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PART I

PREPARATION AND APPLICATION OF POLYMER-SUPPORTED CATALYSTS

PART II

THERMAL DECOMPOSITION OF TRANSITION METAL ALKYLS

By

Biau-Hung Chang

A DISSERTATION

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ABSTRACT

PART I

PREPARATION AND APPLICATION OF POLYMER-SUPPORTED CATALYSTS

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The industrial application of homogeneous catalysts has been expanded greatly in recent years. However, homogeneous catalysts are less widely used than heterogeneous catalysts in the chemical industry mainly due to the difficult separation of the very expensive catalysts from the reaction products. Therefore, heterogenizing homogeneous catalysts by attaching homogeneous catalysts to polymer supports is a significant step in improving their utility and versatility.

In this research, the attachment of transition metal complexes of Ti, Zr, Hf, Nb, Ta, Co, and Rh to 20% cross-linked macroreticular polystyrene-divinylbenzene copolymer beads by cyclopentadienyl ligands has been developed. The organometallic polymer beads have been tested for a variety of catalytic activity. The polymer-attached zirconium and hafnium complexes were effective in hydrogenation of olefins and acetylenes, isomerization of allylbenzene and 1,5-cyclooctadiene, and epoxidation of cyclohexene. The zirconium beads have also been used in hydrozirconation to produce terminal aldehydes. Further observations showed that supported metallocene derivatives were more effective in catalysis than the related compounds in homogeneous solutions and their activities were in the decreasing order, Ti>Zr>Hf. Also, polymer-attached methylene-bridged titanocene dichloride beads were prepared and used for the study of nitrogen fixation.

The pentavalent derivatives of niobium and tantalum containing beads were prepared by the reaction of their pentachlorides with the beads containing tin alkyls. They were active catalysts in hydrogenation of diphenylacetylene, and isomerization of allylbenzene. The tantalum beads were also an active catalyst in dimerization of ethylene.

Mononuclear complexes of cyclopentadienyl cobalt and rhodium dicarbonyls covalently attached to a polystyrene-divinylbenzene copolymer support were prepared from their carbonyl derivatives and cyclopentadiene-substituted beads. The beads have been tested for a number of catalytic reactions. The rhodium containing beads were effective in hydrogenation of olefins, aldehydes and ketones, isomerization of olefins, disproportionation of 1,4-cyclohexadiene and cyclohexene, cyclotrimerization of ethyl propiolate, and hydroformylation of l-pentene and l-hexene. Decomposition of the rhodium catalysts occurs except in hydroformylation, although only slight loss of the carbonyl groups and catalytic activity was observed in cyclotrimerization. The rhodium catalyst appears to be the first example of cyclopentadienyl coordination compound of Rh active in hydroformylation catalysis. The cobalt containing beads have proven to be inactive except in case of the cyclotrimerization of ethyl propiolate.

The second part of this research was a study of the thermal decomposition of some early transition metal alkyl complexes such as Cp_2TiR_2 (R=n-alkyl, neopentyl, neohexyl), and Cp_2VR , Cp_2TaClR_2 , Cp_2MoR_2 and Cp_2WR_2 (R= neohexyl). Two new mechanisms of the thermolysis, γ - and δ -hydrogen eliminations, which involve metallacycles as the intermediates have been proposed and discussed.

To My Wife and My Family.

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PART I

PREPARATION AND APPLICATION OF POLYMER-SUPPORTED CATALYSTS

INTRODUCTION

In an energy conscious world, the chemists have long been interested in ways of minimizing the energy requirements of chemical reactions and to this end have diligently sought out suitable catalysts. The use of both soluble and insoluble catalysts in chemical reactions is almost as old as chemistry itself. Acid catalysis is a typical example of homogeneous catalysis which has been known and applied for a long time. On the other hand, the hydrogenation of unsaturated compounds catalyzed by transition metals such as platinum, palladium, or Raney nickel, a representative example of heterogeneous catalysis, was not developed until the early nineties.

In the last thirty years, the industrial application of processes catalyzed by soluble transition metal compounds has become very significant. Despite this impressive growth, homogeneous catalysts are less widely used than heterogeneous catalysts in the chemical industry and have little application in petroleum refining due to the difficult separation of the very expensive catalysts from the products at the end of the reaction. Nevertheless, homogeneous catalysts demonstrate great selectivity and economic efficiency. Recently, considerable research effort has been expended in developing catalysts that combine as many advantages as possible. There have been two major approaches.

1. Fluid-bed catalysts.¹ The use of fluid-bed catalysts, in which control of the catalyst movement is maintained by the flow of the reactants, represents an attempt to homogenize heterogeneous catalysts. This technique is widely used for the catalytic cracking of petroleum and much other technology.

2. Supported complex catalysts. These catalysts essentially involve a metal complex covalently bound to some form of support. They have also been referred to as hybrid phase catalysts,² heterogenized homogeneous catalysts,³ homoactive heterogeneous catalysts⁴ or solidphase synthesis.⁵ This technique represents an attempt to heterogenize homogeneous catalysts.

The supported homogeneous catalysts are most often insoluble in any solvent, and in this sense, they are indeed quite heterogeneous. However, they are prepared by the same reactions as those used for the homogeneous complexes. The transition metals retain the ligands around them even during the catalytic processes. Moreover, these catalysts function in operating conditions comparable to those used for conventional homogeneous catalysts, for instance at relatively low temperatures. Therefore, these supported homogeneous complex catalysts have several advantages such as overcoming the problem of catalyst separation from the reaction products, retaining the advantages of homogeneous catalysts, having higher selectivity than the conventional heterogeneous catalysts and reducing the chance of poisoning.

Heterogeneous supported catalysts have been developed in order to get a better utilization of the potential catalytic activity by dispersing the metal on an inorganic oxide carrier. Similar effects have also been observed when anchoring a metal complex on a polymer,

the supported catalyst being more active than the homogeneous complex from which it is derived. It is generally agreed that homogeneous catalysis practically always involves at least one intermediate in which the metal atom is coordinatively unsaturated. Such an unsaturated intermediate very often tends to dimerize, which is detrimental to the catalytic activity. It is then conceivable that anchoring the catalyst on a sufficiently rigid support can prevent the association of the isolated and unsaturated catalytic centers, thus preserving all of the potential catalytic activity.

Haag and Whitehurst⁶ reported the carbonylation of allyl chloride catalyzed by either soluble or supported palladium amine complexes. It has been shown the catalytic activity of the supported catalyst increases linearly with the amount of palladium used. On the other hand, the activity of the homogeneous catalyst soon reaches a maximum when its concentration is raised. This corresponds to a parallel increase of the mutual interactions between palladium atoms, leading to aggregation and formation of catalytically inactive oligomeric species. Such an aggregation is not found when the palladium complexes are firmly anchored on a rigid polymer.

Another example of activation of a homogeneous complex by anchoring on a support, reported by Grubbs, Brubaker and coworkers,⁷⁻¹¹ is the hydrogenation of olefins catalyzed by titanocene-supported analogues. The attachment of titanocene species to a rigid polymer resulted in an increase in activity for olefin hydrogenation. Since titanocene species undergo deactivation by polymerization processes, it was proposed that the increase in activity resulted from site

isolation on the polymer. The catalyst activity varies with the loading of the catalyst on the polymer. The relationship between loading and rate is best explained by assuming the material is attached to an almost rigid, immobile surface.

Besides the increasing activity, one can expect also some peculiar selectivity effects from the supported homogeneous catalysts. The use of a polymer raises the question of the diffusion of the substrate from the bulk solution to the catalytic centers, through the pore channels of the polymer. Diffusion barriers are associated with substrate size, polymer crosslinking, swelling power of the solvent used, and relative substrate and polymer polarities. Rhodium(I) hydrogenation catalysts attached to 2% crosslinking polystyrene show decreased reduction rates as olefin size increases or as solvent swelling power decreases.^{12, 13} These effects are mostly associated with diffusion limitations and become more important as catalyst activity increases.¹⁴

All the aims which have been discussed up to now are more or less directed towards the applied aspects of the supported homogeneous catalysis. In fact, the supported homogeneous catalysis may be used as a tool for a new approach of the heterogeneous catalysis. Supported

catalysis is particularly pertinent to the enviroment of the catalytic sites, and of the interactions between these sites. One can hope in this way, to analyze the factors which influence the activities and the selectivities of heterogeneous catalysts.

The choice of a supporting solid depends on the particular catalyst system. Generally speaking, the first property is that the

polymer must bear functional groups which can be used as ligands by the metal, Other parameter, from a chemical standpoint, is inertness to reagents. Concerning the physical properties of the polymer, the desirable characteristics of a support include: good mechanical and thermal stability, porosity, surface area and heat-transfer properties.

A number of materials have been used as the basic supports. It is convenient to describe them as either organic or inorganic supports, although there is a considerable region of overlap. Among these materials, polystyrene and silica have received most attention as organic and inorganic supports, and the techniques used to make these suitable as supports are generally typical of those required for organic and inorganic supports, respectively. Crosslinked polystyrene is available with a wide range of crosslink densities, surface areas and porosities. The basic polymer backbone is chemically inert¹⁵ and the polar properties can be modified by controlled functionalization or by the preparation of appropriate copolymers. These supports, however, have poor mechanical and thermal stabilities and poor heattransfer properties. In this thesis research, 2% and 20% crosslinked polystyrene-divinylbenzene copolymer beads have been used as supports.

A homogeneous catalyst can be heterogenized in a variety of ways. The common methods are to attach the metal complex to a solid support either by deposition or by adsorption, 16 or by an ionic 17 , 18 or a covalent chemical bond. Less common methods involve the polymerization of a complex, bringing a polymerizable function to such a high molecular weight that it becomes insoluble in the medium in which it will be used or by trapping it in a gel or other porous medium. $^{19-23}$

If the complex is electrically neutral, a covalent or a coordinative bond must be used to link it to a support. Thus, polymers have to be functionalized with linking ligands used in homogeneous catalysis such as arene, cyclopentadiene, phosphine, pyridine, cyano, amine, etc.. Numerous techniques have been developed for functionalization of polystyrene with suitable ligands as shown in Figure 1.¹³ These modes allow linking agents to be attached through either nucleophilic or electrophilic reactions and provide great flexibility in the synthetic design. Any transition metal complex can be attached to the polymer by appropriate choice of linking ligands.

