

CHAPTER I

INTRODUCTION

1.1 Chemical Modification of Polymers

Some of the most important commercial polymers are diene polymers, e.g., natural rubber (polyisoprene, PI), styrene butadiene rubber (SBR) and acrylonitrile butadiene copolymers (NBR). Their usefulness to scientists and engineers arises from the fact that they form a base for a variety of chemical modification reactions that are made possible because of the presence of olefinic groups within the polymers.

Chemical modification of polymers is a postpolymerization process. In the broadest sense, chemical modification could include reactions such as crosslinking, grafting, degradation, oxidation, isomerization, and cyclization. Its main use is to produce polymers with desirable physical and chemical properties that are not accessible by standard polymerization techniques. In the past few years, considerable interest has been expressed in the modification of diene polymers by metal-catalyzed reactions such as hydrogenation, hydrosilylation, hydrocyanation, hydrocarboxylation, hydroformylation, and hydroxymethylation. Among these, hydrogenation has been the most widely investigated. The subject has been reviewed previously; however, since the publication of these reviews there has been a surge of new research on the subject, and this current review will illustrate the progress made in the field over the last 15 or so years [1-3].

Hydrogenation in itself simply reduces the degree of unsaturation in the diene polymers. Nevertheless, it leads to significant changes in the chemical and physical properties of the polymers. The reasons for carrying out this process are quite varied, and hydrogenated diene polymers are being used in an ever-growing number of applications, such as in research examining polymer structure and morphology. The major utilization has been in applications that require materials with enhanced resistance to thermal and oxidative degradation. Possibly, the only factor that has prevented hydrogenated polymers from being used in a wider range of applications is the fact that they are relatively expensive to produce. The ever-growing body of research into materials that make use of hydrogenated polymers suggests that this

economic factor is becoming less important or that lower cost processes are becoming more feasible.

Hydrogenation of polymers can be achieved by both catalytic and noncatalytic methods. There are some recent citations of the use of noncatalytic hydrogenation of diene polymers. The main method of noncatalytic hydrogenation is by diimide reduction using hydrazide reagents. This method has one major advantage over others in that it circumvents the need for specialized hydrogenation apparatus. Despite this advantage, studies into the catalytic hydrogenation of the diene polymers are by far more numerous.

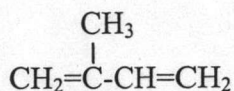
Within the general heading of catalytic hydrogenation there are examples of the use of both heterogeneous and homogeneous catalyst systems. The use of heterogeneous catalysts is still prevalent, but many of the new developments in the field of catalytic hydrogenation over the last few years have involved the use of homogeneous catalysis because it provides a better opportunity to realize quantitative hydrogenation [4].

1.2 Hydrogenation of Natural Rubber

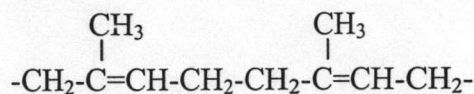
The empirical formula for the natural rubber molecule appeared to be first determined by Faraday who reported his findings in 1826. He concluded that carbon and hydrogen were the only elements present and his results corresponded to the formula of C_5H_8 . Many years later, Weber indicated that the natural rubber molecule was unsaturated since it reacted with bromine to give a material of empirical formula as C_5H_8Br .

Having established the empirical formula, the next step was to determine the arrangement of carbon and hydrogen atoms within the rubber molecule. One approach was to study the products of destructive distillation that was done by Bouchardat and Greville Williams. These reactions gave rise to a variety of products but fractional distillation was found to lead to two main fractions of fairly uniform composition, one with a boiling range of 34-37°C, and the second with a boiling range of 175-176°C [5].

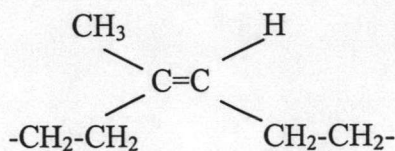
The first isoprene was found to have the formula C_5H_8 , which structure is as follows:



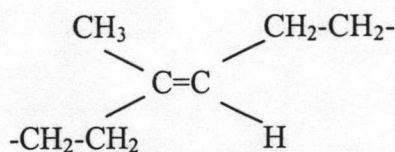
Natural rubber is a polymer of isoprene, in which essentially all the isoprene units are linked together at carbon atom 1 and 4 in a head-to-tail arrangement, and in which all or nearly all the repeating units possess the "cis" configuration.



Head-to-tail arrangement



Cis-1,4-polyisoprene



Trans-1,4-polyisoprene

Natural rubber is a cis-polymer. The structure and unit cell of the crystalline stretched rubber molecule is shown in Figure 1.1.

Hydrogenated natural rubber (NR) is so far only a scientific curiosity, since it has never been produced commercially and may not be on account of the experimental problems usually associated with its preparation. The early processes required either highly purified rubber in dilute solution or the use of very high temperatures that caused degradation. In addition, catalytic hydrogenation requires the catalyst to come into contact with each double bond for the reaction, and thus relatively large amounts of catalyst are essential if the hydrogenation is to be completed in a reasonable period of time. In addition, all traces of catalyst must be removed to avoid rapid oxidation of the product.

Very early work by Pummerer, Burkard, and Harries [6] produced hydorrubber $(\text{C}_5\text{H}_{10})_x$ from dilute solutions of purified rubber using platinum black as catalyst. Only very small amounts were obtained, but these experiments showed that the elastic

properties were retained along with relatively high molecular weight. Other routes, followed by Staudinger et al. [6] employed high temperature and pressure, 0.1% solutions in methyl cyclohexane and a nickel catalyst, and long reaction times with a very high nickel catalyst content at lower temperatures. It is interesting that when both gutta-percha and balata, the transforms of NR, are hydrogenated by similar methods, the result is hydorrubber of essentially the same properties, since the hydrogenation step removes the stereospecificity. One of the more detailed methods of preparation of hydrogenated NR was patented in 1946. Here a relatively high concentration of pale crepe rubber in cyclohexane (2%) was caused to react with hydrogen at 30-35 atm over a nickel-kieselguhr catalyst in an autoclave at 200-220°C for 12 h. The fully hydrogenated product was then obtained from the reaction mixture by the removal of catalyst by flocculation with glacial acetic acid, followed by concentration and precipitation with ethyl alcohol [6]. More recently, Singha et al. [7] investigated a homogeneous catalyst based on a rhodium compound. They reported that 80% hydrogenation of natural rubber was obtained using 1.3 mol% of $\text{RhCl}(\text{PPh}_3)_3$ as a catalyst in toluene at a hydrogen pressure of 40 kg/cm², and a reaction temperature of 100°C for 22 h.

