

I. INTRODUCTION

Rhodium occurs in only very minor concentrations in the earth's surface, primarily as part of nickel or copper-nickel sulfide ores. The extreme rarity of rhodium makes it economically impractical to recover from the sulfide ores alone. However, because it is closely linked to the output of platinum, another constituent of these ores, it is recovered in small amounts. The production of rhodium is about 5% that of platinum, corresponding to the relative ratio of the two metals in the ore. In 1984 South Africa, the second largest source of rhodium after the USSR, exported only 116,000 troy ounces to the Western world.¹

Rhodium has traditionally been used as an alloying agent for platinum and as a constituent of automobile catalytic converters. More recently it has been used in combination with other ligands to form powerful catalysts. (A catalyst is a substance which increases the rate of a thermodynamically allowed reaction by lowering the activation energy of the process, without being consumed itself.) Because of the scarcity of rhodium it is not economical to design industrial processes that do not allow for the complete recovery of the metal after the useful life of the catalyst is over. However, rhodium complexes remain good potential catalysts provided they can be regenerated. Indeed, Johnson Matthey has such a process where rhodium can be regenerated in essentially 100% yield.²

Rhodium(I) Phosphine Catalysts

Homogeneous catalysis by transition-metal complexes plays an important role in industrial chemistry. Neutral and cationic complexes of rhodium(I) are versatile catalysts for hydrogenation, isomerization, dimerization, hydroformylation, and carbonylation reactions. Of particular interest to this dissertation is the catalytic ability of these complexes as it relates to dehydrogenation reactions.

Since rhodium in the +1 oxidation state is a d^8 system, it tends to form square-planar complexes. This geometry makes it coordinatively unsaturated (i.e. possessing a vacant coordination site). This is important for homogeneous catalysis as the substrate can then enter the coordination sphere of the metal, thereby lowering the activation energy barrier by having the reactants in close proximity via neighboring coordination sites.

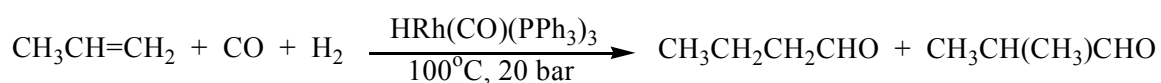
The most famous rhodium(I) phosphine catalyst is Wilkinson's catalyst,^{3,4} $\text{RhCl}(\text{PPh}_3)_3$. It has exhibited activity for hydrogenation,^{3,4} isomerization,⁵ carbonylation,⁶ hydrosilation,⁷ and polymerization reactions⁸. *In situ* catalysts from precursors which form the active catalyst when hydrogenated in the presence of phosphines, such as $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$, have also been prepared.⁹



However, other workers¹⁰ have isolated the hydrogenation catalysts, such as $[\text{Rh}(\text{NBD})(\text{PR}_3)_2]\text{ClO}_4$.

A variety of mixed-donor-set tripod ligands of the type $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ ($X, Y, Z = PPh_2, NR_2, \text{pyrazol-1-yl}$; $R = H, OH$) were reacted with $[Rh(COD)Cl]_2$ and their catalytic activity investigated. It was found that such rhodium tripod ligand complexes make poor hydrogenation catalysts.¹¹

Rhodium-phosphine catalysts have also replaced cobalt catalysts in hydroformylation reactions since lower pressure can be used and a 10:1 selectivity for straight chain over branched products obtained. This process was developed by Union Carbide, Davey Powergas, and Johnson Matthey.^{12,13,14}



Asymmetric Synthesis

A large amount of current research in rhodium-phosphine catalysis has focused on the area of asymmetric synthesis. This involves the transformation of a prochiral substrate (not optically active but containing two non-equivalent faces) into one predominant enantiomer. There are many applications for this in the pharmaceutical industry where often only one enantiomer of a particular compound is biologically active. In order to keep the production of these compounds inexpensive, industry requires complexes that can result in catalytic enantiomeric control of an important synthetic step such as hydrogenation.

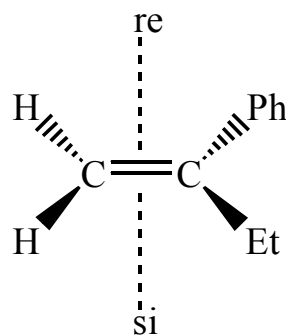
In asymmetric synthesis, the chiral center of the catalyst discriminates between the prochiral features of the bound substrate, leading to a difference in the reaction rates for the formation of the enantiomeric products, making this a kinetic phenomenon. Prochiral substrates are compounds like $\text{CH}_2=\text{C}(\text{Ph})\text{Et}$ where the catalyst can approach from either the re (rectus) or si (sinister) face (Figure 1), and hydrogenation could lead to two possible products, (R)- $\text{CH}_3\text{C}^*\text{H}(\text{Ph})(\text{Et})$ and (S)- $\text{CH}_3\text{C}^*\text{H}(\text{Ph})(\text{Et})$. Determination of the re or si face is accomplished by ordering the three groups around the prochiral carbon according to the Cahn-Ingold-Prelog system. The face containing the sequence in a clockwise direction is the re face, while the face with an anti-clockwise sequence is the si face.¹⁵ With an achiral catalyst the product will be a racemic mixture, whereas with a chiral catalyst one enantiomer will predominate, i.e. it is in enantiomeric excess (e.e.). This excess is often reported as a percentage, calculated as follows:

$$\% \text{ e.e.} = (\text{R} - \text{S}) / (\text{R} + \text{S}) \times 100$$

where the amounts of R and S are expressed as a decimal.

Figure 1

The Two Non-equivalent Faces of a Prochiral Substrate

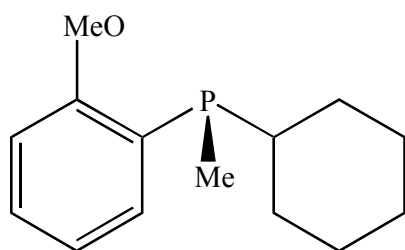


The catalyst-substrate intermediate formed during the reaction contains more than one chiral center, and if the two stereoisomers are not mirror images they are called diastereomers. The % e.e., and thus the success of a catalyst for asymmetric synthesis, depends on the difference in the free energy of activation ΔG^\ddagger of these two diastereomeric transition states. Therefore, the greater the difference in ΔG^\ddagger , the greater the e.e..¹⁶ The e.e. is determined by the first non-reversible step involving a diastereomeric transition state. The factors influencing e.e. are subtle and not well understood but differences in ΔG^\ddagger of only 12 kJ/mol can lead to an e.e. of nearly 100%.¹⁶ Two structural requirements generally believed to increase the enantiomeric excess are a fairly rigid orientation (thus the frequent use of bidentate phosphines over monodentates) and close proximity of the chiral catalyst and the prochiral substrate. Additionally it must be noted that the more stable ground state diastereomer does not always lead to the most stable transition state.^{16,17}

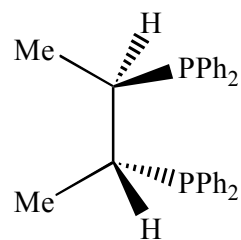
The first attempts to design suitable catalysts for asymmetric synthesis were to modify an existing catalyst, such as $\text{RhCl}(\text{PPh}_3)_3$, by substituting chiral ligands. These ligands could have chirality either centered on the phosphorus itself or on a side chain. In 1968, Horner¹⁸ and Knowles¹⁹ modified Wilkinson's catalyst using monodentate ligands with chirality centered on the phosphorus, but the results for hydrogenation were disappointing (15% e.e.). Major improvements were realized by using bidentate ligands such as DIOP (Figure 2) where the chirality is centered in the backbone. Kagan^{20,21} obtained an e.e. of 80% by using this ligand and an amino acid precursor.