According to the linking ligands, the supported homogeneous catalysts can be divided into two groups: (1) complexes that require mobile, labile supporting ligands, and (2) complexes that exhibit a high degree of unsaturation and are aided by immobile supporting ligands. Good examples of the first class are the group VIII phosphine catalysts, and the early transition element metallocenes provide examples of the second classification.

The attachment of transition metal complexes to solid support by phosphine ligands has been studied extensively. The phosphines in these complexes exchange readily and in general the complexes are easily lost from the supports during the catalytic reactions. Also, the phosphines have high reactivity toward electrophiles,oxygen,and oxidizing agents.

The polymer-attached metal complexes through relatively inert cyclopentadienyl ligands have only recently been studied. Grubbs, Brubaker, and coworkers^{7-11,24-27} reported that titanocene dichloride



Figure 1. Functionalization of polystyrene with ligands.

Cp₂TiCl₂, could be attached to the polystyrene resin by reacting first the cyclopentadienyl groups with methyllithium and then with cyclopentadienyl trichlorotitanium. Upon reduction of the polymeric, "matrix isolated" titanocene dichloride with butyllithium or sodium naphthalide, a gray polymer was obtained that readily catalyzed hydrogenation of olefins and acetylenes (Figure 2).

The reaction of the sodium cyclopentadienide-substituted copolymer with TiCl₄ led to a supported CpTiCl₃ species. Similarly, the polymer-attached CpMCl_n species (M=Zr, Hf, Mo, W, and Nb) can be synthesized by the analogous reactions of polymer-attached cyclopentadienyl anions with anhydrous transition element halides. The reduced supported metallocene halides exhibit a high activity for the hydrogenation and isomerization of unsaturated compounds.²⁶⁻²⁸

A number of polymers containing the ferrocene group have been prepared in recent years due to the thermal stability, moisture stability and air stability of this group. The products obtained during the thermal treatment of ferrocene polymers exhibited catalytic activity in the oxidation and dehydration of alcohols.²⁹

Brintzinger et al 30-31 reported the preparation of mononuclear cyclopentadienyl cobalt, chromium, iron, molybdenum, rhodium and tungsten carbonyl derivatives covalently linked to macroreticular polystyrene and silica gel supports. The cobalt and rhodium derivatives were found to be active catalysts for olefin hydrogenation and hydroformylation reactions.



Figure 2. Scheme for the attachment of Cp_2TiCl_2 to a polymer.

The research work reported here consists of (1) the preparation and characterization of polymer-attached zirconocene and hafnocene species, and the testing of their catalytic activities towards hydrogenation of unsaturated compounds, isomerization of allylbenzene and 1,5-cyclooctadiene, epoxidation of olefins, and hydrozirconation of olefins to produce terminal aldehydes, (2) the preparation of polymerattached methylene-bridged titanocene compounds and their activity toward nitrogen fixation, (3) the preparation and characterization of polymer-attached niobium and tantalum complexes and examination of their catalytic activities, and (4) the synthesis and characterization of polymer-attached cyclopentadienyl cobalt and rhodium dicarbonyls. and study of their applications to the catalytic hydrogenation of olefins, aldehydes and ketones; hydroformylation of olefins; isomerization of allylbenzene and 1,5-cyclooctadiene; disproportionation of cyclohexene and cyclohexadiene; and cyclotrimerization of acetylene derivatives.

RESULTS AND DISCUSSIONS

Homogeneous catalysts have several advantages over heterogeneous catalysts in several aspects such as efficiency, reproducibility, specificity, controllability and selectivity. However, the major disadvantage of the homogeneous catalysts is the need to seperate the reaction products and to recover the catalyst, which is often somewhat more expensive. So it's less useful in industrial applications than a "classical" heterogeneous catalyst. Hybrid catalysts prepared by reaction of organometallic compounds with polymer or metal oxide supports, may combine the advantages of both homogeneous and heterogeneous catalysts. These developments should open new industrial applications.

It has been demonstrated that the attachment of titanocenerelated catalysts to polymers resulted in an increase in activity for the olefin hydrogenation.^{9,10,28} Since titanocene species undergo deactivation by dimerization or polymerization process, it was proposed that this increase in activity resulted from site isolation on the polymer.¹¹ Polymer-attached titanocene has also been proved to be excellent catalysts for the isomerization and epoxidation of olefins and oligomerization of acetylene derivatives.^{26,32}

For the analogous study, zirconocene and hafnocene derivatives, which are isoelectronic and most probably isostructural with the titanium homologs, have been attached to the polystyrene copolymers and their catalytic activities are examined in this thesis research.

Crosslinked polystyrene, available with a wide range of crosslink densities, surface areas, and porosities, has received the most attention as an organic support. Collman and his coworkers³³ have found that 2% crosslinked polystyrene-divinylbenzene copolymers are mobile enough to allow ligands attached to the polymer beads to act as chelates. Consequently, this polymer is not rigid enough to prevent dimerization of attached unstable species. For the research discussed here, 20% crosslinked macroreticular polystyrene-divinylbenzene copolymer beads, ranging in size from 30 to 35 mesh (600 Å average pore size)³⁴ were used as the supports. The 20% crosslinked copolymers are rigid, insoluble and have a large surface area.

The cyclopentadienyl anion has been used as good ligand for a variety of potentially useful metal complexes.³⁵⁻³⁷ It has also provided a remarkably effective means of binding transition metal complexes to the polystyrene-divinylbenzene copolymer and its pentahepto bonding to the metal ensures the formation of a strong, covalent π -bond between the polymer and the metal.

The attachment of cyclopentadienyl groups to polystyrene-divinyl benzene copolymer can be achieved by the reaction of sodium cyclopentadienide with the chloromethylated copolymer beads, which obtained by following the chloromethylation method of Pepper et al.³⁸ The cyclopentadiene is coverted into cyclopentadienide anion by the treatment with methyllithium or butyllithium. The procedures are outlines in Figure 3. A variety of transition metal complexes can be attached to the polymer through the cyclopentadienyl ligands.



Figure 3. Scheme for the attachment of cyclopentadienyl anion to the polystyrene copolymer.

Preparation of Polymer-Attached Bis(cyclopentadienyl)zirconium and Hafnium Dichlorides (P-Cp₂MCl₂; M=Zr, Hf)

Three methods for the preparation of polymer-attached zirconocene and hafnocene dichlorides have been studied. They are (a) reaction of CpMCl₃ with polymer-attached lithium cyclopentadienide, ³⁹ (b) reaction of Cp₂MCl₂ with polymer-attached lithium cyclopentadienide followed by treatment with excess hydrogen chloride gas, ^{40,41} and (c) reaction of MCl₄ with polymer-attached lithium cyclopentadienide followed by the addition of stoichiometric amout of sodium cyclopentadienide, and then by the treatment with small amount of hydrogen chloride gas. The reaction schemes are shown in Figure 4,5 and 6.





Figure 4. Scheme for the preparation of supported Cp₂ZrCl₂ by the reaction of CpZrCl₃ with lithium cyclopentadienidesubstituted polymer.



Figure 5. Scheme for the attachment of Cp_2MCl_2 to polystyrene through the exchange reaction of σ and π cyclopentadienyl ligands.





Figure 6. Scheme for the attachment of Cp₂MCl₂ to polystyrene by the modified method.

Due to the difficult preparation of CpMCl₃, the first procedure is less useful. For the second procedure, the remaining unreacted cyclopentadienyl and vinyl groups on the polymer take up hydrogen chloride when excess hydrogen chloride is used. Therefore, the higher ratio of chloride to metal from elemental analyses than the expected value is observed. After the exchange reaction of $n^1-C_5H_5$ and $n^5-C_5H_5$ rings in Cp₃MCl followed by the treatment with hydrogen chloride gas, the loading of Cp₂MCl₂ on the polymer is only two-thirds of the original concentration of Cp₃MCl.

In order to overcome these problems, the third procedure has been developed to produce higher loading of Cp_2MCl_2 on the polymer. The addition of stoichiometric amount of sodium cyclopentadienide to polymer-attached $CpMCl_3$ mostly gives Cp_2MCl_2 . Although small amount of Cp_3MCl and Cp_4M species can be conceivably produced, they can be easily converted into Cp_2MCl_2 by the treatment with small amount of hydrogen chloride gas. Therefore, the loading of Cp_2MCl_2 on the polymer is almost the same as the original concentration of $CpMCl_3$ and elemental analyses show the ratio of chloride to metal is very close to the expected value.

Preparation of Polymer-Attached Monocyclopentadienyl Zirconium and Hafnium Trichlorides (P-CpMCl₃; M=Zr, Hf)

Brubaker and Chandrasekaran^{27,28} synthesized polymer-attached monocyclopentadienyl zirconium and hafnium trichlorides from the reaction of the lithium cyclopentadienide-substituted copolymer with zirconium tetrachloride and hafnium tetrachloride pyridine adducts respectively, due to the low solubility of the pure tetrachlorides. In the study of supported monocyclopentadienyl zirconium and hafnium trichlorides, it was found that these supported complexes could be prepared by the direct reaction of the lithium cyclopentadienide-substituted polymer and pure tetrachlorides for longer reaction time. Renaut et al⁴² reported that the reaction between dicyclopentadienyl-magnesium and hafnium tetrachloride in decalin gave CpHfCl₃.2THF adduct after removal of Cp₂HfCl₂ with THF. Therefore, the species on the polymer after washing with THF is probably CpMCl₃.2THF adduct.



Figure 7. Scheme for the attachment of CpMCl₃ to the polystyrene copolymer.

Preparation of Polymer-Attached Tris(cyclopentadienyl)zirconium and Hafnium Monochlorides (P-Cp₃MCl; M=Zr, Hf)

Recently the reactivities of $Cp_2Zr(R)Cl^{52-54}$ with a variety of reagents have been studied extensively. In order to compare the reactivity of supported Cp_3MCl with those of the supported $CpMCl_3$ and Cp_2MCl_2 species, the supported Cp_3MCl (M=Zr, Hf) species was prepared. The attachment of Cp_3MCl to the polymer has been achieved by the reaction of Cp_2MCl_2 with polymer-attached lithium cyclopenta-dienide. The reaction scheme is shown below (Figure 8).



Figure 8. Scheme for the attachment of Cp₃MC1 to the polystyrene copolymer.

