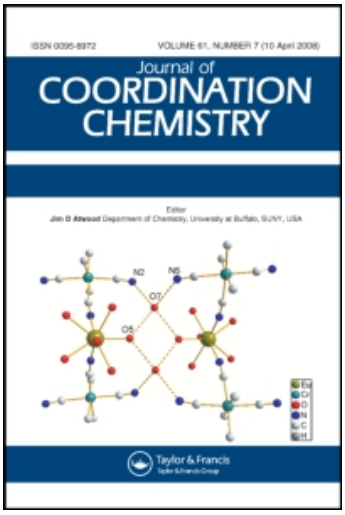

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Mark Barton[a]; Jim D. Atwood[a]
[a] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York, USA

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AQUEOUS SOLUBLE ORGANOMETALLIC COMPLEXES

MARK BARTON and JIM D. ATWOOD*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214, U.S.A.

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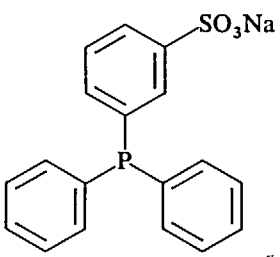
INTRODUCTION

This paper is a survey of the literature on water soluble organometallic complexes. The motivation for this area of research is intrinsic interest in organometallic complexes dissolved in water and in the potential industrial benefits from aqueous soluble catalysts.

The biphasic system for catalytic processes facilitates separation of the organic phase containing substrate and product from the aqueous phase which contains the catalyst. This permits the catalyst to be recycled in the aqueous phase without separation/precipitation and with little attrition of catalyst, thus precluding the problem of extraction typically encountered with homogeneous catalysis. The economic and environmental advantages of working in an aqueous phase are apparent.

Aqueous Soluble Ligands

There are several ligands that solubilize a metal complex in aqueous solution. Generally, a typical ligand used in catalysis is functionalized to enhance its water solubility. The first water soluble phosphine-based ligand was synthesized in 1958, *m*-sulphophenyldiphenylphosphine.[1] This ligand has been given the abbreviations *m*-sP(Ph)$_2$, dpm and TPPMS. In this paper it will be referred to as TPPMS.



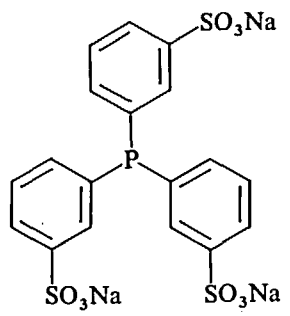
TPPMS

* Author for correspondence.

Hydrophobic transition metal complexes constructed with triphenylphosphine can become water soluble by direct exchange of TPPMS with a PPh_3 ligand.[2] A dichloromethane solution of metal complex, $M_x(PPh_3)_y$, is combined with an aqueous solution of TPPMS, an exchange occurs, and $M_x(PPh_3)_{y-1}$(TPPMS) is extracted into the aqueous phase. Addition of THF to the separated aqueous phase will precipitate the now water soluble complex. The exchange also occurs in media (CH_2Cl_2/THF, 1 : 1) that provide solubility for TPPMS and the triphenylphosphine complex. The reaction may be accomplished either at room temperature or under reflux. The water soluble complex crystallizes with addition of a non-polar solvent or upon cooling.[2] The single phase method gives a superior yield.

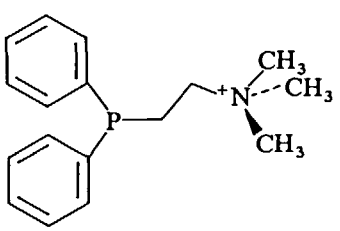
Compounds incorporating TPPMS have been immobilized on anion exchangers to create a stable heterogenized catalyst.[3] Transition metal complexes attached to appropriate supports by ionic/covalent fixation have been successful catalysts for hydrogenation, hydroformylation, and carbonylation and dominate the industrial market for the production of hydrogen.[3-5]

Another frequently cited ligand for assisting in water solubility is the tris(*m*-sulphophenyl)phosphine (TPPTS).[6-16] This ligand, which has been patented by Rhone-Poulenc Industries,[17] is similar to TPPMS, except that all three benzene rings are sulphonated *meta* to the phosphorus bond.



TPPTS

A cationic ligand sometimes selected for the aquation of a catalyst is amphos ($[Ph_2PCH_2CH_2NMe_3^+]$).[18-20] The preparation of metal-carbonyl derivatives can be achieved by using equimolar amounts of metal carbonyl, trimethylamine oxide [$(CH_3)_3NO$] and neutral aminophosphine ($Ph_2PCH_2CH_2NMe_2$) in methylene chloride at low temperatures. A monodentate ligand coordinated through phosphorus results (in good yield).[18] Addition of methyl iodide produces amphos with iodide as the anion.



AMPHOS

Applications to Catalysis

By far the most common area affected by water soluble transition metal complexes is catalysis. Many catalytic processes including hydroformylation, hydrogenation, sulfur removal, nitrogen extraction and oxygen removal have been reported using either a biphasic system or a transition metal phase transfer technique.[21] An application using water soluble ligands in photo-induced catalytic reactions for hydrogenation and hydroformylation of ethene and acetylene has been reported. Photolysis was essential to facilitate catalytic activity.[22,23]

Attempts to utilize water soluble chiral diphosphine derivatives in two phase catalytic hydrogenation of prochiral olefins have been studied.[24-31] The solvent system appears to have a significant impact on enantioselectivity. Water was, of course, one of the solvents tested, and provided the least favourable results with lower enantiomeric excesses. Catalysts with chiral sulphonated phosphines were used to determine the mechanistic route of the reaction.[27]

Carbonylation was performed in a biphasic system on benzyl chloride using $PdCl_2(TPPMS)_2$.[32] Benzylic halides were carbonylated using a sulphonated phosphine-palladium compound with the addition of trialkylamines as a phase transfer agent or under a two phase technique with a high pH. The reduction of aldehydes into their corresponding alcohols was performed under similar conditions with ruthenium as the metal and HCOONa as the hydrogen donor.[33]

In most of the water soluble transition metal catalytic chemistry reviewed, excess ligand was necessary for optimum yields. An exception was hydrogenation using amphos.[19] Also, the hydroxypalladation of allyl alcohol was reported to have the rate expression[34] given below.

$$-d[C_6H_6O]/dt = k[PdCl_4^{2-}][C_6H_6O]/[H^+][Cl^-]^2$$

The rate law implies additional ligand retards conversion. Palladous chloride was made pseudo-catalytic by addition of *p*-benzoquinone to re-oxidize palladium(0) to palladium(II).

For most of the aqueous compounds as well as their organic-soluble analogues, air sensitivity is a problem. Introduction of additional ligand does not increase stability for aqueous soluble complexes in contrast to the lipophilic analogues. Cosolvents in the aqueous phase greatly affected the rate, and varying the total volume of the aqueous phase slightly altered the rates.[35]

A general difference in the water soluble complexes versus their unfunctionalized analogues was that they did not poison with repeated use. The aqueous complexes were capable of reacting without excess ligand. However, the yield was lower. Comparison of $HRh(CO)(TPPTS)_3$ to $HRh(CO)(PPh_3)_3$ using a high pressure NMR technique has been reviewed.[36]

Ionic phosphine ligands permit transition metal phosphine compounds to become aqueous soluble catalysts for all of the reactions previously mentioned. The kinetics of catalytic reactions by complexes of water soluble phosphines have rarely been addressed. The kinetic studies of hydrogenation in the presence of $RhCl(TPPMS)_3$ were described.[37] A detailed kinetic examination of $K[Ru(EDTA)(Cl)]\cdot 2H_2O$ (EDTA = ethylenediaminetetraacetic acid) in the hydroformylation of allyl alcohol was accomplished by Khan *et al.*[38] The reaction conditions were much more severe (50 atm $CO:H_2::1:1$ and 130°C and produced a lower yield of desired product (35% 4-hydroxybutyraldehyde) over a 14 hour period than the water soluble

rhodium system (80°C and 8 atm, CO/H_2 : 1/1, producing a 90% yield). This system is discussed at length in a later section.

