

DEHYDROGENATION OF POLYETHYLENE CATALYZED BY
DIHYDRIDO IRIIDIUM PCP PINCER COMPLEXES

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By
Angela Rouleau

Thesis Committee:

Craig M. Jensen, Chairperson
Roger E. Cramer
Satoshi Takara

DEDICATION

To my parents, who have given me all that any person could ever need – their support, their encouragement and most of all their love.

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ABSTRACT

The dehydrogenation of polyethylene catalyzed by the pincer-ligated PCP iridium complexes, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**1**) and $\text{IrH}_2\{p\text{-OMe-C}_6\text{H}_2\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**2**) have been investigated. The enormous problem of polyethylene is of increasing concern due to its negative environmental impact. This concern stems from the standpoint of environmental protection and conservation of energy.

The degradation of polyethylene has been explored as a potential first step in a novel approach to its degradation and eventual recycling of the monomer products as chemical feedstocks. It has been discovered that the complexes **1** and **2** exhibit remarkably high activity for the transfer dehydrogenation of polyethylene in the presence of the hydrogen acceptor, *tert*-butylethylene, ($\text{Bu}^t\text{HC}=\text{CH}_2$, tbe) at temperatures of 150 °C. Conversions as high as 56% were achieved in perfluorodecalin. The dehydrogenation has been characterized by ^{13}C CPMAS NMR spectroscopy and quantified by gas chromatography.

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LIST OF ABBREVIATIONS

C	Celsius
CPMAS	Cross-Polarised Magic Angle Spinning
kHz	Kilohertz
mg	Milligram
mHz	Megahertz
mL	Milliliter
mmol	Millimole
msec	Millisecond
NMR	Nuclear Magnetic Resonance
ppm	Parts per million
r.t.	Room Temperature
tba	<i>tert</i> -butylethane
tbe	<i>tert</i> -butlyethylene
^t Bu	<i>tert</i> -butyl
μsec	Microsecond
°	Degree

CHAPTER 1

Introduction

1.1. Polyethylene

The most important class of synthetic carbon-chain polymers consists of the various forms of polyethylene. Polyethylene was first synthesized by von Pechmann in his attempt to decompose diazomethane.¹ The first industrial synthesis of polyethylene was developed by the Imperial Chemical Company in 1933.² This early process involved temperatures as high as 250 °C and between 1,000 to 3,000 atmospheres.² This process was expensive, dangerous and costly. An advanced process replaced it in 1953, following the breakthrough discovery of Ziegler-Natta catalysts.² The Ziegler-Natta catalysts allowed for the production of polyethylene at ambient temperatures and pressures through the use of catalysts involving aluminum and other metal alkyls in combination with metal halides.² The discovery of Ziegler-Natta catalysts not only improved the production of polymers but also allowed for the production of linear polyethylene. Subsequent advances in the synthesis of polyethylene have been through the use of catalytic systems based on metallocenes. Discovered by Kaminsky in the early 1980's³ metallocene catalysts have revolutionized how polyethylene is produced. Metallocene catalysis has allowed for the production of polyethylene with new features such as increased impact strength and toughness, better melt characteristics, and improved clarity in films. The key to metallocenes are their ability to be varied to adapt to the specific need of the producer to provide the desired polymer, which has led to the availability of a wide range of polyethylene resins.³

It was quickly discovered that polyethylene polymers have a number of highly desirable qualities. The major application of polyethylene is in packaging; it is mainly used as films and in bottles.⁴ Polyethylene has transformed food distribution because it forms a sterile barrier against microbial contaminants.⁴ The advances in the production of polyethylene coupled with its' utility and durability has led to its domination of the world plastics market. It became the first plastic to cross 10⁹ pounds per year in sales and has held the majority of the plastics market to date as seen in Table 1.1.⁵

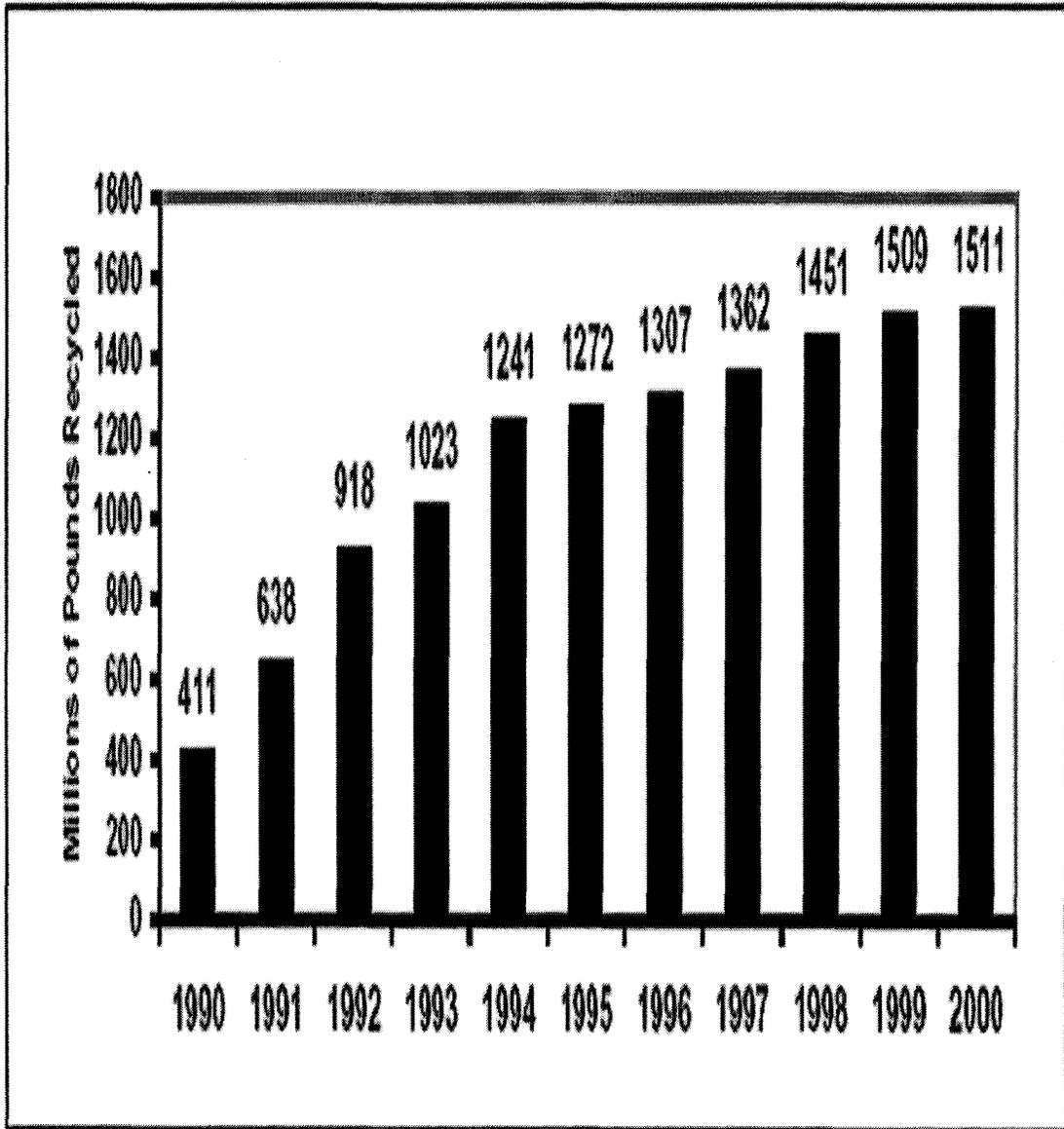
Table 1.1 USA Production Rates of 10 Thermoplastic Polymers for 1995.⁵³

Polymer	Rate (pounds/year)
Polyamide	1.02 x 10 ⁹
Polyester	3.79 x 10 ⁹
Polyethylene:	
Low Density Polyethylene	7.64 x 10 ⁹
Linear Low Density Polyethylene	5.24 x 10 ⁹
High Density Polyethylene	1.12 x 10 ¹⁰
Polypropylene	1.09 x 10 ¹⁰
Polyvinyl Chlorides	1.23 x 10 ¹⁰
Styrene Polymers:	
Polystyrene	5.66 x 10 ⁹
Styrene-Acrylonitrile	1.30 x 10 ⁸

The present usage of polyethylene does not constitute an environmentally sustainable situation. The three principal problems are: source of feedstocks; energy required for the initial production of polyethylene; and difficulties with post-consumer recycling.

The first problem with plastics in general is that their production from original feedstocks is an unsustainable process. Polyethylene plastic feedstocks are petrochemical, so they can be initially produced only as long as there is a viable oil supply. It is estimated that approximately 0.9 kilograms of oil are required for every 1 kilogram of polyethylene produced.⁶ Multiplying this by a billion pounds, shows that a billion kilograms of oil were used solely for plastics in the year that polyethylene broke its sales record. Presently, it is estimated, that total plastics production consumes 8.0×10^7 tons of oil per year, or 10 % of the total world oil refinery output.⁶ Clearly, this is not a long-term sustainable solution and a critical problem as oil becomes scarcer.

The second problem with polyethylene is that of post-consumer reclamation. The growth in the use of polyethylene is proving to be taxing on the waste disposal system. To reduce the demand for landfill space and the consumption of limited petroleum reserves, the recycling of polymers, as indicated in Figure 1.2, has steadily increased in recent years.



Source: R. W. Beck, Inc.

Figure 1.2 Growth in Post-Consumer Plastic Bottle Recycling.⁵⁴

1.2. Degradation of Polyethylene

Plastics have become an inextricable part of our society. Because of the inescapable need of plastics in our modern society, a way has to be found to produce them that does not drain non-renewable sources. There are greater environmental effects to consider in addition to our dependence on an unsustainable resource. Presently, the disposal of plastics can only be dealt with in one of three ways: burial, recycling, or incineration.

Landfills provide a benign method of disposing of plastics, however, there is the disadvantage of space. Plastics waste now constitutes about 10% of weight and 20% of volume of landfills.⁷ This crisis will not diminish as plastics are non-degradable and thus may eventually consume a disproportionate amount of landfill space. As reported by the EPA plastics compromised an estimated 400,000 tons of municipal waste in 1960 and an astonishing 19.8 million tons by 1994.⁷

As indicated in Table 1.3, the energy savings, in addition to the decrease in environmental impact, makes recycling the most viable option in the disposal of plastics.

Table 1.3 Energy Savings of Several Recycling Options.⁵⁵

Recycling Option	Energy Saving (MJ/kg)
Mechanical (bottles)	38.4
Mechanical (films)	30.0
Syngas	10.0
Hydrogenation	23.8
Thermolysis	29.3
Monocombustion	26.4
Municipal waste incineration	15.9

The recycling of plastics can be broken into four categories - primary, secondary, tertiary and quaternary. Primary and secondary recycling refers to the use of physical processes to recycle the materials into products in which the basic polymer is not altered.⁸ Primary and secondary recycling is often referred to as mechanical recycling. Mechanical recycling refers to practices involving the grinding, melting and regranulation of used plastics.⁹ These methods are largely employed by industry. Mechanical recycling is limited both by the low purity of the polymeric wastes and the limited market for the recycled products.⁹

Tertiary recycling often refers to the processes, which convert plastics into high valued products such as fuel or petrochemical feedstocks. This process is suitable for polymeric materials, and involves their conversion into smaller hydrocarbon intermediates.¹⁰ Tertiary recycling may also be referred to as feedstock recycling. Feedstock recycling is the most promising option and includes chemical depolymerization, gasification and partial oxidation, thermal degradation, catalytic cracking and reforming, and hydrogenation.⁹

Chemical depolymerization includes hydrolysis, glycolysis, methanolysis, and pyrolysis. Hydrolysis, glycolysis and methanolysis are the reverse reaction of polymerization, as indicated in Figure 1.4.⁹