Preparation of Polymer-Attached Methylene-Bridged Bis(cyclopentadienyl)zirconium Dichloride

The attachment of Cp_2ZrCl_2 to a polymer has been described above. The higher loading of Cp_2ZrCl_2 on the polymer can be achieved by using methylene-bridged cyclopentadiene-substituted polymer which contains higher concentration of cyclopentadienyl groups. The concentration of metal complexes attached by this way usually can be increased to twice that of non-bridged cyclopentadiene-substituted polymer. The reaction scheme is shown in Figure 9.

Far Infrared Studies

An understanding of the factors which control the change in catalytic activity on polymer attachment has been difficult to determine due to the lack of good methods for the analysis of the structure of the catalyst on the polymer. Several techniques have been found useful for this analysis in our laboratory. Elemental analysis gives the loading of the catalyst and the ratio of metal to chloride. Electron microprobe analysis^{27,28} allows the rapid determination of the distribution of the catalyst inside of a polymer bead. Recently the ³¹P NMR spectroscopy has been used for the analysis of low cross-linked phosphinated polystyrenes.^{43,44} The IR analysis, although successful in some cases, is normally hindered by high background absorption of the polymer and the low loadings used.



Figure 9. Scheme for the preparation of polymer-attached methylene-bridged Cp₂ZrCl₂.
The study of far infrared spectra of metallocene chlorides allows assignments to be made for the metal-ring and metal-ligand stretching modes. Since the far infrared spectra for the titanocene systems show a good correlation between the polymer-attached and unattached species, 27,28 a similar investigation of the zirconocene and hafnocene systems was undertaken as a further means of identifying the species on the polymer. It is indicated that there is also a good correlation between the attached and unattached zirconocene and hafnocene chlorides (Figure 10 and 11). These absorption bands are in substantial agreement with those reported in the literature. 45,46 The band assignments are deduced from these reported data and are listed in Table 1 and 2.

Table 1. Far infrared bands (cm^{-1}) of polymer-attached and unattached Cp_2ZrCl_2 .

Assignments	Cp ₂ ZrC Obs.	Calc.	5,46 Cp ₂ ZrCl ₂	P-Cp ₂ ZrCl ₂	
v _s (Zr-Cp)	358	350	361	355	
ν _a (Zr-Cp)	358	368	361	355	
v _s (Zr-Cl)	333	329	332	330	
v _a (Zr-Cl)	333	332	332	330	
tilt	310	•••	31 0	306	
tilt	266	•••	265	269	

Assignments	Cp ₂ HfC Obs.	Calc.	Cp ₂ HfC1 ₂	P-Cp ₂ HfC1 ₂
ν _s (Hf-Cp)	360	349	360	360(sh)
ν _a (Hf-Cp)	360	338	360	33 5
ν _s (Hf-Cl)	31 0	314	312	308
ν _a (Hf-Cl)	310	310	312	308
tilt	264	•••	265	265
tilt	284	•••	285	285(sh)

Table 2. Far infrared bands (cm^{-1}) of polymer-attached and unattached Cp₂HfCl₂.

Hydrogenation Studies

Titanocene and its hydrides are useful catalysts for the hydrogenation of unsaturated compounds. However, these complexes readily dimerize or polymerize to form catalytically inactive materials.^{47, 48} To prevent the dimerization, it has been achieved by attaching the titanocene precursor to a rigid polymer support. On reduction, a catalyst is produced whose hydrogenation efficiency is greater than a corresponding nonattached species.^{9, 10}

Zirconocene and hafnocene are also found to be active catalysts for the hydrogenation of alkenes. Their activities in hydrogenation have been increased after attachment to the polymer. For example, the rates of hydrogen uptake for 1-hexene catalyzed by reduced nonattached and attached Cp_2ZrCl_2 are 0.12 mL and 0.95 mL/m mmol of metal









at room temperature respectively. Previous hydrogenations reported with homogeneous cyclopentadienyl zirconium catalysts were carried out only at high temperature and high pressure.⁴⁹ Supported zirconocene and hafnocene complexes are also active hydrogenation catalysts for alkynes. The rates of hydrogen uptake for diphenylacetylene catalyzed by supported zirconocene and hafnocene catalysts are 3.6 mL and 2.7 mL/m mmol of metal at 100° , respectively. It is shown that diphenylacetylene is hydrogenated to give trans-stilbene and further to give 1,2-diphenylethane (Figure 12 and 13). Some catalytic hydrogenation of unsaturated compounds in the presence of supported titanocene catalysts is also examined and indicates a reduced activity for the heavier metals.

Isomerization

Allylbenzene and 1,5-cyclooctadiene, when treated with reduction product of polymer-attached zirconocene and hafnocene chlorides, appear to undergo a rapid double bond migration. The exact mechanism by which they act, whether of the addition-elimination or π -allyl type, is still not certain. Allylbenzene can be isomerized to form the more stable conjugated system, cis- and trans-propenylbenzene (Figure 14-17). Similarly, 1,5-cyclooctadiene is effectively isomerized to 1,3-cyclooctadiene with 1,4-cyclooctadiene as the intermediate product (Figure 18-21). The catalysts produced by reducing the supported metallocene chlorides under hydrogen are more active than those generated under argon. For example, the catalyst produced, by reducing the supported Cp₂ZrCl₂ under argon, can only effect about 50% isomerization of







Figure 13. Hydrogenation of diphenylacetylene catalyzed by supported Cp_2HFCl_2 .

allylbenzene in 5 h, while the catalyst obtained under hydrogen brings the isomerization to an extent of 90% under the same conditions. The reduction of metallocene chlorides under hydrogen probably generates metallocene hydrides such as Cp_2ZrH_2 and Cp_2HfH_2 and the isomerization most probably proceeds through the addition-elimination mechanism.

A comparison of isomerization activity is examined, it is shown that $CpMCl_3$ is the most efficient catalyst, followed by Cp_2MCl_2 , with Cp_3MCl being least active under the conditions employed (Figure 14, 16 and 17; Figure 18 and 20; Figure 19 and 21). A reduced activity for the heavier metal is also indicated (Figure 14 and 15; Figure 18 and 19; Figure 20 and 21). The catalyst can be repeatly used without much reduced activity (Figure 14).

Other experiments indicate that polymer-attached zirconocene and hafnocene catalysts are also good catalysts for cis-trans isomerization. Cis-stilbene, when treated with these catalysts, is isomerized rapidly to trans-stilbene. But no appreciable amount of isomerization products was observed for 1,5-hexadiyne, β -pinene and 1-octene.

The isomerization of allylbenzene and 1,5-cyclooctadiene catalyzed by the reduction product of the supported titanocene chlorides has been studied by C. P. Lau.^{26, 32} To compare its activity with those of zirconocene and hafnocene catalysts, it is found that their activities are in the decreasing order, Ti>Zr>Hf.



Figure 14. Isomerization of allylbenzene catalyzed by supported Cp_2ZrCl_2 .



Figure 15. Isomerization of allylbenzene catalyzed by supported Cp_2HFCl_2 .



Figure 16. Isomerization of allylbenzene catalyzed by supported $CpZrCl_3$.



Figure 17. Isomerization of allylbenzene catalyzed by supported Cp_3ZrCl .



Figure 18. Isomerization of 1,5-cyclooctadiene catalyzed by supported Cp_2ZrCl_2 .



Figure 19. Isomerization of 1,5-cyclooctadiene catalyzed by supported Cp_2HfCl_2 .



Figure 20. Isomerization of 1,5-cyclooctadiene catalyzed by supported CpZrCl₃.



Figure 21. Isomerization of 1,5-cyclooctadiene catalyzed by supported CpHfCl₃.

Epoxidation

It is known^{50, 51} that compounds of certain transition metals, notably Mo, W, Ti and V catalyze the liquid-phase epoxidation of olefins with alkyl hydroperoxides.



Both homogeneous and heterogeneous catalysts^{50, 51} have been described. Brubaker and Lau^{26, 32} have demonstrated that polymerattached titanocene dichloride and trichloride can be used as catalysts for the epoxidation of cyclohexene and cyclooctene with t-butyl hydroperoxide. Similarly, the epoxidation of cyclohexene with t-butyl hydroperoxide in the presence of polymer-attached zirconocene and hafnocene catalysts has been studied. Polymer-attached zirconocene and hafnocene chlorides are active catalysts for the epoxidation, but their activities are relatively lower than that of the supported titanocene catalysts. The results are given in Table 3. The yields of major product, epoxycyclohexane, are ranged from 9% to 22%. Some other by-products,⁵¹ possibly 3-t-butylperoxy-1-cyclohexene, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, trans-cyclohexane-1,2-diol, 2-hydroxycyclohexanone and 2,3-epoxy-cyclohexan-1-ol, were not examined.

The continuous decrease in the activity of the catalysts, possibly due to the autoretardation by the co-product t-butanol, has been observed. However, the catalysts can be regenerated by passing anhydrous hydrogen chloride gas into the beads suspended in THF. The regenerated catalysts are reused for the epoxidation without much loss of activity. The detailed mechanism of epoxidation catalyzed by these supported catalysts was not determined.

Table 3. Catalytic epoxidation of cyclohexene.

Catalysts(wt.) (loading)	Solvent	Time(h)	Product(%) (epoxycyclohexane)	
P -Cp ₂ ZrCl ₂ (0.1444g) (0.63 mmol Zr/g)	benzene	18	16	
P -Cp ₂ ZrCl ₂ (0.1448g) (0.63 mmol Zr/g)	cyclohexane	18	19	
P -Cp ₂ ZrCl ₂ (0.1448g) (recycled) ^a	cyclohexa ne	18	15	
P -Cp ₂ ZrCl ₂ (0.1467g) (0.63 mmol Zr/g)	benzene	48	20	
P -CpZrCl ₃ (0.2756g) (0.33 mmol Zr/g)	cyclohexane	18	22	
P -Cp ₂ HfCl ₂ (0.2007g) (0.45 mmol Hf/g)	cyclohexane	4 8	9	
P -CpHfCl ₃ (0.3075g) (0.29 mmol Hf/g)	cyclohexane	48	11	

a Catalyst used was recycled from previous reaction.

Hydrozirconation of Alkenes

Schwartz <u>et al</u>⁵²⁻⁵⁴ have demonstrated that Cp_2ZrClH will react with olefins and alkynes to produce terminal alkyl and alkenyl zirconium derivatives. These zirconocene alkyls and alkenyls will react with a number of reagents to produce terminally functionalized alkanes and alkenes in high yield. The most interesting reaction is the production of terminal aldehydes from olefins (Figure 22). The development of hydrozirconation illustrates that the introduction of new procedures will continue to be an exciting aspect of organic synthesis because of the broad scope and high reactivity of organometallic complexes.