DISCUSSION

Hydroformylation and Hydrogenation

Kalck *et al.* have studied the hydroformylation, hydrogenation and the water–gas shift reaction using the water soluble tris(*m*-sulphophenyl)phosphine, TPPTS, prepared by Rhone-Poulenc Recherche, which has patents related to the use of TPPTS (including hydroformylation of propylene to butyric aldehyde by a biphasic rhodium system).[17,39] Three rhodium complexes were examined: $Rh_2(\mu\text{-S-tBu})_2(CO)_2(TPPTS)_2$, $HRh(CO)(TPPTS)_3$ and $[Rh(COD)(TPPTS)_2]^+$ (COD = cyclooctadiene). The cationic species was an extension of the research on the monosulphonated triphenylphosphine complex, $[Rh(COD)(TPPMS)_2]^+$ which was found to be active in the water–gas shift reaction.[40] The dirhodium compound significantly outperformed the mono metal complexes with regard to conversion and straight chain yield (see Table I). The following discussion pertains to $Rh_2(\mu\text{-S-tBu})_2(CO)_2(TPPTS)_2$.

The focus was primarily on the hydroformylation of 1-hexene using a biphasic system.[6–9] The complex was placed in 25 cm^3 water (pH = 6, T = 80°C) with gaseous carbon monoxide (P_{CO} = 8 bar) and the other liquid phase consisted of 40 mmol (5 cm^3) of olefin. After a fifteen hour reaction, 100% conversion was attained with 97% selectivity in heptanal. The ratio of linear aldehyde to branched aldehyde product was 36 : 1.[9] In order to achieve this result, ten equivalents of non-complexed TPPTS were added to generate a P/Rh ratio of 6 in the aqueous solution. These experiments were concatonated, reusing the aqueous phase each time. They observed no leakage of rhodium into the organic layer; analysis indicated less than 0.5 ppm (w/w) rhodium was present in the organic phase. For the consecutive experiments, there was no attenuation of catalytic activity.

It was determined that the dinuclear complex hydroformylated with a P/Rh ratio of unity and was not poisoned (unlike its hydrophobic analogue, $Rh_2(CO)_2(\mu\text{-S-tBu})_2(PPh_3)_2$); however, when the reaction was performed without excess TPPTS, the results were less favourable (about 75% yield in *n*-heptanal). A P/Rh ratio of three improved the results. An approximate selectivity of 95% in linear aldehyde occurred using the bimetallic water soluble catalyst.

These results are exceptionally positive when compared to their homogeneous catalyst analogue $Rh(CO)(PPh_3)_3$, A, and $Rh_2(\mu\text{-S-tBu})_2(CO)_2(PPh_3)_2$, B. Hydroformylation was attempted under a variety of experimental conditions.[6] The conditions, P_{CO} = 8 bar, T = 80°C, gave an 8% yield in eighteen hours. Ethoxyethanol was used as solvent, triethylamine as cocatalyst and excess triphenylphosphine (P/Rh ratio = 13/3). In addition to the low yield, up to 40% of the product isomerized. Complex A was converted to the inactive compound $PhRh(CO)(PPh_3)_2$ and complex B, also inactive, transformed into $Rh_2(CO)_4(PPh_3)_4$.

A series of hydroformylation experiments were conducted with $Rh_2(CO)_2(\mu\text{-S-R})_2(TPPTS)_2$ varying the thiolato ligands (R = tBu, CH_2–Ph, CH_3, Ph, C_6F_5, $-CH_2-$).[9] The turnover rates differ no more than 70 percent with C_6F_5 at 18 min^{-1} and CH_3 at 30 min^{-1}. The *n*/*i* ratio (straight/branched) had a range of 11 with *t*-Bu on the high end at 24 and C_6F_5 at the low end with 13. The interface of the two

TABLE I
Summary of catalytic reactions with rhodium complexes.

Complex	Selectivity (%)	Turn Over Frequency*	Conversion Rate (%)	Reference
$Rh_2(\mu\text{-S-t-Bu})_2(CO)_2(TPPTS)_2$	(heptanal) 94.8	a1 28 h^{-1}	53 in 15 hrs	1, 2, 3, 4
$(Rh(COD)(TPPTS)_2)ClO_4$	(heptanol) 93.8	a1 5.3 h^{-1}	20 in 15 hrs	1, 2, 3
$RhH(CO)(TPPTS)_3$	(heptanol) 90.0	a1 6.6 h^{-1}	25 in 15 hrs	1, 2
$Rh_2(\mu\text{-S-t-Bu})_2(CO)_2(TPPTS)_2$	(heptanol) 97	a1 –	100 in 18 hrs	4
$Rh_2(\mu\text{-S-Me})_2(CO)_2(TPPTS)_2$	(butanal) 93	b1 1820 h^{-1}	100 in 1 hr	4
$RuHCl(TPPMS)_3$	(heptanal) 75	a1 –	20 in 24 hrs	5
$RhCl(TPPMS)_3 \cdot H_2O$	(hexane) 72.5	a2 –	72.5 in 24 hrs	5
$RuHCl(TPPMS)_3 \cdot 2H_2O$	(hexane) 55	a2 –	55 in 24 hrs	5
$RhCl(TPPMS)_3$	1.8	c2 40 TON	1.8	6
$[Rh(amphos)_2(MeOH)_2]^+ + 1$ equivalent $(amphos)NO_3^-$	(heptanal) 90	a1 –	90–95 in 24 hrs	10
$Rh_2(\mu\text{-S-t-(Bu)}_2(CO)_2(TPPTS)_2$	β-aldehyde 3/γ-aldehyde 97	d1 –	62 in 24 hrs	4
$[Ir(C_5Me_5)(bpy)Cl]Cl$		3 20 TON		7
$[Co(CO)_3(amphos)]_2(PF_6)_2$	(heptanal) 68	a1 151 TON	27 in 24 hrs	18

* a, 1-hexene; b, propene; c, ethylene, d, other substrate; 1, hydroformylation; 2, hydrogenation; 3, WGSR.

phases was thought to exert more influence over the results than the bridging sulfur ligand. This observation contrasts significantly from the homogeneous analogue, $Rh_2(CO)_2(\mu\text{-S-R})_2(PPh_3)_3$. The R-group had a greater impact on catalytic activity.[41]

Kalck offered three explanations of the increased activity of $Rh_2(CO)_2(\mu\text{-S-R})_2(TPPTS)_2$; (1): the bridging ligand simplifies ligand transfer from one metal centre to the other, lowering E_a for coordination of olefin; (2): the sigma donation from the ligands to the metal centre reduces charge density; (3): the ability to back bond throughout the compound increases stability. The cooperative effect between the two rhodium atoms permitted the hydroformylation mechanism (oxidative addition, coordination of alkene, hydride transfer, CO insertion, reductive elimination) to operate more efficiently.

The pH was varied for the three metal complexes. The other conditions were held constant (T = 80°C, P_{CO} = 8 bar, P/Rh = 6, t = 15 hours, 5 cm^3 of a buffer, 20 cm^3 of water, 40 mmol of hexene). Table II shows the results for hydroformylation of hexene in acidic media. The dirhodium complex had optimum catalytic activity at a pH of 4.8. The complex $[Rh(COD)(TPPTS)_2]ClO_4$ had its best performance when the experiment was run at a pH of 3.7. $HRh(CO)(TPPTS)_3$ was not evaluated with varied pH values due to its lower linear-to-branched product ratio. At lower pH values, rhodium leached into the organic phase.[7] When the experiment was run in alkaline solution, the ligand TPPTS was oxidized to OTPPTS.

TABLE II
Hydroformylation of 1-hexene with varied pH values.

Precursor*	pH	Conversion Rate (%)	Turnover (hours^{-1})	Selectivity in Heptanal (%), [n/i]
A	6	53	28	(94.7), [18]
A	4.8	75	40	(95.8), [28]
A	3.7	40	21	(95.5), [22]
B	6	20	5.3	(93.8), [15]
B	4.8	35	9.3	(95.8), [23]
B	3.7	60	16	(95), [19]
C	6	25	6.6	(90), [9]

* A = $Rh_2(\mu\text{-S-tBu})_2(CO)_2(TPPTS)_2$; B = $[Rh(COD)(TPPTS)_2]ClO_4$; C = $HRh(CO)(TPPTS)_3$.