Figure 2

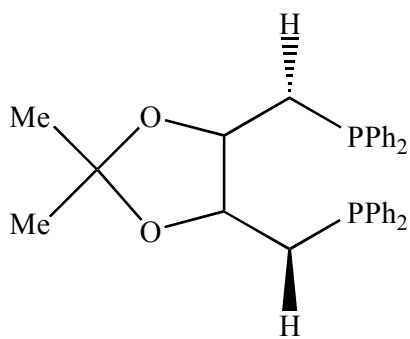
Structures of some Chiral Phosphines



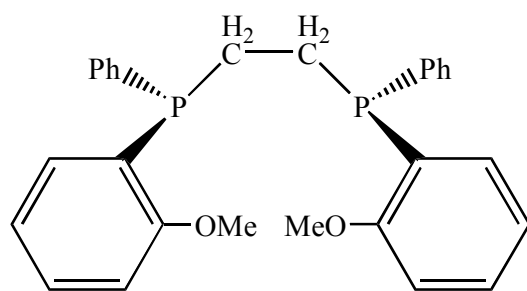
CAMP



CHIRAPHOS

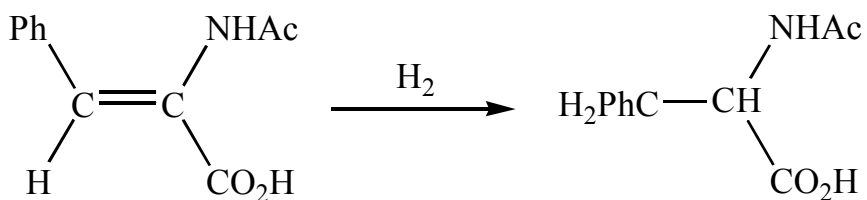


DIOP



DIPAMP

Another factor found to affect the % e.e. is the olefin used. These can be of two types, either a simple olefin like the example $\text{CH}_2=\text{C}(\text{Ph})\text{Et}$ shown above, or an olefin containing a polar group next to the double bond such as the amino acid precursor used in Kagan's DIOP study (see below).



It has been determined that enantiomeric excesses are generally higher with amino acid precursors. Kagan found evidence of this by running the same reaction above using DIOP but with a simple olefin in place of the amino acid precursor. This reaction gave an e.e. of only 15%, compared to the previous 80%. It is believed that the oxygen of the carboxylic acid group binds to the rhodium, thereby forming the preferred rigid structure. These type of interactions with the metal, whether from the substrate or from the ligand, appear to be very important. For example, when Knowles²² used the monodentate ligand CAMP (Figure 2) with chirality on the phosphorus and an amino acid precursor he achieved an e.e. of 90%. This large e.e. was attributed to the weak interactions between the ligand and the o-anisyl group.

More recently it has been discovered that phosphites and phosphinites can also be highly effective ligands for enantioselective rhodium-catalyzed hydrogenation.²³ Some of the most effective have been phosphine-phosphites which gave enantiomeric excesses up to 98.8%.²⁴

From 1968-1972 most of the catalysts were synthesized *in situ* by adding phosphine to $[\text{RhCl}(\text{olefin})_2]_2$. However, studies found that isolated cationic complexes such as $[\text{Rh}(\text{COD})(\text{DIOP})]^+$ gave a more active catalyst with greater reproducibility in the results.²⁵ This increased activity was not limited to just hydrogenations. For example, $[\text{Rh}(\text{DPPP})_2]\text{BF}_4$ will decarbonylate aldehydes with rates more than double that of $\text{RhCl}(\text{PPh}_3)_3$ and with turnovers in excess of 100,000.^{26,27}

Structure of Rhodium Bis-Phosphines

In summary, it has been found that for good enantiomeric excesses it is necessary to have a structure not far removed from an achiral catalyst, preferably containing a bidentate ligand. Such complexes can either have a *cis* or *trans* geometry, but the majority of studies relating to asymmetric synthesis were conducted with *cis* complexes. Most have used cationic complexes of the general formula $[\text{Rh}(\text{olefin})(\text{bis-phosphine})]^+$, where a *cis* geometry is forced upon the complex by using a diolefin such as COD or NBD.^{17,25} It has been found that if the bidentate ligand has a backbone long enough to span *trans* then the hydrogenation results in methanol appear more varied than with *cis*-chelating ligands.²⁸ For example, on hydrogenation of $[\text{Rh}(\text{NBD})\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2]^+$ two species initially form, a solvent adduct and a C-H activated species, until eventually the

dihydride $[\text{RhH}_2(\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2)(\text{MeOH})_2]^+$ is formed. In contrast, upon using bis-phosphines which are too short to span *trans*, the solvate species is prevalent and no dihydride forms.^{28,29,30} Neutral complexes of the type $[\text{Rh}(\text{CO})\text{Cl}(\text{bis-phosphine})]$ have also been prepared and found to have a *trans* geometry, except $[\text{Rh}(\text{CO})\text{Cl}(\text{DPPE})]$ which is *cis*.^{31,32}

Although the majority of complexes studied for use in asymmetric synthesis have been *cis*, there is still much interest in pursuing complexes possessing a *trans* geometry. While previous studies have focused on chirality in the catalyst being centered on the ligands, it is theoretically possible to center it directly on the metal center. This could be accomplished through use of an unsymmetrical bidentate phosphine of the general formula $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2'$ capable of *trans*-chelating. This would block one site of the rhodium from attack, making the metal chiral (Figure 3). High enantiomeric excesses could be expected as the chiral centers in the catalyst-substrate intermediate would be in close proximity. However, if a dimeric complex were formed the rhodium would not be chiral as the hydrocarbon backbone of the phosphine would not be protecting the fifth coordination site. But if a prochiral substrate were to bind to a rhodium in a 'head-to-tail' dimer the metal center would then become chiral (Figure 4). The same is true for square-planar monomeric complexes containing a *cis*-chelated unsymmetrical bis-phosphine as coordination of a substrate would again produce a chiral rhodium (Figure 5). Although the complexes discussed in this work contain symmetrical bis tertiary phosphines, unsymmetrical ligands could be used as easily.

Figure 3

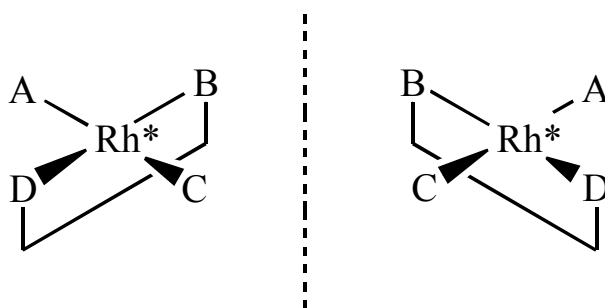
Optical Isomers in Square Planar *Trans* Chelates

Figure 4

'Head-to-Head' and 'Head-to-Tail' Structural Isomers

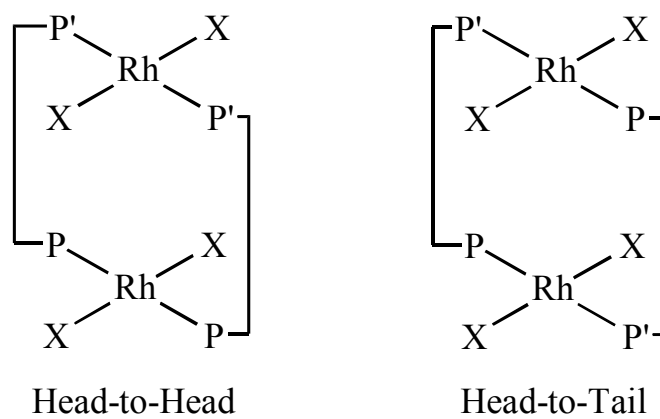
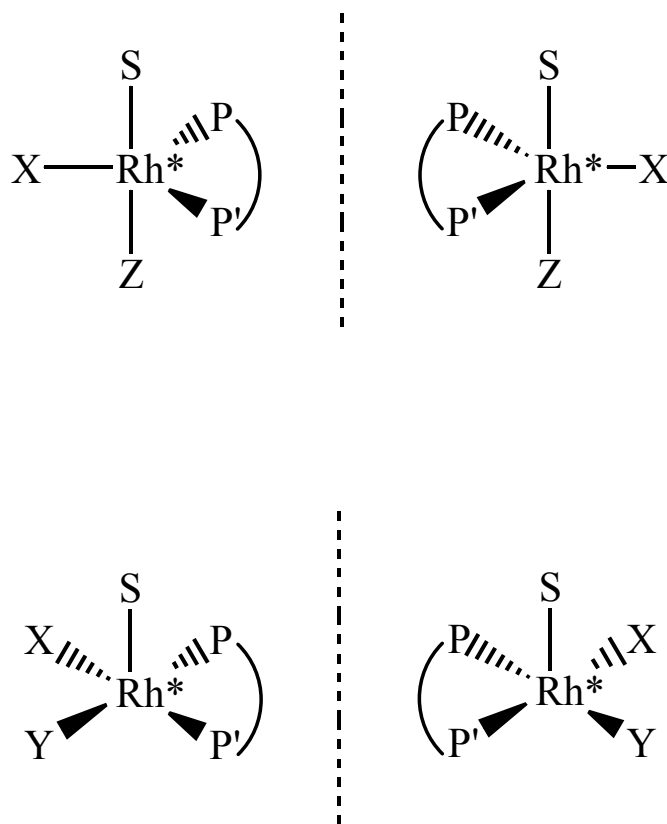