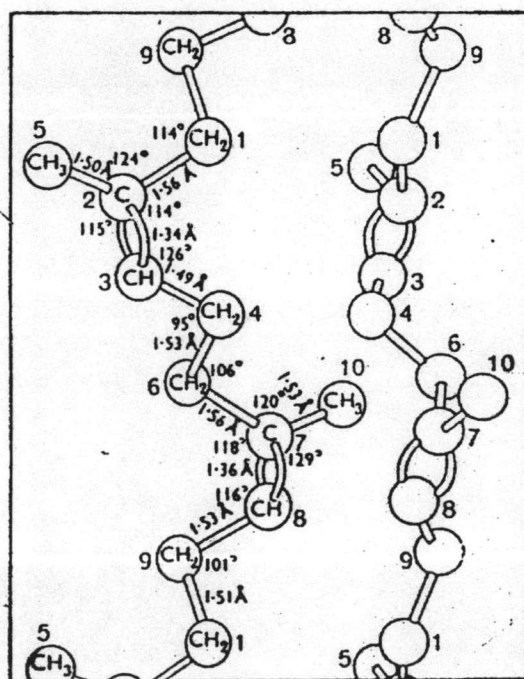


Figure 1.1 Unit cell structure of the natural rubber molecule [5].

Hydrogenated rubber is colorless and transparent. It is a plastic elastic waxy solid with the peculiar characteristic of pulling out into fine threads when stretched. Unfortunately, the limited scale of its preparation so far has precluded the measurement of any technological properties. It is known that fully hydrogenated NR is unaffected by the chemical reagents that normally attack unmodified natural rubber owing to the removal of the unsaturation. However, this also results in it being difficult to vulcanize in the conventional manner. Potential applications have been considered to be in the cable industry, which would utilize its insulation properties, and possibly for adhesive application.

1.3 Homogeneous Catalyst for Rubber Hydrogenation

Previous research on rubber hydrogenation showed that the most widely reported catalysts were those based on rhodium, ruthenium, and palladium [8-10]. While mononuclear osmium and iridium complexes have been largely overlooked, new research has demonstrated their ability to facilitate a variety of reactions, including the selective hydrogenation of compounds containing sensitive functional groups.

1.3.1 Catalytic Chemistry of $\text{OsHCl}(\text{CO})(\text{PR}_3)_2$ (**1a**, R=Cy; **1b**, R=*i*-Pr)

The synthesis of $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$ by refluxing a solution of PCy_3 and K_2OsCl_6 in methoxyethanol was first reported by Moers [11]. Although **1a** and **1b** are coordinatively unsaturated, they are monomeric in both the solid phase and in solution [11, 12]. Their structure is square pyramidal, with the bulky phosphines *trans* disposed within a plane shared by Cl and CO (Figure 1.2). Moers [13] attests that osmium lies essentially in the basal plane of **1a**, leaving a vacant coordination site *trans* to the hydride which is of considerable dimension. However, the coordination of a third bulky phosphine has not been detected for either **1a** or **1b**.

The addition of a host of small molecules to form stable, six coordinate complexes of **1a** and **1b** has been observed. Moers et al. [14, 15] have demonstrated the coordinative capacity of pyridine, SO_2 , CS_2 and CO to **1a**. Esteruelas and Werner have characterized the analogous CO complex of **1b** as well as an octahedral product of PMe_3 or $\text{P}(\text{OMe})_3$ addition [12]. The use of a 2:1 PMe_3 to Os ratio did not result in

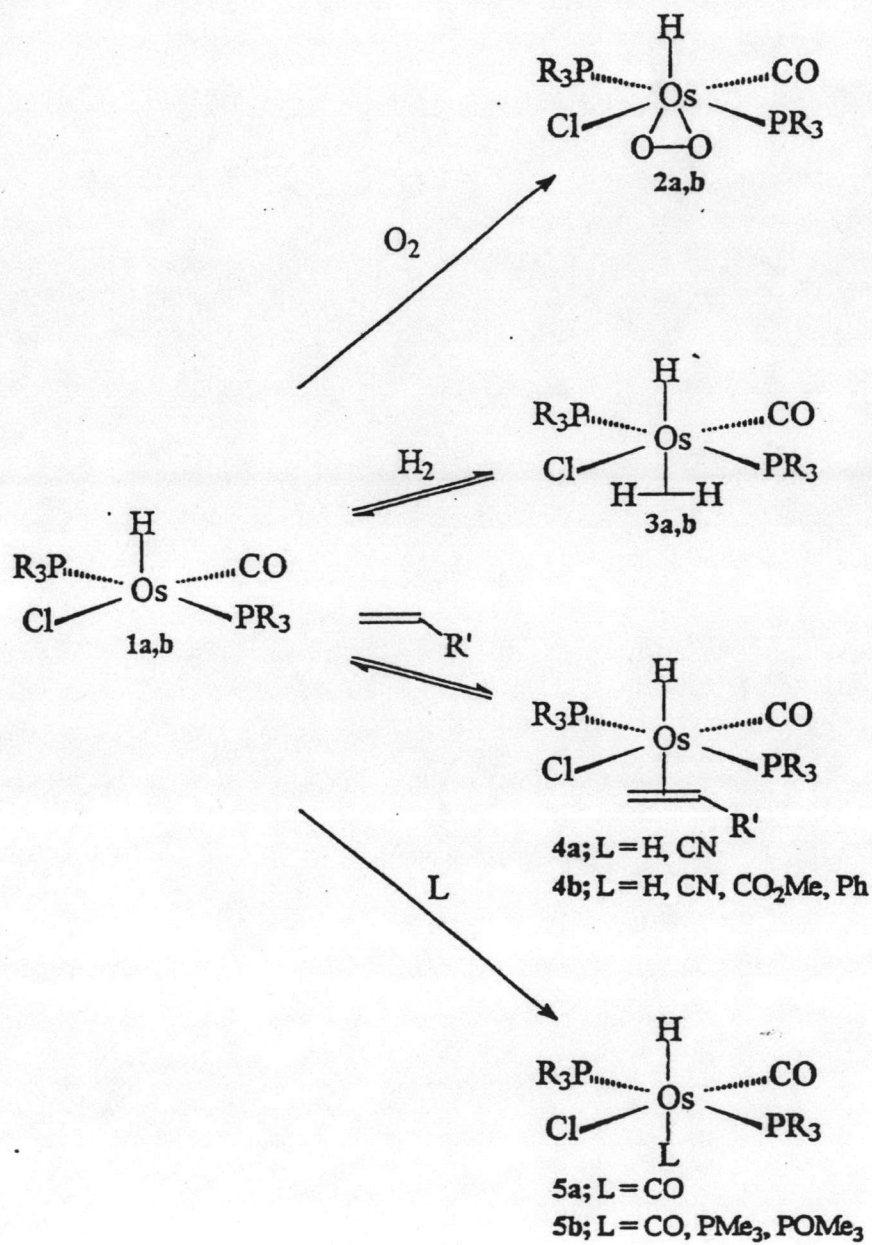


Figure 1.2 Characterized reactions of **1a,b** [13].

the displacement of a bulky phosphine to form a bis PMe_3 complex. The addition of larger alkyl phosphines was not observed, due to what is believed to be a steric limitation.