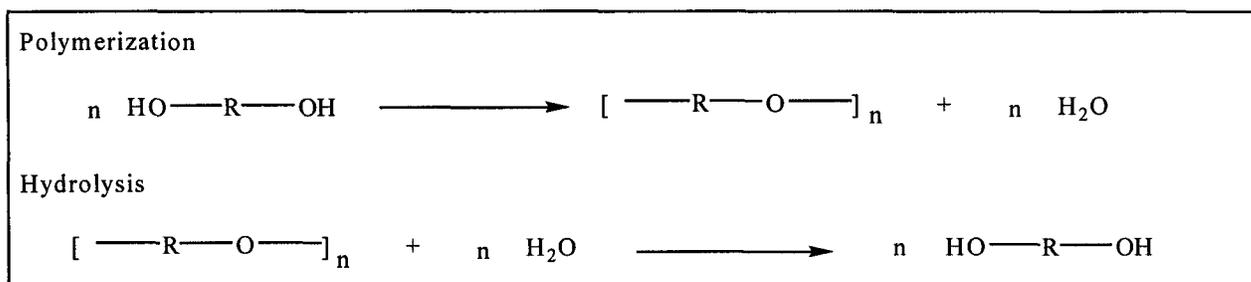


Figure 1.4 Depolymerization of a Polymer by Hydrolysis.⁵⁶

Hydrolysis involves the introduction of water into the polymer resulting in the splitting of the compound into fragments with the hydroxyl group being incorporated into one fragment, and the hydrogen atom into the other fragment. Glycolysis involves the introduction of ethylene glycol into the polymer. This process is used industrially to recover valuable raw materials from clean internal scrap plastics.¹⁰ Methanolysis involves the introduction of methanol into polymers, which are then broken down into basic molecules. Hydrolysis, glycolysis, and methanolysis have no significant advantage over mechanical recycling, as they require pure plastic materials, which can be much more easily remoulded.¹¹

Pyrolysis is an interesting chemical process where plastics are heated in the absence of oxygen.¹² The covalent bonds are broken in a more random fashion, which produces a mixture of varying chain length olefins and aromatic compounds.¹² These mixtures are sometimes used as a direct replacement for petroleum in oil refineries, where the mixture of organic compounds produced may be fractionated into purer, more valuable products.¹²

Gasification and partial oxidation are processes, which result in the production of synthetic gas. This process converts the hydrogen and carbon in the original feedstock into reusable synthetic gas by controlling the amount of oxygen present.¹³ Partial oxidation describes the net effect of various exothermic and endothermic reactions, which includes the complete combustion of part of the feed to CO₂ and H₂O.¹⁴

Thermal degradation involves the heating of plastics from approximately 200 °C to 400 °C.¹¹ At this temperature the plastics are converted into liquid petroleum products, which may be refined and transformed into a wide variety of products.¹¹

Catalytic cracking uses catalysts, which may be composed of zeolite, aluminum hydrosilicate, bauxite or silica-alumina to crack various feedstocks into smaller hydrocarbons.¹⁵

Hydrogenation of polymers takes pyrolysis one-step further. It produces even more pure gases and oils through a combination of heat, pressure and hydrogen.¹²

Quaternary recycling is used to recover energy from used plastic products and may also be referred to as energy recovery. Energy recovery, or incineration, is suitable for mixed/contaminated plastics.⁸ Incineration is used in the disposal of over 16 % of all municipal wastes.⁷ More than two-thirds of the incinerators in the United States burn garbage in waste-to-energy facilities that use heat energy to generate steam or electricity.⁷ Potential hazardous emissions from incinerating plastics include hydrogen chloride, dioxin, cadmium, and fine particulate matter.⁷ Even with the recent introduction of stricter air pollution standards there is considerable public opposition to incineration and should be thought of as a last resort in the disposal of plastics.

Currently, none of these methods are both economically and environmentally viable. The recycling of polymers is not a closed loop, where a material is reformed into new products repeatedly. Most polymeric materials are recycled only once, and the product made of recycled polymer is discarded after use. Polyethylene is not recycled due to the restrictions that arise from fears that contaminants surviving the recycling process would, as an example, be able to move into foods and beverages from containers.⁸ Because recycled polyethylene cannot be used in the same products as originally used, the need for virgin raw materials is not reduced, as indicated in Figure 1.5. The values of the bars in Figure 1.5 represent the number of additional pounds of virgin packaging

produced for each additional pound recycled. A ratio greater than 1.0 means that growth in recycling is not even keeping up with growth in virgin production. Therefore, unfortunately recycling cannot go far enough in reducing the need for original feedstocks. However, the tertiary method or feedstock recycling has the greatest potential since valuable chemicals are produced from plastic wastes.

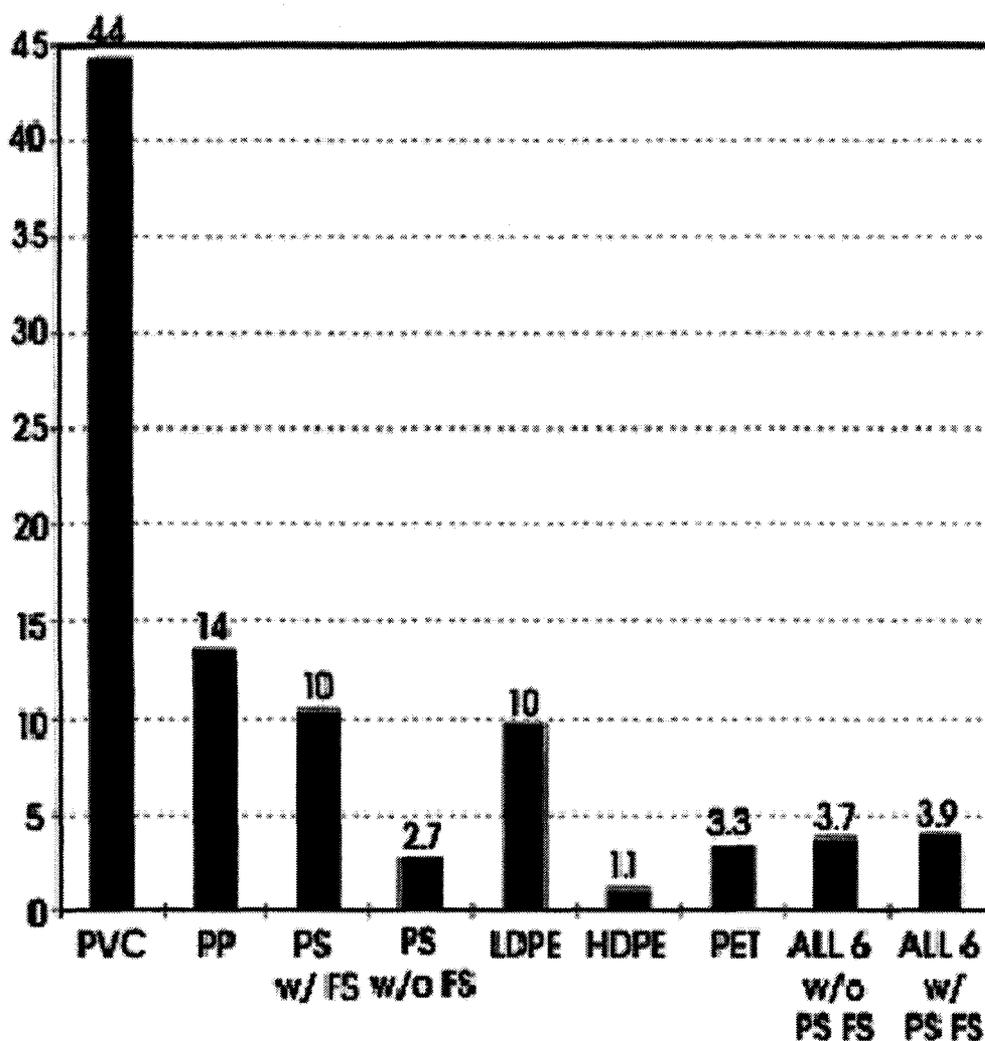


Figure 1.5 Growth in Virgin Production vs. Growth in Recycling of Various Plastic Packaging Resins 1990-1996.⁵⁷

1.3. Current Research on the Degradation of Polyethylene

Although no recycling method is currently considered both economically and/or environmentally viable the use of catalytic degradative processes is providing new alternatives. Until recently, catalytic methods for polyolefin degradation at low temperatures and pressures were unknown. Polyolefins are chemically inert and there are thermodynamic limitations to achieving the reverse of the Ziegler-Natta polymerization.¹⁶

However, recent findings by Dufaud and Basset,¹⁶ Uemichi *et al.*,¹⁷ and Pifer and Sen,¹⁸ have provided new hope in dealing with the limitations of catalytic degradation of plastics, and has led to the prospects of developing new methods for recycling.

Dufaud and Basset have described the degradation of polyethylene and polypropylene under a low hydrogen pressure and a moderate temperature of 150 °C.¹⁶ In this experiment ethylene and propylene were polymerized by a zirconium monohydride on aluminosilica gel. The polymer was formed by insertion of ethylene or propylene into the Zr-H bond followed by multiple insertion of the monomers into the resulting Zr-alkyl bonds.¹⁶ The polymer bound to the catalyst was cleaved hydrogenolytically to methane, ethane and higher alkanes. This experiment, although remarkable, produced no monomers.

Uemichi *et al.*, reported chemical recycling where polyolefins were decomposed in high yield to useful chemical feedstocks. In chemical recycling the catalyst would be required to be more selective than those required for fuel recovery.¹⁷ Uemichi *et al.* report on the catalytic degradation of low-density polyethylene under a helium stream and at temperatures of 400 °C to 525 °C.¹⁷ The catalyst employed was H-Ga-silicate, which

produced upon degradation aromatic hydrocarbons.¹⁷ This experiment again produced no monomers and was more successful at the higher temperature of 525 °C.

Pifer and Sen describe the oxidative degradation of polystyrene, polyethylene and polypropylene into organic molecules including monomers.¹⁸ The polymers were reacted with nitrogen oxides and dioxygen at 170 °C, producing moderate yields of monomers.¹⁸

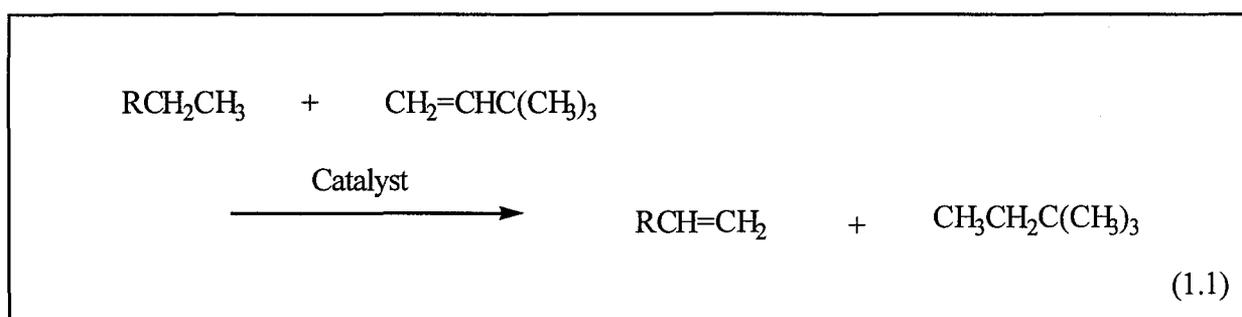
Despite the progress reported in these recent publications, the need for viable high yield methods for the degradation of polyethylene into monomers at mild conditions still persists.

1.4. Dehydrogenation

Polyethylene is abundant, inexpensive and would make an ideal source of feedstocks. However, aliphatic C-H bonds (the basic building block of polyethylene) lack reactivity. This is due to their lack of donor and/or acceptor character. This is evident by the position of the low-lying HOMO σ -orbital and the high-lying σ^* -orbital. This leads to a very strong C-H bond, in the order of 90-100 kcal/mol as well as a very nonpolar C-H bond with a usual pK_a of 45-60. As a result the selective functionalization of alkanes has long posed a formidable challenge to chemists.

Attempts to activate C-H bonds has a long and prolific history. Shilov performed initial work in 1969 in which the first reaction involving the activation of C-H bonds in alkanes was discovered.¹⁹ The next decade was marked with vigorous developments in this area by Crabtree,²⁰ Bergman,²¹ and Graham²². In 1979, Crabtree reported on a number of iridium complexes, $[\text{IrH}_2\text{-(olefinic)}_2\text{-(PPh}_3)_2]^+$, which performed alkane dehydrogenation. This was the first report of the stoichiometric dehydrogenation of alkanes to alkenes by soluble transition metal complexes.²⁰ In 1982, Bergman observed the reaction of $\text{Cp}^*\text{IrH}_2(\text{PMe}_3)$ where $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ with saturated hydrocarbons such as C_6H_{12} and CMe_4 to form the alkyl hydride complexes $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(\text{R})$ where ($\text{R} = \text{C}_6\text{H}_{11}, \text{CH}_2\text{CMe}_3$).²¹ This was the first direct observation of the activation of an alkane C-H bond at a metal center.²¹ In 1983, Graham *et al.* achieved the activation of the C-H bond of methane using the iridium complex $\text{Cp}^*\text{Ir}(\text{CO})_2$.²² The research carried out by these groups employed late transition metals (especially Rh and/or Ir) with vacant coordination sites.²⁰⁻²² These metals have been shown through experiment and calculations to be the best suited for alkane C-H bond activations.²³

In 1983, Baudry *et al.* reported the use of the first homogeneous catalysts for the transfer hydrogenation of alkanes to alkenes.²⁴ Transfer dehydrogenation is the most common method of dehydrogenation. In this reaction hydrogen is transferred from alkanes to hydrogen acceptors such as *tert*-butylethylene (tbe) as shown in equation 1.1.²⁴⁻³³



In 1991, the first efficient thermochemical system for the transfer dehydrogenation of alkanes was achieved by Goldman and co-workers using $\text{Rh}(\text{CO})\text{Cl}(\text{PMe}_3)_2$ as a catalyst under a hydrogen atmosphere.²⁸ Unfortunately, all systems up till this time tended to suffer from very slow reaction rates and rapid catalyst decomposition.^{20,24-37,30,34,35}

A new system needed to be introduced which could catalytically activate alkane C-H bonds by a metal complex, the system should possess catalytic activity that would be high under mild conditions and have high product selectivity.

