in the following way: I) In the deposition procedure some of the TPPTS is oxidized to OTPPTS so the actual moles ligand / moles Rh ratio is lower than the moles P / moles Rh ratio. II) It has been noted that chelating phosphines lead to a lower n/b ratio due to the impossibility of the P atoms to be trans to each other in the catalytic cycle[69]. The same argument can, most likely, be applied in this case assuming a restricted movement of the ligands.

The lack of hydroformylation activity of SAPC towards *t,t*-2,4-hexadien-1-ol and 2-acetyl-5-methylfuran is not surprising since their double bonds have additional stabilization derived from the fact of being conjugated and aromatic double bonds respectively.

Having proved that the hydroformylation reaction occurs at the interface, Figure 23 on page 100 shows a scheme of the mechanism that we postulate operates. The main difference with the homogeneous one is that the reactant and the catalyst are in different phases, the consequences of which have already been discussed.
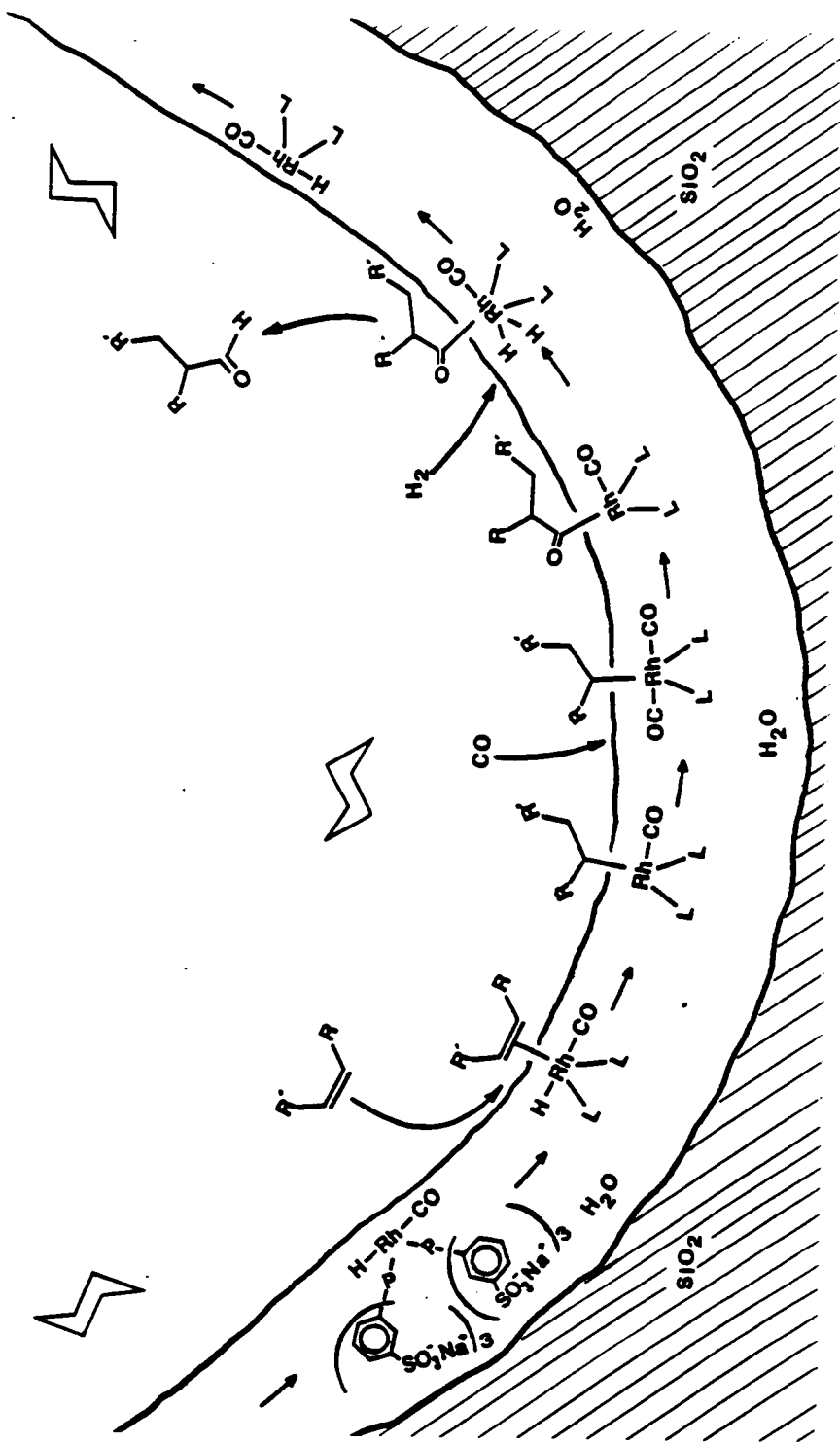
Figure 23. PLAUSIBLE HYDROFORMYLATION MECHANISM USING SAPC