Figure 22. Scheme for the synthesis of aldehydes from hydrozirconation of alkenes.

If one can attach Cp_2ZrCl_2 to a polymer support, zirconocene dichloride can be recovered by filtration and re-used for hydrozirconation after hydrolysis of an acyl zirconium complex with dilute aqueous hydrochloric acid solution. Attempt to use the polymer-attached Cp_2ZrCl_2 reagents for the hydrozirconation of olefins to produce terminal aldehydes did not meet with much success. The results are given in Table 4.

The zirconium hydride, Cp₂Zr(H)Cl, was first prepared by Wailes <u>et al</u>^{49, 55} from Cp_2ZrCl_2 and LiAlH₄ or LiAl(0-t-Bu)₃H. Schwartz et al⁵² reported that it could be easily prepared by treatment of zirconocene dichloride in THF with a stoichiometric amount of $NaAlH_{2}(OR)_{2}$ (Vitride). Both procedures give high yield of zirconocene hydridochloride. The preparation of polymer-attached Cp₂Zr(H)Cl from Vitride and supported Cp_2ZrCl_2 , which was prepared from Method b or c, has been difficult to achieve, possibly due to the remaining unreacted cyclopentadienyl groups on the polymer taking up some alumium hydride reagents and the optimum amount of Vitride is difficult to determine. For example, with a Cp_2TCl_2 -substituted polymer with a loading of 0.32 mmol of Cp₂ZrCl₂ per g of polymer, there are 1.58 mmol of unreacted cyclopentadienyl groups per g of polymer remaining on the polymer after attachment of Cp₂ZrCl₂ to the polymer. The remaining unreacted cyclopentadienyl groups on the polymer will react with Vitride to give cyclopentadienide. Attempts to increase the formation of supported Cp₂Zr(H)Cl by varying the molar ratio of Vitride to zirconocene dichloride from one half to two are not successful. The polymerattached methylene-bridged Cp₂ZrCl₂ beads with higher loading of zirconium were also used, but no improvement in the production of

aldehydes was observed.

To solve the above problems, the polymer-attached Cp_2ZrCl_2 beads which prepared from the reaction of $CpZrCl_3$ and lithium cyclopentadienide-substituted copolymer beads (Method a) were used. The remaining cyclopentadienide groups instead of cyclopentadienyl groups on the polymer will not take up the aluminum hydride reagents. Therefore, polymer-attached $Cp_2Zr(H)Cl$ can be easily prepared by treatment of supported Cp_2ZrCl_2 with a stoichiometric amount of Vitride, and then used in hydrozirconation to produce aldehydes with high yields. However, the recovered beads from previous reaction can not be reused in hydrozirconation because the cyclopentadienide groups remaining on the polymer are converted into cyclopentadienyl groups after hydrolysis with dilute aqueous HCl.

Wailes <u>et al</u>⁵⁵ reported that the IR spectrum of $Cp_2Zr(H)Cl$ showed one broad Zr-H stretching band at 1390 cm⁻¹. Attempts to determine the species on the polymer after the reaction of supported Cp_2ZrCl_2 with Vitride are not successful due to the background absorption of the polymer and the low loadings used.

MC. OT	roiymer	Reactants	Used	Olefins	Pressure	A1 dehydes ^a
(loadti	ng, mmol Zr/g)	mol Zr	mmol Vitride		of CO(ps1)	(%)
6.2 g	(0.32)	2.0	1.0	1-hexene	60	o
7.1 g	(0.27)	1.9	1.0	l-pentene	80	ο
5.7 g	(0.32)	1.8	2.0]-pentene	80	O
5.0 g	(0.67)	3.3	1.7	1-hexene	45	o
5.0 g	(0.67)	3.3	3.0	1-hexene	80	0
5.0 g	(0.67)	3.3	4.0	1-pentene	80	n-hexanal (9%)
5.0 g	(0.67)	3.3	6.0]-pentene	80	0
8 .4 g	(0.81) ^b	6.8	9.4	1- hexene	80	0
11.0 g	(0.81) ^b	8.9	12.0	1-hexene	100	n-heptanal (21%)
10.5 g	(0.81) ^b	8.5	16.0]-hexene	100	n-heptanal (12%)
6.6 g	(0.42) ^C	2.77	1.39	1-hexene	80	n-heptanal (72%)
10.5 g	(0.42) ^C	4.41	2.21	3-hexene	100	n-heptanal (70%

Table 4. Synthesis of aldehydes from hydrozirconation of alkenes with polymer-attached Cp₂ZrCl₂.

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Wt. of P	olymer	Reactant	s Used	Olefins	Pressure	A1 dehydes ^a
(loading	• mmol Zr/g)	mmol Zr	mmol Vitride		of CO (psi)	(%)
10.2 g	(0.42) ^C	4.28	2.14	1-hexene	100	n-heptanal (81%)
10.2 g	(0.42) ^d	4.28	2.14	1-hexene	100	n-heptanal (trace)

- a. The yields are based on zirconocene dichloride.
- b. Polymer-attached methylene bridged Cp₂ZrCl₂ was used.
- Polymer-attached $Cp_2 ZrCl_2$ which prepared from the reaction of $Cp ZrCl_3$ and lithium cyclopentadienide-substituted polymer (Method C) was used. ບ່
- d. Recycled from the previous reaction.

Reduction of Carbon Monoxide to Alcohols by Polymer-Attached Cp₂ZrCl₂ Catalysts

Schwartz <u>et al</u>⁵⁶ reported that diisobutyl aluminum hydride (DIBAH) in the presence of Cp_2ZrCl_2 as a catalyst could reduce carbon monoxide at room temperature to give, on hydrolysis, a mixture of linear aliphatic alcohols. Reduction of CO by DIBAH in the presence of polymerattached Cp_2ZrCl_2 catalyst has been studied. The reaction mixture after hydrolysis gave the indication of methanol and propanol as shown by GLC analysis. Unfortunately, the amount is too small to be isolated for further analysis.

ESR Studies

The ESR spectra of the reduced polymer-attached Cp_2TiCl_2 species have been reported by C. P. Lau.²⁶ It has been claimed that the species formed by reduction of polymer-supported Cp_2TiCl_2 under argon is the supported titanocene, while that generated under hydrogen is the supported titanocene monohydride. The ESR spectra of reduced species formed by the reaction of polymer-attached Cp_2ZrCl_2 with n-butyllithium give a singlet signal regardless of the reduction carried out under argon or hydrogen (Figure 23 and 24). The siglet is possibly due to supported zirconocene formed by reduction.



Figure 23. The ESR spectrum of the reduced species of polymer-attached Cp₂ZrCl₂ beads under argon.

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Figure 24. The ESR spectrum of the reduced species of polymer-attached Cp₂ZrCl₂ beads under hydrogen.

Nitrogen Fixation Studies

Since the first report⁵⁷ of an uncharacterized but isolable dicyclopentadienyltitanium dinitrogen complex, homogeneous titanocene has been intensively studied and used for nitrogen fixation. $^{58-67}$ The titanocene dinitrogen complexes can be generated by the reaction of titanocene dichloride with a variety of reducing agents in a nitrogen atmosphere. At times considerable confusion has arisen over the nature of the dinitrogen complexes. But it is believed that a dinuclear titanium complex is involved in the process of titanocene nitrogen fixation.

Attempts to fix nitrogen were made by Kroll⁶⁸ and Chandrasekaran²⁷ using crosslinked copolymer-supported titanocene. No significant amount of ammonia was produced by the polymer-supported titanocene, possibly due to the titanocene centers being separated too far to fix nitrogen as a dinuclear Ti complex. This leads to the expectation that if the titanocene centers are brought closer by methylene-bridged ligands, then some nitrogen fixation should be observed. This was found out to be the case. The results of nitrogen fixation by using polymersupported methylene-bridged titanocene are given in Table 5 and 6.

Two approaches for the preparation of polymer-supported methylenebridged titanocene dichloride have been developed. First approach starts with cyclopentadienide-substituted copolymer beads which prepared from the reaction of chloromethylated copolymer beads with sodium cyclopentadienide, followed by reacting with alkyl lithium reagents. The reaction of cyclopentadienide-substituted polymer with methylene chloride,followed by reacting with sodium cyclopentadienide, gives

methylene-bridged cyclopentadiene-substituted polymer. The methylenebridged cyclopentadienyl groups are converted into cyclopentadienide, then reacted with CpTiCl₃ to give supported methylene-bridged titanocene dichloride. The reaction scheme is shown in Figure 25.

Chloromethyl ethers are suspected carcinogens and are used in the step of chloromethylation. In order to overcome this problem, the second approach starting with polystyrene beads was developed. Direct lithiation $^{113-115}$ of cross-linked polystyrenes with butyllithium-tetramethylethylenediamine (BuLi.TMEDA), followed by reacting with carbon tetrachloride, gives trichloromethylated beads. Further reaction of trichloromethylated polymer with sodium cyclopentadienide and then removal of the chlorine atom gives methylene-bridged cyclopenta-diene-substituted polymer. The methylene-bridged cyclopentadiene-substituted polymer beads are then treated with butyllithium and CpTiCl₃ to give supported methylene-bridged titanocene dichloride. The reaction scheme is shown in Figure 26.

Titanocene Dichloride(g)	Reaction Temp.(^O C)	Reactan mmol Ti	ts Used mmol NaNp	Produce mmol NH3	cts Produced mmol NH ₃ /mmol Ti
H omogeneous (0.1684 g)	-40	0.676	6.8	0.04	0.06
Homogeneous (0.2279 g)	-40	0.915	17.0	0.06	0.07
Homogeneous (0.3020 g)	25	1.213	22.5	0.01	0.01
20% supported Methylene-Bridge (0.523 g)	ed -40	0.366	3.7	0.00	0.00
2% Supported Methylene-Bridge (1.201 g)	ed -40	1.869	34.7	0.00	0.00

Table 5. van Tamelin nitrogen fixations (flow system).