The introduction of the PCP pincer complex $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$, in 1996, provided a more active and robust catalyst for aliphatic dehydrogenation reactions.³⁶ This catalyst has unusual long-term stability at temperatures as high as 200 °C with 20 turnover per minute reported.^{33, 36} Upon consideration of Figure 1.6 it is apparent that the dehydrogenation of various cyclic compounds, as well as straight chain alkanes is achieved. Figure 1.6 also indicates that the catalyst is also able to tolerate aromatics.

Straight chain alkanes are normally less susceptible to transfer dehydrogenation than their cyclic counterparts. It has been previously observed that cyclic alkanes are more reactive than their linear counterpart.³⁶ The PCP pincer was an efficient and robust catalyst in the dehydrogenation of straight chain alkanes³⁶ such as undecane, this then suggests that the dehydrogenation of larger alkyl chains alkanes and even polymers such as polyethylene might be possible.

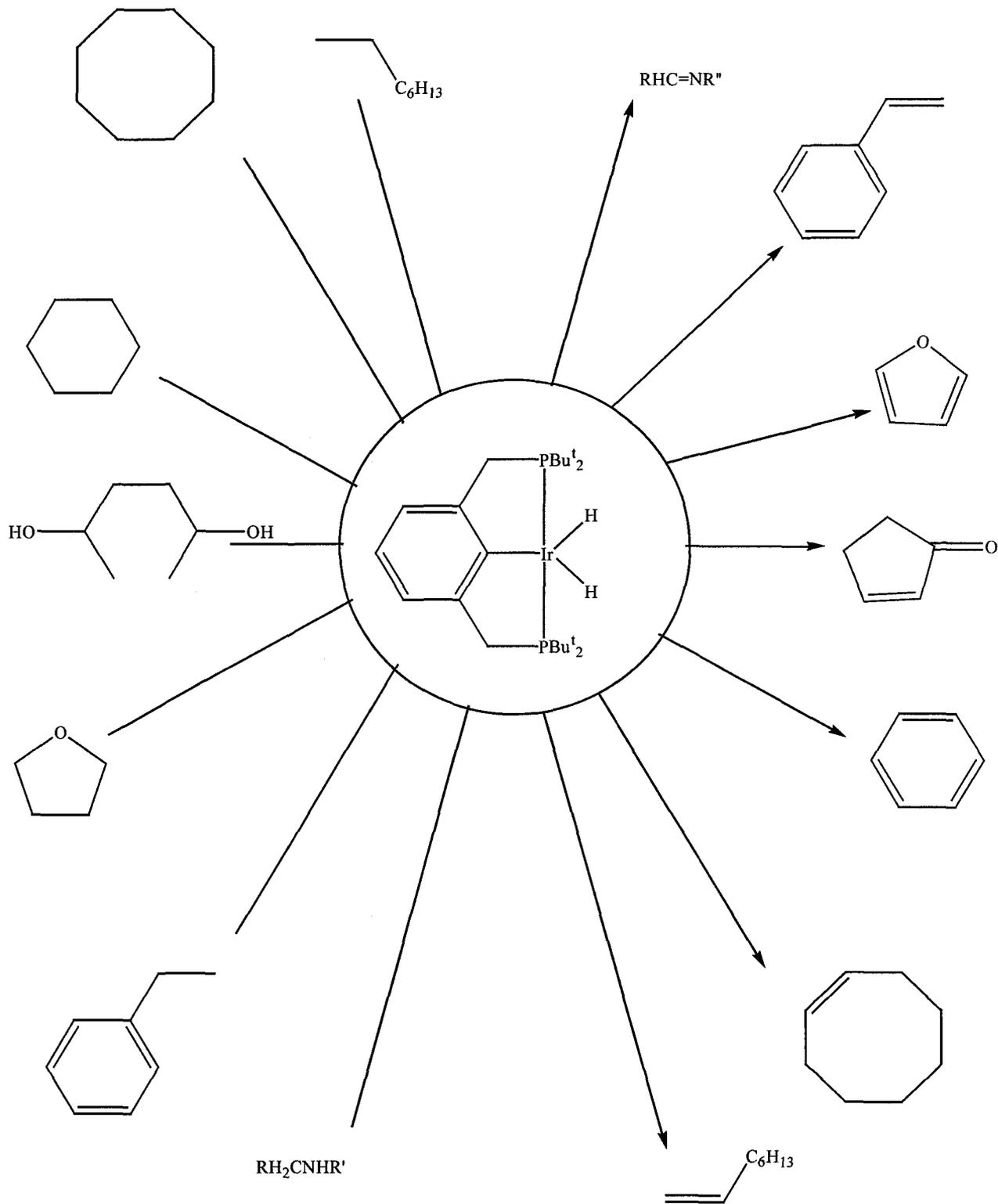


Figure 1.6 Transfer Dehydrogenation of Various Compounds by the PCP Pincer Catalyst $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{PBU}^t_2)_2\}$.³⁶

1.5. Perfluorinated Solvents

Previous work employing the PCP catalyst in the dehydrogenation of alkanes did not need to consider a solvent, as the alkane itself acted both as the substrate and solvent. However, in the dehydrogenation of polyethylene the alkane is a solid and therefore a solvent is required. Upon careful consideration, perfluorinated solvents appeared to be excellent candidates. The advantages of employing perfluorinated solvents in catalytic systems has been indicated by the work of Horvath and Rabai,³⁷ and Barrett *et al.*³⁸

Although perfluorinated hydrocarbons are well known, they have only recently been considered as a useful class of solvents in inorganic chemistry. As such they made an excellent choice in the dehydrogenation of polyethylene as they addressed the issues of ease of separation, temperature requirements and the concern of dehydrogenation of the solvent versus the polymer substrate.

Complex transition metal catalysts employ expensive metals and/or ligands. Thus the separation and the recovery of the catalyst are of high priority. Perfluorinated solvents have a high density, and low miscibility with other common organic solvents, which makes their separation on completion of the reaction facile. Separation can be easily accomplished by filtration (when solid products are formed) or decantation when a biphasic solution is obtained.³⁹

In addition to these conveniences of work-up of reactions perfluorocarbons are extremely inert and are available in a wide range of boiling points which makes them also useful for carrying out reactions under vigorous conditions.³⁹ These characteristics are especially attractive in the dehydrogenation of polyethylene as the solubility of

polyethylene requires a solvent which can undergo heating to 150 °C without decomposition.

Another advantage is that perfluorinated solvents do not contain C-H bonds. This was especially appealing as it removed any possible competition between the dehydrogenation of the solvent versus the dehydrogenation of the polymer substrate. This ensured that the quantification of the hydrogenation of *tert*-butylethylene acceptor reflected a complimentary amount of dehydrogenation of polyethylene.

Additionally, perfluorinated solvents' chemical inertness, their low miscibility and easy recovery after the reaction also made them an attractive choice of solvent.

1.6. Scope of Thesis

This thesis presents a novel approach to the dehydrogenation of polyethylene. The dehydrogenation of polyethylene was achieved through the use of a robust and active catalyst $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**1**) and its derivative $\text{IrH}_2\{p\text{-OMe-C}_6\text{H}_2\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**2**). This system also employs perfluorinated solvents, which are a largely untapped solvent resource for catalytic systems.

^{13}C CPMAS NMR and gas chromatography were utilized to characterize and quantify the percent conversion of the units of saturation to the units of unsaturation in polyethylene.

This thesis also provides direction for future considerations and research. It is hoped that this research will lead to a potential method for the complete degradation of polyethylene, which will satisfy both environmental and economic constraints.

CHAPTER 2

Catalytic Dehydrogenation of Polyethylene by Dihydrido Iridium PCP Pincer Complexes: Portal to a New Method of Polyolefin Recycling?

2.1. Introduction

The utilization of “disposable” plastic polymers has proliferated at a staggering rate. Over 0.5 million tons of polyethylene alone are produced annually⁵ to meet the demand created by the ubiquity of its packaging applications.⁴ The production of plastic polymers consumes 8.0×10^7 tons of oil per year, or 10% of the total world refinery output.⁶ Furthermore, it was estimated in 1994 that more than 19 million tons of these materials are annually discarded as municipal waste.⁷ Processes have been developed for the recycling of waste plastic polymers. However, their application is quite limited due to unfavorable economics and other practical limitations. Thus, the development of a chemical method that could convert this waste material into valuable chemical feedstocks would be a key component in the establishment of a long-term, sustainable basis for the utilization of plastic polymers.

The degradation of polyolefins is a particularly challenging problem as they are, to a great degree, chemically inert and their depolymerization is subject to thermodynamic limitations. A method for their degradation that is both economically and environmentally viable has not been developed.⁵ This deficiency in technology is alarming in view of the millions of tons of polyolefin waste that accumulates each year. Dufaud and Basset,¹⁶ Uemichi et al.,¹⁷ and Pifer and Sen¹⁸ have recently explored methods for the catalytic degradation of polyolefins. Unfortunately, the utility of these

processes is generally limited by the failure to produce monomers, unsatisfactory yields and/or requisite reaction conditions that are too severe. Therefore, the development of a catalytic system for the degradation of polyolefins that operates under mild conditions to give satisfactory yields of monomers would be of great importance.

Hydrido iridium PCP pincer complexes have been found to be highly efficient and robust catalysts for aliphatic dehydrogenations, including linear alkanes.^{25,34,36,40-42} We reasoned that the introduction of unsaturations into the aliphatic chains of polyolefins resulting from catalytic dehydrogenation by the iridium pincer complexes could be an important first step in a degradation process involving a subsequent catalytic reaction such as a metathesis depolymerization.⁴³⁻⁴⁷ It was, therefore, of interest to explore the activity of the iridium PCP pincer complexes, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**1**) and $\text{IrH}_2\{p\text{-MeO-C}_6\text{H}_2\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**2**) as catalysts for the dehydrogenation of polyethylene.

2.2. Experimental Section

2.3. General Details. All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. The following were purchased from and used without further purification: perfluorodecalin, *tert*-butylethylene, dichloromethane, light density polyethylene (avg. Mw. 130,000), medium density polyethylene (avg. Mw. 6,300), and high-density polyethylene (avg. Mw. 125,000) from Aldrich Chemical Company. Professor Goldman of Rutgers University provided the complex $\text{IrH}_2\{p\text{-MeO-C}_6\text{H}_2\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**2**), which was used without further purification. The complex $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**1**) was prepared by the literature method.³⁰

The ^{13}C CPMAS spectra were recorded on a Varian Unity Inova 400 WB Multinuclear NMR Spectrometer operating at 400.012 MHz for ^1H (100.69 MHz for ^{13}C). Spectra were recorded using a standard CPMAS sequence.^{48, 49} ^1H $\pi/2$ pulses were 3.7 μsec . and spin lock times were 2 msec. A recycle delay of 7 sec was used for signal averaging. ^1H decoupling was at a field strength of 110 kHz. A Chemagnetics 3.2 mm H-X CPMAS probe (Varian NMR Instruments, Ft. Collins, CO) was used to acquire the spectra. The samples were spun with $\omega_{\text{b}} = 8$ kHz at the magic angle of 54.7° to the external magnetic field. Typically 8000 scans were signal-averaged for each spectrum. ^{13}C spectra were acquired with a 25 msec acquisition times and a sweep width of 50 kHz. 40 Hz line broadening was used before FT. The spectra were zero filled to a final size of 8000 points. Chemical shifts are referenced to external HMB (hexamethylbenzene) with the methyl peak set to 17 ppm, and are accurate to ± 0.3 ppm. Subtraction of background signal from the spinner module and rotor were performed using a data set from an empty rotor acquired with the same parameters as the sample spectra.