An interesting reaction was performed to compare the amount of hydrogen produced from water in the hydroformylation reaction *versus* the water–gas shift reaction (WGSR).[6,8] The hydroformylation process, conducted in the absence of olefin, resulted in the WGSR. After the reactions, there was a total accounting for hydrogen evolution. This included capturing H_2 in the gas phase, and determining the amount of hydrogen consumed in the hydroformylation run. The results are presented in Table III. The reactions with olefins produced 4 to 5 times the amount of hydrogen as the WGSR. Kalck *et al.* suggested a common intermediate in the reaction scheme is a dihydride (RhH_2) which is produced in the WGSR and utilized in the hydroformylation process.[42]

The ligand sodium phenylphosphinobenzene-*m*-sulphonate (TPPMS), prepared by Wilkinson *et al.*,[2] was exchanged with triphenylphosphine in various metal complexes to afford solubility in water. The functionalized ligand was extracted into the aqueous phase and precipitated with THF. Hydrated and nonhydrated forms of the

ligand result from reaction either in the presence or absence of water. The reactivity of the compounds was altered very little, but the physical properties were changed. The nonhydrated complexes were not as crystalline and were more sensitive to air and had greater solubility in THF. The temperatures at which they decompose were lower than for their hydrated forms.

TABLE III
Comparison of hydrogen produced from the WGSR and hydroformylation.

pH	H_2 Evolution (mmole)	Conversion of Hexene to Aldehyde (Percent)	H_2 Total (mmole)
4.8[a]	5.3	75	35
4.8[b]	7.5		7.5
6[a]	4.8	53	25
6[b]	6.3		6.3

[a] 40 mmol of 1-hexene. [b] No olefin.

Two phase catalysis was examined with the catalyst dissolved in water and hydrogenation/hydroformylation of a separate unsaturated organic phase. They noted little or no colouring of the organic layer, indicating that the catalyst remained in the aqueous phase; however, a small amount of emulsion existed between the two phases which reduced the efficiency of separation.

$RhCl(TPPMS)_3$ and $HRuCl(TPPMS)_3$ provided catalytic hydrogenation of olefins. A biphasic system that avoided air was utilized (see Table IV).[2] The rhodium complex outperformed the ruthenium compound in conversion and selectivity. The results hold for hydrogenation and hydroformylation. The reactions were more successful when excess TPPMS was added. Their inchoative examination of hydroformylation led them to the species $HRh(CO)(TPPMS)_3$. Results were not published; however, it was noted that in all the environments tested, an orange colour was present in the organic layer after reaction.

TABLE IV
Catalytic hydrogenation of alkenes.*

Catalyst	Concentration ($mmol/dm^3$)	Temp (°C)	Alkene	Product Distribution (%) A	B	C
D	1.9	25	1-hexene	72.5	22.5	5
D	2.4	25	2-hexenes	9	29	62
D	2.3	25	cyclohexene	14		86
E	2.9	80	1-hexene	55	13	32
E	3.4	80	2-hexenes	31	28	41
E	3.6	80	cyclohexene	21		79

* A = hexane, B = *trans*-2-hexene, C = *cis*-2-hexene + 1-hexene, D = $RhCl(TPPMS)_3 \cdot 4H_2O$, E = $HRuCl(TPPMS)_3 \cdot 2H_2O$.

During the initial studies of the rhodium-TPPMS system, the hydrogenation reaction proceeded a little differently.[35] An example is the hydrogenation of cyclohexene. The stoichiometric amount of ligand (TPPMS) was added to the aqueous solution with cosolvent (methanol, ethanol, dimethylacetamide or dimeth-

oxyethane) in an argon atmosphere. The corresponding amount of $RhCl_3 \cdot 3H_2O$ was then added to this solution. Initially, the solvent turned red in colour, followed by orange which indicated the ligand reacted with the metal complex. The solution was constantly stirred. The penultimate step consisted of addition of hydrogen, and the solution colour changed from orange to pale yellow. Finally, olefin was added to the solution 0.5 hours after the hydrogen addition. For the majority of the runs, the temperature was 50°C and the P/Rh ratio was 6. Table V shows the influence of cosolvent. All cosolvents separated with a clear organic phase. Quantitative analysis of the product, cyclohexane, as compared to the amount of hydrogen used, indicated that no side reactions occurred. Table VI presents the effects of volume and concentration differences on the rate of reaction. Halving the concentration by doubling the aqueous volume increased the rate by 27%. When the volume was held constant and the molar concentration of rhodium was doubled, the rate increased by 53%. The authors conclude the reaction rate is controlled by the solubility of the olefin in the aqueous phase rather than the interface. Precipitation of salt ($NaBF_4$) in the aqueous phase reduced the reaction rate and there was no increase in rate when surfactants were added.

TABLE V
The effect of cosolvent.

Cosolvent	Rate [cm^3 of H_2 uptake/min]
methanol	1.5
ethanol	1.3
dimethylacetamide	0.1
dimethoxyethane	0.5

* Note: cosolvents isopropanol, acetone, and dioxane effected the precipitation of rhodium.

TABLE VI
Influence of aqueous volume/metal concentration.

Aqueous Phase Volume (cm^3)	[Rh]	Rate [cm^3 of H_2 uptake/min]
35	1.1×10^{-3} M	1.5
70	0.55×10^{-3} M	1.9
35	2.2×10^{-3} M	2.3

A paper by Joo provides some insight to the kinetics of the catalyst $Rh(TPPMS)_3Cl$ in hydrogenations of fumaric, maleic, crotonic, and cinnamic acids.[37] When excess ligand was avoided, a linear increase in rate with increasing catalyst concentration and increasing partial pressure of hydrogen was observed. The rate levelled off with additional substrate. The equation is

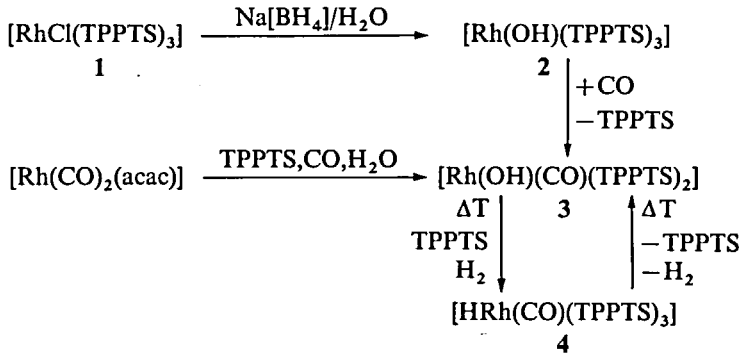
$$\text{rate} = -d[H_2]/dt = \frac{kK[Rh]_0[\text{Substrate}]_0[H_2]}{1 + K[\text{Substrate}]_0}$$

where $[x]_0$ refers to initial concentrations and K is the equilibrium constant for the

intermediate catalyst–substrate complex. Addition of TPPMS had a tremendous impact on the rate, although the impact varied with substrate. An induction period was created when excess ligand was present and for crotonic acid the hydrogenation was almost completely inhibited. These findings were explained by defining multiple mechanistic paths for the reduction of olefin and permitting each substrate to follow the most stable route available.

An interesting NMR study of the rhodium hydroformylation system compared the water soluble TPPTS ligand to its hydrophobic analogue PPh_3.[36] $Rh(CO)_2(acac)$ was reacted with TPPTS (P/Rh = 3.5) in an aqueous solution having a pH of 13. The reaction was run under an atmosphere of carbon monoxide. The products were $HRh(CO)(TPPTS)_3$ and some OTPPTS. NMR and IR techniques were used to confirm the overall structure which is very similar to $HRh(CO)(PPh_3)_3$. The main differences in results for the hydrophilic and lipophilic catalysts are the higher *n/i* ratios for complexes of TPPTS and the greater activity of the PPh_3 complex during hydroformylation (when the P/Rh ratio is kept to a minimum). Two intermediates for the mechanism of the hydroformylation process were $HRh(CO)(PR_3)_2$ and $HRh(CO)_2(PR_3)$. When 200 atmospheres of CO/H_2 1 : 1 were mixed with $HRh(CO)(TPPTS)_3$/(P/Rh = 6), $HRh(CO)_2(TPPTS)_2$, the precursor for $HRh(CO)_2(TPPTS)$, was not detected. The authors suggest this may be the reason for the higher *n/i* ratio for the water soluble complex. For the species $HRh(CO)(PPh_3)_3$, substitution to $HRh(CO)_2(PPh_3)_2$ was achieved at 30 atmospheres CO/H_2(1 : 1); this was the only complex detected. Activation energies for the dissociation of a PR_3 ligand were determined; PPh_3 dissociation had an activation energy of 19 kcal/mole (± 1 kcal/mole) and the TPPTS dissociation energy was 30 kcal/mole (± 1 kcal/mole).* The rationale for the increase in activation energy of the water soluble ligand may involve hydrogen bonding of the sulfonate group in the aqueous solution.