A displacement of the chloride of **1b** by an acetate anion to yield an air-stable, microcrystalline solid has been reported [12]. An IR spectrum indicates that the acetate group is bonded through both oxygen atoms as shown in Figure 1.3. This type of reaction has the potential to interfere with the hydrogenation of copolymers that contain significant amounts of the carboxylate salts derived from surfactant.

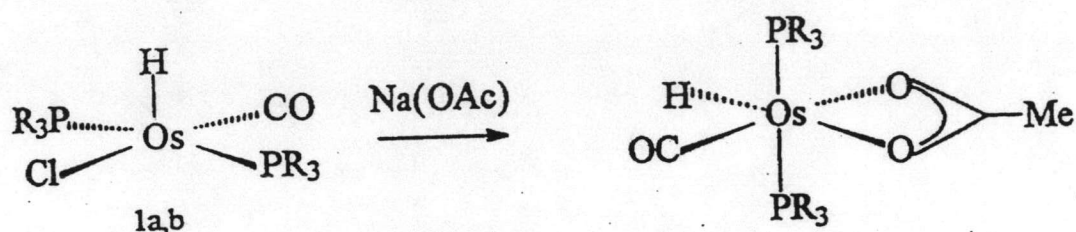


Figure 1.3 A displacement of the chloride of **1b** by an acetate anion [12].

Exposed to traces of oxygen the solid form of **1a** and **1b** (Figure 1.2) yield the diamagnetic dioxygen adducts **2a** [15] and **2b** [16]. The dioxygen ligand is very strongly bound, as indicated by the shift of $\nu_{\text{O-O}}$ in the IR from 1580 cm^{-1} for free O_2 to 820 cm^{-1} for **2a** and **2b**, respectively. The substantial single bond character of bound O_2 is characteristic of a η^2 -peroxo coordination mode [16]. In spite of this strong association, a displacement of dioxygen from **2b** was proposed by Andriollo et al. [17] when employed as a catalyst precursor. Note that over extended periods of time, pure solutions of Os- O_2 complexes are not necessarily stable.

A variety of small olefins have been shown to produce six coordinate complexes of **1a** and **1b** (Figure 1.2). Unactivated olefin such as ethylene must be present in excess to maintain stable adducts. However, electron withdrawing substituents such as CN, CO_2Me or CO stabilize the Os-olefin bond enough to produce isolable octahedral complexes. Esteruelas and Werner [12] observed no direct evidence for the production of stable metal-alkyls of **1b** that could form by the insertion of olefin into the osmium-hydride bond. However, in a later report they provide convincing evidence to support

the insertion of styrene at room temperature according to the scheme presented in Figure 1.4 [17].

In benzene solution with styrene, the hydride region of a $^1\text{H-NMR}$ spectrum of **1b** is reported to undergo significant changes. The hydride triplet of **1b** at -31.9 ppm disappears, to be replaced by a broad resonance at -27.9 ppm. In a separated experiment, the addition of styrene to $\text{OsDCl}(\text{CO})(\text{P}i\text{-Pr}_3)_2$ initiated an H-D exchange as the hydride signal at -27.9 ppm was restored at the expense of the olefin signal. Andriollo et al. [17] rationalized these observations as a rapid equilibrium (Figure 1.3) which produced an exchange averaged signal for the hydride of **1b**.

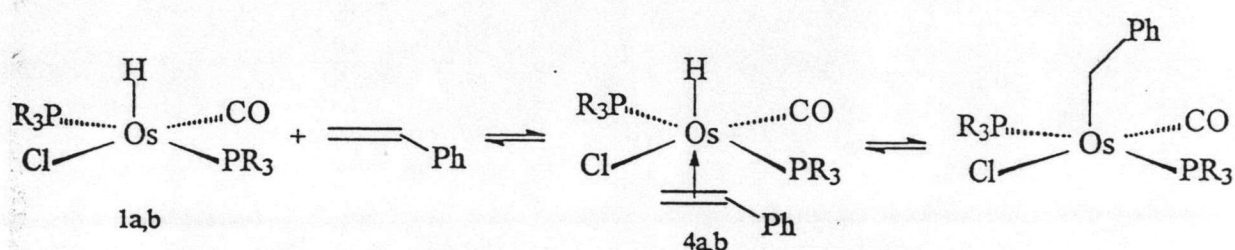


Figure 1.4 Styrene insertion into the Os-H bond of **1b** [17].

The only other olefin to be scrutinized for Os-alkyl formation is *trans*- PhHC=CHCOMe , or benzylideneacetone [18]. At room temperature in benzene, four equivalents of substrate failed to produce any changes to the $^1\text{H-NMR}$ spectrum of **1b**. Under identical conditions, the H-D exchange that had been reported for styrene was not observed. It should be noted that the unsubstituted analogue of benzylideneacetone, $\text{H}_2\text{C=CHCOMe}$, forms a very stable π -olefin complex that is unchanged after heating to 70°C in benzene for 24 hours [12]. It would therefore appear that the coordinating ability of an olefin is strongly influenced by the bulk of its substituents.

Complex **1b** has been shown to activate molecular hydrogen by a rather uncommon η^2 -coordination mode [16]. Consistent with other small molecule additions, dihydrogen coordinates *trans* to the hydride to create what is formally an Os (II) complex (Figure 1.5). Removal of an H_2 atmosphere rapidly transforms the

dihydrogen adduct back into **1b**. This instability has precluded the isolation of **3b**. It has therefore been characterized by spectroscopic means only.