Identity and purity of the products was established by gas chromatography with a gas chromatograph GC HP 5980A with flame ionization detector (FID), equipped with a HP-1 capillary column (25 m) from Hewlett Packard (25 $^\circ\text{C}$ isothermal for 1 minute, 1 $^\circ\text{C}/\text{min}$. to 45 $^\circ\text{C}$).

2.4. General Procedure.

Dehydrogenation of Polyethylene (Method A). A Schlenk flask was charged with the prescribed polyethylene (30 mg, 1.07 mmol), $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (60 mg, 0.10 mmol), toluene or mesitylene or octane (2.5 mL), and *tert*-butylethylene (1.5 mL, 11.64 mmol) under 1 atm of argon at 25 °C. The tube was charged with a magnetic stir bar and sealed, and fully immersed in a 150 °C silicon oil bath. After 168 hours, the mixture was cooled to r.t. and the organic phase was analyzed and quantified by gas chromatography. Following removal of the solvent by vacuum filtration, the solid residue was extracted with THF (3 x 10 mL). A brown solid was obtained. ^{13}C CPMAS NMR (100.69 MHz, hexamethylbenzene) δ :125.0 (CH=CH), δ : 17.0 (CH₃).

Dehydrogenation of Polyethylene (Method B). A Schlenk flask was charged with the prescribed polyethylene (30 mg, 1.07 mmol), $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (30 mg, 0.05 mmol), perfluorodecalin (2.5 mL), and *tert*-butylethylene (1.5 mL, 11.64 mmol) under 1 atm of argon at 25 °C. The tube was charged with a magnetic stir bar and sealed, and fully immersed in a 150 °C silicon oil bath. After 168 hours, the mixture was cooled to r.t. and the organic phase was analyzed and quantified by gas chromatography. Following removal of the solvent by vacuum filtration, the solid residue was extracted with THF (3 x 10 mL). A brown solid was obtained. ^{13}C CPMAS NMR (100.69 MHz, hexamethylbenzene) δ :125.0 (CH=CH), δ : 17.0 (CH₃).

Dehydrogenation of Polyethylene (Method C). A Schlenk flask was charged with the prescribed polyethylene (30 mg, 1.07 mmol), $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (60 mg, 0.10 mol) perfluorodecalin (2.5 mL), and *tert*-butylethylene (1.5 mL, 11.64 mmol) under 1 atm of argon at 25 °C. The tube was charged with a magnetic stir bar and sealed, and

fully immersed in a 150 °C silicon oil bath. After the prescribed time, the mixture was cooled to r.t. and the organic phase was analyzed and quantified by gas chromatography. Following removal of the solvent by vacuum filtration, the solid residue was extracted with THF (3 x 10 mL). A brown solid was obtained. ¹³C CPMAS NMR (100.69 MHz, hexamethylbenzene) δ:125.0 (CH=CH), δ: 17.0 (CH₃).

Dehydrogenation of Polyethylene (Method D). A Schlenk flask was charged with the prescribed polyethylene (30 mg, 1.07 mmol), IrH₂{*p*-MeO-C₆H₂-2,6-(CH₂PBu^t)₂} (60 mg, .10 mmol), perfluorodecalin (2.5 mL), and *tert*-butylethylene (1.5 mL, 11.64 mmol) under 1 atm of argon at 25 °C. The tube was charged with a magnetic stir bar and sealed, and fully immersed in a 150 °C silicon oil bath. After 168 hours, the mixture was cooled to r.t. and the organic phase was analyzed and quantified by gas chromatography. Following removal of the solvent by vacuum filtration, the solid residue was extracted with THF (3 x 10 mL). A brown solid was obtained. ¹³C CPMAS NMR (100.69 MHz, hexamethylbenzene) δ:125.0 (CH=CH), δ: 17.0 (CH₃).

Dehydrogenation of Medium Density Polyethylene (Method E). A Schlenk flask was charged with the prescribed polyethylene (30 mg, 1.07 mmol), IrH₂{C₆H₃-2,6-(CH₂PBu^t)₂} (60 mg, 0.10 mmol), perfluorodecalin (2.5 mL), and *tert*-butylethylene (0.2 mL, 1.55 mmol) under 1 atm of argon at 25 °C. The tube was charged with a magnetic stir bar and sealed, and fully immersed in a 150 °C silicon oil bath. After 168 hours, the mixture was cooled to r.t. and the organic phase was analyzed and quantified by gas chromatography. Following removal of the solvent by vacuum filtration, the solid residue was extracted with THF (3 x 10 mL). A brown solid was obtained. ¹³C CPMAS NMR (100.69 MHz, hexamethylbenzene) δ:125.0 (CH=CH), δ: 17.0 (CH₃).

2.5. Results and Discussion

The design of the initial experiments were based on previous studies of the iridium PCP pincer complexes in which aromatic solvents were employed.⁵⁰ However, characterization by ¹³C CPMAS NMR and quantification by gas chromatography indicated very low catalytic activity. The finding that only extremely limited dehydrogenation of polyethylene occurred in our initial experiments was surprising in view of the turnover numbers of >1000 that are attained when **1** is employed as a catalyst for the dehydrogenation of low molecular alkanes.^{31-33,36} We reasoned that the dehydrogenation of polyethylene might be inhibited by competitive coordination of the arene solvent to **1**. Thus, a second round of experiments was carried out in non-coordinating, perfluorodecalin solvent. Although **1** and polyethylene are insoluble in perfluorodecalin at 25 °C, it was found to readily dissolve upon heating to 150 °C.

Samples of polyethylene following the catalytic degradation were characterized by ¹³C CPMAS NMR (Figure 2.1 – 2.8). Occurrences of signals in the olefinic region of the ¹³C NMR spectra were indicative of the presence of significant unsaturation. The hydrogenation of tbe to tba was monitored by GC and was used to show the extent of transfer dehydrogenation. The ratio of one unit of tbe hydrogenated is equal to one unit of C₂H₄ dehydrogenated. The amount of tba produced was quantified by the ratio of tba to tbe. The number of moles of tba produced is equal to the number of moles of C₂H₄ dehydrogenated. Polyethylene was the limiting reagent and tbe was in excess by ten-fold. Therefore, all tba to tbe ratios were multiplied by 100 to get the % dehydrogenation within polyethylene.

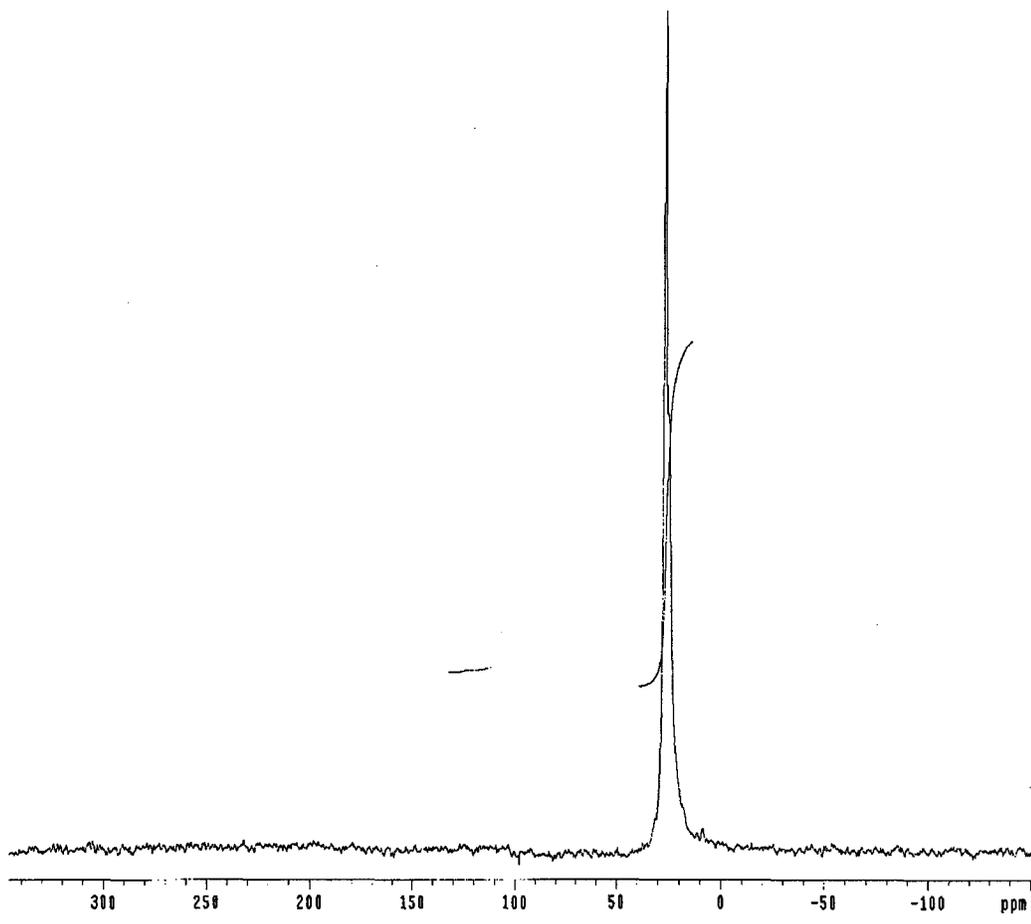


Figure 2.1. ^{13}C NMR Spectrum of Dehydrogenated Light Density Polyethylene (Method B).

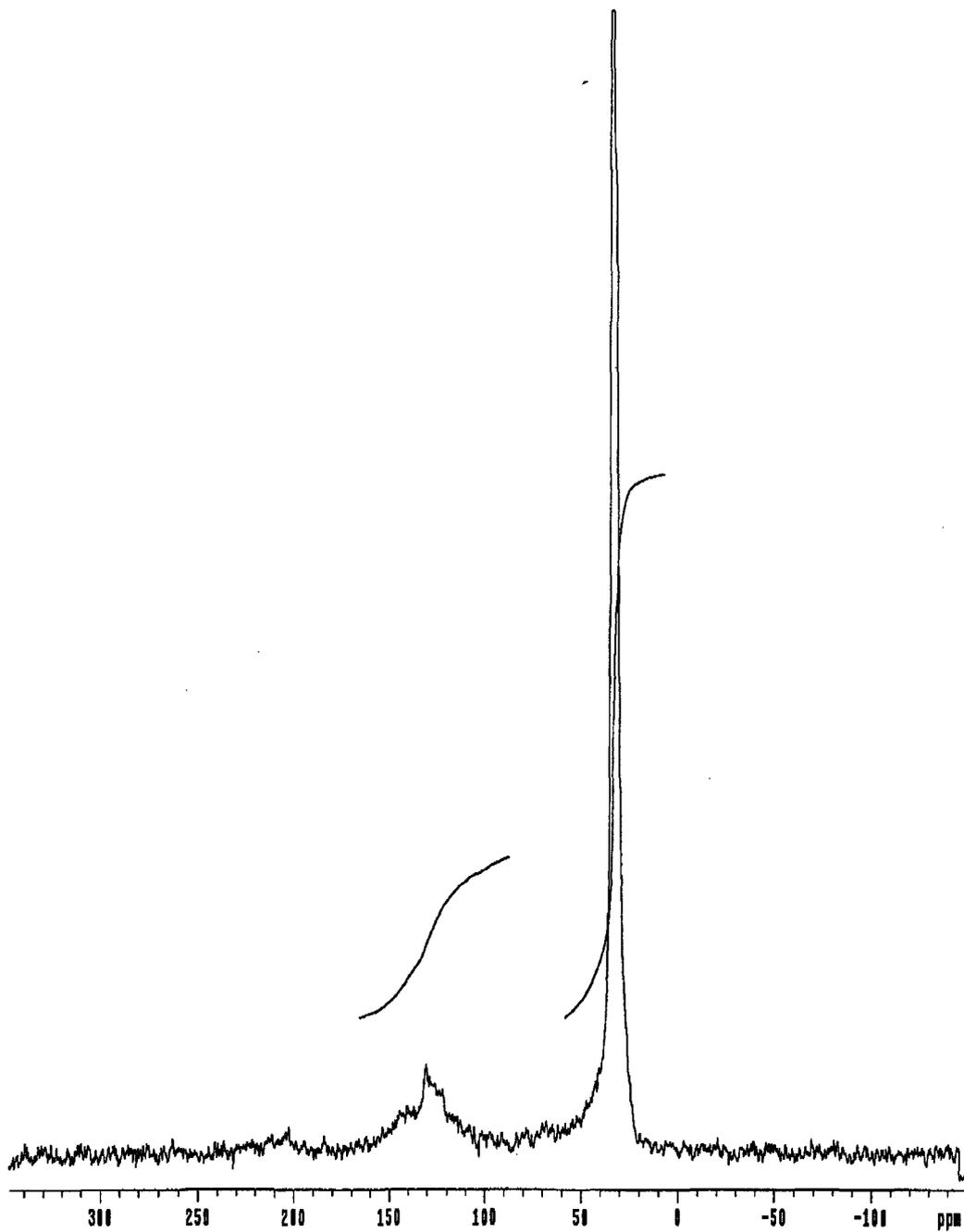


Figure 2.2. ^{13}C NMR Spectrum of Dehydrogenated Light Density Polyethylene (Method C).