5.7 Attempts to find a selectivity change.

The criterion established for the selection of molecules to hydroformylate proves to be too restrictive for the olefins commercially available. From the olefins used, only allyl 9-decenyl ether (not commercially available) strictly complies with the requirements. Also, cis-1,2,3,6-tetrahydrophtalic anhydride (THPA) is an example of the type of reactants having a double bond with a diasterotopic face. THPA does not react probably because of some type of strong interaction between the two carbonyls and the complex.

The molecular structure drawn in the previous chapter for the hydroformylation of stigmasterol is the one given by the handbook CRC[70], the molecule complies with the set of requirements. The stigmasterol that Sigma[71] sells has another structure and the reaction taking place is the isomerization of the non polar double bond as shown in the following scheme:
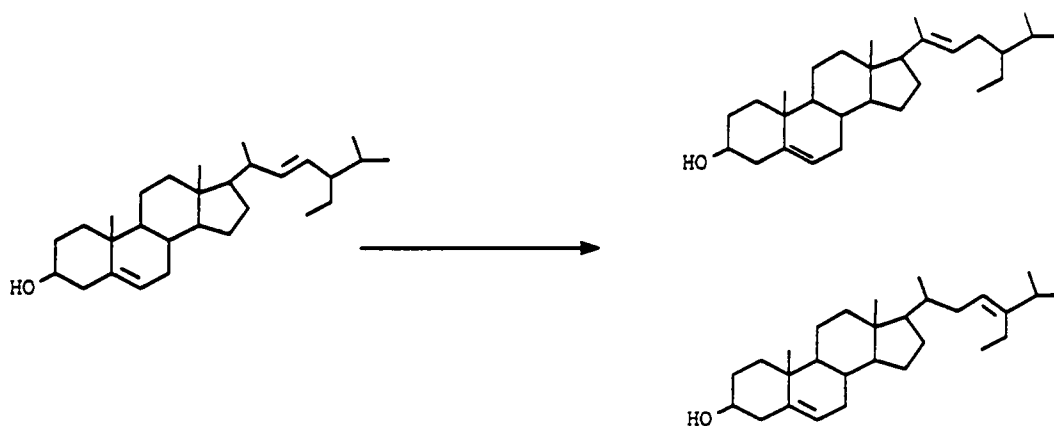
A ^{1}H NMR analysis on one of the products indicates very clearly the migration of the double bond to the position indicated in the previous scheme. The higher conversions are obtained using CHCl$_3$ as solvent, probably because of some residual acidity.

The yields in the synthesis of allyl 9-decenyl ether are low. This is probably because the NaH was partly deactivated. A more common practice in organic synthesis is to use a suspension in mineral oil.

No selectivity differences between homogeneous catalysis and SAPC were found. However, these results do not prove that it is not possible to obtain selectivity variations. One problem is that the minimum reasonable temperature in a reaction like hydroformylation is probably too high for this type of selectivity to be significant. A high temperature favors disorder in any possible orientation caused by the presence of the interface[72]. A reaction carried out at a lower temperature has better probabilities of success. Such reaction could be the hydrogenation of a double bond. Hydrogenation reactions can be carried out at room temperature using catalysts similar to Wilkinson's.