Figure 5

Optical Isomers in *Cis*-Chelates with Unsymmetrical Bis-Phosphine Ligands

The bidentate ligand backbone in these complexes can be either flexible or rigid. Both type of ligands are known to form *trans*-chelates with rhodium. One advantage of a rigid backbone is that it rules out some of the backbone conformers otherwise possible with a flexible alkyl chain. The great catalytic success of rhodium complexes containing the chiral phosphine CHIRAPHOS (Figure 2) has been attributed to rigidity.^{33,34} However, the counterpoint to this is the possibility of a too-rigid backbone preventing small molecules like hydrogen from entering the coordination sphere of the metal. In fact, this may explain the tenfold decrease in catalytic activity in rhodium complexes using the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene compared to triphenylphosphine.³⁵ Additionally, some symmetrical ligands such as BPBP (2,2'-bis(diphenylphosphino)biphenyl) have no asymmetric center when unbound, but upon complexation to metals form one due to restricted rotation of the two phenyl rings.³⁶

Chirality at the rhodium in these types of compounds depends on the complexes being inert, i.e. non-labile. If one enantiomer were isolated in the solid state and the ligands labile, the result on dissolution would be a racemic mixture. However, an optically active rhodium complex containing the ligand BPBP, $[\text{Rh}(\text{COD})(\text{BPBP})]^+$, was not racemized during catalytic use,³⁷ so perhaps racemization with unsymmetrical bidentate ligands will not be a problem.

The first example of a *trans*-chelated square-planar bis(tertiary phosphine) complex, $[\text{NiBr}_2\{(\text{cy})_2\text{P}(\text{CH}_2)_3\text{Pcy}_2\}]$, was synthesized in 1961 by Isslieb and Hohlfield.³⁸ Until recently chelate rings with more than eight members were believed to be unstable with regards to open-chain (polymeric) structures. Although there are now examples of larger chelates with a variety of transition metals, *trans*-chelation is still relatively rare compared to *cis*-chelation, and the factors leading to formation of a *trans* vs. *cis* structure are not well understood.³⁹

Shaw and co-workers have prepared several of these large-ring chelate complexes with Pt(II), Pd(II), Rh(I), and Ir(I) using a variety of long-chain phosphines of the type ${}^t\text{Bu}_2\text{P}(\text{CH}_2)_n\text{P}{}^t\text{Bu}_2$ ($n = 5-10, 12$),^{40,41} ${}^t\text{Bu}_2\text{P}(\text{CH}_2)_4\text{C}\equiv\text{C}(\text{CH}_2)_4\text{P}{}^t\text{Bu}_2$,⁴² and ${}^t\text{Bu}_2\text{PC}\equiv\text{C}(\text{CH}_2)_n\text{C}\equiv\text{C} \text{P}{}^t\text{Bu}_2$ ($n = 4$ or 5).⁴² Shaw proposes that bulky substituents on phosphorus, such as ${}^t\text{Bu}$, give favorable conformational and internal entropy effects for the formation of large rings compared to less sterically demanding groups such as phenyls. Additionally, he argues that the non-bonding interaction between a ${}^t\text{Bu}$ group and other ligands on the metal (eg. Cl, CO, etc.) produces favorable conformational effects that lead to *trans*-bonding. For example, the restricted rotation about the Rh- ${}^t\text{Bu}_2$ and P-C bonds, caused by the bulky ${}^t\text{Bu}$ groups, means that the internal rotational entropy lost on cyclization is not as great as with less sterically demanding phosphines. Shaw's inability to synthesize *trans*-bonded species with these types of phosphines (eg. those containing Me and Ph substituents) lends credence to his argument.

However, Alcock *et al.* were able to successfully synthesize *trans*-bonded square-planar complexes with phosphino ether ligands of the general formula

$\text{Ph}_2\text{P}(\text{CH}_2)_2(\text{OCH}_2\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3$ - POP, POOP, POOOP respectively)

demonstrating that bulky substituents are not a prerequisite for large-ring chelates.^{43,44}

For the neutral complex $[\text{Rh}(\text{CO})\text{Cl}(\text{POP})]_2$ the X-ray structure revealed a dimeric structure which appears to dissociate in solution into a monomeric species (based on molecular weight evidence in benzene solution), showing that 8-membered chelate rings with the phosphorus atoms spanning the square plane are possible. In contrast, cationic complexes of the general formula $[\text{Rh}(\text{CO})\text{L}]\text{PF}_6$ were shown by X-ray to be square-planar monomers. However, each of these structures were stabilized either by an oxygen in the ligand donating to the metal center or by a solvent molecule trapped in the large ring. For example, POP is actually terdentate in $[\text{Rh}(\text{CO})(\text{POP})]\text{PF}_6$ with donation from both the phosphorus atoms and the oxygen. In the case of $[\text{Rh}(\text{CO})(\text{POOOP})]\text{PF}_6$ X-ray reveals a very strongly held water molecule incorporated in the ring, while the corresponding complex with POOP has a less tightly held ethanol molecule.

Hill and McAuliffe have synthesized *trans*-complexes of the type $[\text{MX}_2\text{L}]$, where $\text{M} = \text{Pd}$ or Pt and $\text{X} = \text{Cl}, \text{Br}, \text{I},$ or NCS , using ligands of the general formula $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 6, 8, 10, 12$).^{45,46} Studies on $[\text{PtCl}_2\text{L}]$ showed that for *trans*-chelation, monomer formation was at a maximum for a 15-membered ring where $\text{L} = \text{DPPDOD}$ (87% monomer, 13% dimer), while larger ligands such as DPPHD gave dimeric complexes (8% monomer, 92% dimer). This maximum for a 15-membered ring was explained in terms of ring strain. The ring contribution to the phosphorus chemical shift, ΔR , was found to be 0 for the DPPDOD complex indicating the least amount of ring strain for this configuration.

Rhodium complexes of the general formula $[\text{Rh}(\text{CO})\text{Cl}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 1, 2, 3, 4$) have been synthesized by Sanger who determined them all to be dimeric, except $n = 2$ which *cis* chelates.³¹ Clark synthesized $[\text{Rh}(\text{CO})\text{Cl}(\text{DPPH})]_2$ and determined it to be a dimer based on molecular weight measurements.⁴⁷ One last example of a rhodium square-planar complex chelated with flexible ligands is $[\text{Rh}(\text{CO})\text{Cl}\{\text{Cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\}]$ which is a 7-membered chelate containing a diphosphine spanning the *trans* positions on the square plane.⁴⁸

A different approach to forming square-planar *trans*-chelated complexes is to design a ligand with a rigid backbone which will chelate in this fashion due to steric constraints. By far the best known example of one of these ‘tailored’ ligands is Venanzi’s L = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene.⁴⁹ The donor atoms are at an optimal distance to *trans*-chelate a variety of transition metals, including rhodium, as demonstrated for $[\text{Rh}(\text{CO})\text{ClL}]$ and $[\text{Rh}(\text{CO})(\text{CH}_3\text{CN})\text{L}]\text{BF}_4$.^{50,51} The X-ray structure of $[\text{Rh}(\text{CO})\text{ClL}]$ verified the *trans* arrangement but with a slightly distorted square plane containing a P-Rh-P bond angle of 174.7° . Marty has synthesized 3,3'-oxybis(diphenylphosphino)methylbenzene, which is more flexible and easier to make than Venanzi’s ligand.⁵² Upon complexing this ligand with Ni(II), Pd(II), Pt(II), Rh(I), and Ag(I) he found moderate flexibility not to be an impediment to *trans*-chelation.⁵³

The remaining *trans*-chelated monomeric rhodium complexes with bis phosphines exhibit some kind of restricted rotation in the ligand backbone, unlike the $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ series. For example, the X-ray structure of $[\text{Rh}(\text{CO})\text{Cl}\{\text{}^t\text{Bu}_2\text{P}(\text{CH}_2)_4\text{C}\equiv\text{C}(\text{CH}_2)_4\text{P}^t\text{Bu}_2\}]$ showed a 13-membered ring complex,⁵⁴

whereas the corresponding complex without a triple bond was a dimer.⁵⁵ Bennett synthesized $[\text{RhCl}(\text{CO})(\text{BDPBZ})]$ ($\text{BDPBZ} = \text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{PPh}_2\text{-o}$) which, based on molecular weight data in chloroform, appears to be a monomer.³² *In situ* synthesis of $[\text{Rh}(\text{CO})_2(\text{BDPBZ})]^+$ from the above and AgBF_4 also yielded a *trans* structure, presumably monomeric, although it was not isolated in the solid state.