A ^1H -NMR spectrum of **1b** at 240K under H_2 exhibits a broad resonance at -1.8 ppm (η^2 -bonded H_2) and a triplet at -6.5 ppm corresponding to the apical hydride ligand [19]. The minimum spin lattice relaxation times ($T_{1\text{min}}$) of these signals are 6.5 ms and 296 ms, respectively. Relatively fast relaxation is expected for η^2 -bonded H_2 , due to the efficiency of dipole interactions between two protons so close in space. Classical hydrides on the other hand, being located much further from other protons, have a less efficient relaxation mechanism and therefore longer T_1 's [20].

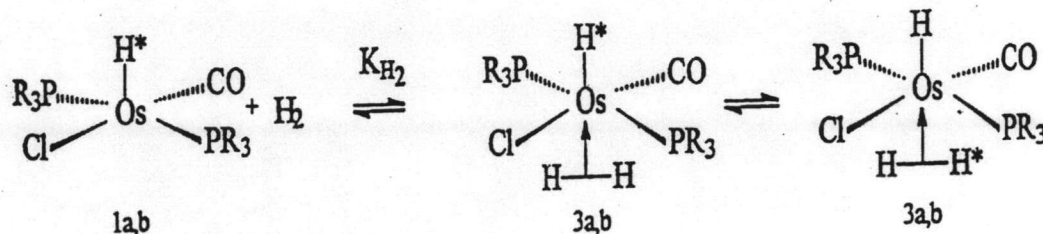


Figure 1.5 Coordination of molecular hydrogen by **1b** [16].

At 240K, Bakhmutov et al. [19] resolved a distinct dihydrogen signal at $\delta = -1.8$ ppm. At higher temperatures an exchange between free and bound H_2 was observed at a rate which varied from slow to fast on the NMR timescale. In the fast exchange domain they have estimated the equilibrium constant, K_{H_2} , to range from 2572 M^{-1} at 40°C to 143 M^{-1} at 80°C . Also at 80°C , the rate for H_2 loss (k_{-1}) from **3b** was reported to be $7.1 \times 10^5 \text{ s}^{-1}$. Clearly, the rate of H_2 exchange and the population of dissociated products are favoured by extreme temperature.

Esteruelas et al. [18] have noted that the exposure of **1b** to D_2 at room temperature produces $\text{OsD}(\text{D}_2)\text{Cl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ by H-D exchange. The transition state of this Os-H/Os- H_2 exchange process may be relevant to olefin hydrogenation, in that a seven-coordinate trihydride complex may serve as a hydrogenation transition state. To produce such a complex, bound dihydrogen must add oxidatively to the metal

centre. Alternatively, Bakhmutov et al. [19] suggest that $\eta^2\text{-H}_2$ could migrate from its *trans* position to form a transient *cis* H/H₂, 3-centred, Os(H₃) complex. Given the present state of knowledge, an assignment of either a trihydride or a three-centred Os (H₃) pathway for this exchange may be unjustified.

1.3.2 Catalytic Chemistry of [Ir(cod)py(PCy₃)]PF₆ (Crabtree's Catalyst)

The complexes [Ir(cod)L₂](PF₆) (**6**, cod = 1,5-cyclooctadiene; L = tertiary phosphine), first studied Osborn [21], presented a test of these ideas. The chlorinated solvents, CHCl₃, C₆H₅Cl, and, best of all, CH₂Cl₂, are the only viable solvents for catalytic hydrogenation with these cationic iridium catalysts, presumably since they all have high polarity but negligible coordinating power. The catalyst is tolerant of several functional groups, such as CO₂R, on the olefin, but those which are good ligands, such as CH₂OH, or strong bases, such as NR₂, can cause a loss of activity of the catalyst. Deliberate deprotonation of the catalyst system with NEt₃ leads to the formation of [IrH₅L₂], known to be a poor catalyst.

The mixed-ligand complexes [Ir(cod)L(py)]PF₆ (**7**), however, proved to be the most active catalysts of any particularly for hindered substrates, such as Me₂C=CMe₂. The catalysts derived from **6** and **7** are insensitive to substitution at the olefin, a feature in which they resemble heterogeneous catalysts far more than they resemble any other homogeneous system. One should allow about an order of magnitude rate differential to account for the 25°C temperature difference between the measurements made at 0°C. The catalysts derived from **6** and **7** are entirely homogeneous, colorless and yellow solutions, respectively, and they have no tendency to deposit metallic iridium even after prolonged contact with hydrogen. In non-coordinating solvents only, they are much more active than their rhodium analogues [22].

Crabtree et al. [23, 24] found that the reduction of the more hindered olefins does not proceed to completion. This is due to an irreversible deactivation process, which occurs even for unhindered olefins when the substrate has been consumed. Catalysts derived from **6** turn yellow on deactivation. Unsuccessful efforts were made to prevent deactivation using coordinating solvents or weakly coordinating ligands, or by changing the number and type of ligands in the precursor complex.

The original starting work in iridium chemistry came from an important early observation by Morris [23]. It is found that the catalyst precursor **6**, as a red CH₂Cl₂

solution., decolorizes on admission of hydrogen to the reaction flask. One day, he decided to see what would happen if he immediately pumped the hydrogen away again. He found that the color of the solution turned back to red. The color changes could even be cycled four or five times by admitting and then removing the hydrogen. Complex 6 could be reisolated unchanged, and in moderate yield, after the cycle of color changes. This suggested that a colorless intermediate might be formed in the reaction and might be stable enough at least to observe if not to isolate.

A concentrated solution of 6 in CD_2Cl_2 in an NMR tube also decolorizes rapidly at -80°C on passing hydrogen for a few seconds, and the solution is stable for at least several hours at -80°C . The product from the ^1H -NMR at that temperature is the simple cationic adduct $\text{cis}[\text{IrH}_2(\text{cod})\text{L}_2]^+$ (Figure 1.6). This was the first example known of a dihydrido olefin complex. Such complexes had been presumed to be the key intermediates in homogeneous hydrogenation, but had never been observed [25].

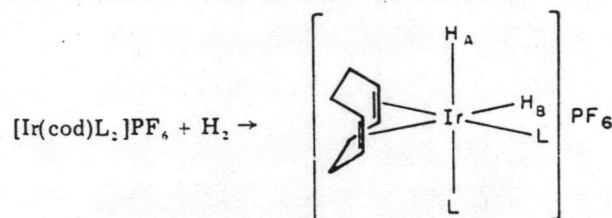


Figure 1.6 The simple cationic adduct [25].

Two hydride resonances were observed, a triplet, due to H_B coupling to two cis phosphorus nuclei, and a doublet of doublets, due to H_A coupling to one trans and one cis phosphorus nucleus. Four sharp resonances, due to the four inequivalent (cod) vinyl protons, were also present; these resonances have proved to be a reliable guide to the structure of a variety of types of iridium complexes containing 1,5-cyclooctadiene. The PMePh_2 complex also showed two PMe doublets, as expected for two inequivalent cis ligands.