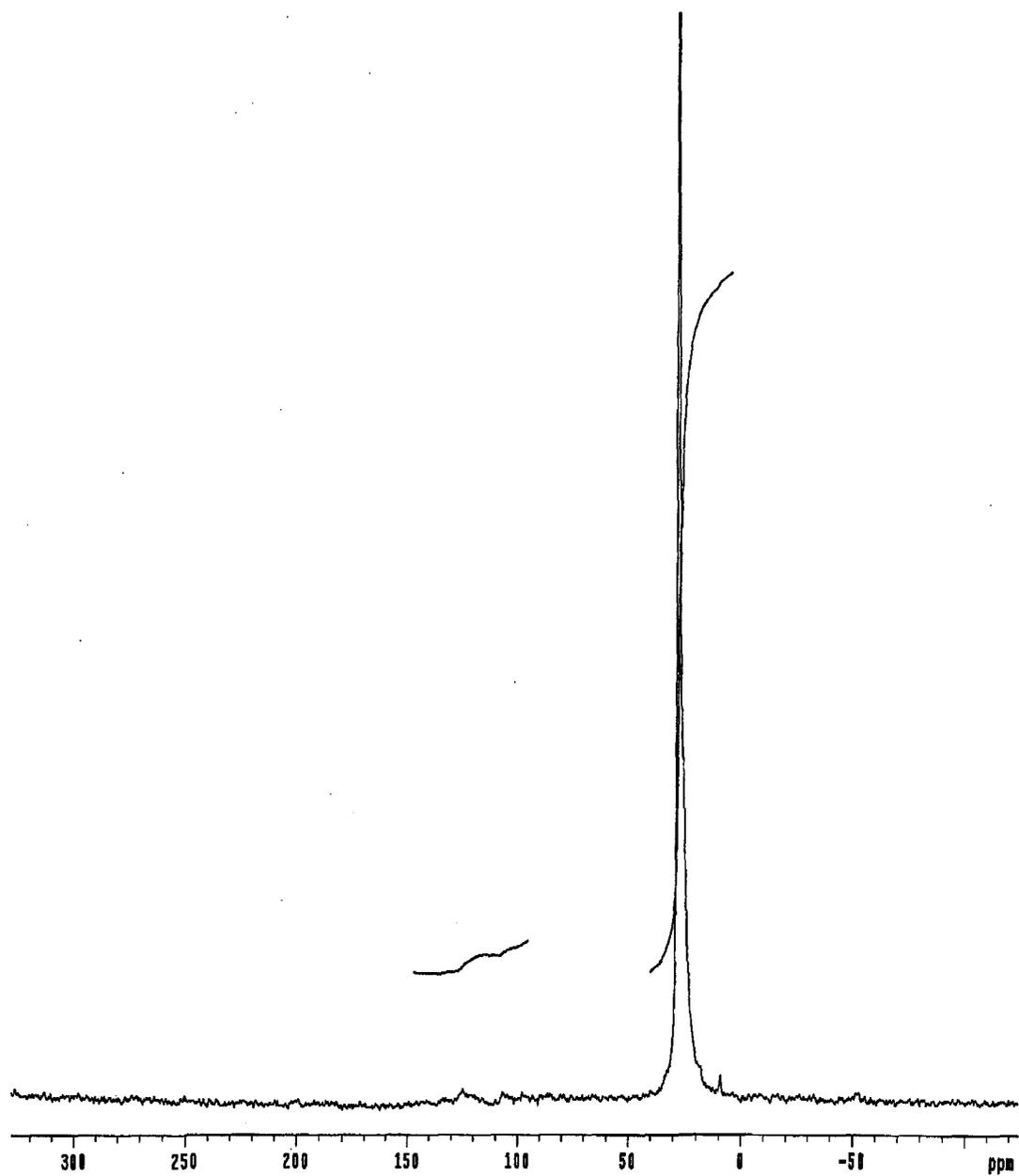


Figure 2.3. ^{13}C NMR Spectrum of Dehydrogenated Medium Density Polyethylene (Method B).

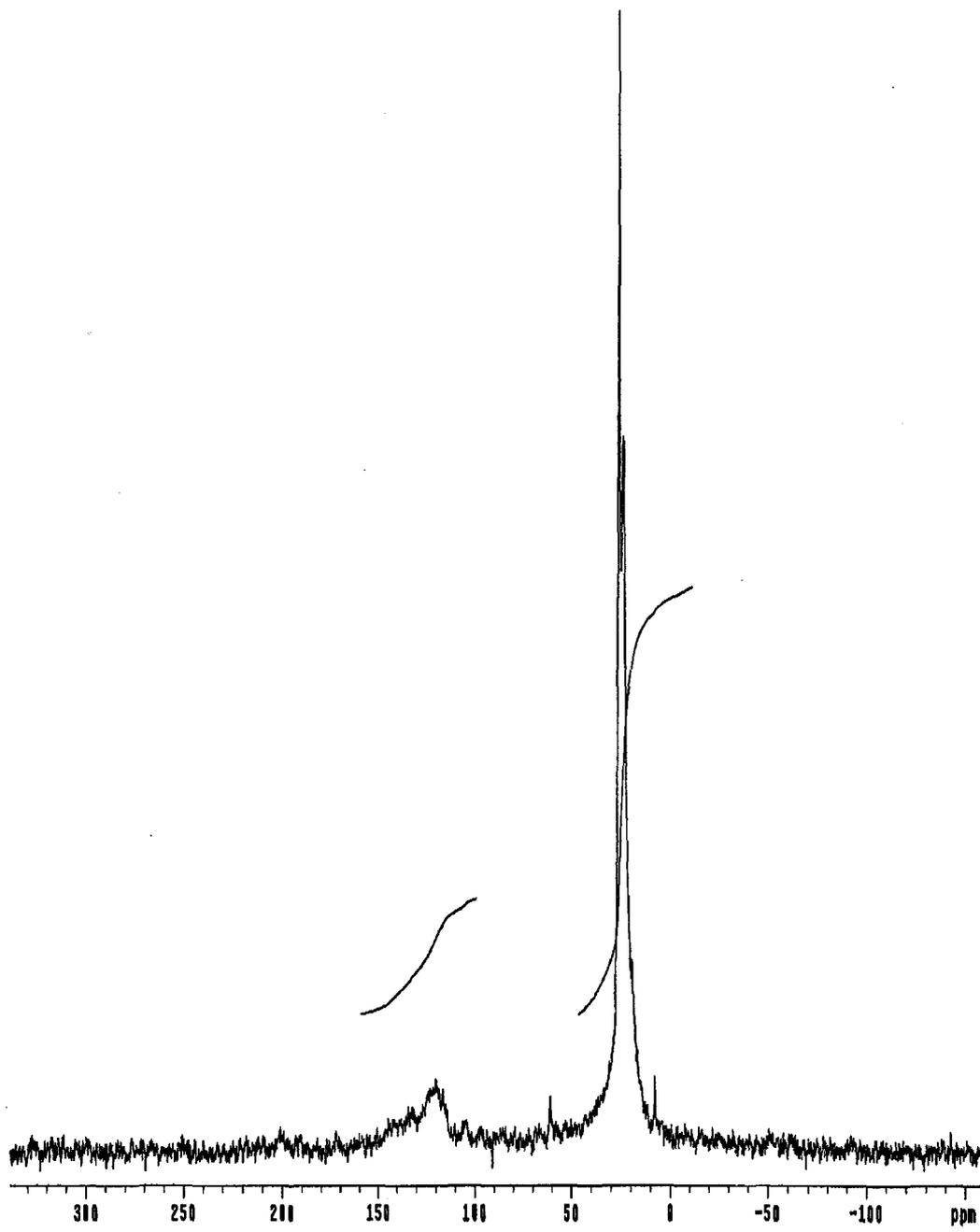


Figure 2.4. ^{13}C NMR Spectrum of Dehydrogenated Medium Density Polyethylene (Method C).

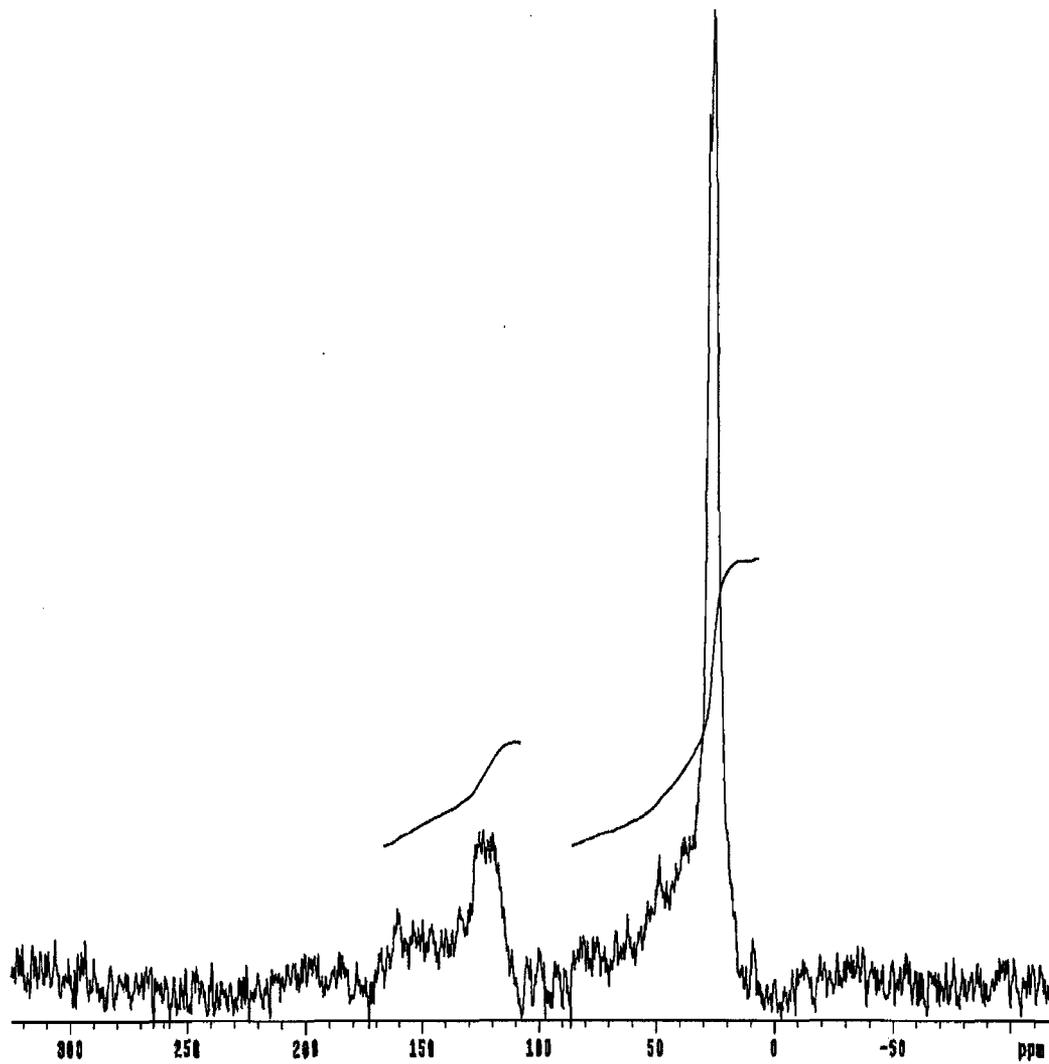


Figure 2.5. ^{13}C NMR Spectrum of Dehydrogenated Medium Density Polyethylene (Method D).