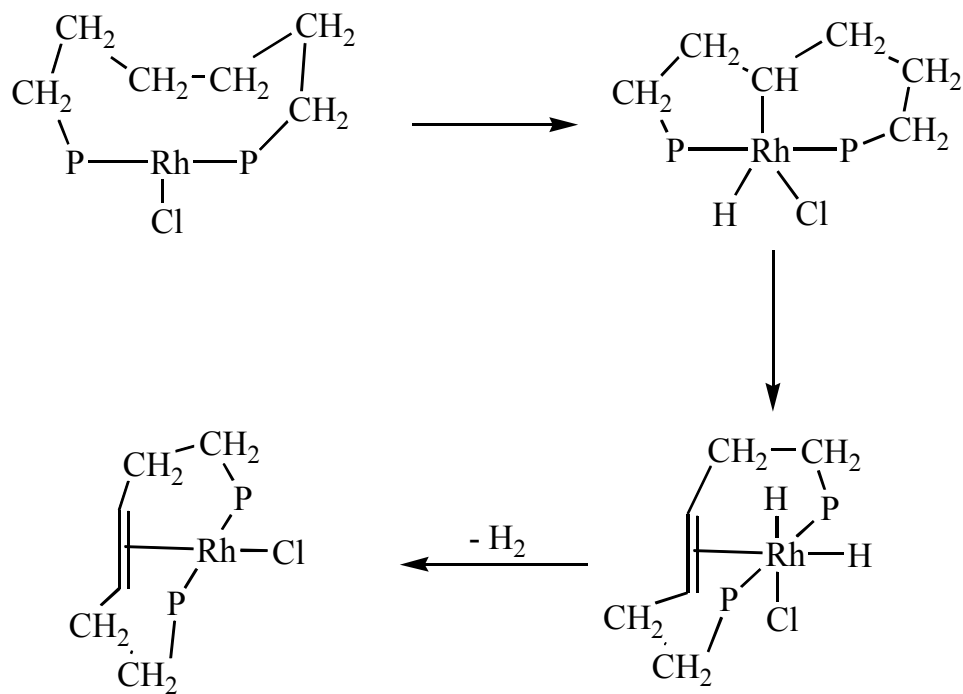
Dehydrogenation

The activation of alkanes by soluble transition-metal species has inspired considerable interest, though such catalysts need to be resistant to dimerization or β -elimination of their ligands as these represent major deactivation pathways.⁵⁶ It has been shown that the alkyl backbones in long-chain bis tertiary phosphines can undergo dehydrogenation and cyclometallation reactions with rhodium. For example, Clark found that upon refluxing in mesitylene, DPPH undergoes dehydrogenation with $[\text{Rh}(\text{COD})\text{Cl}]_2$ to yield $[\text{RhCl}(\text{BPPH})]$, where $\text{BPPH} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2$, with a *trans* geometry at the double bond.⁴⁷ This type of reaction is also known to occur with BDPBZ. When the same reaction was run with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 5, 7, 8$) he found that no dehydrogenation occurred. However, dehydrogenation was observed in this work for the $n = 8$ case in the electrospray mass spectrum (see Results, Section 3).

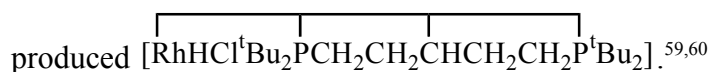
Clark's proposed mechanism for the dehydrogenation is shown in Figure 6. In this mechanism it is the C_3 position of the hydrocarbon backbone that is metallated. This is also known to occur with Pt complexes of the straight-chain phosphines $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$ and $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$.^{57,58} In Shaw's studies with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and

Figure 6

Mechanism Proposed by Clark for the Dehydrogenation of DPPH



$t\text{Bu}_2\text{P}(\text{CH}_2)_5\text{P}^t\text{Bu}_2$ he too determined this position was the one cyclometallated and



Similar results were obtained by Clark with the ligand 2,2'-bis(*o*-diphenylphosphino)bibenzyl which was dehydrogenated with various rhodium complexes to give the planar rhodium(I) complex $\text{RhCl}(\textit{o}\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{PPh}_2\text{-}\textit{o})$.⁶¹ In this case, attack at the C₃ position to form a five-membered ring is the only possibility and occurs despite the rigid phenyl groups (Figure 7).

Shaw also demonstrated that the substituents on phosphorus were of enormous importance in determining the likelihood of cyclometallation (Figure 8). This information is important to the current work as cyclometallation is one of the primary steps in dehydrogenation. He found that if R₁, R₂ are small (e.g. methyls) then metallation would usually not occur; if R₁, R₂ are larger (e.g. phenyls) it would sometimes occur and sometimes not; but if R₁, R₂ were very bulky (e.g. $t\text{Bu}$) then metallation occurs readily and rapidly. In every case he examined it was found that the tendency to metallate increased in the order:



and that steric effects were clearly dominant over electronic.⁶² These results closely resemble the Thorpe-Ingold or *gem*-dialkyl effect known by organic chemists for many years.

Figure 7

Mechanism Proposed by Clark for the Dehydrogenation
of 2,2'-Bis(*O*-Diphenylphosphino)Bibenzyl

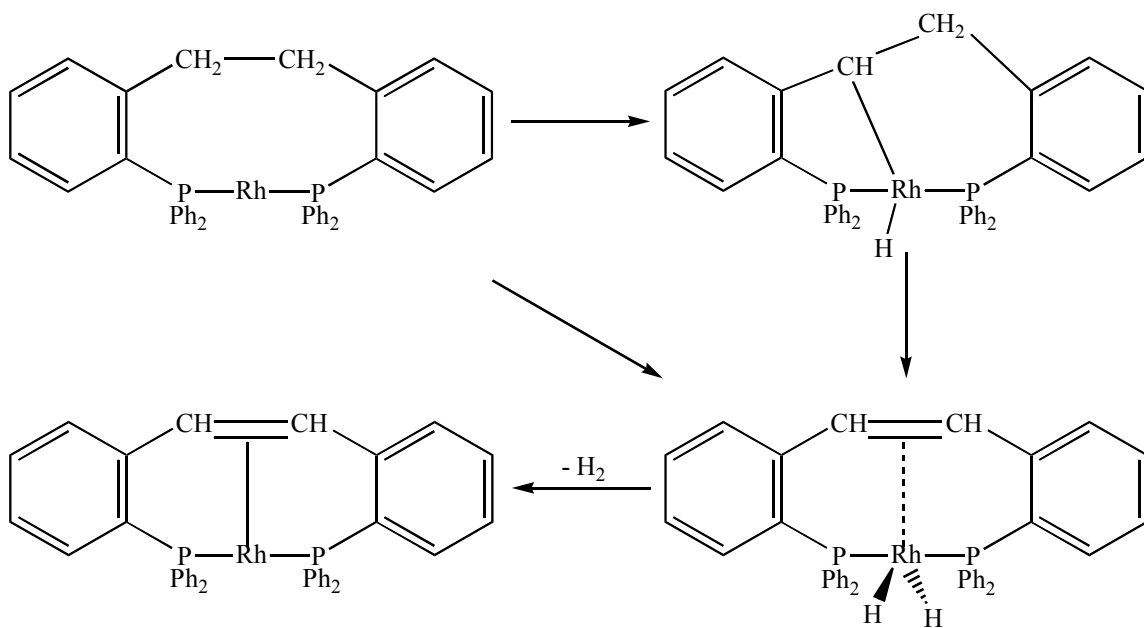
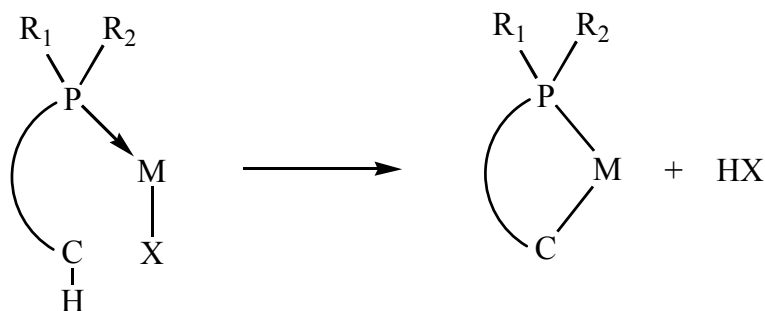