Titanocene	Reactar	ts Used	Prod	lucts Produced
Dichloride(g)	mmol Ti	mmol NaNp	mmol NH3	mmol NH ₃ /mmol Ti
Homogeneous (0.28 g)	1.11	17.0	0.50	0.45
Homogeneous (0.40 g)	1.61	40.0	0.89	0.55
20% Supported (5.11 g)	2.30	38.9	0.02	0.01
20% Supported Methylene-Bridged (2.30 g)	2.45	60.0	0.15	0.06
20% Supported Methylene-Bridged (0.84 g)	0.89	40.0	0.10	0.11
20% Supported Dimethylene-Bridged (2.13 g)	1.83	35.2	0.16	0.15
20% Supported Trimethylene-Bridged (1.36 g)	1.50	39.5	0.14	0.16
20% Supported Tetramethylene-Bridged (2.19 g)	1.97	40.6	0.11	0.13
2% Supported Methylene-Bridged (1.24 g)	1.93	50.0	0.19	0.10
2% Supported Methylene-Bridged (1.42 g)	2.21	100.0	0.30	0.13

Table 6. Vol'Pin-Shur nitrogen fixations (at 1500 psi of N_2).



Figure 25. Scheme for the preparation of polymer-attached methylene-bridged Cp₂TiCl₂ via chloromethylation.



Figure 26. Scheme for the preparation of polymer-attached methylene-bridged Cp₂TiCl₂ via lithiation.

Preparation and Study of Polymer-Attached Titanocene Dicarbonyl (P -Cp₂Ti(CO)₂)

Titanocene dicarbonyl has been reported as an active catalyst for the hydrogenation of diphenylacetylene.⁶⁹⁻⁷¹ Huffman <u>et al</u>⁷² reported a homogeneous hydrogenation of carbon monoxide to methane using $Cp_2Ti(CO)_2$. The synthesis of $Cp_2Ti(CO)_2$, all starting from titanium(IV) derivatives,⁷³⁻⁷⁶ e.g. Cp_2TiR_2 (R=CH₂Ph or Me) has been reported. Recently, Floriani <u>et al</u>⁷⁷ reported a convinient synthetic route gave high yield of $Cp_2Ti(CO)_2$ from the widely available and well-characterized $Cp_2Ti(BH_4)$.

Polymer-attached $Cp_2Ti(CO)_2$ has been prepared by Lau²⁶ from the reaction of supported titanocene dibutyl beads with carbon monoxide. The preparation of supported $Cp_2Ti(CO)_2$ in this research is from the carbonylation of supported titanocene tetrahydroborate in the presence of tridthylamine. The reaction scheme is shown in Figure 27. The I.R. spectrum of the supported $Cp_2Ti(CO)_2$ beads shows two strong CO stretching bands at 1880 and 1965 cm⁻¹ (Figure 28). The CO stretching bands are much more intense than those of dicarbonyl beads prepared from the polymer-attached Cp_2TiCl_2 with butyllithium under CO atmosphere.

The supported titanocene dicarbonyl species is an active catalyst for the hydrogenation of diphenylacetylene to give 1,2-diphenylethylene and 1,2-diphenylethane under 10 atm of hydrogen and at 100° . However, this supported dicarbonyl is not active catalyst for the hydrogenation of olefins at room temperature or for the isomerization of allylbenzene at 145° .

Irradiation of dicarbonyl beads with U.V. light showed disappearance of two strong CO stretching bands and the color changed from brown to greyish brown. After stirred under 10 atm of CO, the greyish brown beads showed two weak CO stretching bands at 1880 and 1965 $\rm cm^{-1}$.

The study of hydrogenation of carbon monoxide to methane using supported $Cp_2Ti(CO)_2$ was not successful, possibly due to the active metal centers isolated on the rigid polymer.



Figure 27. Scheme for the preparation of polymer-attachedCp₂Ti(CO)₂.



Figure 28. IR spectrum of polymer-attached Cp₂Ti(CO)₂.

Polymer-Attached Niobium and Tantalum Complexes

Recently Schrock <u>et al</u>⁷⁸ reported in a series of papers some new chemistry of niobium and tantalum. The complexes of niobium and tantalum containing a single n^5 -cyclopentadienyl ligand are, in contrast to the bis(n^5 -cyclopentadienyl) complexes, not easily available.⁷⁹ The complexes of niobium such as CpNbCl₃ and Cp₂NbCl₂ have been attached to the polystyrene beads and proved to be active catalysts in the hydrogenation of olefins and isomerization of allylbenzene by Lau,²⁶ but attempt to attach CpNbCl₄ to the polymer was not successful. The synthesis of CpMCl₄ (M=Nb and Ta) has only recently been described.^{79,80} Therefore, stimulated by those reports, the attachment of CpMCl₄ (M=Nb and Ta) to the polymer was developed and their catalytic activities were also examined.

Preparation of Polymer-Attached CpMCl₄ (M=Nb and Ta)

The complexes $CpMCl_4$ (M=Nb and Ta) were prepared recently from the reaction of MCl_5 with $CpSnR_3$ (R=CH₃ or n-Bu)^{79, 80} or $MgCp_2$.⁷⁹ The attachment of $CpMCl_4$ species to the polymer can be achieved by the reaction scheme shown in Figure 29.

Treatment of the cyclopentadiene-substituted copolymer beads with n-butyllithium followed by the addition of R_3SnCl (R=Me or n-Bu) gave pale yellow polymer-attached CpSnR₃ beads. Then the direct reaction of supported CpSnR₃ with MCl₅ gave supported CpMCl₄ beads. These species were confirmed by the comparison of their colors with unattached species and by elemental analyses. This method is good for attaching CpMCl_n species to polymers.



Figure 29. Scheme for the preparation of polymer-attached $CpMCl_A$ (M=Nb, Ta).

Preparation of Polymer-Attached $(n^{1}-Benzy1)$ Niobium and Tantalum Chlorides (P -Ph-CH₂MCl_n, M=Nb and Ta)

Transition metal complexes attached to polymers by means of phosphine, nitrogen of π -bonded ligands have been studied extensively. However, polymers where the transition metal complex is attached to the matrix by a carbon-to-metal σ -bond have rarely been studied. ⁸¹⁻⁸⁵ Pittman <u>et al</u>⁸²⁻⁸⁴ found the use of metal carbonyl anions provided convenient routes to incorporate transition metal carbonyl moieties into polymers. In this research, polymer-bound (n¹-benzyl)niobium and tantalum chlorides have been prepared by treating polymer-bound

 $(n^{1}-benzy1)$ tin alkyls with anhydrous niobium and tantalum pentachlorides respectively. Polymer-bound $(n^{1}-benzy1)$ trimethyltin can be prepared in good yield by treating chloromethylated polystyrene beads with trimethylstannyllithium which was prepared by treatment of a tetrahydrofuran solution of hexamethyldistannane with methyllithium.⁸⁶ The proposed reaction may be illustrated in Figure 30. This method provides convenient routes for attaching transition metal halides to polymers through a n^{1} -benzyl ligand.



Figure 30. Scheme for the preparation of polymer-attached $(n^{1}-PhCH_{2})MCl_{4}$ (M=Nb and Ta)

Olefin Dimerization Catalyzed by Polymer-Attached Tantalum Complexes

Recently Schrock <u>et al</u>^{87, 88} reported that a neopentylidene complex, TaCp(CHCMe₃)Cl₂, reacts with ethylene to give a tantallocyclopentane complex, CpCl₂TaCH₂CH₂CH₂CH₂. They also demonstrated that the tantallocyclopentane complex could be intermediates in selective dimerization of ethylene to give 1-butene. The dimerization of ethylene catalyzed by polymer-attached CpTaCl₄ was carried out as follows:

The polymer-attached CpTaCl₄ beads were treated with two equivalents of neopentyllithium in pentane. The color of beads changed from yellow to brown. The brown beads were washed with pentane, the pressure bottle was then pressurized with 60 psi of ethylene and the mixture was stirred for 2 h. The solvent and ethylene were then removed by means of vacuum. Mesitylene was added and the mixture was stirred at 80 psi of ethylene at 100° . From the GLC analysis of the reaction mixture, it indicated that 1-butene was formed selectively and catalytically with a turnover of 18. When the brown beads were treated with 60 psi of ethylene and then treated with 90 psi of CO, a dicarbonyl complex, supported CpTaCl₂(CO)₂⁸⁷ was formed (v_{CO} : 2040 and 1960 cm⁻¹). The reaction scheme is shown in Figure 31.



Figure 31. Scheme for the dimerization of ethylene catalyzed by polymer-attached CpTaCl₄.

Hydrogenation Catalyzed by Polymer-Attached Niobium and Tantalum Complexes

 Lau^{26} reported the reduction product of polymer-attached CpNbCl₃ was an active catalyst in the hydrogenation of olefins. Similarly, the catalytic activities of polymer-attached $CpNbCl_4$, $CpTaCl_4$ and $(n^{1}-benzy1)$ niobium and tantalum chlorides were examined in this research. It was found that no hydrogen uptake was observed for the hydrogenation of olefins at room temperature using these reduced beads. However, the reduction products of these beads are active catalysts in the hydrogenation of diphenylacetylene at 100° and at 1 atm of H₂. For example, diphenylacetylene (1.5 mmol) was hydrogenated to give 1.2-diphenylethane via trans-stilbene as an intermediate within 23 h, when 0.63 g of supported $CpTaCl_4$ beads (0.79 mmol Ta/g of beads) was used. The reduced polymer-attached CpNbCl_A beads were much less reactive and brought the hydrogenation to an extent of 20% under the same conditions. The hydrogenations catalyzed by reduction products of polymer-bound $(n^{1}-benzyl)$ niobium and tantalum chlorides were not examined in detail in this case.

Isomerization Catalyzed by Polymer-Attached Niobium and Tantalum Complexes

The polymer-attached $CpTaCl_4$ beads were treated with excess of n-BuLi in hexane under atmospheric pressure of hydrogen. An active isomerization catalyst, red beads, was formed. The same procedures were carried out for polymer-attached $CpNbCl_4$ beads. The generated
reduced species, black beads, was much less reactive than that of supported $CpTaCl_4$. The isomerizations of allylbenzene catalyzed by these reduced beads were shown in Figure 32. The reduction products of polymer-bound $(n^1-benzyl)$ niobium and tantalum chlorides are also active isomerization catalysts and are as reactive as those of supported $CpNbCl_4$ and $CpTaCl_4$ in the isomerization of allylbenzene respectively.



Figure 32. Isomerization of allylbenzene catalyzed by reduced species of polymer-attached $CpMCl_A$ (M=Nb and Ta).