The cis complexes were also formed with chelating phosphines as ligands [e.g., where $\text{L}_2 = 1,2$ -diphenylphosphinoethane (dpe)]. Crabtree et al. [26] found one

example in which the metal has no tertiary phosphines at all in the coordination sphere: $\text{cis-}[\text{IrH}_2(\text{cod})_2]^+$, formed by H_2 addition to $[\text{Ir}(\text{cod})_2]^+$ at -80°C . This example is particularly interesting, because it had been thought that hydrogen addition to an olefin complex was forbidden, since an olefin is an electron-withdrawing and therefore deactivating ligand.

In one case ($\text{L}_2 = \text{dpe}$), they isolated the crystalline adduct with Et_2O at -80°C . The IR spectrum of the solid, which is just stable at room temperature, shows two Ir-H vibrations, as expected for a cis arrangement of these ligands. When the solution is warmed to -20°C , in the absence of excess H_2 , hydrogen is in part lost to give **6**. Some hydrogen is transferred to the coordinated olefin to give $[\text{Ir}_2\text{H}_5\text{L}_4]\text{PF}_6$, cyclooctane, and HPF_6 . In the presence of excess H_2 the complexes are completely hydrogenated on warming.

The $[\text{IrH}_2(\text{cod})\text{L}_2]^+$ might be an intermediate in the reduction of excess (cod) as substrate by the catalyst precursor **6**. The initial activation of the precursor **6** ($\text{L} = \text{PPh}_3$ or PmePh_2) does indeed give the cis hydrogen adduct (Figure 1.6). Unexpectedly, however, once the initial mole of (cod) originally coordinated to the metal has been hydrogenated via $\text{cis-}[\text{IrH}_2(\text{cod})\text{L}_2]\text{PF}_6$ (**8**), a new cation [26] succeeds **8** as the principal iridium-containing species in solution (see Figure 1.7). This cation is $\text{cis-}[\text{IrH}_2(\text{cod})\text{L}_2]^+$ (**9**), the (cod) ligand of which derives from the excess (cod) used as substrate for the catalyst. In contrast to the cis isomer **8**, the cis, trans-dihydride **9** does not readily transfer its hydrogen to the coordinated olefin. The complexes appear to be stable in solution, at least over short periods, at ca. 40°C . One example ($\text{L} = \text{PMePh}_2$) can be isolated with Et_2O as a white crystalline solid, which only decomposes rapidly in air at ca. 85°C .

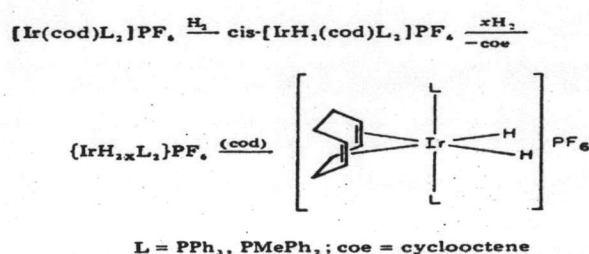


Figure 1.7 A new cation succeeds **8** as the principal iridium-containing species in solution [26].

The principal species present in classical homogeneous hydrogenation systems have to dissociate a solvent or other ligand before the olefin substrate can gain access to the active site. In the iridium system, in contrast, the principal species present seem to be dihydrido olefin complexes, probably various isomers of $[\text{IrH}_2(\text{olefin})_2\text{L}_2]^+$, which can collapse directly to alkane, without further associative or dissociative steps. In this case, they seem to resemble heterogeneous rather than homogeneous hydrogenation catalysts; this may account for their high activity. The corresponding rhodium complexes $[\text{Rh}(\text{cod})\text{L}_2]\text{PF}_6$ are at least an order of magnitude less active under analogous conditions, and do not reduce tri- or tetrasubstituted olefins. Perhaps olefin dihydride complexes are not formed in the rhodium system. It is possible that the principal active rhodium species are similar to the catalytically active, hydrogen-bridged clusters $[\text{RhHL}'_2]_n$ ($n = 2$ or 3 , $\text{L}' = \text{P}(\text{OR})_3$) recently isolated by Muetterties et al. and formed in the hydrogenation of $[\text{Rh}(\text{C}_3\text{H}_5\text{L}'_2)]$ [22].

1.4 Literature Review

1.4.1 Hydrogenation of Acrylonitrile-Butadiene Copolymers

Parent et al. [27] studied $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhH}(\text{PPh}_3)_4$ catalyzed hydrogenation of acrylonitrile-butadiene copolymers. Both $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhH}(\text{PPh}_3)_4$ function as efficient catalyst systems for the selective hydrogenation of nitrile rubber (NBR) under relatively severe reaction conditions. Observed influences of process conditions on the rate of hydrogenation are consistent with behavior reported at mild temperatures and pressures near ambient. This knowledge has led to a straight forward extrapolation of a mild reaction condition mechanism for the $\text{RhCl}(\text{PPh}_3)_3$ system that is supported by rate and selectivity data. Uniform viscosities of hydrogenated nitrile rubber sample (HNBR) suggest that while the copolymer's nitrile functionality undoubtedly form complexes with coordinatively unsaturated rhodium species, this coordination does not lead to detectable levels of nitrile reduction.

Martin et al. [9] carried out a detailed study of the hydrogenation of nitrile-butadiene rubber and other substrates catalyzed by Ru (II) complexes. Development of a computer controlled apparatus for measurement of gas uptake at elevated temperatures and pressures has made possible a study of the kinetics of NBR

hydrogenation at conditions approaching those that are used in commercial operations. Complexes of $\text{Ru}(\text{X})\text{Cl}(\text{CO})\text{L}_2$ where $\text{X} = \text{H}$ or β -styryl ($\text{CH}=\text{CH}(\text{Ph})$) and L is a bulky phosphine such as tricyclohexyl- or triisopropyl-phosphine, are excellent catalysts for the hydrogenation of $\text{C}=\text{C}$ in a variety of polymers and are superior to other Ru complexes for the hydrogenation of $\text{C}=\text{C}$ present in nitrile-butadiene rubber.