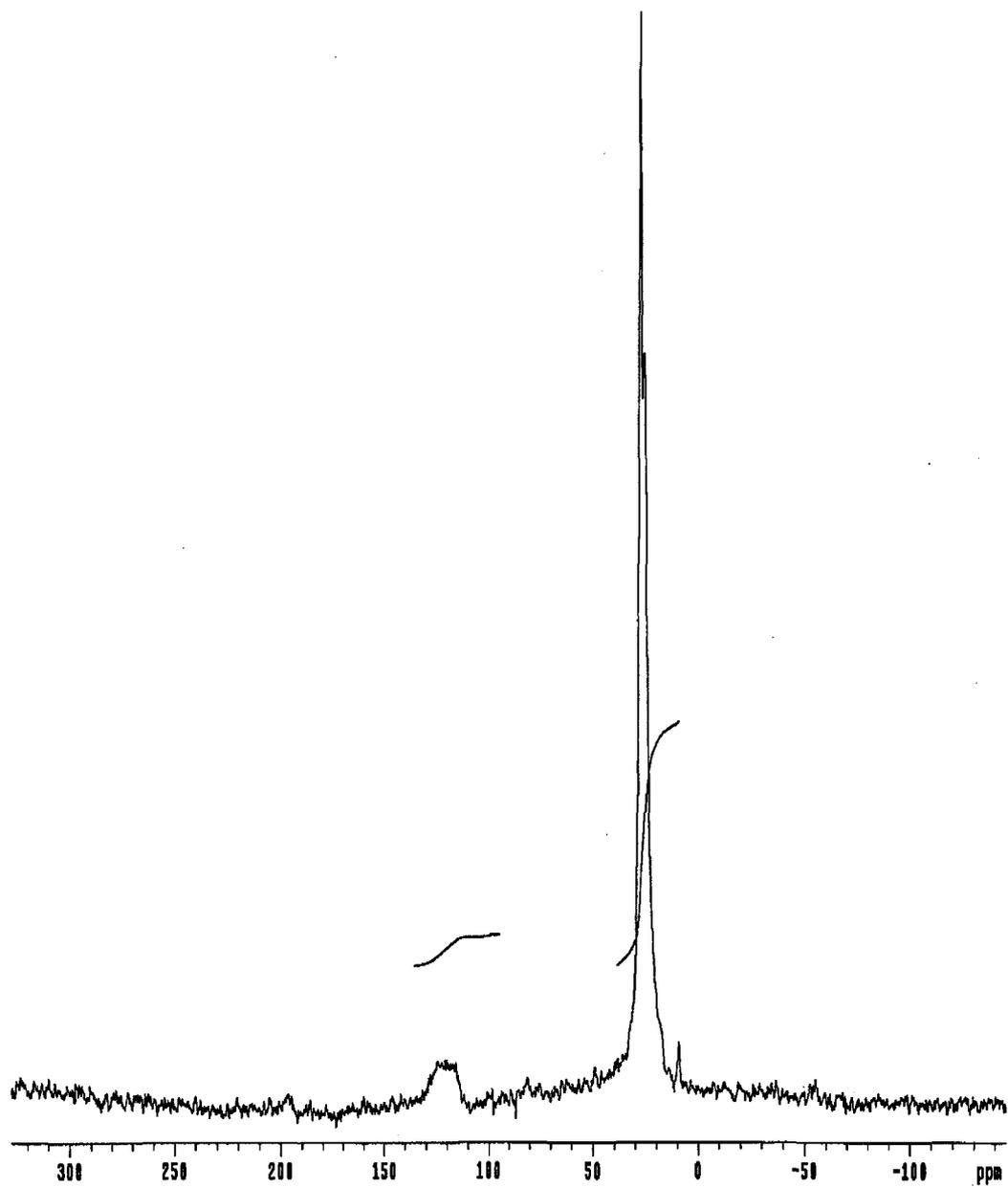


Figure 2.6. ^{13}C NMR Spectrum of Dehydrogenated Medium Density Polyethylene (Method E).

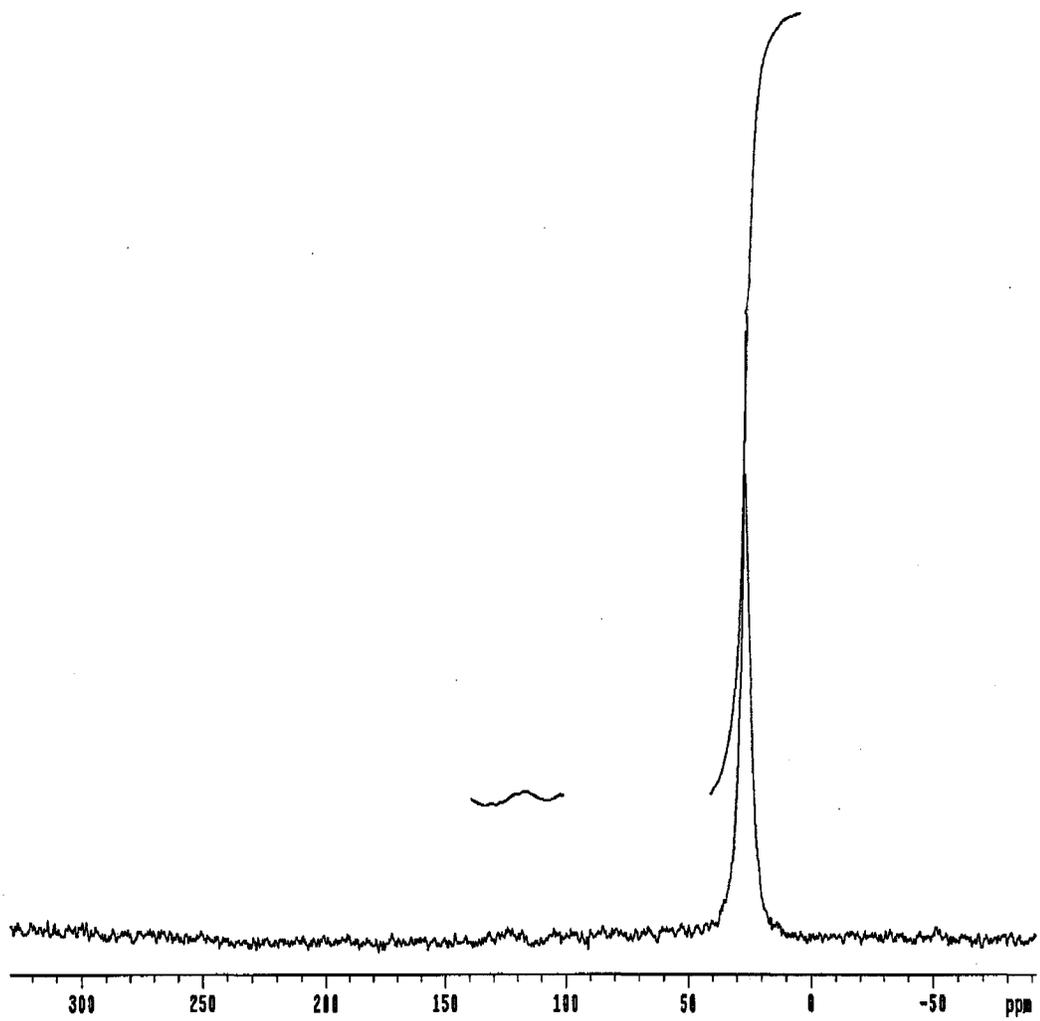


Figure 2.7. ^{13}C NMR Spectrum of Dehydrogenated High Density Polyethylene (Method B).

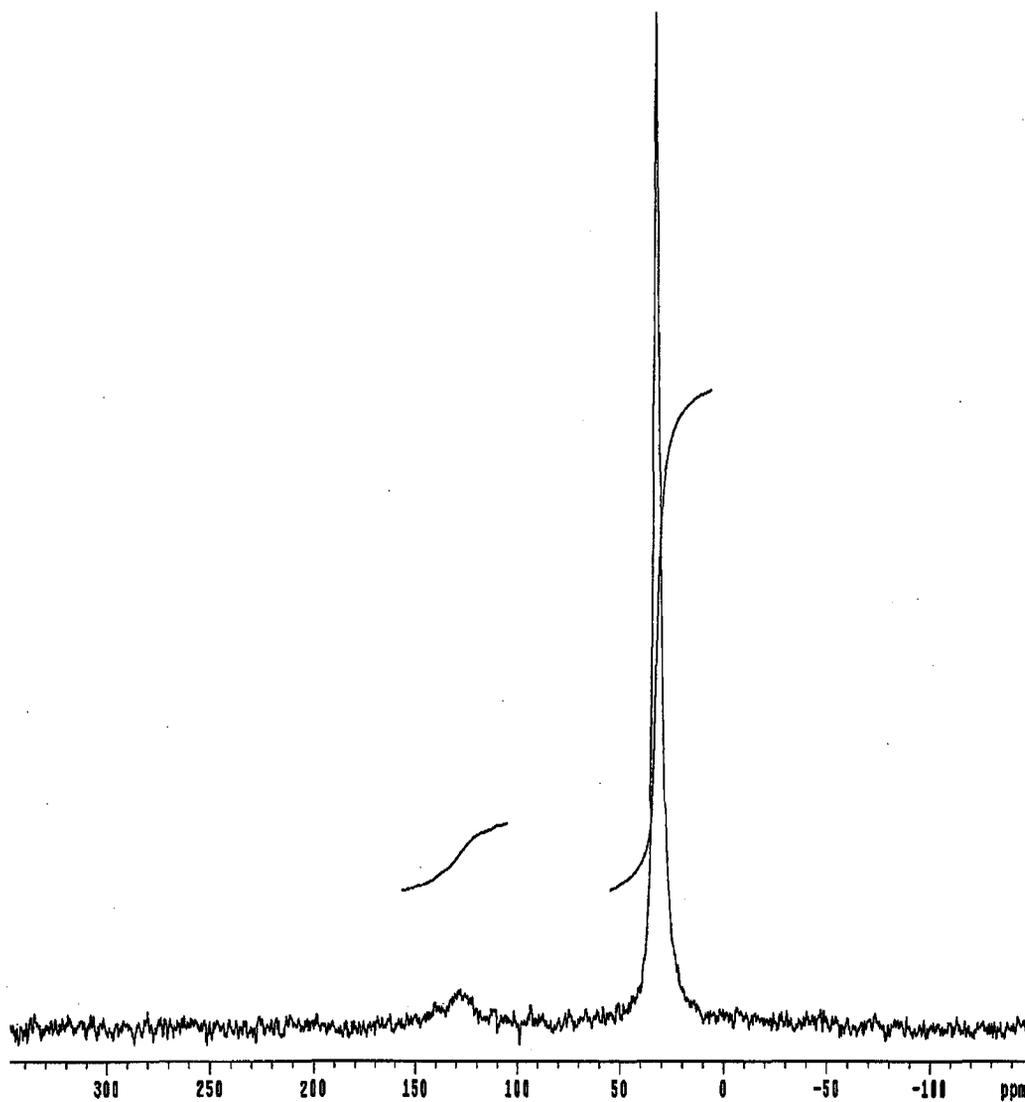
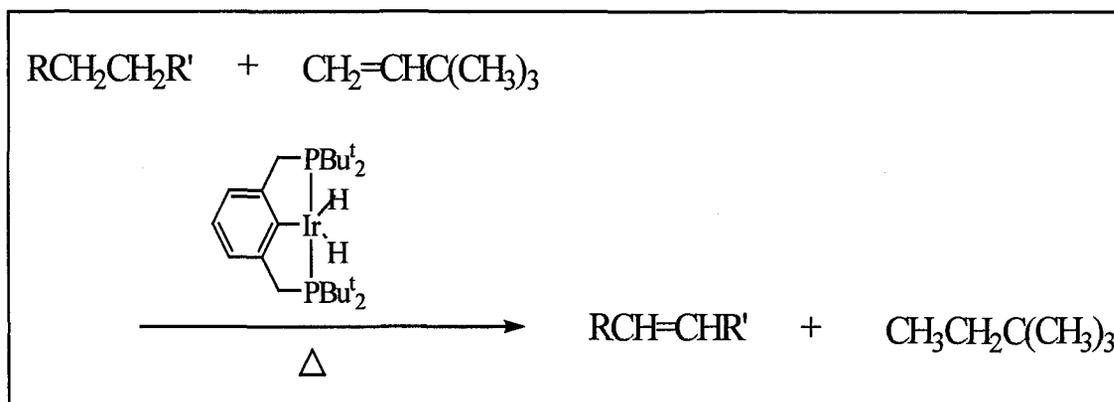


Figure 2.8. ^{13}C NMR Spectrum of Dehydrogenated High Density Polyethylene (Method C).

GC analysis of the reaction mixtures showed that the change of solvent resulted in a dramatic increase in the amount of tbe that was hydrogenated to tba. As seen in Figures 2.1- 2.8, the ^{13}C CPMAS NMR spectrum of the isolated polymeric material verified that a very substantial number of unsaturations were introduced into the polyethylene.