Polymer-Attached Cyclopentadienyl Cobalt and Rhodium Dicarbonyls

Cobalt and rhodium have been the focus of most research and are metals of choice for commercial hydroformylation of olefins and related synthetic reactions. Many low oxidation state cobalt and rhodium catalysts have been supported on a polymer network through phosphine ligands.^{13, 89-98} Interestingly, the catalytic properties of polymer-supported cyclopentadienyl cobalt and rhodium carbonyl derivatives are rarely studied,⁹⁹ although compounds of this kind are easily synthesized and characterized. The use of cobalt and rhodium complexes attached to polymers through the reasonably inert cyclopentadienyl groups is reported here. It is shown that polystyreneattached cyclopentadienyl cobalt and rhodium dicarbonyl complexes are active hydrogenation, isomerization, disproportionation, cyclotrimerization and hydroformylation catalysts.

Preparation of Polymer-Attached Cyclopentadienyldicarbonylcobalt

Two methods for the synthesis of polymer-attached cyclopentadienylcarbonylcobalt, photochemical and thermal techniques, have been developed.

In a photochemical reaction, a mixture of cyclopentadienesubstituted polystyrene-divinylbenzene copolymer beads and $Co_2(CO)_8$ in benzene was irradiated with UV light under argon. After being washed and dried <u>in vacuo</u>, the beads showed two strong CO stretching bands at 2020 and 1960 cm⁻¹ (Figure 35)

Similar procedures were carried out in a thermal method, except

a steam bath was used to reflux the reaction mixture. The beads showed the same CO stretches in the IR. The reaction scheme is illustrated in Figure 33.



Figure 33. Scheme for the preparation of polymer-attached $CpCo(CO)_2$.

Preparation of Polymer-Attached Cyclopentadienyldicarbonylrhodium

Polymer-attached $CpRh(CO)_2$ beads were prepared from the reaction of the $\{Rh(CO)_2Cl\}_2$ dimer and cyclopentadienide ion-substituted copolymer, which was obtained by treating the cyclopentadienesubstituted copolymer beads with n-BuLi in THF or hexane. The copolymer beads show two strong CO stretching peaks at 2040 cm⁻¹ and 1980 cm⁻¹ (Figure 36). The reaction scheme is shown in Figure 34.



Figure 34. Scheme for the preparation of polymer-attached CpRh(CO)₂.





Hydrogenation of Olefins

Rhodium complexes coordinatively bonded to polymer-supported cyclopentadiene ligands are active olefin hydrogenation catalysts. During these reactions the color of the catalyst changed to black. The two IR CO stretching peaks of the catalyst recovered from the reactions show the same decrease. This result should probably be interpreted in terms of the formation rhodium metal. The results are given in Table 7. Some or perhaps all of the catalysis may be due to Rh(0). Polymer-attached $CpCo(CO)_2$ is not an active hydrogenation catalyst under these conditions.

Hydrogenation of Ketones and Aldehydes

Polymer-attached CpRh(CO)_2 will hydrogenate aldehydes and some ketones. Acetone is most easily hydrogenated. When acetophenone is the substrate, the aromatic ring is also hydrogenated, as has been observed for rhodium compounds¹⁰² and would be the metal of choice for total reduction. Other ketones were not hydrogenated. Aldehydes are hydrogenated somewhat selectively by polymer-attached CpRh(CO)_2 . The black catalyst recovered from the reactions exhibited two CO stretches that were considerably diminished and suggests that Rh metal has formed and accounted for the catalytic activity. The results are given in Table 8.

Olefin (1.2 M in hexane)	Hydrogenation rate				
	(mL H ₂ /m/mmol)				
1-hexene	23.0				
1-octene	20.0				
2-octene	17.0				
1-dodecene	5.2				
cyclohexene	19.2				
l-methylcyclohexene	2.9				
l,3-cyclooctadiene	0.3				
l,5-cyclooctadiene	2.9				
β-pinene	1.3				
phenylacetylene	(cyclotrimerization)				
styrene	20.1				
allylbenzene	19.6				
allyl alcohol	18.8				
methylvinyl ketone	5.7				

Table 7. Hydrogenation rates for polymer-attached $CpRh(CO)_2$ beads at 25⁰ and 1 atm.

Molar Ratio Substrate Reaction Product Yield(%) Note Substrate/Rh Time(h) Temperature Acetone 313 24 No Reaction 25⁰ 100 Acetone 313 12 2-Propanol 3-Pentanone 153 24 No Reaction 24 No Reaction Cyclohexanone 160 Cyclohexanone 152 24 Cyclohexanol 1 Temperature 150⁰ Pressure 150 psi 7 1-Phenylethanol 36 Acetophenone 221 221 1-Phenylethanol 75 Acetophenone 15 1-Cyclohexylethanol 25 Benzaldehyde 161 24 Benzyl Alcohol 8 Benzaldehyde 158 36 Benzyl Alcohol 17 Temperature 150⁰ 170 48 n-Butanol 51 n-Butanal 3-Phenylpropanol33 3-Phenylpropanal 219 24 n-Hexanal 159 24 n-Hexanol 50 159 48 n-Hexanol 65 n-Hexanal

Table 8. Hydrogenation of ketones and aldehydes with polymer-attached $CpRh(CO)_2$. Temperature 100⁰; Pressure H₂; 7.8 atm.

Isomerization

Allylbenzene can be isomerized to form the more stable cis and trans-propenylbenzene by using a polymer-attached $CpRh(CO)_2$ catalyst. The catalyst was reused repeatedly without loss of activity. The isomerization of 1.5-cyclooctadiene gives a mixture of 1.3- and 1,4-cyclooctadiene. Comparison of the results shows that the rate of isomerization of 1,5-cyclooctadiene is much slower than that of allylbenzene. The two CO stretches of the catalysts are much less intense in the spectra of resins recovered from the isomerization reaction of 1,5-cyclooctadiene than those of the catalysts recovered from the isomerization reaction of allylbenzene and might be due, in part, to the formation of rhodium diene complex during the reaction. The results for the isomerization of allylbenzene, 1,5-cyclooctadiene and cis-stilbene are shown in Table 9. During the reaction, the catalyst changed to black. The two CO stretches of the recovered black catalysts were much weaker than those of the fresh beads. Thermal CO elimination is indicated. Rhodium metal may be the active catalyst. Polymer-attached $CpCo(CO)_2$ was not an active isomerization catalyst under these conditions.

μloq	mer-attached C	pRh(CO) ₂ .			
Reaction	Molar Ratio	Temperature	Produ	cts (mole per cer	it)
Time (h)	Substrate/Rh	(0 ⁰)			
allylbenzene			allylbenzene	.cis-propenyl-	trans-propenyl-
80	375	25	83.0	benzene 2.1	benzene 14.g
0	500	145	8.2	8.2	83.6
e	500	145	O	0.6	0.10
2	500 ⁸	145	8.5	8.8	82.7
1,5-cycloocta- diene	ъ.		1,5-cycloocta- diene	1,4-cycloocta- diene	l,3-cycloocta- diene
19	500	145	55,3	10.1	34.6
67	500	145	34.8	6.0	59.2
96	500	145	25.1	4.5	70.4
cis-stilbene			cis-stilbene		trans-stilbene
60	800	145	40.6		59.4
55	335	145	3.2		96.8
^a Catalyst used 1	was recycled f	rom previous react	ion.		

The isomerization of allylbenzene, 1,5-cyclooctadiene, and cis-stilbene by Table 9.

Disproportionation

The disproportionation of 1,4-cyclohexadiene catalyzed by polymer-attached $CpRh(CO)_2$ initially gave benzene, cyclohexene, and cyclohexane and finally only benzene and cyclohexane. Cyclohexene also disproportioned to give benzene and cyclohexane within an hour. Thus, polymer-attached $CoRh(CO)_2$ is also a good catalyst for olefin disproportionation. The black beads recovered from the reactions still contain CO ligands according to IR spectra but the CO intensities were much less intense than those of the initial material. Again Rh(0) is indicated as the active catalyst. The results are given in Table 10.

Table 10. The disproportionation of 1,4-cyclohexadiene and cyclohexene by polymer-attached CpRh(CO)₂. Temperature 145⁰.

nexadiene				
1000	8.7	49.9	35.3	6.1
1000	2.3	62.4	12.0	23.3
1000	0	66.9	0	33.1
ne				
930		31.1	7.5	61.5
930		33.2	0	66.8
	1000 1000 1000 ne 930 930	1000 8.7 1000 2.3 1000 0 ne 930 930	1000 8.7 49.9 1000 2.3 62.4 1000 0 66.9 ne 930 31.1 930 33.2	1000 8.7 49.9 35.3 1000 2.3 62.4 12.0 1000 0 66.9 0 ne 930 31.1 7.5 930 33.2 0

Cyclotrimerization of Ethyl Propiolate

Homogeneous $CpCo(CO)_2$ and $CpRh(CO)_2$ serve as active catalysts for cyclotrimerization of a wide variety of acetylenic compounds.¹⁰³ Ethyl propiolate is one of the most reactive substrates. Reactions were carried out by stirring a suspension of the catalyst beads in the presence of ethyl propiolate in benzene, under argon. The reaction mixture was heated for periods of 6 to 48 h at 80°. Work-up of the benzene reaction mixtures with polymer-attached $CpRh(CO)_2$ beads led to a yield of 17.5% 1,3,5-tricarbethoxybenzene and 52.5% of 1,2,4-tricarbethoxybenzene by weight based on the amount of ethyl propiolate used. Ethyl propiolate was only converted in 20.5% yield to a mixture consisting of 2.4% 1,3,5-tricarbethoxybenzene and 18.1% of 1,2,4-trisubstituted isomer by using polymer-attached $CpCo(CO)_2$. Same loss of intensity in the CO stretches was noted. The results are given in Table 11.

The dark brown catalyst recovered from the reaction mixture was active in a second reaction converting only a slightly lower percentage of ethyl propiolate. These dark brown beads contain coordinated CO ligands and exhibit intense ester CO absorptions in IR.

Table 11. Cyclotrimerizations^a of ethyl propiolate with polymerattached $CpCo(CO)_2$ and $CpRh(CO)_2$.

Polymer-Attached	Molar Ratio Reaction		Conver-	Products(%) ^b		
catalyst (g)	Substrate/M	Time	sion ^a	1,3,5-Tri-	1,2,4-Tri-	
	(M=Co or Rh)	(h)		benzene	benzene	
CpCo(CO) ₂ (0.14)	435	48	20.5	2.4	18.1	
recycled ^C (0.14)	435	48	17.6	1.7	15.9	
CpRh(CO) ₂ (0.24)	812	6	38.0	14.0	24.0	
recycled ^C (0.24)	812	6	30.0	10.0	20.0	
CpRh(CO) ₂ (0.30)	661	32	70.0	17.5	52.5	

^aPer cent by weight converted to cyclized products. ^bWeight per cent based on the amount of ethyl propiolate used. ^CPolymer supported reagent used was recycled under argon from preceding reaction.