Chapter 6

CONCLUSIONS

The following conclusions can be drawn from the research documented in this dissertation:

i)   A new method for the heterogenation of organometallic complexes was developed: Supported Aqueous Phase Catalysts.

ii) A new procedure for the synthesis of ClRh(TPPTS)$_3$ was found.

iii) A procedure for the synthesis and purification of HRh(CO)(TPPTS)$_3$ was established.

iv) An effective procedure for the deposition of an aqueous phase which contains an organometallic complex onto the surface area of a narrow PVD support was developed.

v)   HRh(CO)(TPPTS)$_3$ is able to be deposited onto the surface area of a glass support when using the described procedure.

vi) A HRh(CO)(TPPTS)$_3$-based SAPC exhibits catalytic activity for the hydroformylation of non-conjugated, non-aromatic olefins.

vii) The activity and stability of a HRh(CO)(TPPTS)$_3$-based SAPC show a strong dependence on water content.

viii)A HRh(CO)(TPPTS)$_3$-based SAPC performs catalysis at the interface between a polar phase and a non polar phase.

ix) A HRh(CO)(TPPTS)$_3$-based SAPC does not leach detectable amounts of rhodium to the reactant/product solution when subjected to hydroformylation conditions.

Chapter 7

RECOMMENDATIONS FOR FUTURE WORK

A HRh(CO)(TPPTS)$_3$-based SAPC was investigated and its most general features were shown. However, much remains to be known in terms of a complete characterization of the system as a hydroformylation catalyst.

Further studies concerning the present system. Studies related to the kinetics of the SAPC hydroformylation should shed light on the nature of the reaction by a comparison with the homogeneous results. Those studies should include the influence of the H$_2$ and CO pressure, temperature, and nature of the olefin. The studies should be able to differentiate between kinetic and transport effects. Several supports with different pore diameters should be used in order to obtain more evidence concerning the influence of the pore radius and the surface area in the activity of the catalyst. The influence of the amount of catalyst loaded into the support on the activity of the catalyst should also be studied. Investigations aimed at optimizing the deposition procedure should include the adaptation of the NMR technique used to determine the PVD (mentioned in a previous chapter). A more complete study of the influence of the molar ratio P/Rh on the activity and selectivity should be carried out.

Modifications to the present system. The changes of the activity and selectivity of

the catalyst caused by the use of water-soluble cosolvents in the catalytic layer, such as ethanol, ethylene glycol and glycerine, should be studied. A systematic study of the various organic solvents that can be used to dissolve the reactants would also constitute valuable information when different substrates are hydroformylated. The influence of different polar cosolvents and different organic solvents on the Rh leaching and catalyst stability should also be investigated.

Other complexes, other reactions Currently, the hydroformylation of long-chain olefins is performed with the use of a Co-based catalyst. One of the reasons for its use consists in the difficulty in separating the catalyst from the products in an economical way if Rh is used as catalyst. Another reason is the ability of the Co-based catalyst to isomerize olefins that are converted to linear aldehydes. For SAPC to be able to compete in that process, a system able to isomerize as well as hydroformylate olefins should be developed. An additional desirable feature would be that the hydrogenation of the aldehydes to alcohols could be performed in the same reactor. The development of such a system would be highly desirable.

The preparation of a member of the SAPC family which is able to catalyze a selected reaction at low temperature may permit better study of the effect of geometry at an interface. As it was mentioned in the previous chapter, a hydrogenation reaction is a good candidate. Neither ClRh(TPPTS)₃ nor HRh(CO)(TPPTS)₃ give hydrogenation activity. The central atom could be varied to provide for the desired activity, or the ligands could be changed leaving Rh as the central atom. TPPTS has been demonstrated to be useful in maintaining a complex on the support without leaching. For that reason TPPTS should be left as a ligand, or at least replaced with a very similar one. Other water soluble complexes (based on Rh(I), Pt(II), Pd(II) and Mo(0)) using TPPTS as ligand have been prepared[37a] and may be tried as active species for SAPC. Other reactions using SAPC that can be explored are dimerization,

codimerization, hydrocyanation and metathesis of olefins and arene-olefin coupling.

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