Guo et al. [28] studied catalytic hydrogenation of nitrile-butadiene copolymer emulsion. Two processes have been developed for the selective hydrogenation of the $\text{C}=\text{C}$ bonds in NBR emulsions in the presence of a number of $\text{RuCl}(\text{PPh}_3)_3$ complex catalysts. One of the processes was carried out in a homogeneous system, in which an organic solvent, which could dissolve the NBR polymer and catalyst and which was compatible with the emulsion, was used. The other process was carried out in a heterogeneous system, in which an organic solvent, which was capable of dissolving the catalyst and swelling the polymer particle but was not miscible with the aqueous emulsion phase, was used. In both processes, quantitative hydrogenation of the $\text{C}=\text{C}$ bonds of the NBR emulsion was achieved in the presence of $\text{RuCl}(\text{PPh}_3)_3$. It was also found that the addition of certain types of additives can improve the activities of the Ru based catalysts.

Parent et al. [8] studied $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ catalyzed hydrogenation of acrylonitrile-butadiene copolymers. In chlorobenzene, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ is an efficient catalyst precursor for the selective hydrogenation of olefin resident within acrylonitrile-butadiene copolymers. The reaction rate is first order with respect to $[\text{Os}]$, implying that the active complex is mononuclear. Both nitrile and phosphine reduce the catalyst activity, nitrile by coordination to the metal center and phosphine presumably by the inhibition of a required dissociation reaction. Nitrile coordination appears to induce a second-order dependence of the reaction rate with respect to hydrogen, which diminishes at high pressures. In contrast, hydrogenation of substrates lacking nitrile are virtually indifferent to hydrogen pressure at all pressures. A reaction mechanism, wherein $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ molecules of hydrogen are involved in the rate-limiting reaction, accounts for the unique behavior of this system.

Parent et al. [29] investigated the ligand exchange processes of $\text{OsHCl}(\text{CO})(\text{L})(\text{PR}_3)_2$ ($\text{L} = \text{vacant}, \text{H}_2, \text{RCN}', \text{O}_2$; $\text{R} = \text{Cy}, i\text{-Pr}$). The reactivity of complexes formed

by the addition of O₂, H₂ and RCN' to OsHCl(CO)(L)(PR₃)₂ (1a: R = Cy; 1b: R = *i*-Pr) was examined. Under 24 bar H₂ and 65°C, the dioxygen ligand of OsHCl(CO)(O₂)(PR₃)₂ (2a,b) is displaced to yield the trans-hydridodihydrogen complexes OsHCl(CO)(η^2 -H₂)(PR₃)₂ (3a,b). Measurements of the equilibrium constant, $K_{H_2} = [3a]/[1a][H_2]$, for the direct addition of H₂ to 1a yield $\Delta H^\circ = -49.1 \pm 2.4$ kJ/mol and $\Delta S^\circ = -95.7 \pm 7.9$ kJ/mol K. 1a,b react reversibly with aryl and alkyl nitriles to produce the isolable complexes, OsHCl(CO)(RCN')(PR₃)₂ (4a,b). The phosphine ligands of 1a,b and 3a,b exchange with unbound, bulky alkyl phosphines at a rate that is slow relative to the NMR timescale. In the presence of excess PCy₃, complex 3b yields the exchange products OsHCl(η^2 -H₂)(CO)(*Pi*-PR₃)(Pcy₃) and 3a. While a tris-phosphine complex cannot be detected, limited kinetic data characterize the exchange as an associative process.

Mao et al. [30] studied catalytic hydrogenation of acrylonitrile-butadiene copolymers by a series of osmium complexes. The activity of a series of osmium complexes as catalyst for the hydrogenation of nitrile-butadiene copolymers (NBR) was studied under 3.42 MPa hydrogen pressures and at 130°C in monochlorobenzene. On the basis of the correlation of phosphine ligand properties with the catalytic activities of complexes, the complexes studied are divided into three classes: class I (bulky monophosphines with Tolman's cone angle $\geq 160^\circ$) OsHCl(CO)(O₂)(PR₃)₂ (PR₃ = PiPr₃, PCy₃, PCy₂Ph); class II (small monophosphines) OsHCl(CO)(CO)(PR₃)₃ (PR₃ = PPh₃, P(*m*-C₆H₄Me)₃); class III (diphosphines) OsHCl(CO)(PPh₃)₂(dpp) (dpp = Ph₂P(CH₂)₃PPh₂). In general, the activity of these complexes decreases as follows; class I > class II > class III. This trend is mainly attributed to the ease of dissociation of a ligand from an 18-electron complex to generate a 16-electron species in the catalytic process. In the case of complexes of the class I as catalysts, their activities increase in the order: PCy₂Ph \ll PiPr₃ < PCy₃. While this activity trend does not appear to correlate with the steric effect based on Tolman's cone angles, it is in good agreement with the electronic effect, which is evaluated based on the infrared ν_{CO} values of these complexes. The catalytic activity of these complexes increases with the decrease of ν_{CO} value, which is consistent with the increase of the donor power of phosphine ligands. This indicates that the activity of these complexes are predominately dependent on the electronic properties of phosphine ligands and, in

conjunction with the kinetic isotope effect, that the rate determining step of the catalytic process would be H₂ bond breaking related process or an olefin insertion into an Os-H bond.

Parent et al. [31] studied the selectivity of the OsHCl(CO)(O₂)(PCy₃)₂ catalyzed hydrogenation of nitrile-butadiene rubber. The quality of HNBR produced using OsHCl(CO)(O₂)(PCy₃)₂ was enhanced by low catalyst concentrations and high H₂ pressure. Although a viscosity-modifying additive such as octylamine reduces the extent of crosslinking, it cannot render HNBR equivalent to a rhodium product and its presence has a detrimental effect on the hydrogenation rate. Kinetic studies of the crosslinking process have revealed an influence of residual olefin that cannot be rationalized by the prevailing crosslinking mechanism purely on the basis of hydrogenation of CN group.

Hu [31] studied the hydrogenation of nitrile-butadiene rubber using [Ir(COD)py(PCy₃)]PF₆ (Crabtree catalyst). Crabtree catalyst application in the hydrogenation of NBR was investigated. In non-coordinating solvents like chlorobenzene, the Crabtree catalyst is an efficient catalyst precursor for the selective hydrogenation of olefin resident within NBR. The reaction rate is first order with respect to [Ir] and hydrogen pressure, implying that the active complex is mononuclear. Both nitrile and phosphine reduce the catalyst activity, by coordination to the metal center. Different type of butadiene units may be hydrogenated via different pathways.