Through variations of the experimental parameters it was observed that the dehydrogenation of the polymer substrate was found to be maximized at a catalyst concentration of 40 mM and 168 hours of reaction time. At 150 °C the reaction proceeds with the dehydrogenation of polyethylene by *tert*-butylethylene (tbe), as indicated by the production of *tert*-butylethane (tba). The net catalytic process is shown in Scheme 2.9.

Scheme 2.9 Catalytic Dehydrogenation of Polyethylene by $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$.



Iridium catalysts are sensitive to their environment. Therefore the dehydrogenation reactions, which employ iridium catalysts, must consider several factors for the optimization of their system. These factors to be considered are the ratio between catalyst and substrate, solvent effects, reaction temperature, the structure of the ligand, and the concentration of hydrogen acceptor.

To determine the conditions needed to optimize the reaction an initial study was performed which varied the ratio between catalyst and substrate. The ratios employed from previous dehydrogenation reactions were considered in selecting the ratio of substrate to catalyst for this system.^{31-32, 50} As observed in previous dehydrogenation reactions, as the ratio of catalyst to substrate is increased, the reaction yield increased.⁵⁰ Our results were in agreement with our expectations as is observed in Table 2.10.

In chemistry, there is a direct correlation between structure and reactivity. In organometallics the relationship between structure and reactivity is under constant exploration. Researchers have modified the structure of the PCP pincer using the numerous modifications as indicated in figure 2.12. Modifications have included substitutions at (a) the alkyl groups on the donor group (b) the benzene ring (c) the CH₂ groups and (d) the donor groups.

Goldman has recently reported an improved catalyst, which is a derivative of the PCP ligand as seen in Figure 2.13.⁵¹ In compound **2** an electron-donating methoxy group is introduced at the para position of the benzene ring of the pincer ligand backbone.

Table 2.10 Summary of the Results of Studies of the Catalytic Dehydrogenation of Polyethylene using Iridium PCP Pincer Complexes.

Catalyst (mmol)	tbe (mmol)	Duration (hr)	Polyethylene	Conversion (%)*
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-CH}_2\text{PBU}^t_2\}_2$ (0.05)	11.64	168	Light Density	24.1 ± 0.3
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-CH}_2\text{PBU}^t_2\}_2$ (0.10)	11.64	168	Light Density	44.5 ± 1.2
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.05)	11.64	168	Medium Density	30.2 ± 1.4
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	11.64	24	Medium Density	8.7
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	11.64	72	Medium Density	19.4
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	1.55	168	Medium Density	24.1 ± 0.6
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	11.64	168	Medium Density	51.9 ± 2.2
$\text{IrH}_2\{\text{p-MeO-C}_6\text{H}_2\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	11.64	168	Medium Density	61.0
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	0	168	Medium Density	0
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	0	504	Medium Density	0
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.05)	11.64	168	High Density	32.5 ± 1.3
$\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ (0.10)	11.64	168	High Density	55.8 ± 1.5

* All values, with standard deviations, are based on an average of three experiments.

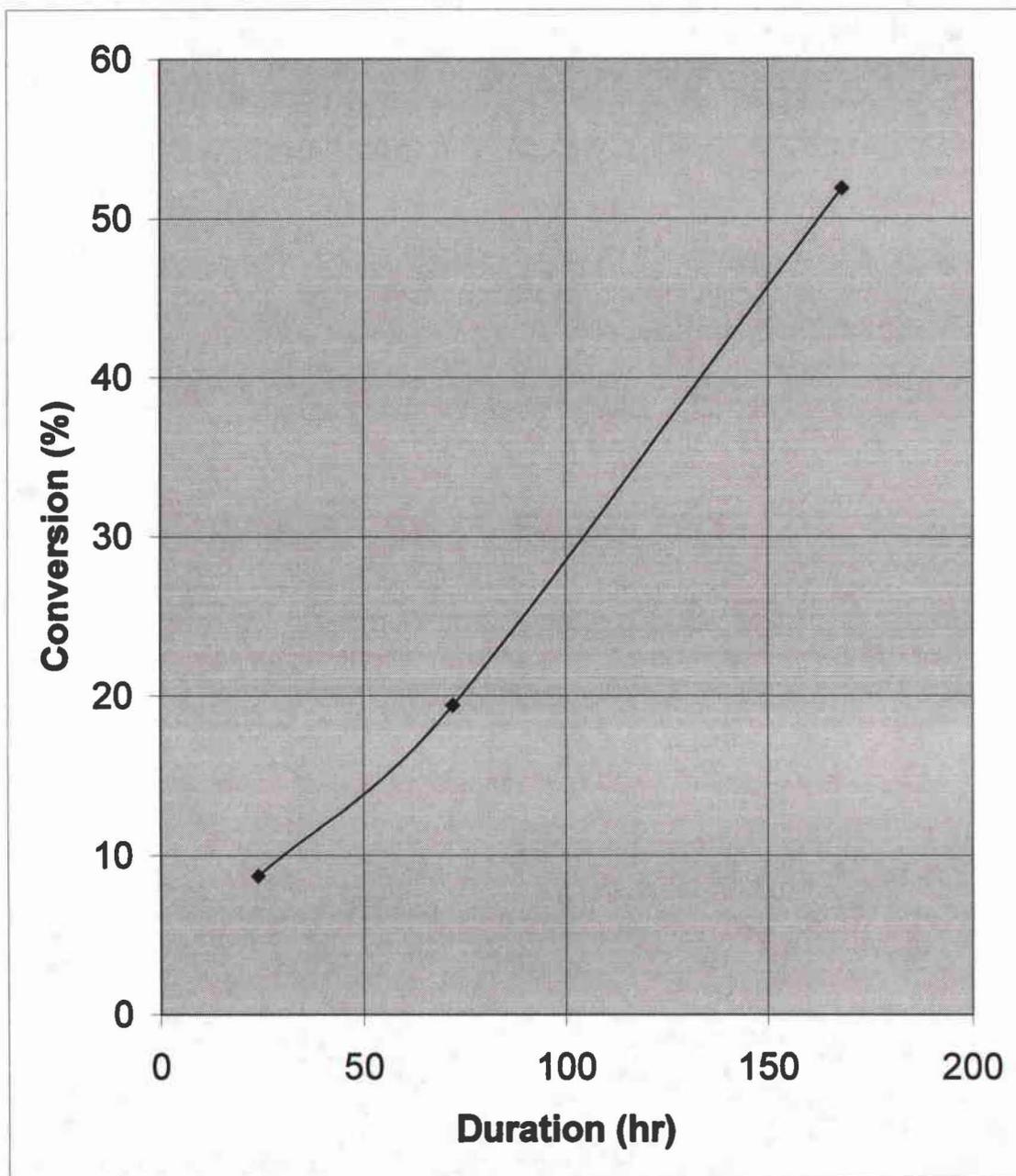


Figure 2.11 Catalytic Dehydrogenation of Polyethylene Versus Time.

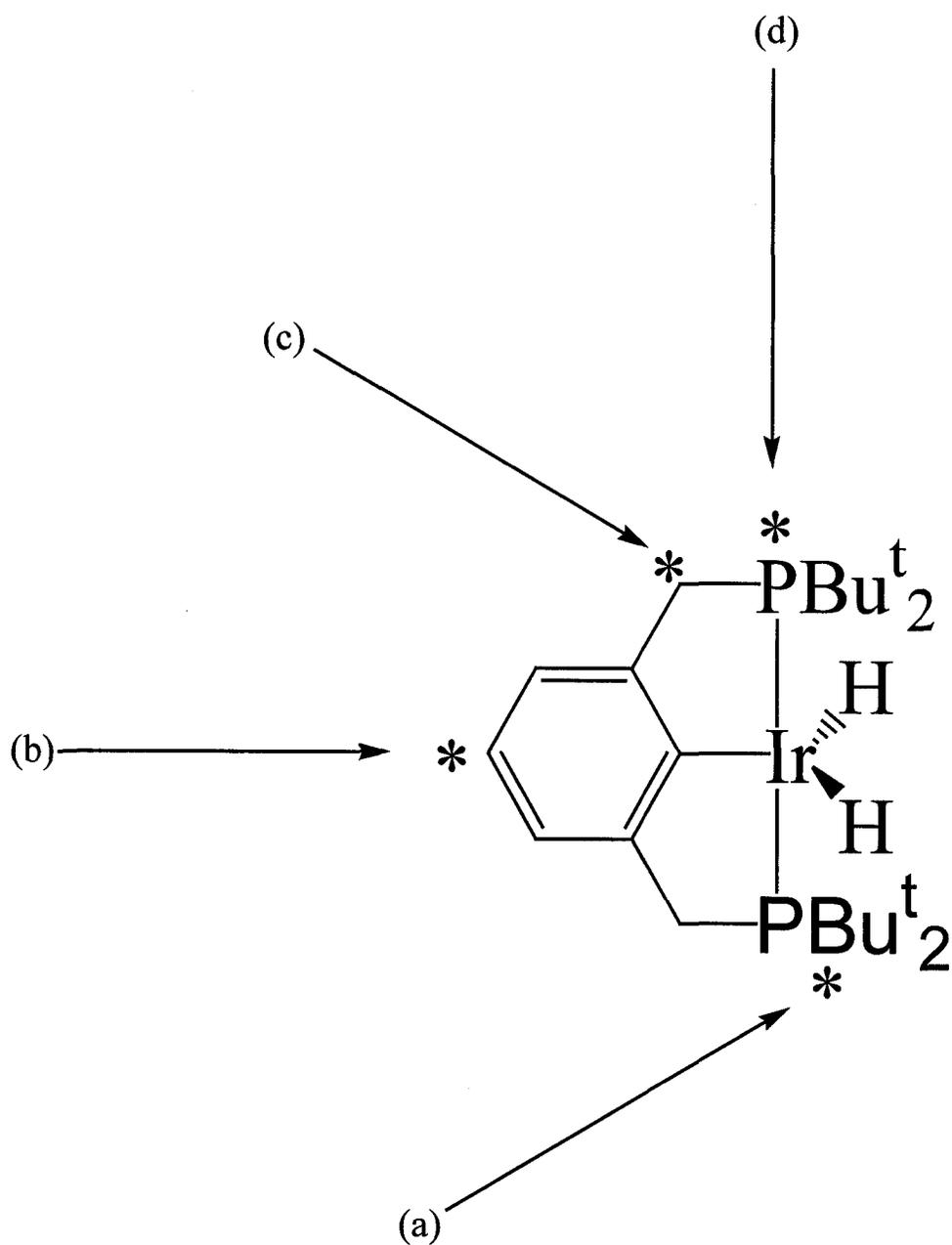
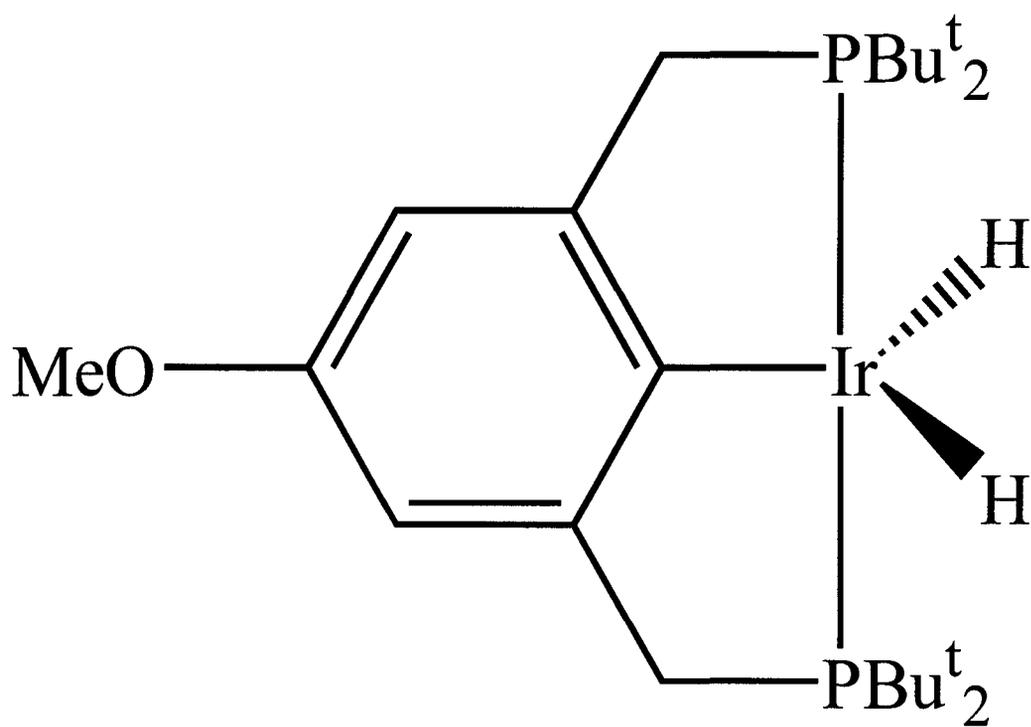


Figure 2.12 Possible Sites of Modifications on $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{PBU}^t_2)_2\}$.