TPPTS is extremely water soluble with an aqueous concentration of approximately 1,100 g dm^{-3}.[16] The ligand contains one water molecule per sodium ion. TPPTS will exchange with ligands from transition metal salts in aqueous solution. Some products are not stable and will exchange with water to form hydroxo complexes (Scheme 1).[15] Complex **4** is the hydroformylation catalyst and will form the hydroxo complex, **3**, when heated. The reaction drives the equilibrium back to **4**, facilitating the catalytic reaction.



Scheme 1 (in aqueous solution)

* 1 cal = 4.184 J.

TPPTS complexes have very similar ^{31}P NMR data when compared to their hydrophobic (PPh_3) analogues. The coordination number of a TPPTS compound *versus* a PPh_3 analog will generally be lower. This tendency is considered to be due to the higher charge density of the ligand (*e.g.* $Ni(PPh_3)_4$ *versus* $Ni(TPPTS)_3$). It is possible to lower the sodium ion concentration by substituting the ligand in a complex where the transition metal balances the negative charge, *e.g.* $Na_8[Ag^I$-(TPPTS-without sodium)$_3$ + NaX, where X is the dissociated ligand. $Ag(TPPTS)_3$ would have 9 sodium ions; the corresponding PPh_3 compound, $[Ag(PPh_3)_4^+]$, has a coordination number of four.

Herrmann and coworkers have prepared a number of new water soluble complexes based on $TPPTS{\cdot}3H_2O$.[43-45] They found that gel permeation chromatography is useful for the separation and purification of complexes of Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Ag and Au.[43]

Use of TPPTS based rhodium catalysts in hydrogenation reactions requires mild conditions. The catalyst is not air sensitive and can be easily handled and stored[11] when prepared using a slight variation of Wilkinson's procedure for $ClRh(PPh_3)_3$.[46] Some 0.002 mol of $RhCl_3{\cdot}3H_2O$ and 0.006 mole of TPPTS were mixed in 30 cm^3 of deoxygenated water/ethanol (1 : 1). After refluxing the solution for 2 hours, it was cooled and the solvent was removed under vacuum. The biphasic hydrogenation of olefin involved adding 50 mg of brown residue (catalyst), 3 cm^3 of distilled water and 0.01 mol of olefin to a 50 cm^3 flask. Conversion of styrene to ethyl benzene required 40 hours to obtain 100% conversion with a product yield of 90–95%. Other olefins were also hydrogenated.[11] The rate of hydrogenation was dependent on steric factors. Analysis of the catalyst precursor showed that a significant amount (70%) of TPPTS was rapidly oxidized to phosphine oxide (OTPPTS) during hydrogenation. Apparently, the catalyst is not a typical coordination compound, but may consist of colloidal rhodium salts and OTPPTS.

In another paper, Larpent *et al.*[10] demonstrated that a redox process takes place between rhodium(III), water and TPPTS in the absence of any other oxygen source. Deaerated water was utilized under nitrogen with 3 equivalents of TPPTS and 1 equivalent of $RhCl_3$ reacting at room temperature for 21 hours. Analysis indicated unreacted TPPTS, OTPPTS, and *ca* 50% of rhodium was in the form of $ClRh(TPPTS)_3$. It is unclear as to the fate of the remaining rhodium. The rate of oxidation of ligand was related to the ratio $TPPTS/RhCl_3$. A lower ratio caused rapid oxidation of TPPTS to OTPPTS and, inversely, a higher ratio slowed the process. For example, at a ratio of 1, at t = 0.2 hours, 20% of TPPTS is oxidized. Under the same conditions at a ratio of 10 at t = 10 hours, 4% of TPPTS is oxidized. The redox reaction was conducted with isotopic $^{18}OH_2$ to determine that water was the source of oxygen for OTPPTS. The results indicated that 55% of the phosphine oxide contained the isotope. The authors stated that the remaining oxygen must come from two sources, $RhCl{\cdot}3H_2O$ or *via* handling after termination of the reaction.

Confirmation of a hydroxy rhodium(III) intermediate was possible with a proton NMR study. The reaction

$$RhCl_3 + H_2O \rightleftharpoons RhCl_2(OH) + H^+ + Cl^-$$

initiated the redox process and generated a rapid decrease in pH. Even in the presence of oxygen, manipulation of the equilibrium by adding either acid or chloride permitted the retardation of TPPTS oxidation.

Completion of the oxidative process occurs *via* the following processes.

$$RhCl_2(OH)\cdot 3H_2O + TPPTS \longrightarrow (TPPTS)Rh^{III}Cl_2(OH) \longrightarrow Rh^{I}Cl + OTPPTS + H^+ + Cl^-$$

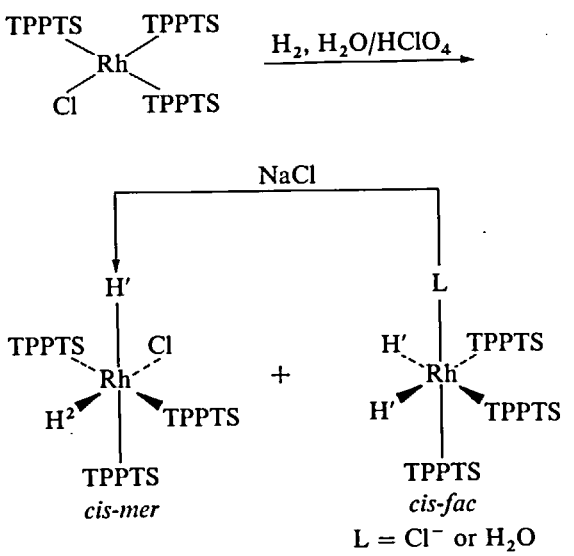
$$Rh^{I}Cl + 3TPPTS \longrightarrow ClRh(TPPTS)_3$$

$$ClRh(TPPTS)_3 \rightleftharpoons TPPTS + ClRh(TPPTS)_2$$

$$2ClRh(TPPTS)_2 \rightleftharpoons [ClRh(TPPTS)_2]_2$$

Dissociation of $ClRh(TPPTS)_3$ to the coordinatively unsaturated $ClRh(TPPTS)_2$ species allowed dimerization. These compounds were identified by ^{31}P NMR. The redox process becomes catalytic when performed under an atmosphere of O_2.[14]

When $ClRh(TPPTS)_3$ was placed under an atmosphere of H_2 with molar concentrations of either NaCl or HCl, a stable *cis-mer* dihydride was formed at 35°C (see scheme 2).[12]



Scheme 2

Clear, well-resolved ^{31}P and ^{1}H NMR spectra indicated that dissociation and isomerization do not occur at this temperature.

A 60% *cis-mer* and *cis-fac* mixture was created when 1 M $HClO_4$ was used to retard oxidation of TPPTS. The equilibrium resolves to a 50/50 mix after a period of time. A small amount of aqueous NaCl added to the solution, instantly drove the *cis-fac* to the *cis-mer* configuration (100% conversion).

The lack of stability of these compounds prohibits them from performing well as catalysts. The ionic species prevent dissociation of chloride and oxidation of TPPTS. Their study indicated that hydrogen absorption commenced after oxidation of TPPTS.