Hydroformylation

It is well known that Group VIII transition metal complexes, such as those of Rh and Co, are good catalysts for hydroformylation of olefins. Recently, much attention has been directed towards the polymeric phosphine-attached rhodium complexes for hydroformylation of olefins. But the use of rhodium complexes coordinatively bonded to polymeric cyclopentadiene ligands has not been examined extensively. The results of hydroformylation with polymer-attached $CpRh(CO)_2$ catalysts are presented in Table 12. No hydroformylation was observed for polymer-attached $CpCo(CO)_2$ catalyst even at 110° , under 120 atm pressures of CO and H₂.

The selectivity of linear/branched aldehydes was about 1 when the H_2/CO ratio was 1. At equal pressures, the selectivity increased as temperature increased. Similarly, the selectivity increased as pressure increased at constant temperature.

The selectivity varied slightly by the addition of triphenylphosphine. For example, the selectivity increased from 1.24 to 2.06 when the P/Rh ratio increased from 0 to 20. But when the P/Rh ratio was raised to 50, the selectivity dropped to 1.23. The selectivity also varied slightly when the H_2/CO ratio was changed.

The dark brown beads recovered from the hydroformylation reactions showed two CO stretches as strong as those of the fresh beads and were reused without loss of activity.

	polymer-at	tached Cpkn(C	·/ ₂ ·				
Weight of	Substrate	Molar Ratio	Time	Temp	Pressure	^a Yield ^d	Selecti- vity
Catalyst(g)	Substrate/Rh	(h)	(°C)	(psig)	(%)	(Linear/ Branched)
0.109	1-Pentene	430	20	20	1500	50.7	0.83
0.119		394	9	40	1000	53.6	1.00
0.071		660	12	80	500	93.9	0.95
0.071 ^e		660	12	80	50 0	88.2	0.90
0.093		504	8	80	500 ^b	89.1	1.35
0.090		520	9	80	500 ^C	86.2	0.83
0.101		464	3	80	1000	89.2	1.34
0.130		360	24	110	100	26.0	0.92
0.181		259	4	110	1000	100	1.18
0.112		418	3	110	150 0	10 0	1.24
0.108		434	3	110	1500 ^b	97.0	1.51
0.132		355	3	110	1500 ^C	83.1	0.86
0.143 ^f		328	5	110	1500	99.0	1.27
0.111 ⁹		422	5	110	1500	91.1	2.06
0.144 ^h		325	5	110	1500	100	1.23
0.099	1-Hexene	414	10	110	1500	98.3	1.69

Table 12. Hydroformylations of 1-pentene and 1-hexene catalyzed by

 ${}^{a}H_{2}/C0 = 1/1$. ${}^{b}H_{2}/C0 = 1/3$. ${}^{C}H_{2}/C0 = 3/1$. d Yields are based on olefins consumed. Only small amount of pentane (\sim 5%) formed during the reactjions. ${}^{e}Catalyst$ used was recycled from preceding reaction. ${}^{f}Triphenylphosphine$ was added, P/Rh = 5/1. ${}^{g}P/Rh = 20/1$. ${}^{h}P/Rh = 50/1$.

Cyclopentadienyldicarbonyl rhodium, $(C_5H_5)Rh(CO)_2$, is well known to form dinuclear species, $(C_5H_5)_3Rh_3(CO)_3$, at elevated temperatures or under photolytic conditions.¹⁰⁴⁻¹⁰⁶ These rhodium carbonyl clusters appear to be quite inert due to a substantially increased metal-metal bond strength. If the cyclopentadienylrhodium dicarbonyl species is attached to a rigid polymer support, then the coordinatively unsaturated intermediates, generated by thermal CO elimination, chould be isolated from each other. These isolated intermediates provide an efficient pathway for the formation of a reactive hydride as a necessary prerequisite for a subsequent olefin hydroformylation reaction. The proposed mechanism is shown in Figure 37.

Mechanisms

The mechanisms of the above catalytic processes are presumed to be analogous to those proposed for the homogeneous rhodium catalysts, but detailed mechanistic studies have not been made. Either dissociation of CO, or a reduction of the cyclopentadienyl coordination below n^5 must precede olefin binding and (in hydrogenation or hydroformylation) hydrogen addition.¹⁰⁷

Since olefin isomerization and disproportionation are carried out at 145⁰, it is possible that decomposition, possibly to rhodium metal, occurred and the rhodium metal has been responsible for the isomerization and disproportionation. Several samples that had been used in the disproportionation of cyclohexene for 24 and 48 h were tested for their effectiveness as catalysts in cyclotrimerization of ethyl propiolate. The fresh catalyst gave an 81% yield of cyclic trimers



Figure 37. Scheme for the mechanism of hydroformylation reaction catalyzed by polymer-attached cpRh(c0)2.

after 24 h, while the one that had been used in disproportionation for 24 h gave only 62% and the 48 h sample only 35%. Thus it appears that decomposition of the catalyst had indeed occurred and may account for its ability to catalyze the **iso**merization and disproportionation processes.

It is clear that polymer-attached $CpRh(CO)_2$ is an excellent hydroformylation catalyst and, under the conditions described, does not decompose. Decomposition does occur under the conditions given for hydrogenation, isomerization, and disproportionation of olefins, and for cyclotrimerization of alkynes. It is possible that the decomposition product (Rh(0)?) is responsible for the catalysis. Gubitosa and Brintzinger⁹⁹⁻¹⁰¹ reported that supported CpRh(CO)₂ served as a hydrogenation catalyst and did not note decomposition of the catalyst.

Gubitosa and Brintzinger also found that polymer-attached CpCo(CO)₂ was an effective hydrogenation and hydroformylation catalysts. In our hands no catalytic activity was found, but it was not possible for us to duplicate their experiments exactly.

EXPERIMENTAL

General

Manipulations involving air-sensitive materials were performed under argon in Schlenk-type vessels. Where necessary, transfers were make in an argon-filled glove box.

NMR spectra were obtained by use of a Varian T-60 spectrometer. Electron spin resonance (ESR) spectra were obtained by use of a varian E-4 Spectrometer. IR spectra were recorded on Perkin-Elmer 457 or 237B spectrophotometers. Samples were prepared by crushing the polystyrene beads in a ball mill under anaerobic conditions and mulling the powder with dry nujol in a dry glovebox. Gas chromatography, GLC, analyses were performed by use of Varian model 1400 analytical gas chromatograph and a model 920 gas chromatograph.

All solvents used were A. C. S. reagent grade. Tetrahydrofuran (THF), hexane, cyclohexane, toluene, xylene and benzene were distilled from sodium-benzophenone under argon. All alkenes used for hydrogenations were at least 95% pure, and were further purified by distillation from sodium under argon. Allyl benzene and 1,5-cyclooctadiene were dried through an activated alumina column and distilled under vacuum. N,N,N',N'-tetramethylethylenediamine (TMEDA) was dried over molecular sieves (4A) for 4 h before distilling under argon. Analytical grade cis-stilbene, aldehydes and ketones were used without further purification. Ethyl propiolate was distilled under vacuum and a center cut collected. The reagents, n-butyl lithium, allylbenzene, l-hexene,

cyclohexene, 1-octene, 3-hexene, 1,5-cyclooctadiene, ethyl propiolate, trimethyltin chloride, tri-n-butyltin chloride, hexamethyldistannane and chloromethyl ethyl ether were obtained from Aldrich Chemical Co. 1-Pentene was obtained from J.T. Baker Chemical Co. Dicobalt octacarbonyl, chlorodicarbonylrhodium dimer and cyclopentadienyltitanium trichloride were obtained from Strem Chemicals Inc. Zirconium tetrachloride, hafnium tetrachloride, niobium pentachloride, tantalum pentachloride, bis(cyclopentadienyl)zirconium dichloride and bis(cyclopentadienyl)hafnium dichloride were obtained from Alfa Chemical Co. Sodium bis(2-methoxyethoxy)aluminum hydride (Vitride) was obtained from Eastmen Kodak Co.

The 20% cross-linked polystyrene-divinylbenzene copolymer beads were a gift from the Dow Chemical Co. and were washed to remove impurities before use. They were washed with 10% HCl (aq.), 10% NaOH (aq.), H_2O , H_2O -CH₃OH (1:1), CH₃OH, CH₃OH-CH₂Cl₂ and benzene and then dried under vacuum.

Analytical Methods

Chloride in the chloromethylated beads was removed from the copolymer beads with boiling pyridine and determined by Volhard technique. 108 Similarly, chloride from the supported metallocene chlorides beads was removed from the copolymer with boiling 2 N KOH solution for 24 h and determined by the same technique. Titanium, zirconium and hafnium were determined by ignition of the metal-containing polymer at 1000° for 24 h and weighed as the oxides. 109

Other elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation of Cyclopentadiene-Substituted Copolymer

Typically, following the chloromethylation method of Pepper, et al 38 , 50 g of washed and dried copolymer beads was taken into a 1 L, three-necked, flask with a drying tube and an overhead stirrer. About 180 mL of chloromethyl ethyl ether (chloromethyl ethyl ether is a "cancer suspect agent" because the related compound (a possible contaminant), bis-(chloromethyl)ether, is a carcinogen) was added and the mixture was stirred for 2 h. A solution prepared by cautiously adding 8.5 mL of $SnCl_A$ to 80 mL of ice-chilled chloromethyl ethyl ether was then introduced slowly through a dropping funnel. After the reaction mixture was stirred vigorously at room temperature for 18 h, the ether was removed by suction and a dispersion tube. The beads were washed with four 250 mL portions of 50% aqueous dioxane, aqueous dioxane containing 10% HCl (v/v) and finally with dry dioxane until the washings were chloride free. The chloride analysis of the chloromethylated beads after it had been dried for 2 days in vacuo yielded 1.45 mmol of Cl/g of beads or 16.7% chloromethylation of the styrene rings.