Figure 8

Cyclometallation of Carbon Atoms in Organic Groups on Tertiary Phosphines



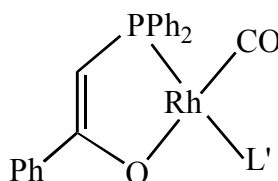
It's only since 1988 that the first efficient homogenous catalytic systems for the dehydrogenation of alkanes have been reported. Initially, $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ was found to catalyze photochemical alkane dehydrogenation.^{63,64,65} More recently, Goldman and co-workers reported that $\text{Rh}(\text{PMe}_3)_2\text{CIL}$ ($\text{L} = \text{CO}, \text{PMe}_3, \text{P}^i\text{Pr}_3$) and $[\text{Rh}(\text{PMe}_3)_2\text{Cl}]_2$ catalyzed extremely efficient thermal transfer-dehydrogenation.⁶⁶ The latter system requires both sacrificial hydrogen acceptors (olefins) and, somewhat surprisingly, a hydrogen atmosphere to be operative. Such complexes are reported to effect transfer-dehydrogenation in the absence of H_2 , but with much lower rates and total catalytic turnovers, even at much greater temperatures.⁶⁷ Complexes with tridentate ligands, $(\eta^3\text{-PXP})\text{RhL}'$ ($\text{PXP} = (\text{Me}_2\text{PCH}_2\text{Me}_2\text{Si})_2\text{N}, \text{Me}_2\text{PCH}_2(2,6\text{-C}_6\text{H}_3)\text{CH}_2\text{PMe}_2$; $\text{L}' = \text{CO}, \text{C}_2\text{H}_4$), were also found to catalyze thermal or photochemical dehydrogenation of cyclooctane with limited activity.⁶⁷

Miller and Knox reported efficient transfer-dehydrogenation of alkanes with $[\text{RhCl}(\text{AsPh}_3)_2]_2$ and $[\text{RhCl}(\text{CO})(\text{AsMe}_3)_2]$ as catalytic precursors under 3.4 MPa of

hydrogen at 60-100°C with turnover rates reaching 600/hr.⁶⁸ Braunstein and co-workers have used a variety of rhodium carbonyl phosphino enolate complexes (Figure 9, L' = PPh₃, PPh₂(*p*-tolyl), P(*p*-C₆H₄F)₃) to catalyze the dehydrogenation of cyclooctane in the presence of norbornene.⁶⁹

Figure 9

Structure of Rhodium Carbonyl Phosphino Enolate Complexes



They found that the value of K, the ratio between the cyclooctene and norbornane products, increases slightly in the order L' = PPh₂(*p*-tolyl) < PPh₃ < P(*p*-C₆H₄F)₃, with decreasing phosphine basicity. However, the potentially chelating keto phosphine Ph₂PCH₂C(O)Ph considerably decreased the dehydrogenation reaction, while P(*o*-tolyl)₃ was completely inactive.⁷⁰ This latter observation may be attributed to a cyclometallation side reaction which would provide a pathway for catalyst deactivation.^{71,72} Alkane activation is known to be especially sensitive to this.⁷³

The catalysis of 2-propanol dehydrogenation has also been explored extensively, being the reverse of acetone hydrogenation. Knowing that NEt₃ induced ketone hydrogenation in Wilkinson's catalyst, RhCl(PPh₃)₃, Matsubara and Saito investigated the effect of NEt₃ on dehydrogenation.⁷⁴ While RhCl(PPh₃)₃ itself was inactive for 2-

propanol dehydrogenation, the addition of NEt_3 aroused the catalytic activity to generate equimolar amounts of hydrogen and acetone. This is believed to be caused by the *in situ* transformation of $\text{RhCl}(\text{PPh}_3)_3$ into an active hydrido species, $\text{RhH}(\text{PPh}_3)_4$. The formation of this hydrido phosphine complex initiates dehydrogenation in solution. By studying $\text{RhH}(\text{PPh}_3)_4$ directly they deduced that the presence of a base, such as NEt_3 , allows the formation of an alkoxide ion and promotes its attack to give $[\text{RhH}(\text{OCHMe}_2)(\text{PPh}_3)_3]^-$, where one of the PPh_3 ligands is lost. This alkoxide complex then releases acetone and gives $[\text{Rh}(\text{H})_2(\text{PPh}_3)_3]^-$. Subsequent protonation leads to $\text{Rh}(\text{H})_3(\text{PPh}_3)_3$ which loses dihydrogen to give the parent complex $\text{RhH}(\text{PPh}_3)_4$ with PPh_3 coordination.

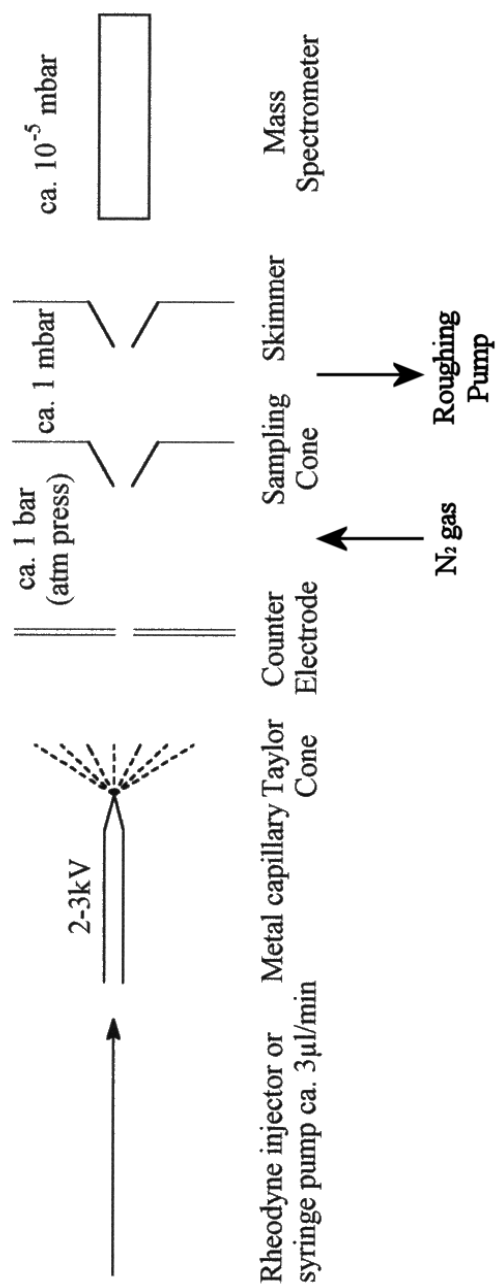
Electrospray Mass Spectrometry

Electrospray mass spectrometry (ESMS) is a relatively new technique capable of very gentle transfer, with little or no fragmentation, of pre-existing ions from solution to the gas phase. Although the electrospray nebulization process was first developed in the late 1960's,⁷⁵ it was not closely examined until 1979.⁷⁶ It was after this time that Fenn and co-workers first combined electrospray ionization (ESI) with a modern spectrometer (MS), thus giving birth to ESMS.⁷⁷

Several steps are involved in producing charged ions in the gas phase.⁷⁸ First, a solution of the electrolyte to be studied is prepared at a concentration of 1×10^{-3} - 1×10^{-5} (mol/L). This is delivered at a constant flow rate of about $3 \mu\text{l}/\text{min}$ to a metal capillary (Figure 10). There are two common ways of doing this: (1) by using a Rheodyne injector

Figure 10

Scheme of a Typical Electrospray Mass Spectrometer (ESMS)



fitted with a 10 μ l sample loop,⁷⁹ or (2) by using a syringe pump which delivers at a constant flow rate. The advantage of the first is that it uses less analyte, resulting in less frequent cleaning of the mass analyzer. The advantage of the syringe pump is that the sample is injected over a longer time period allowing more data acquisition.