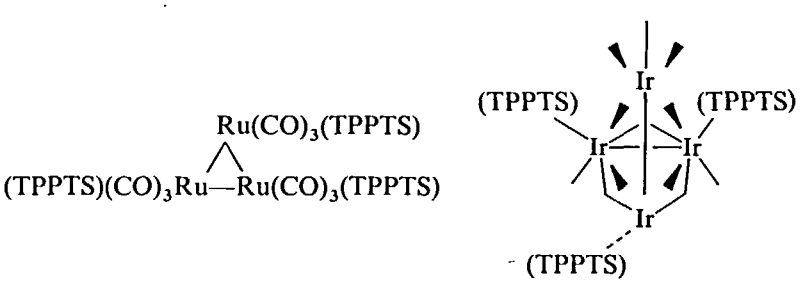
Photosensitized Catalysis

Water soluble transition metal complexes were used for catalytic, photo-induced, water–gas shift reactions, hydrogenation and hydroformylation.[22,23] Chlorotris-(3-diphenylphosphinobenzene-*m*-sulphonate)rhodium, $[ClRh(TPPMS)_3]$, was the catalyst for the hydrogenation of ethylene/acetylene and the hydroformylation of ethylene. The aqueous solution was buffered to a pH of 4.5 and contained trisbipyridineruthenium(II), $[Ru(bpy)_3]^{2+}$, as a photosensitizer with ascorbate for electron donation. The system generated H_2 when exposed to a 150W Xenon arc ($\lambda > 400$ nm) without the olefin. When either ethylene or acetylene was added, hydrogenation occurred. In comparing the experiments with and without substrate, the amount of hydrogen evolved without olefin was equal to the amount of hydrogen evolved with olefin when hydrogenation of the substrate was taken into account. An equivalent amount of hydrogen produced from the above experiment was added to an acidic solution with the catalyst $ClRh(TPPMS)_3$ and olefin, and then stirred in the dark for 24 hours. This control experiment showed no hydrogenation of acetylene or ethylene. Apparently, at a pressure of 0.1 atm, (the pressure produced by the evolution of H_2 in the experiment), H_2 will not hydrogenate ethylene or acetylene without an active catalyst. Hydroformylation was achieved when carbon monoxide was introduced to the solution. Simultaneous evolution of H_2 and propionaldehyde resulted without hydrogenation of ethylene.

$[Ir(C_5Me_5)(bpy)Cl]Cl$ is water soluble and effected the evolution of 3.4 cm^3 of H_2 in the WGSR (see Table I). The experiments indicated that pH was significant with respect to reaction rate. Carbon dioxide formation was accelerated in a solution with a high pH, and formation of molecular hydrogen was accelerated in a low pH solution. A pH of seven provided the best results in the series of tests which used the catalyst with 25 equivalents of bpy in solution for a 24 hour period. The reaction was accomplished under one atmosphere of carbon monoxide. The solution with a pH of 5.0 produced an overall turnover number of 3.4. A pH of 8.4 generated a turnover number of 10.2. The solution with a pH of 7.0 rendered a 13.3 turnover number.[23] The data suggest that both mechanistic steps, *i.e.*, the oxidation of CO and the generation of molecular hydrogen, are significant in influencing the rate.

Aqueous Clusters

Fontal has synthesized a new group of water soluble clusters.[47] The ligand selected was $P[C_6H_4\text{-}m\text{-}SO_3^-Na^+(H_2O)]_3$ (TPPTS). The following structures were obtained.

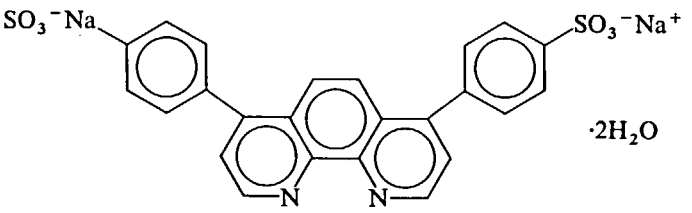


COMPOUND 1 COMPOUND 2

The compound $Os_3(CO)_{10}(TPPTS)_2$ was also listed as a water soluble species, but a structure was not provided. The clusters were stable in air to some extent. The data

provided for compound 1 indicated that it may be exposed to air (while in an aqueous solution) over 15 days without degradation.

A large water soluble cluster has been reported by Schmid *et al.*[48] A four shell platinum cluster of composition $Pt_{309}Phen_{36}{}^{*}O_{30 \pm 10}$ was synthesized by agitating a solution of acetic acid and platinum(II) acetate with Phen* (volumetric ratio 15 : 2) under hydrogen gas. The mixture was stirred until H_2 was no longer absorbed (approximately 3 hours). The black/brown solution was then oxidized with air. The complex is water soluble and air stable. The platinum cluster has a cubeoctahedral structure with cubic close-packed (ccp) atoms.



Phen*

Cationic Complexes

The amphos ligand has been used with cobalt to make the complex $[Co(CO)_3(amphos)]_2(PF_6)_2$.[20] This compound was used in the hydroformylation of 1-hexene (see Table I) through two routes. A biphasic system with the catalyst in the aqueous phase and hexene in the other provides one route. The second method involved fixing the complex to a cation exchange resin. The complex was made by adding 21.0 mmol of 1-dimethylamino-2-diphenylphosphinoethane dissolved in 20 cm^3 of benzene to a solution of 100 cm^3 of benzene containing 10.5 mmol of $Co_2(CO)_8$. The solution was stirred for an hour at room temperature under nitrogen. The pressure was reduced to remove solvent and the residue was recrystallized from methylene chloride/hexane to produce brown crystals of $[Co(CO)_3(Ph_2PCH_2CH_2NMe_2)]_2$. Methyl iodide was added to precipitate $[Co(CO)_3(Ph_2PCH_2CH_2NMe_3)]_2I_2$.

The results of the hydroformylation of 1-hexene were not as impressive as for other systems. However, excess amphos was not introduced. $[Co(CO)_3(amphos)]_2(PF_6)_2$ was dissolved in water (buffered to a pH range of 5–7) and reacted with olefin. The reaction was carried out for twenty four hours at a temperature of 100°C and a pressure of 88 bar. The H_2 to CO ratio was 1.5 to 1. The conversion of 1-hexene was less than 30% and of that, *n*-heptanal made up 35%.

TABLE VII
Homogeneous catalyst.*

Catalyst[a]	TON[b]	% Linear aldehyde	% Branched aldehyde	% Linear alcohol	Overall *n/i* ratio
1	120	82	18	0	4.6
2	67	82	18	0	4.6

*Yields based on amount of 1-hexene converted at 100°C.

[a]1: $Co_2(CO)_8$; 2: $[Co(CO)_3(amphos)]_2(PF_6)_2$. [b]Maximum turnover number (TON) = 120.

The authors also compared $Co_2(CO)_8$ and $[Co(CO)_3(amphos)]_2(PF_6)_2$ in the hydroformylation of 1-hexene in benzene (see Table VII). $[Co(CO)_3(amphos)]_2(PF_6)_2$ had limited solubility in benzene and was only about half as effective as $Co_2(CO)_8$.

Iron, molybdenum and tungsten carbonyl complexes containing amphos were prepared[18] from the parent carbonyls $Fe(CO)_5$, $Mo(CO)_6$ and $W(CO)_6$. The metal carbonyls were treated with neutral aminophosphine, $Ph_2PCH_2CH_2NMe_2$, and trimethylamine oxide (Me_3NO), using equimolar amounts of all three, producing the monosubstituted products $Fe(CO)_4(Ph_2PCH_2CH_2NMe_2)$, $Mo(CO)_5(Ph_2PCH_2CH_2NMe_2)$ and $W(CO)_5(Ph_2PCH_2CH_2NMe_2)$. Addition of methyl iodide gave $[Fe(CO)_4(amphos)]^+I^-$, $[Mo(CO)_5(amphos)]^+I$ and $[W(CO)_5(amphos)]^+I^-$. NMR studies were performed on the three complexes. Free amphos was compared to coordinated amphos; the methyl proton resonances remain constant but the ^{31}P resonance shifts downfield. The data imply that amphos is a monodentate ligand coordinated through phosphorus. The I.R. spectra in the carbonyl region indicate that the complexes are monosubstituted. The three complexes are reported to be reasonably soluble in 1 : 1 aqueous methanol and 3 : 1 aqueous acetonitrile. An alternative approach to the synthesis of amphos salts has been accomplished by oxidation of the phosphine using hydrogen peroxide.[49] The alkylation proceeded with attachment occurring to the amine end of the phosphine oxide. Then, the phosphine oxide was reduced using trichlorosilane (approximate yield 70%).