Bhattacharjee et al. [10] prepared the hydrogenated nitrile rubber using palladium acetate as the homogeneous catalyst system. The effect of different reaction parameters on the level of hydrogenation was studied. The extent of hydrogenation increased with increase in reaction time, temperature, pressure, and catalyst concentration. A maximum conversion of 96% could be achieved. The degree of hydrogenation was estimated from IR and NMR spectroscopy. The selectivity of the catalyst in reducing -C=C- in presence of -CN was supported by IR and ¹³C-NMR spectra. ESCA studies further confirmed this observation. Properties of hydrogenated nitrile rubber were investigated by various techniques such as gel permeation chromatography (GPC), glass transition temperature (T_g), stress-strain behavior and rheological measurements. GPC studies showed no significant change in molecular

weights of the products after the reaction. T_g value decreased with an increase in the level of hydrogenation. The ultimate stress improved significantly with the increase in the extent of hydrogenation. The die swell decreased with hydrogenation and at a particular shear rate. The kinetics of the NBR hydrogenation was investigated. With the increase hydrogen pressure and catalyst concentration, the rate of reaction increased. The reaction was apparently first order with respect to olefinic substrate at higher hydrogen pressure. The apparent activation energy, enthalpy, and entropy of the reaction are calculated as 29.9 kJ/mol, 27.42 kJ/mol, and -0.20 kJ/mol K, respectively.

Yi et al. [33] studied acid-promoted homogeneous hydrogenation of alkenes catalyzed by the ruthenium-hydride complex $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$: evidence for the formation of 14-electron species from the selective entrapment of the phosphine ligand. The addition of 1.0 equiv of $\text{HBF}_4 \cdot \text{OEt}_2$ led to a ca. 2-3 fold increase in the catalyst activity of $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ (1a) toward the hydrogenation of alkenes. The stoichiometric reaction of 1a with $\text{HBF}_4 \cdot \text{OEt}_2$ produced a 1:3:5 mixture of the new ruthenium-hydride species $\text{RuHCl}(\text{CO})(\text{PCy}_3)$ (2) and $\text{Cy}_3\text{PH}^+\text{BF}_4^-$. The catalyst activity of the isolated 2/ Cy_3PH^+ mixture was found to be similar to 1a/ $\text{HBF}_4 \cdot \text{OEt}_2$. The complex 2 slowly decomposed in C_6H_6 solution to give a novel tetrameric complex.

1.4.2 Hydrogenation of Styrene-Butadiene Rubber, Styrene-*b*-Butadiene-*b*-Styrene Copolymers, and Polybutadiene

Mohammadi et al. [34] studied the homogeneous catalytic hydrogenation of polybutadiene. Detailed kinetic and mechanistic studies for the homogeneous hydrogenation of polybutadiene, in the presence of $\text{RhCl}(\text{PPh}_3)_3$ as catalyst, have been carried out by monitoring the amount of hydrogen consumed. At sub-atmospheric pressure (<101 kPa) and temperature of 20 - 50°C , $\text{RhCl}(\text{PPh}_3)_3$ was found, based on hydrogen consumption, infrared, ^1H and ^{13}C NMR spectroscopic measurements, to provide quantitative hydrogenation of the carbon-carbon unsaturation present in polybutadiene. The reaction kinetics, in presence of excess PPh_3 , showed a first-order behaviour with respect to total $[\text{Rh}]$ as well as with respect to $[\text{C}=\text{C}]$. At low $[\text{H}_2]$, the reaction exhibited a first-order dependence on $[\text{H}_2]$ which tended toward a zero-order dependence at higher values of $[\text{H}_2]$. An inverse dependence with respect to the added

[PPh₃] is observed. The kinetic results are consistent with a mechanism in which an initial complexation between the active catalyst, RhClH₂(PPh₃)₂, and the C=C unsaturation present in the polybutadiene occurs. At the given reaction conditions, the RhCl(PPh₃)₃ catalyst showed selectivity for the hydrogenation of 1,2 (vinyl) addition units over 1,4 (internal) addition units present in the polybutadiene.

Doi et al. [35] investigated the microstructure and thermal properties of hydrogenated polybutadienes. Hydrogenation of 1,4-, atactic 1,2, and syndiotactic 1,2-polybutadienes have been conducted at 100°C under 50 bar of H₂ in the presence of soluble RhCl(PPh₃)₃ catalyst, and completely hydrogenated polybutadiene (HPB) of different molecular weights was prepared. The chain microstructure of HPB samples was well characterized by their ¹³C-NMR spectra. The melting temperature of quenched HPB samples with ~10% 1,2 addition decrease with an increase in M_w, which is associated with a decrease in the crystallinity. The glass transition temperature of syndiotactic HPB with nearly 100% 1,2 addition is higher by ~9°C than the value of isotactic poly(1-butene). It is concluded that the isotactic sequences of 1-butene units possess a less restricted segmental mobility than do the syndiotactic sequences.

Roa et al. [36] investigated the structure of hydrogenated polybutadiene catalyzed by RuCl₂(PPh₃)₃. The RuCl₂(PPh₃)₃ complex was found to be a suitable catalyst for the hydrogenation of polybutadiene rubber. The catalytic hydrogenation of polybutadiene was carried out in an autoclave in toluene with the ruthenium complex under 50 bar hydrogen pressure at 100°C. The resulting polymeric products were analyzed by IR and NMR spectroscopic and DSC techniques. ¹³C-NMR spectroscopy was employed for estimating chain branching. NMR results for the products indicated that hydrogenation of polybutadiene was complete in 6 h using 0.3 mol% of catalyst. A comparative evaluation of samples of hydrogenated polybutadiene obtained by the polymerization of butadiene using Co²⁺, Ni²⁺, and Nd³⁺ based catalyst systems was described.

Gilliom et al. [37] studied the bulk catalytic hydrogenation of a polyolefin. Specifically, polybutadienes could be hydrogenated to good conversions under moderate conditions in the absence of added solvent by using molecular catalysts. The

most effective catalyst found for use in this bulk modification is the Crabtree catalyst, $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$. While exploring the sensitivity of the hydrogen uptake rate to the physical form of the polymer, they observed an interesting phenomenon. When the polymer was fabricated as a full-density pellet, the hydrogenation produced a marked reaction front. The polymer was hydrogenated from the outside in.