(2)

Figure 2.13 Goldman's Modifications of the Parent PCP Catalyst, $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{PBu}^t_2)_2\}$.

During the course of these studies, it was reported that the derivative complex of **1**, $\text{IrH}_2\{p\text{-MeO-C}_6\text{H}_4\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**2**) catalyzed the transfer hydrogenation of poly-1-hexene.⁵¹ In view of the higher activity that has been reported for the *p*-OMe-PCP derivative as a catalyst for alkane dehydrogenation,⁵¹ it was of interest to compare its activity to that of **1** as a catalyst for the dehydrogenation of polyethylene. As seen in Table 2.10, utilization of **2** as the catalyst was found to result in a small but significant increase in the extent of the dehydrogenation of medium density polyethylene from 52 to 61%.

The results indicate that under our system the modified catalyst, **2**, has higher activity. The higher activity may be attributed to the electronic effect of the methoxy group, which is at the para position on the benzene ring. It has been shown that increasing the electron density at the metal center promotes oxidative addition of C-H bonds.⁵⁸ It has been proposed that the electron-donating groups enhance dehydrogenation by facilitating oxidative addition and β -hydride elimination.⁵⁸

The observation that the extent of polymer dehydrogenation increases with increasing density of the polyethylene provides an important insight into this catalytic system. Clearly, the effectiveness of the PCP pincer catalysts is highly sensitive to branching of the polymer chains. This finding is congruous with the observations that these catalysts are highly selective for the dehydrogenation of terminal positions of linear alkanes³⁶ and the methyl group of methylcyclohexane.³² Therefore the formation of internal unsaturations in these substrates is the result of much slower, secondary olefin isomerization reactions. Apparently, unsaturations can not be produced in the branching positions of polyethylene by the PCP pincer catalysts through direct dehydrogenation.

Thus the more extensive dehydrogenation of polyethylene that can be achieved upon substitution of **1** by **2** in the catalytic system is apparently due to an enhanced ability of **2** to create internal substitutions in the polymer through the catalytic isomerization of C-C double bonds to form internal C-C double bonds.

Another important factor that was considered in optimizing this system was the solvent. Previous dehydrogenation experiments encountered solvent issues in the form of product inhibition.⁵² Product inhibition was avoided in the dehydrogenation of polyethylene by carrying out the reactions in dilute solutions of perfluorodecalin. Perfluorodecalin is an excellent choice in solvent because it addresses the issues of ease of separation, temperature requirements and it eliminates any concern of the dehydrogenation of the solvent versus the alkane.

The reaction temperature of 150 °C was chosen based on results of previous experiments.³⁴⁻³⁶ Previous dehydrogenation reactions found that the amounts of products obtained when using the iridium PCP pincer were restricted by thermodynamics. Lower levels of products are obtained below 150 °C, and temperatures above 200 °C are avoided due to decomposition of the catalyst.

As a final optimization of the system we considered the amount of hydrogen acceptor to employ. Previous studies indicated alkene inhibition problems with the hydrogen acceptor concentrations when they were in excess of 300 times that of the concentration of the catalyst.³¹ To avoid alkene inhibition, a the concentration at 20 times and 120 times the concentration of catalyst were chosen as indicated in Table 2.10. As expected the results indicate that the experiment, which employed 120 times the the concentration to catalyst, showed higher levels of dehydrogenation. Apparently it seems

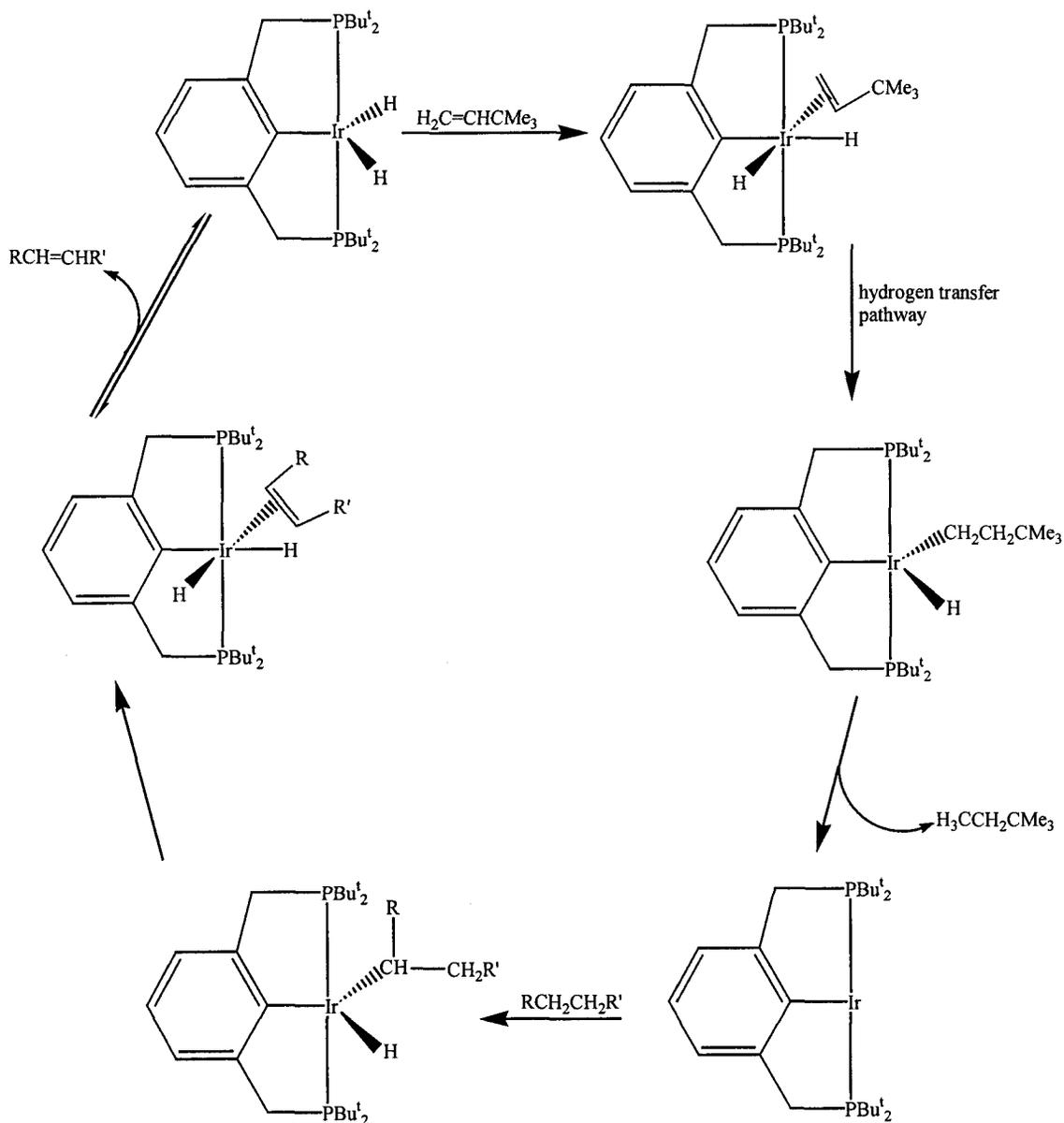
that the excess of tbe is there for transfer hydrogenation, which is attempting to out-compete the internal transfer dehydrogenation of polyethylene. All attempts to carry out the catalytic dehydrogenation of polyethylene in the absence of a sacrificial hydrogen acceptor were not observed.

Finally the consideration of the overall mechanism of the dehydrogenation of polyethylene must be deliberated. The overall mechanism of the transfer dehydrogenation of alkanes, and for that matter polyethylene, by $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$ is largely unexplored.³⁶ However, the initial process in the catalytic sequence is undoubtedly the dehydrogenation of the dihydride by the hydrogen acceptor to produce the intermediate $\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$.³⁶ This initial step occurs with the olefin insertion of the tbe group. This is followed by hydrogen migration to form tba, which undergoes reductive elimination to give the intermediate $\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$. This reaction has been studied in detail and occurs cleanly at 25 °C.⁵⁹ This initial step has been shown to be irreversible with the observation of no deuterium scrambling.⁵⁹

The elimination of tba in the initial process is believed to be triggered by an agostic interaction with a methyl C-H bond of a tert-methyl group. This hypothesis has been supported by the observation of deuterium scrambling.⁵⁹

The polyethylene dehydrogenation process is believed to occur through a reversal of the hydrogenation of tbe.³⁶ This process proceeds through the oxidative addition of the C-H bond in the polyethylene substrate. This is then followed by the β -hydride elimination from the resulting alkyl group and then is followed by the elimination of the product polyolefin to regenerate the active species $\text{Ir}\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBU}^t_2)_2\}$, as indicated in Scheme 2.14.

Scheme 2.14 Proposed Mechanism of the Dehydrogenation of Polyethylene by $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PBu}^t_2)_2\}$.



2.6. Conclusion

The iridium dihydrido complexes $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**1**), and $\text{IrH}_2\{p\text{-OMe-C}_6\text{H}_4\text{-}2,6\text{-(CH}_2\text{P}^t\text{Bu}_2)_2\}$ (**2**), catalyze the transfer-dehydrogenation of polyethylene in the presence of the hydrogen acceptor *tert*-butylethylene at temperatures of 150 °C. Rates of dehydrogenation as high as 56 % were achieved in perfluorodecalin.

Our product quantification shows that there is a direct relationship between the catalyst to substrate ratio and reaction yield. This study also indicates that there is a preference for the linear, high density polyethylene.

To our knowledge, this is the first report of a homogeneous catalytic system for the dehydrogenation of polyethylene. The practicability of the system suffers from several obvious problems such as the requirement of a sacrificial hydrogen acceptor and insufficient catalyst efficiency. However, it does represent the first step toward the development of a novel approach to the degradation of polyethylene to recyclable chemical feedstocks.

CHAPTER 3

Future Directions

The dihydrido iridium PCP pincer complexes have been found to be active and robust catalysts for the dehydrogenation of polyethylene. This stage represents a major step towards the development of viable methods for the complete dehydrogenation of polymers.

Polyethylene is effectively converted to its polybutadiene analog through oxidative addition and subsequent β -hydride elimination at the primary methyl groups leading to the isomerization of internal olefins. Thus after dehydrogenation of the polymer it can then be subjected to various methods of breaking carbon-carbon double bonds, such as oxidative addition or olefin metathesis.

A possible method that is being considered is represented in Figure 3.1.

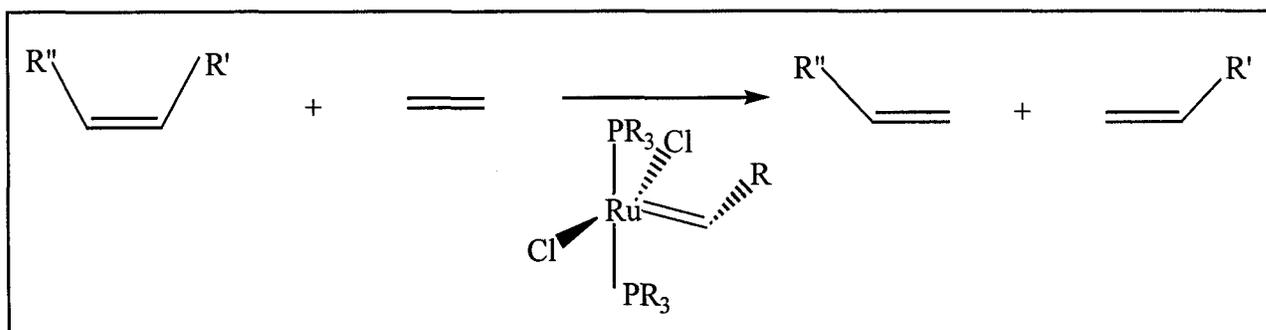


Figure 3.1 Metathesis of Dehydrogenated Polyethylene by Grubb's Catalyst.

As indicated in Figure 3.1 the alkene, which has been dehydrogenated with the PCP pincer complexes, will then undergo acyclic diene metathesis depolymerization to produce small olefins. The olefin metathesis could be achieved through the use of Grubb's catalyst or other related catalysts. However, Grubb's catalyst would be an optimum choice due to its stability, and good functional group compatibility.

The dehydrogenated polyethylene may also be studied for its electrical and material properties.

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