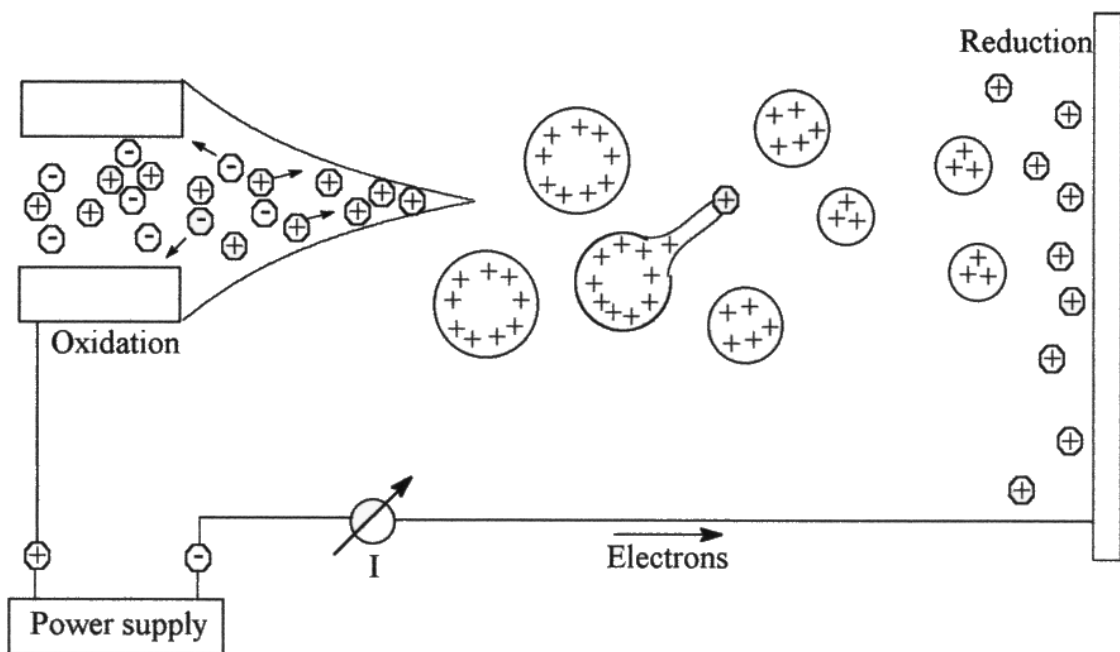
Second, the liquid sample (analyte in the solvent or mobile phase) with a purge of nebulizing gas, typically nitrogen, flows through a heated (ca. 60°C) stainless steel capillary to which a voltage of 2-3 kV has been applied. This high voltage creates a powerful electric field which charges the surface of the liquid (electrophoretic charging) and induces a partial charge separation in the electrolyte solution. When the capillary is of positive polarity, the surface of the liquid emerging from the capillary tip is enriched with positive ions. The opposite would be true for a negative polarity capillary,^{80,81} but only the former case will be considered.

The liquid surface with its excess charge is unstable, which combined with the effect of the nebulizer gas, results in a fine spray of droplets directed towards the counter electrode. These droplets form a cone called the Taylor cone. This cone has a concentration gradient, becoming filled primarily with positively charged ions at the tip, while the negatively charged ions remain at the capillary (Figure 11).

Once the droplets are released from the Taylor cone they pass through an orifice at the counter electrode into the mass spectrometric sampling system where they begin to decrease in size. Solvent evaporation occurs as a result of a combination of the heated capillary, passing through a curtain of dry nitrogen gas (the bath gas), and a pressure gradient created by the 1 mbar pressure region beyond the sampling cone. This

Figure 11

Scheme of Processes in Electrospray Ionization (ESI)



shrinkage of the drops continues until they get down to about 1 μm or the Rayleigh limit where the charge of the droplet is sufficient to overcome the surface tension that holds it together.^{81,82} Most of the uncharged material and solvent vapor are pulled away from the sampling cone by the bath gas and diffusion pumps.

The fission of solvated ion droplets continue until they decrease in size to a radius of 8-10 nm and are suitable to enter the gas phase. This process is not well understood, but there are two popular mechanisms proposed for this gaseous ion formation. One theory, called the single ion in droplet theory (SIDT), proposes that the droplets must continue to shrink until they contain only a single ion. Thus, when the solvent evaporates it leaves only a single ion in the gas phase.⁸¹ Another theory proposed by Iribarne and Thomson, called Iribarne emission, is that the droplet fissions continue until the electric field at the droplet surface is powerful enough to desorb ions into the gas phase.⁷⁶

Next, the ions are drawn through the sampling cone, which has a variable voltage (often referred to as the “cone voltage”), and then through the skimmer into the mass analyzer. The higher the potential on the sampling cone, the greater the kinetic energy of the generated ions resulting in more energetic collisions with the solvent molecules and greater collisionally induced dissociation (CID), or fragmentation of clusters and ions.^{83,84}

One of the unique abilities of the ESI process is the production of ions of high charge, distinguishing ESMS from other mass spectrometric techniques. These multiply charged ions yield m/z values of generally up to 2500, within the m/z upper limit of today's mass spectrometers.⁸⁵ This has made it of great interest to the study of large biomolecules such as proteins.⁸⁶ Normally molecules of such high molecular weights (>

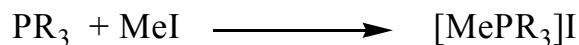
10,000 amu) are outside the range of conventional techniques, but one of the primary features of ESI is its soft ionization which produces multicharged molecular ions giving peaks in a more convenient mass/charge region.

Group 9 Transition Metal Complexes and ESMS

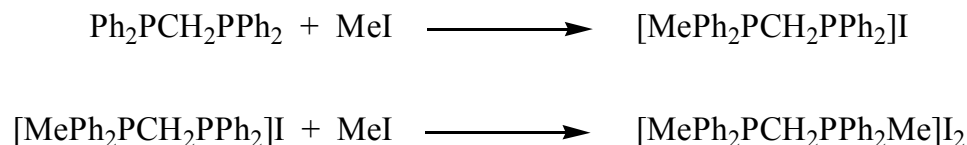
The following section is a brief review of what has been reported in the literature on the use of electrospray mass spectrometry (ESMS) in regards to group 9 (cobalt, rhodium, iridium) transition metal complexes. Additional attention will be given to phosphines, a particular interest of this work.

The first phosphine derivative examined using ESMS was reported by Yamashita and Fenn,⁷⁷ two of the pioneers of electrospray mass spectrometry. They mixed together a number of tetraalkyl-ammonium and -phosphonium salts dissolved in a 50:50 mixture of methanol:water. The ESMS spectrum revealed the intact ion peaks for each of the ions, including the $[\text{P}(\text{C}_4\text{H}_9)_4]^+$ phosphonium ion.

More recently, ESMS studies of phosphonium salts have been extended to include derivatives of polyphosphines.⁸⁷ Reaction of a simple phosphine with MeI is known to form the corresponding methylphosphonium cation



and similar reactions proceed in a stepwise manner with polyphosphines.

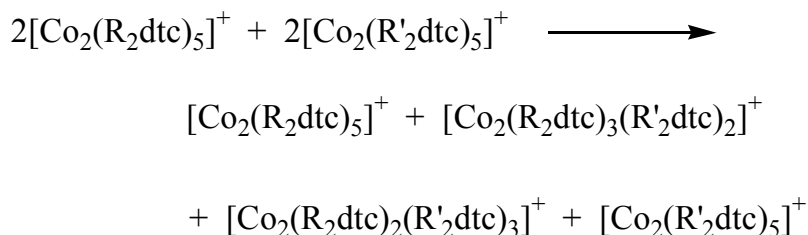


The identities of the products in solution were confirmed by ^{31}P NMR measurements. In almost every case, the intact cations were observed by ESMS and their identification agreed with that deduced from the NMR spectra. Also, peaks were often observed that corresponded to the addition of an oxygen atom to the remaining phosphine groups in the cation to form a phosphine oxide. This effect is often observed in the ES mass spectra of metal phosphine complexes and may be due to oxidation within the electrospray ion source, or, in some cases, to oxidation of the phosphine in dilute solution.⁸⁸

The first transition metal complexes studied by ESMS were $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ (bipy = 2,2'-bipyridyl) and $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ (phen = 1,10-phenanthroline).⁸⁹ For $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ solutions at low levels of collisional activation, the doubly-charged intact cation was the base peak in the mass spectrum. Also observed were a series of minor peaks corresponding to adduction of one to four acetonitrile solvent molecules. Increasing the collision energy led to removal of the weakly bound solvent molecules, while still higher energies produced fragmentation in which both one and two bipyridyl ligands were lost. Similar behavior was observed for the phenanthroline complex. However, the corresponding complex $[\text{Ru}(\text{bpz})_3]\text{Cl}_2$ (bpz = bipyrazine) produced different results in

that $[\text{Ru}(\text{bpz})_2\text{Cl}]^+$ was identified as the base peak in its mass spectrum.⁹⁰ This result is consistent with the known facile loss of the bipyrazine ligand for this compound in solution and demonstrates the ability of ESMS to monitor reactions in solution.