Sarkar et al. [38] studied thermoplastic elastomeric hydrogenated styrene-butadiene elastomer (HSBR). Thermoplastic elastomeric HSBR was prepared by diimide reduction of SBR in the latex. The standard energy change at 298K is -44.7×10^4 kJ/mol, indicating that the formation of HSBR is thermodynamically feasible. The value of heat change of the reaction at constant volume is -41.6×10^4 kJ/mol. The effect of different reaction parameters on the level of hydrogenation, calculated from NMR spectroscopy, was also investigated. The degree of hydrogenation increases with the increase in reaction time, temperature, the concentration of reactants and catalyst. A maximum of 94% hydrogenation was obtained under the following conditions: time, 4 h; temperature, 45°C; pH, 9.36; cupric sulphate catalyst concentration, 0.0064 mmol; hydrazine concentration, 0.20 mol; and hydrogen peroxide concentration, 0.26 mol. The diimide reduction of SBR is first-order with respect to olefinic substrate, and the apparent activation energy is 9.5 kJ/mol. The glass transition temperature increases with the increase in saturation level due to development of crystalline.

Barrios et al. [39] studied the selective hydrogenation of butadiene-styrene copolymers (SBR) using Ziegler-Natta type catalyst. The SBR dissolved in cyclohexane, were homogeneously hydrogenated using a Ziegler-Natta type catalyst, prepared with nickel acetylacetonate and n-butyllithium. The only species, which was not present in both parts of the global process, is the catalyst for the homogeneous hydrogenation: nickel acetylacetonate. Three types of SBR were investigated on the basis of their monomeric distribution: diblock (D-SBR), triblock with polystyrene extremes (T-SBR) and random (R-SBR). All the copolymers studied were synthesized by anionic solution polymerization. The precursors and corresponding hydrogenated polymers were analyzed by IR and ^1H -NMR spectroscopy to determine the 1,2-vinyl and 1,4-trans double bond content in the butadiene portion of the copolymers.

Tsiang et al. [40] studied hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene block copolymers (SBS) using a metallocene/*n*-butyllithium catalyst. A metallocene catalyst system, primarily the bis(η^5 -cyclopentadienyl)cobalt (Cp_2Co) combined with *n*-butyllithium (*n*-BuLi), was found to be active for the hydrogenation of SBS. Data from the UV spectroscopy of the catalyst system indicated that one of the Cp ligand in the original Cp_2Co was substituted by the butyl group forming a CpCoBu as the major catalytic species. The kinetics of the hydrogenation reaction were studied by monitoring the extent of saturation of double bonds on the polybutadiene segment of the copolymer using IR spectroscopy. The temperature dependence of the hydrogenation rate was analyzed and the activation energy was determined as 14.11 kcal/mol of the double bond.

1.4.3 Hydrogenation of Natural Rubber

Gan et al. [41] studied hydrogenation of natural rubber using nickel 2-ethylhexanoate catalyst in combination with triisobutylaluminum. Kinetic study for the homogeneous hydrogenation of natural rubber was carried out by monitoring the change in hydrogen pressure in a Parr reactor of fixed volume. $^1\text{H-NMR}$ spectroscopy provides the measurements of the extent of hydrogenation. The reaction kinetics, in the presence of a fixed amount of catalyst, showed an overall second-order reaction with respect to $[\text{H}_2]$ and $[\text{C}=\text{C}]$. The reaction has relatively low apparent activation energy of 26.0 kJ/mol and is therefore suitable for the hydrogenation of natural rubber at ambient conditions to minimize side reactions. The impurities in commercial rubbers have a slight effect on the catalyst activity.

Singha et al. [7] studied homogeneous catalytic hydrogenation of natural rubber using $\text{RhCl}(\text{PPh}_3)_3$. Hydrogenation of natural rubber in toluene was carried out using $\text{RhCl}(\text{PPh}_3)_3$ as a catalyst in the temperature range of 40 to 100°C and with 10 to 40 kg/cm² of hydrogen pressure. Quantitative hydrogenation could be achieved after 22 h using 1.3 mol% catalyst at 100°C and 40 kg/cm² hydrogen pressure. This was confirmed by quantitative hydrogen absorption, IR, NMR and iodine value. Hydrogenation increases the thermal stability of the hydrogenated natural rubber without affecting its glass transition temperature.

Velichkova et al. [42] investigated the solution properties of hydrogenated styrene-isoprene block copolymers. Styrene-isoprene block copolymers with different degree of monomer distribution are hydrogenated with homogeneous nickel 2-ethylhexanoate and triisobutyl aluminium catalysts. The products were characterized by means of IR and $^1\text{H-NMR}$ spectroscopy, GPC, viscometry, and light scattering. Hydrogenation proceeded without destruction and selectively for olefinic unsaturation. The hydrogenated copolymers were homogeneous in molecular weights and chain composition. The influence of the copolymer structure on the solution properties in selective solvents was established. In cyclohexane an equilibrium between micelle associates and individual polymer coils, monomolecular micelles, or micelle aggregates were observed, depending on the type of the copolymer. The micellization in base-lubricating oil leads to micelle fractions with a different degree of association.

1.5 Scope of the Research

The principal objective of this research is to investigate the hydrogenation of cis-1,4-poly(isoprene) and natural rubber in the presence of homogeneous organotransition metal catalysts. Natural rubber is a polymer of poly(isoprene) in which all or nearly all the repeating units possess the cis configuration. Thus, synthetic cis-1,4-poly(isoprene), was used as a model for natural rubber hydrogenation studies. The $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ complexes were used as homogeneous catalysts for hydrogenation of cis-1,4-poly(isoprene). Chapter 1 of this thesis presents a review of relevant literature. The focus on homogeneous catalyst for rubber hydrogenation is included.

The following two chapters summarize research projects that serve as a foundation to the hydrogenation of natural rubber. Kinetic studies of cis-1,4-poly(isoprene) hydrogenation catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ are detailed in Chapter 2 and Chapter 3, respectively. The hydrogenation studies were carried out using an automated gas uptake apparatus. The influence of main effects and their interactions were estimated using two-level factorial design. On the basis of kinetic studies, plausible reaction mechanisms have been suggested and rate laws have been developed. This research work advances our understanding of the natural rubber hydrogenation while hydrogenation of cis-1,4-poly(isoprene) catalyzed by two catalyst systems were compared.

Chapter 4 relates an initial study of the hydrogenation of natural rubber catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. The hydrogenation of natural rubber was carried out in a Parr reactor and gas uptake apparatus. The hydrogenated natural rubber products were characterized using IR, $^1\text{H-NMR}$ spectroscopy. The effects of acid and solvent on the natural rubber hydrogenation were investigated.

The main body of the thesis is closed with a characterization of hydrogenated cis-1,4-poly(isoprene) and natural rubber products using thermal analysis technique (Chapter 5). The thermal properties (glass transition temperature (T_g) and degradation temperature) of hydrogenated cis-1,4-poly(isoprene) and natural rubber products are reported. Chapter 6 summarizes the important conclusions of the thesis and recommends directions for future work.