Amphos was coordinated with rhodium to make $[Rh(amphos)_2(MeOH)_2]^{3+}$. This complex is water soluble.[19] $[(Norbornadiene)RhCl]_2$ in a methanol solution with two equivalents of amphos nitrate generated $[NBDRhCl(amphos)]NO_3$. The *bis* product was prepared by the following scheme

NBD = norbornadiene

$$[NBDRhCl(amphos)]NO_3 + H_2 \longrightarrow Rh + Norbornane$$

$$[NBDRhCl(amphos)]NO_3 + amphos \longrightarrow [NBDRh(amphos)_2]^{3+}$$

$$[NBDRh(amphos)_2]^{3+} + H_2 \xrightarrow{Cl^-} [RhH_2Cl(amphos)_2(MeOH)]^{2+} + [RhH_2(amphos)_2(MeOH)_2]^{3+}$$

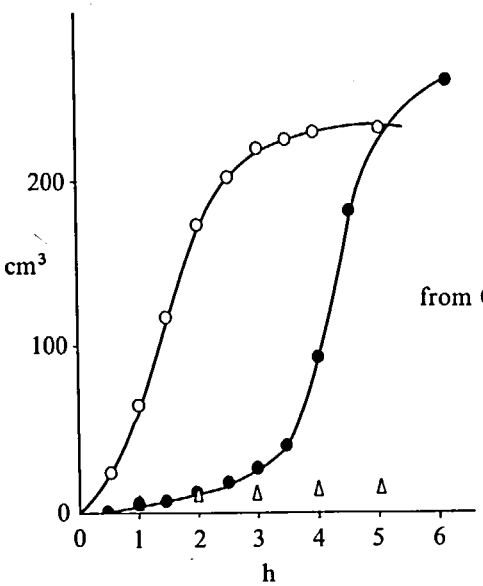
$$\longrightarrow [Rh(amphos)_2(MeOH)_2]^{3+} + H_2$$

$[Rh(amphos)_2(MeOH)_2]^{3+}$ is capable of hydrogenating maleic and crotonic acid in methanol and aqueous solution using one atmosphere of hydrogen. It was stated that $[Rh(amphos)_2(MeOH)_2]^{3+}$ is more active than the triphenylphosphine analogue and is sixfold more active in methanol than in water. Excess amphos nitrate lowered the activity in contrast to the other water soluble ligands (TPPMS and TPPTS). The amphos rhodium system is stable for about an hour when exposed to air, unlike the TPPMS and TPPTS systems. In order for hydroformylation of 1-hexene to occur, it was necessary to add one equivalent of amphos nitrate to produce heptanal in 90–95% yields. This was accomplished over 24 hours at 90°C with 40 atmospheres of CO/H_2 at a ratio of 1 : 1. Less than 0.1% of rhodium entered into the organic phase for the twenty-four hour period.

Two Phase Carbonylation

Carbonylation of benzyl chloride was studied using a two phase catalytic approach with an organotransition metal complex that was amphiphilic in order to avoid addition of phase transfer agents.[32] $PdCl_2(TPPMS)_2$ was selected as the catalyst. The complex was made by starting with $Ph_2P(C_6H_4SO_3Na)$ (0.41 g) in 30 cm^3 of ethanol and adding $PdCl_2(PhCN)_2$[50] (0.2 g). The solution was stirred for five minutes at 40°C. The product, a yellow powder, precipitated from the yellow solution.[2] $PdCl_2(TPPMS)_2 \cdot 3H_2O$ is quite soluble in water (248 mg/500 mg H_2O) and significantly less soluble in non polar organic solvents (3 mg/15 cm^3 anisole).

Benzyl chloride was carbonylated with $PdCl_2(TPPMS)_2$, $PdCl_2(TPPMS)_2$ and excess TPPMS (P/Pd = 4) and $PdCl_2(PPh_3)_2$. The reaction took place under 1 atmosphere of carbon monoxide at 50°C.



Absorption rates of carbon monoxide in aq. NaOH/*n*-heptane.
Catalyst: (○); $PdCl_2(TPPMS)_2$; (●); $PdCl_2(TPPMS)_2$/TPPMS; (△); $PdCl_2(PPh_3)_2$.
Conditions: catalyst 0.1 mmol; $C_6H_5CH_2Cl$ 10 mmol, 2.5 M NaOH 10 cm^3; *n*-heptane 8.9 cm^3; CO 1 atm; reaction temp. 50°C.

Carbonylation did not occur until Pd(II) was reduced to Pd(0). A long induction period was present when excess ligand was introduced. The extra TPPMS slowed the reduction of palladium(II) to palladium(0). After the reaction commenced, the rate appeared to be influenced by additional ligand. Various solvents were tested to determine their impact on the carbonylation of benzyl chloride. Table VIII lists the results. The more polar solvent (*n*-butanol) provides the faster rate; however, the selectivity decreases. The yield in *n*-butanol for phenylacetic acid was only 54% compared to *ca* 90% for the other solvents. $PdCl_2(PPh_3)_2$ failed to compete successfully with $PdCl_2(TPPMS)_2$ except in *n*-butanol.

TABLE VIII
Carbonylation of benzyl chloride with $PdCl_2L_2$.

Ligand	Solvent	hr	Yields* % A	B	C
TPPMS	*n*-heptane	5	9.6	89	3.9
PPh_3	*n*-heptane	12	0.9	2.3	89
TPPMS	benzene	12	10.5	93	5.7
PPh_3	benzene	12	4.2	39	60.7
TPPMS	anisole	12	10.1	92	7.7
PPh_3	anisole	12	7.4	61	38.7
TPPMS	*n*-butanol	2	9.9	54	42.9
PPh_3	*n*-butanol	3	9.7	79	18.3

* A = CO uptake (mmol); B = phenylacetic acid; C = other.

A study was performed to determine if water soluble palladium complexes would be capable of transporting hydrophobic organic species into the aqueous phase of a two phase reaction system.[51] The term "counter phase transport" was coined in describing the phenomenon (as opposed to the transport of lipophobic anions from the aqueous phase into an organic layer by crown ethers). The catalytic reduction of allyl acetate to propene under biphasic conditions using either $PdCl_2[P(n\text{-}Bu)_3]_2$ or $PdCl_2[P(CH_2(CH_2CH_2O)_3Me)_3]_2$ was accomplished in a special apparatus.[51] The amounts of propene generated in the aqueous volume and the organic/interface are shown in Table IX. The water solubility of $PdCl_2[P(CH_2(CH_2CH_2O)_3Me)_3]_2$ led to counter phase transport of allyl acetate from the organic to the aqueous phase.[51]

$PdCl_2(TPPMS)_2$ was selected for the two phase carbonylation of allyl chloride. Atmospheric pressure of carbon monoxide reacting with the catalyst and substrate at a temperature of 30°C produced 80–90% yields in 3-butenoic acid.[52] The addition of sodium hydroxide (2.5 M) was required before any CO gas was absorbed. The solvents were benzene and alkaline water.

TABLE IX
Biphasic reduction of allyl acetate.

Catalyst	Organic Phase	Propene Evolution (%) Aqueous	Organic*
$PdCl_2[P(n\text{-}Bu)_3]_2$	Heptane	12	88
	Toluene	15	85
$PdCl_2[P(CH_2(CH_2CH_2O)_3Me)_3]_2$	Heptane	98	2
	Toluene	23	77

* Organic = organic phase and interface.

A water soluble transition metal complex was utilized in the reduction of a carbonyl to its corresponding alcohol without hydrogenation of the unsaturated moieties of the substrate.[33] The reaction was run in a two phase system with a nitrogen purge. The ligand permitting the catalyst into the aqueous phase was

m-sulphophenyldiphenyl-phosphine (TPPMS). The ruthenium complex consisted of $RuCl_2$(TPPMS). Cinnamaldehyde, l-citronellal and citral were reduced to their analogous alcohols without isomerization or loss of unsaturation and in good yield (>90%; see Table I).

Water–Gas Shift Reaction

The water–gas shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2 + 42\,kJ\ mole^{-1}$$

is the most common industrial system for producing hydrogen. K[Ru(HEDTA)(CO)] is water soluble and is capable of generating a turnover frequency of 350 h^{-1} at 50°C and 15 atm of CO.[53] The turnover number is the highest yet reported with an activation energy of 6.15 kJ $mole^{-1}$, an entropy activation of 2.45 e.u. and an enthalpy of activation of 3.35 kJ $mole^{-1}$.[53] A linear dependence of rate of CO consumption on [CO] was demonstrated. A similar relationship with catalyst concentration was found (0.25–1.0 mmol) until saturation kinetics appeared and the rate levelled off. The process was tested at 1 atm CO and ambient temperature. A 75% conversion of carbon monoxide was accomplished in 4 hours.