Studies with group 9 transition metals (cobalt, rhodium, and iridium) utilizing ESMS have been scarce to date. In 1990 Kebarle and coworkers observed the hydrated ions $[\text{M}(\text{H}_2\text{O})_n]^{2+}$ ($n = 7-14$) for a range of divalent transition metals including Mn, Fe, Co, Ni, Cu, and Zn.^{91,92,93} Later, Colton and co-workers studied the dimeric cation $[\text{Co}_2(\text{Et}_2\text{dtc})_5]^+$ ($\text{Et}_2\text{dtc} = \text{S}_2\text{CNEt}_2$, diethyldithiocarbamate) formed by the oxidation of $\text{Co}(\text{Et}_2\text{dtc})_3$ using NO^+ . The ES mass spectrum showed the intact $[\text{Co}_2(\text{Et}_2\text{dtc})_5]^+$.⁹⁴ ESMS also showed exchange of $[\text{Co}(\text{R}_2\text{dtc})_2]^+$ units according to the following reaction:



This exchange has previously been observed using ^{59}Co NMR spectroscopy.⁹⁵ Van Berkel and Zhou used cyclic voltammetry, UV-vis spectrophotometry, and ESMS to investigate another oxidation reaction, this time of $\text{Co}(\text{OEP})$ ($\text{OEP} = \text{octaethylporphyrin}$) by chemical electron-transfer reagents such as $\text{CH}_2\text{Cl}_2/0.1\% \text{CF}_3\text{COOH}$, which are essentially oxidizing solvents.⁹⁶

A very detailed ESMS study has been carried out on the species formed in solution between the ligands shown in Figure 12 and a variety of transition metals, including Co(II).^{97,98,99} The bidentate ligand L¹, an analog of bipy, reacted with Co(II) to give [Co(L¹)₃]²⁺ which was observed by ESMS. Previous stability constant studies showed that the ligand L² forms the triple helical cation [Co₂(L²)₃]⁴⁺ with Co(II), and the ES mass spectrum showed essentially one peak assigned to this intact ion.

A ruthenium(II)-rhodium(III) mixed metal species was examined by ESMS. The complex contained bipy and was bridged by dPr (Figure 13 for structure). The mass spectrum of the product, [(bipy)₂Ru(dPr)Rh(bipy)₂](ClO₄)₅, gave peaks assigned to the intact cation (5⁺) and adducts with 1-3 perchlorate anions.⁹⁰ The spectrum of the bridged rhodium(III) dimer [Rh(bpy)₂]₂B_αH₂(ClO₄)₆ (Figure 13 for structure of B_αH₂) was also obtained. The three metal-containing species each involved loss of 2H and contained 0-2 perchlorate anions ([M-6X-2H]⁴⁺, [M-5X-2H]³⁺, [M-4X-2H]²⁺ where X = ClO₄⁻).⁹⁰

Also studied by Arakawa and co-workers was the complex Co(bpy)₃(ClO₄)₃. The distinctive feature in the mass spectrum was the appearance of reduced Co(II) complex ions. Possible explanations include chemical reduction/oxidation in the solvent system prior to the spraying, electrochemical reduction at the metal/solution interface of the ESI needle used as a high-voltage contact, and reduction induced by collisional activation. The absorption spectrum showed no signs of Co(II) so it must be a phenomenon arising during the ESMS technique. Van Berkel *et al.* have presented data showing that the origin of radical cations observed in ESMS is due to electrochemical oxidation in the ESI needle.¹⁰⁰ However, electrochemical reduction during the spraying may be impossible in

Figure 12

Ligands Studied with Co(II) using ESMS

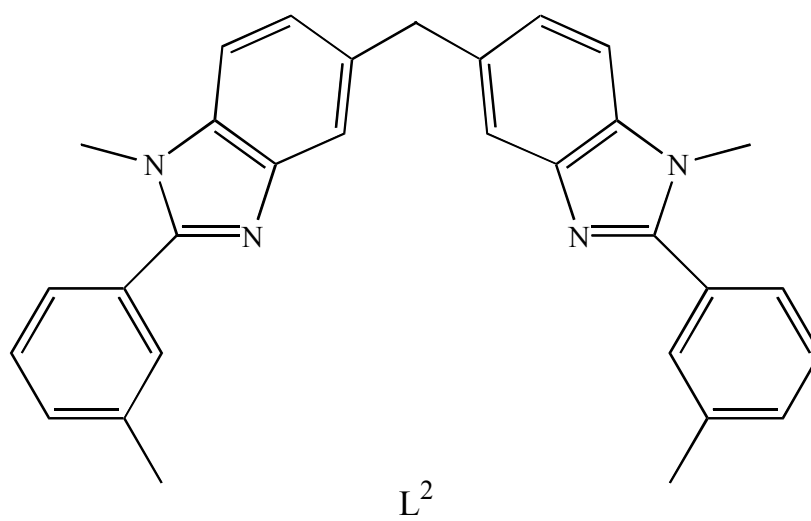
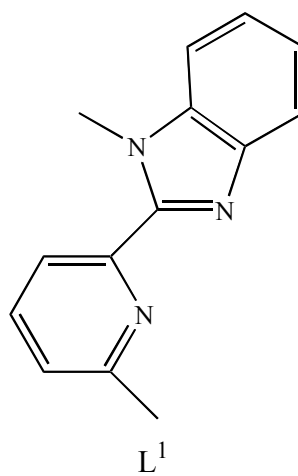
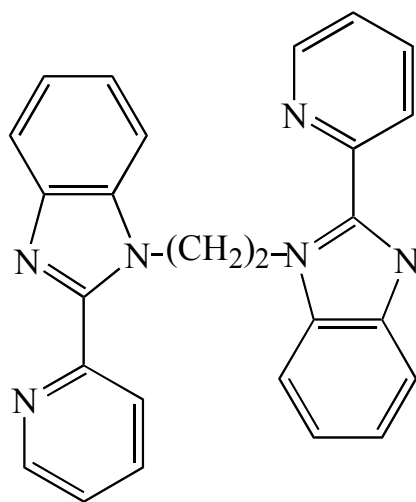
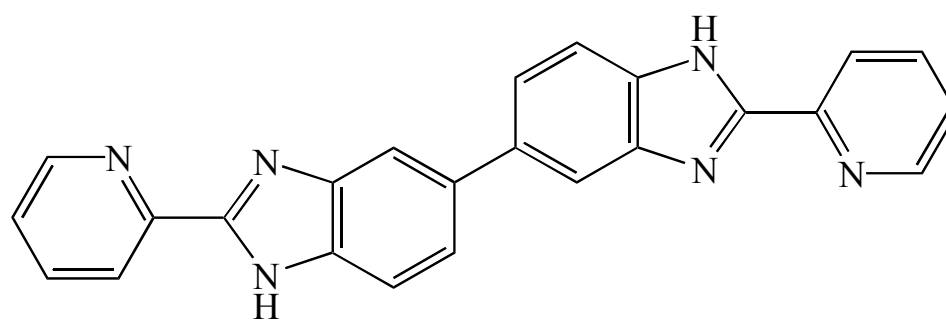


Figure 13

Ligands Studied with Ru(II) and Rh(III) using ESMS



dPr

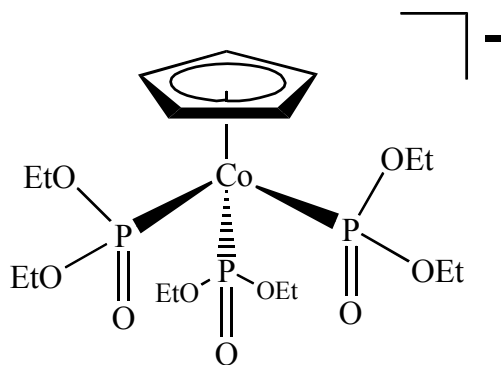
 $B_\alpha H_2$

the positive ESMS mode. Arakawa proposed that the production of Co(II) is due to charge reductions caused by collisional activation.⁹⁰

Colton and Kläui reported some interesting results with the tripodal oxygen ligand $[\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]^-$ (Figure 14).¹⁰¹ Using this anion they formed salts with various metals, including sodium, potassium, cesium, and lithium. The sodium salt had the unusual property of being soluble in both water and pentane. The X-ray structure of the sodium salt showed the complex to be trimeric ($\text{Na}_3 [\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]_3$) where each ligand is bidentate to one sodium ion with the third oxygen bridging to another sodium ion. This encapsulates the three sodium ions in a hydrophobic cavity surrounded by lipophilic cyclopentadienyl rings and 18 ethoxy groups.