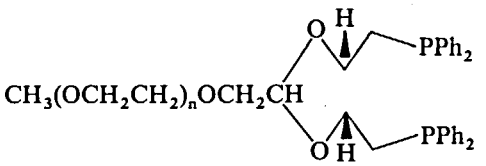
TABLE X
Asymmetric reduction of prochiral olefins.

Substrate	Ligand	Solvents	e.e.*(%)	Configuration
c_1	a_{18}	$EtOH/H_2O$	60/30	*S/S*
c_1	a_5	$EtOH/H_2O$[f]	42/12	*R/R*
c_1	a_{16}	$EtOH/H_2O$	43/11	*R/R*
c_1	a_{42}	$EtOH/H_2O$	46/10	*R/R*
c_2	a_{18}	$EtOH/EtOH^a/H_2O^a$	53/35/28	*S/S/S*
c_2	a_5	$EtOH/H_2O$	64/0	*R*
c_2	a_{16}	$EtOH/H_2O^b$	69/30	*R/R*
c_2	a_{42}	EtOH	65	*R*
c_2	a_{42}	$H_2O^b/H_2O^{b,c}/H_2O^{b,d}/H_2O^{b,c}$	30/28/28/32	*R/R/R/R*
c_2	a_{42}	X**/Y***	21/10	*R/R*
d	a_{18}	$EtOH/H_2O$	7/7	*R/R*
d	a_5	$EtOH/H_2O$[f]	41/10	*S/S*
d	a_{16}	$EtOH/H_2O$	39/20	*S/S*
d	a_{42}	$EtOH/H_2O$	47/9	*S/S*

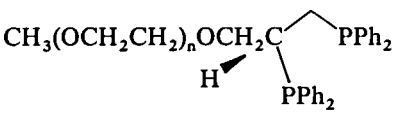
[a] $PH_2 = 5$ atm, [b] [substrate]/[Rh] = 50, [c] [substrate] = 0.25 M, [d] [substrate] = 0.01 M, [f] catalyst not soluble.
* e.e. = enantiomeric excess. X** = $AcOEt/H_2O$(1 : 1).[c] Y*** = $AcOEt/H_2O$(1 : 1).[c]

Chiral Compounds

For the study of the reduction of prochiral species, asymmetric polyoxa-1,2- and 1,4-diphosphines were used to create cationic rhodium(I) complexes.[24,25] The compounds were water soluble and examined in an aqueous phase and in ethanol. The diphosphines have the following structures.

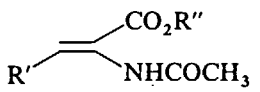


1,4-bisphosphine a_5 : n = 5 (MW = 280)
a_{16} : n = 16 (MW = 450)
a_{42} : n = 42 (MW = 1900)

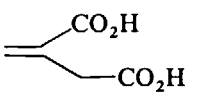


1,2-bisphosphine a_{18} : n = 18 (MW = 835)

substrates

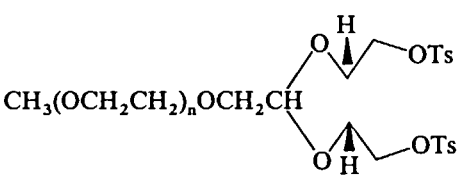


C_1 : R′ = R″ = H
C_2 : R′ = Ph, R″ = H
C_3 : R′ = Ph, R″ = CH_3



d

The alcohol, $CH_3(OCH_2CH_2)_nOH$ (n = 5, 15, 42) in chloracetaldehydedimethylacetal at 100°C was treated with sodium hydride. Hydrolysis produced $CH_3(OCH_2CH_2)_nOCH_2CH(OCH_3)_2$. Acetalization followed in a low pH solution using (4*R*, 5*R*)-*trans*-4,5-di-*O*-tosylthreitol which resulted in the following species.



The ditosylates reacted with lithium diphenylphosphine to generate the 1,4-diphosphine. The product was purified by flash chromatography.

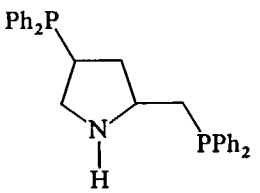
The rhodium complex, $[Rh(COD)(a_n)]^+ClO_4^-$ was prepared according to previously published methods.[29] The smaller chain, a_5, proved to be somewhat insoluble when water was used as solvent. This hindered the performance of the catalyst and is reflected in the rate, *i.e.*, with substrate c_1, a_5 produced a turnover of 1.7 min^{-1} *versus* 26.8 min^{-1} in ethanol.[29] The chain length of the 1,4-bisdiphenylphosphines appears to have little effect on the enantioselectivity in ethanol.[29] Data are available for the rate of a_5 and a_{16} in ethanol on substrate c_1 and c_2. Both catalysts produced a turnover of 26.8 min^{-1} for c_1. Using c_2 as the substrate, the rate was 11.2 min^{-1} and 14.3 min^{-1} for a_5 and a_{16} respectively. The size of the 1,2 bisdiphenylphosphine (a_{18}) allows comparison to the 1,4 bisdiphenylphosphine, a_{16}. For substrate c_1 in ethanol, a_{18} had 40 percent more enantioselectivity than a_{16}. However, a_{16} outperformed a_{18}

on substrates c_2 and c_3 by 23 and 82 percent, respectively (in ethanol). The significant difference between the complexes of 1,2 and 1,4-diphosphines was in the product configuration. When one ligand produced a rectus (*R*) configuration, the other produced a sinister (*S*) configuration.

The most obvious difference in all of the runs (except one) was the loss of enantioselectivity when the hydrogenation was run in water compared to ethanol. The e.e. plummeted in water; 11 and 10% *vs* 43 and 46% for α-acetamidoacrylic, c_1, 30 and 36% compared to 69 and 65% for α-acetamidocinnamic acid, c_2 and 9 and 20% *versus* 47 and 39% for itaconic acid, d. The rate was also lower in water which may be due to the higher solubility of hydrogen in ethanol. Lowering substrate concentration showed little change on the e.e. A two solvent system of ethylacetate/water dropped enantiomeric excesses to 21% from 30% in pure water and 65% in neat ethanol.

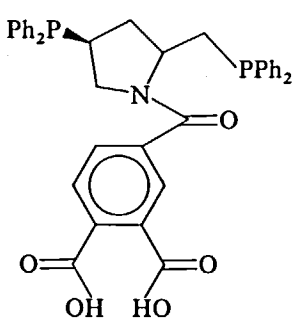
It was suggested that the competition between the two diastereomers is significantly influenced by solvation. The limiting enantioselectivity can be determined by the difference in transition state free energies. Water may reduce the difference in T.S. free energies through solvation, hence lowering enantioselectivity.

An extension of this work by the same authors has shown improved enantioselectivity in water using different chiral ligands.[26] Trimellitic anhydride acid chloride acylation of PPM{2-[(diphenylphosphino)methyl]-4-(diphenylphosphino)-pyrrolidine] produces the diphosphine (1) with an 80% yield.

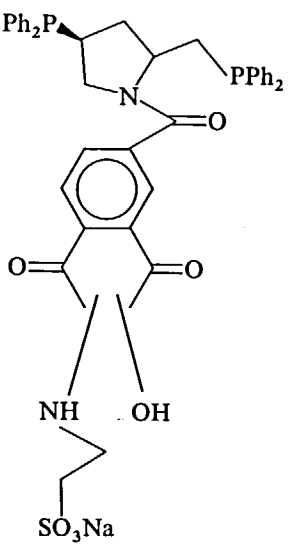


1

The implementation of Whiteside's procedure[30] with either sodium hydroxide or sodium taurinate generates the diphosphines (2) or (3), respectively.



2



3

The prochiral substrates were the same as in the previous work (c_1, c_2, and d). The results are tabulated in Table XI. It should be noted that (3) is the only ligand that allowed the complex $[Rh(COD)(a_n)]^+ClO_4^-$, (n = 1, 2, 3) into the aqueous phase. A 0.1 M Na_2HPO_4 aqueous solution solubilized (2).

TABLE XI

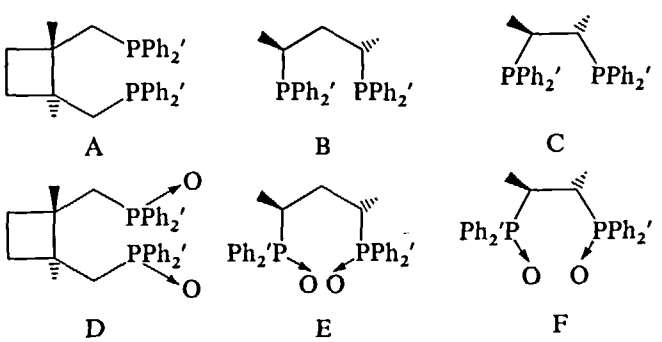
E.e. of asymmetric reduction of olefins with 1 atm of H_2.

Substrate	Ligand	Solvent	e.e.	Configuration	Minutes
c_1	1	EtOH	34	*R*	18
c_1	2	EtOH	35	*R*	18
c_1	2	H_2O/Na_2HPO_4	31	*R*	300
c_1	3	EtOH	57	*R*	12
c_1	3	H_2O	34	*R*	18
c_2	1	EtOH	87	*R*	12
c_2	2	EtOH	82	*R*	90
c_2	2	$H_2O/NaHPO_4$	60	*R*[a]	24 h
c_2	3	EtOH	No reaction		
c_2	3	H_2O	No reaction		
d	1	EtOH	74	*S*	12
d	2	EtOH	58	*S*	12
d	2	H_2O/Na_2HPO_4	16	*S*	24 h
d	3	EtOH	65	*S*	12
d	3	H_2O	59	*S*	24 h

[a] $P(H_2) = 5$ atm

Focussing specifically on (3) clearly demonstrated improved enantiomeric excesses with the exception of α-acetamidocinnamic acid, c_2, which did not hydrogenate either in alcohol or water.

Enantiomeric excess was used to determine the homogeneous/heterogeneous state of rhodium complexes in aqueous solutions.[27] Three chiral sulphonated ligands were used, cyclobutanediop (CBD), A, skewphos, B, and chiraphos, C. In addition, their corresponding oxidized phosphines (D, E, F) were also examined. The water soluble compounds were made from the corresponding phosphines.[30] Two mmol of diphosphine were added to a solution of 30% SO_3 in H_2SO_4 (10 cm^3) and stirred for 24 hours. The solution was then poured into 30 grams of ice and neutralized with NaOH. 200 cm^3 of methanol was added and the sodium sulfate was allowed to separate. When the solvent evaporated, the residue consisted of the sulfonated diphosphine.[31]



Ph' = $C_6H_5SO_3Na$(*meta*)

The hydrogenation reaction was demonstrated, and the e.e. was measured. Table XII lists the results.

The first three runs presented the highest values of enantioselectivity. The aqueous phase was without colour or turbidity. Runs 4–6 showed a decrease in e.e. and the solution turned cloudy with time. The last set of runs, 7–9, utilized the analogous phosphine oxides which produced rapid reduction without stereospecificity and generated a turbid solution.

TABLE XII
Hydrogenation using asymmetric ligands in Rh complexes.

Run	Catalyst Precursor	Ligand	Ph_2(atm)	Opt. Yield (%)
1	$[Rh(COD)Cl]_2$	A	1.1	21
2	$[Rh(COD)Cl]_2$	B	6	31
3	$[Rh(COD)Cl]_2$	C	6	61
4	$RhCl_3 \cdot 3H_2O$	A	1.1	5
5	$RhCl_3 \cdot 3H_2O$	B	6	15
6	$RhCl_3 \cdot 3H_2O$	C	6	20
7	$[Rh(COD)Cl]_2$	D	1.1	0
8	$[Rh(COD)Cl]_2$	E	6	0
9	$[Rh(COD(Cl]_2$	F	6	0
10	$RhCl_3 \cdot 3H_2O$	D	1.1	0

The data imply that the aqueous system consisting of $[Rh(COD)Cl]_2$ with a chiral tetrasulphonated phosphine reacts homogeneously and the aqueous phase can be recycled for the reduction of olefin without loss of enantiomeric excess. The Rh(I)/phosphine oxide system is a heterogeneous catalyst that operates with colloidal rhodium particles dispersed in the aqueous phase (this was confirmed by light scattering techniques). The $RhCl_3 \cdot 3H_2O$ system initiated the catalytic process with Rh(III). When the metal was reduced to Rh(I), the phosphine was oxidized. After this, the enantioselectivity dropped as more and more oxidation of the phosphine continued, hence the lower e.e. on the second set of runs. This system started out homogeneous and ended up heterogeneous. Water, as well as various water/ethanol blends, was examined using $[Rh(COD)A]^+ClO_4^-$ as a catalyst. Table XIII provides the information. The data show the e.e. and $\log(\%S/\%R)$ appear to have a proprotionally inverse relationship with dilution by water. This observation was noted in much of the work reviewed regarding enantiomeric excess. The solvophobicity parameter appears to have a linear relationship with the aqueous percentage of solution.

TABLE XIII
Asymmetric reduction of c_2 using $[Rh(COD)A]^+ClO_4^-$.

Solvent	Sp	e.e.(%)	$\log(\%S/\%R)$
ethanol/water (100/0)	0.1440	52	0.501
ethanol/water (75/25)	0.2500	46	0.432
ethanol/water (50/50)	0.4495	42	0.389
ethanol/water (25/75)	0.7600	36	0.327
ethanol/water (0/100)	1.0000	28	0.250

TABLE XIV
Reference information.

	Rh	Ru	Pd	Pt	Ir	Cu	Co	Fe	Mo	W	Ag	Os	Mn	Ni	Au
LIGAND															
TPPMS	4, 2, 3, 21, 22, 35, 37, 54	2, 3, 21, 33, 54	32, 51, 52	48											
TPPTS	6 thru 15, 21, 36, 43–45	43, 47	43	43	43, 47		43	43			15, 43	47	43	43	43
AMPHOS	19, 21						20	18	18	18					
EDTA		39, 53 59													
Cl	4, 14, 21, 60		34, 52												
CO								21					21		
DIOP	24, 25, 27 28, 29, 31														
Other	26		51		23	5									

Biochemistry

Hydrogenation can be considered a chemical modification of the lipid moieties of biomembranes creating physiological alterations. The potential utility of water soluble transition metal complexes for this activity was explored.[54-57]

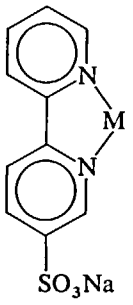
A comparison of the performances of the complexes $RuCl_2(TPPMS)_2$ and $RhCl(TPPMS)_3$ was accomplished by Joo.[54] The compounds were prepared by Wilkinson's procedure.[2] The hydrogenation of fatty acids (soybean phosphatidyl choline) was run in a reactor mixed at the rate of 50 r.p.m. under 1 bar total pressure and a temperature of 20°C. The ruthenium compound demonstrated superior conversion abilities over rhodium at 20°C (ruthenium hydrogenated approximately twice as much as rhodium) in the saturation of soybean phosphatidylcholine fatty acid components. The activity of the two catalysts changed dramatically when the temperature was varied and the other reaction parameters were held constant. The catalysts performed equally (in activity) at 33°C. The rhodium complex is known to split molecular hydrogen homolytically, whereas $RuCl_2(TPPMS)_2$ incorporates a monohydridic mechanism. For the purpose of hydrogenating plant membranes under natural physiological conditions (room temperature and atmospheric pressure), the ruthenium catalyst generates a superior rate.

Use of $Pd(TPPTS)_3$ to catalyze alkylation of biological molecules in a natural environment has been reported.[58] Coupling of alkynes with unprotected iodonucleotides, iodonucleosides and an iodoamino acid provided an alternative approach to T-505.[58]

Conclusion

Table XIV is the compilation of references surveyed in this communication. The references are broken down into the transition metals and ligands that are applicable. This area of chemistry is still under initial development with much work to be done. The potential industrial applications are significant.

Since the submission of this review, a new ligand that imparts aqueous solubility to metal carbonyl complexes has been reported.[a,b]



Sulfonation of bipyridine provides a bidentate ligand that coordinates to metal carbonyl complexes. The sodium salts have reasonable aqueous solubility.

[a] W.A. Herrmann, W.R. Thiel and J.G. Kuchler, *Chem. Ber.*, **123** 1953 (1990).
[b] W.A. Herrmann, W.R. Thiel, J.G. Kuchler, J. Behm and E. Herdtweck, *Chem. Ber.*, **123** 1963 (1990).

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