Figure 14

Structure of the Tripodal Oxygen Ligand $[\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]^-$



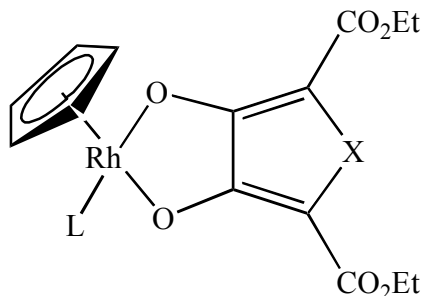
The electrospray mass spectrum of $\text{Na} [\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]$ in methanol showed monomers, dimers, and the trimeric unit $[\text{HNa}_3 [\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]_3]^+$ (m/z 1675) which are also found in the solid state, in non-aqueous solvents, and even in acidic

aqueous media. The presence of these polymeric species was also confirmed using negative ion ESMS.¹⁰² It was unclear whether the monomers, dimers, and trimers were all present simultaneously in solution, or if the monomers and dimers were fragments derived from the trimers during collision within the ion source. In an attempt to verify that they are not collisionally induced products, Colton monitored the relative intensities of monomers and dimers as the cone voltage was increased. It would be expected that these intensities would increase with cone voltage if they were a product of fragmentation from the trimers, but this was not observed; and in fact the peaks corresponding to the dimers decreased. Peaks due to monomers also decreased, but the appearance of a new monomer peak was not observed. This suggests that monomers, dimers, and trimers exist simultaneously for this system and that breakdown of dimers to monomers is not a facile process in the gas phase.¹⁰¹

ESMS has also been used to study the coordination chemistry of complexes of the

type $[\text{Rh}\{\overline{\text{OCC}(\text{CO}_2\text{Et})\text{XC}(\text{CO}_2\text{Et})\text{CO}}\}(\eta^5\text{-C}_5\text{Me}_5)\text{L}]$ where X = O or S and L =

PPh_3 , pyridine (py), or $\text{P}(\text{OPh})_3$.¹⁰³



The complexes were studied by $^{13}\text{C}\{^1\text{H}\}$, ^1H , and $^{31}\text{P}\{^1\text{H}\}$ NMR. ESMS was used to study the lability of the ligands which were trapped with various reagents to obtain products such as E=PPh_3 (where $\text{E} = \text{O}, \text{S}, \text{Se}$). Different ligands showed different coordinating tendencies towards the rhodium center.

They also added AgNO_3 to a solution of

$[\text{Rh}\{\overline{\text{OCC}(\text{CO}_2\text{Et})\text{SC}(\text{CO}_2\text{Et})\text{CO}}\}(\eta^5\text{-C}_5\text{Me}_5)\text{PPh}_3]$. After standing for approximately

ten minutes, the electrospray mass spectrum showed that the parent ion

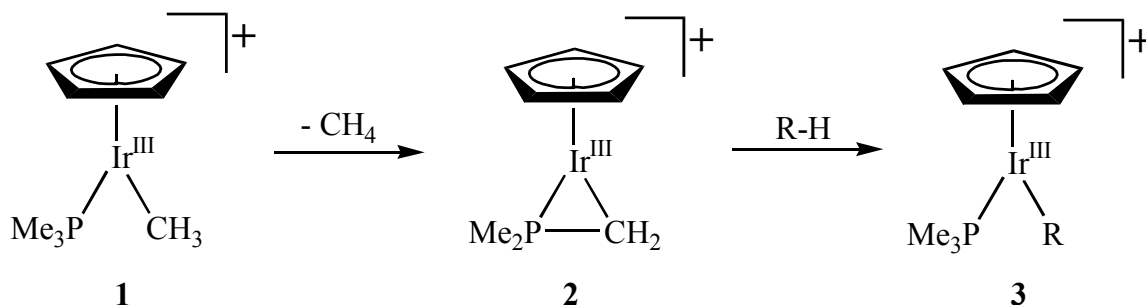
$[\text{Rh}\{\overline{\text{OCC}(\text{CO}_2\text{Et})\text{SC}(\text{CO}_2\text{Et})\text{CO}}\}(\eta^5\text{-C}_5\text{Me}_5)\text{PPh}_3 + \text{H}]^+$ had almost disappeared and

the major peak was identified as $[(\text{Ph}_3\text{P})\text{Ag}(\text{NCMe})]^+$ (m/z 410). Also present were other peaks, including $[\text{AgPPh}_3]^+$ (m/z 369). It is assumed that as the PPh_3 dissociates from the rhodium complex it is complexed to the Ag^+ ion, preventing recombination with the rhodium center.¹⁰³

ESMS has also been used to determine reaction intermediates. In a study of cationic iridium(III) complexes the previously proposed associative mechanism proceeding through an 18 electron iridium(V) intermediate was shown to be incorrect.¹⁰⁴ Instead, the following mechanism was validated by ESMS (Figure 15).

Figure 15

Proposed Associative Exchange Mechanism for Iridium(III)



R-H = pentane, cyclohexane, or benzene

The electrospray mass spectrum of the $[\text{CpIr}(\text{PMe}_3)(\text{CH}_3)(\text{CH}_3\text{CN})]^+$ starting material showed the intact cation of $[\text{CpIr}(\text{PMe}_3)(\text{CH}_3)(\text{CH}_3\text{CN})]^+$ at low cone voltages (35V). Upon increasing the cone voltage to 60V, this ion peak undergoes collisionally induced dissociation to remove the CH_3CN , giving cation **1** (Figure 15) and a small amount of cation **2** (Figure 15). When R-H was mixed with the bath gas, N_2 , then cation **2** was depleted and cation **3** (Figure 15) observed. The lack of change in the signal from **1** indicated that it is not as reactive to addition of R-H as **2**. All this evidence lends credence to the reaction proceeding through a 16-electron intermediate, as shown in **2**.¹⁰⁴

One of the most ambitious studies was conducted in 1999 by Kim and Chen who used electrospray ionization tandem mass spectrometry (ESI-MS/MS) to model homogenous catalytic hydrogenation in the gas phase.¹⁰⁵ Their ESI-MS/MS consists of an octopole, quadrupole, octopole, quadrupole (O1/Q1/O2/Q2) configuration behind a conventional ESI source. This allowed them to have a “daughter-ion mode” where Q1 is

used to mass-select ions of a single mass produced in O1 and react or collide them with a target gas in O2 and then analyze them in Q2. Using this they selectively prepared and monitored the subsequent gas-phase reactions of $[\text{Rh}(\text{PMe}_3)_2]^+$ and $[\text{Rh}(\text{PMe}_3)_2(\text{H})_2]^+$. $[\text{Rh}(\text{PMe}_3)_2]^+$ resembles the key reactive intermediate in catalytic hydrogenation reactions by rhodium or ruthenium complexes, and furthermore exhibits gas-phase ion-molecule chemistry with hydrocarbons and molecular hydrogen that shows parallels to solution-phase homogeneous catalytic hydrogenation.^{106,107} Through a combination of isotopic labeling and multistep reaction sequences they mapped two mechanistic pathways in the hydrogenation sequence and defined the structural requirements for a gas-phase mimic of the solution-phase solution. (See Results, Section 3 for more on this)

Prior to this work, Chen and co-workers also used ESI-MS/MS to study gas-phase C-H activation by $[\text{CpIr}(\text{PMe}_3)(\text{CH}_3)]^+$,^{108,109} oxo-transfer reaction by $[\text{O}=\text{Mn}^{\text{V}}(\text{salen})]^+$,¹¹⁰ the Ziegler-Natta polymerization of olefins by $[\text{Cp}_2\text{Zr-R}]^+$,¹¹¹ and olefin metathesis by $[\text{Cl}_2\text{Ru}(=\text{CHPh})(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{NMe}_3)_2]^{2+}$.¹¹²

Conclusions

Neutral and cationic complexes of rhodium phosphines are well-known as powerful catalysts for hydrogenation, isomerization, dimerization, hydroformylation, and carbonylation reactions. Their catalytic activity for asymmetric synthesis in regards to hydrogenation is well documented, but less is known pertaining to dehydrogenation reactions.

The factors affecting *cis* vs *trans* and monomer vs dimer formation of these complexes are not entirely understood, but several theories with a few examples have arisen. The effect of structure on catalytic activity is clear, but the exact specifics are not.

Finally, over the last 20 years, electrospray mass spectrometry has emerged as one of the preeminent techniques for the study of cationic species in solution. It can be extended to study even neutral species when converted to a related ion. Even intermediates or species in rapid exchange, which are difficult to observe in NMR, can be studied easily by ESMS. The increased sensitivity of this technique reduces the long collection times sometime required in NMR, while also allowing very low concentrations of samples to be used. ESMS is also a versatile technique in regards to the information that can be gathered. At higher cone voltages ESMS closely resembles FAB mass spectroscopy with increased fragmentation, but at lower cone voltages the spectra obtained give an accurate qualitative picture of the species present in solution.

Focus Statement

The primary aim of this research is:

- 1) Study of the solution structures of cationic rhodium(I) bis-phosphine complexes primarily by ESMS and complemented by ^{31}P NMR and previous FAB MS results.
- 2) Examination by ESMS of the ligand backbone dehydrogenation in the bidentate phosphine ligands of rhodium(I) complexes at higher cone voltages. FAB MS data from prior work will be used complementary to this.
- 3) Examination by ESMS of loss of formaldehyde and methanol from rhodium(I) carbonyl complexes with bidentate phosphine ligands at higher cone voltages. Results from previous FAB MS studies will be used to supplement this as well.

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