The chloromethylated beads obtained above were suspended in 100 mL dry, air-free THF and 100 mL of 2.0 M sodium cyclopentadienide in THF. After the mixture was stirred for 6 days at room temperature, excess sodium cyclopentadienide and THF were removed by filtration. The beads were washed with ethanol/THF (1/1) and THF until the

washings were chloride free and then were dried under vacuum. The beads contain 0.04 mmol of Cl/g of beads. Thus the cyclopentadiene content was 1.41 mmol C_5H_5/g of beads determined by the difference between the Cl contents before and after reaction with sodium cyclopentadienide.

Preparation of Polymer-Attached Biscyclopentadienyl Zirconium and Hafnium Dichlorides (P-Cp₂MCl₂; M=Zr, Hf)

Method a:

Magnesium cyclopentadienide, 100 Mg(C₅H₅)₂, may be prepared by the direct reaction of magnesium metal with cyclopentadiene vapor at 500⁰ to 600⁰ under argon. The pure white crystalline Mg(C₅H₅)₂ was then obtained by sublimation in a vacuum at 60⁰ and identified by its melting point and IR spectrum.

Monocyclopentadienyl zirconium trichloride was also prepared by the reported procedure.¹¹² Treatment of $ZrCl_4$ in xylene with $Mg(C_5H_5)_2$ (0.5 mol. equiv.) gave $CpZrCl_3$. The pure $CpZrCl_3$ was obtained by sublimation under vacuum (10⁻⁴ mmHg) at 90⁰.

In a typical reaction, 2 g of cyclopentadiene-substituted copolymer beads (0.5 mmol Cp/g of beads) was treated with excess butyllithium in THF and the mixture was stirred for 2 days under argon. The excess of n-BuLi was removed and the beads were washed with THF. They were then suspended in 30 mL of THF, and CpZrCl₃ (1.3 mmol) was added. The reaction mixture was stirred for 2 days. The solution was then removed and the beads were washed with THF in a soxhlet extractor for 3 days. The product, yellowesh beads, was dried under vacuum. Anal. Calcd: Cl/Zr, 2.00. Found: Zr, 0.420 mmol/g of beads; Cl, 0.827 mmol/g of beads; Cl/Zr, 1.97.

Method b:

In a typical reaction, 2 g of cyclopentadiene-substituted copolymer beads (1.41 mmol Cp/g of beads) was treated with excess butyllithium in THF and the mixture was stirred for 2 days under argon. The excess of n-BuLi was removed and the beads were washed with THF. They were then suspended in 20 mL of THF, and 2 g of $Cp_2MCl_2(M=Zr,$ Hf) was added. The reaction mixture was stirred for 3 days, then treated with excess anhydrous hydrogen chloride gas for 4 h. The solution was removed and the beads were washed with THF in a soxhlet extractor for 5 days. The product, brownish yellow beads, was dried under vacuum. Anal. Calcd. for supported zirconocene dichloride: C1/Zr, 2.00. Found: Zr, 0.142 mmol/g of beads; Cl, 0.328 mmol/g of beads; Cl/Zr, 2.31. Anal. Calcd. for supported hafnocene dichloride: C1/MF, 2.00. Found: Hf, 0.126 mmol/g of beads; Cl, 0.302 mmol/g of beads; Cl/Hf, 2.40.

Method c:

Typically, 10 g of polymer-attached $CpZrCl_3$ (0.636 mmol Zr/g of beads) or $CpHfCl_3$ (0.463 mmol Hf/g of beads) were suspended in 10 mL of THF and 3.1 mL (2.3 mL for $CpHfCl_3$) of 2.2 M sodium cyclopenta-dienide in THF was added. After the reaction mixture was stirred for 5 days, the beads were washed with THF several times. Then a small

amount of hydrogen chloride gas was introduced and allowed to stir for 24 h. After being washed with THF in a soxhlet extractor for 3 days, the yellow beads were dried <u>in vacuo</u> for 2 days. Anal. Calcd. for supported zirconocene dichloride: Cl/Zr, 2.00. Found: Zr, 0.627 mmol/g of beads; Cl, 1.223 mmol/g of beads; Cl/Zr, 1.95. Anal. Calcd. for supported hafnocene dichloride: Cl/Hf, 2.00. Found: Hf, 0.450 mmol/g of beads; Cl, 0.869 mmol/g of beads; Cl/Hf, 1.93.

Preparation of Polymer-Attached Monocyclopentadienyl Zirconium and Hafnium Trichloride (P-CpMCl₃; M=Zr, Hf)

About 5 g of polymer-attached lithium cyclopentadienide beads (1.41 mmol Cp/g of beads) was suspended in 40 mL of benzene and 2 g of MCl₄ (M=Zr, Hf) was added. The reaction mixture was stirred for 7 days. The solution was then removed. After being washed with THF in a soxhlet extractor for 4 days, the product, cream colored beads, was dried. Anal. Calcd. for supported CpZrCl₃: Cl/Zr, 3.00. Found: Zr, 0.338 mmol/g of beads; Cl, 0.953 mmol/g of beads; Cl/Zr, 2.82. Anal. Calcd. for supported CpHfCl₃: Cl/Hf, 3.00. Found: Hf, 0.428 mmol/g of beads; Cl, 1.198 mmol/g of beads; Cl/Hf, 2.79.

Preparation of Polymer-Attached Tricyclopentadienyl Zirconium and <u>Hafnium Monochloride</u> (P-Cp₃MCl; M=Zr, Hf)

The polymer-attached lithium cyclopentadienide beads were suspended in THF and a two-fold excess of Cp_2ZrCl was added. The reaction mixture was stirred for 3 days. The excess of Cp_2ZrCl_2 was

removed and the beads were then washed with THF in a soxhlet extractor until excess chloride had been removed. The product, yellow beads, was dried. Anal. Calcd. for supported Cp_3ZrCl : 1.00. Found: Zr, 0.302 mmol/g of beads; Cl, 0.297 mmol/g of beads; Cl/Zr, 0.98. Anal. Calcd. for supported Cp_3HfCl : 1.00. Found: Hf, 0.345 mmol/g of beads; Cl, 0.328 mmol/g of beads; Cl/Hf, 0.95.

Far Infrared Studies

The far infrared spectra in the $100-500 \text{ cm}^{-1}$ region were obtained by use of a Digilab Model FTS-16 fourier transform spectrophotometer. The samples were prepared by crushing the polystyrene-divinylbenzene copolymer beads in a ball mill under anaerobic conditions and mulling the powder with dry nujol in a glove box. The spectra were recorded with the samples mounted between polyethylene plates in a dry nitrogen atmosphere. The spectra were obtained by scanning the samples (nujol mull) 1000 times with a resolution of 4 cm⁻¹ and a sampling interval of 8 microns.

Hydrogenation Studies

The polymer-attached catalysts were weighed into a 100 mL roundbottomed flask with a side arm. The beads were suspended in 5 mL n-hexane and treated with 3 mL of 2.0 M n-butyllithium in n-hexane for 2 days. The excess of n-butyllithium was removed and the beads were washed with n-hexane several times. Then 8.5 mL hexane was injected into the flask and 1.5 mL 1-hexene was added. The reaction mixture was stirred at a constant stirring rate, while the temperature

was maintained at 25° . The rate of hydrogen uptake was measured by using an 100 mL gas buret.

For the hydrogenation of diphenylacetylene, the catalyst was suspended in 5 mL toluene, then 0.267 g (1.5 mmol) of diphenylacetylene in 5 mL toluene was added into the flask. The rate of hydrogen was measured at 100° and at normal atmospheric pressure. A small amount of reaction mixture was drawn out periodically and then chromatographed by GLC on a 8 ft x 1/8 in 15% SE-30/Chromosorb P column. The relative amounts of diphenylacetylene, trans-stilbene and 1,2-diphenylethane were measured by integration.

Isomerization

The reduction of polymer-attached zirconocene and hafnocene chloride beads with excess n-butyllithium in hexane was carried out under hydrogen at room temperature for 2 days. The excess of n-butyllithium was removed and the beads were washed with hexane several times and dried under vacuum. Allylbenzene or 1,5-cyclooctadiene was then added and allowed to stir under argon at 145° . A small amount of reaction mixture was drawn out periodically and chromatographed by GLC on a 8 ft x 1/8 in 15%SE-30/Chromosorb P column. The relative amounts of allylbenzene, cis-propenylbenzene and trans-propenylbenzene were measured by integration. The relative amounts of 1,3-, 1,4- and 1,5-cyclooctadiene were measured by GLC integration and NMR integra± tion.

Epoxidation

Reactions were carried out under an atmosphere of argon. A quantity of 5 mL benzene or cyclohexane, 3 mL cyclohexene (30 mmol) and the catalyst (0.09 mmol Zr of Hf) was warmed to 80° and 8 mL of 80% tert-butyl hydroperoxide (60 mmol) was added. Aliquots were removed at time intervals and analyzed by GLC on 16 ft x 1/8 in 20% Carbowax/Chromosorb W and 8 ft x 1/8 in 15% SE-30/Chromosorb P columns. Chlorobenzene was used as an internal standard.

Hydrozirconation of Olefins

Typically, the reduction of 5 g of polymer-attached Cp_2ZrCl_2 beads (3.3 mmol Zr) with Vitride (1.7 mmol) in THF was carried out in a 200 mL pressure bottle under argon for 2 days. After the beads were washed with THF and benzene several times, a quantity of 2 mL of 1-hexene and 10 mL of benzene was added and allowed to stir for 2 days. The argon was then removed and carbon monoxide was introduced (150 psi). The reaction mixture was allowed to stir for 2 days at room temperature and then hydrolyzed with dilute aqueous hydrochloric acid. The solution was taken out and extracted with ether. The extract was concentrated and then analyzed for aldehydes by GLC on a 16 ft x 1/8 in 20% Carbowax/Chromosorb W column.

Preparation of Polymer-Attached Methylene Bridged-bis(cyclopentadienyl) Zirconium Dichloride

About 30 g of cyclopentadienide ion-substituted copolymer beads (2.2 mmol Cp/g of beads) was suspended in 80 mL of THF and the reaction flask was cooled in an ice bath. Then, 30 mL of freshly distilled methylene chloride was added slowly. The dark red beads changed to yellow immediately. After stirred at room temperature for one day, the beads were washed with THF in a soxhlet extractor and dried under a vacuum. The chloride analysis gave 2.0 mmol Cl/g of beads. To the yellowish beads suspended in 80 mL of THF, three fold excess of sodium cyclopentadienide in THF was added. After stirred for 5 days, the beads were dried under vacuum. The product, yellowish methylene bridged cyclopentadiene-substituted copolymer beads, contains 0.05 mmol Cl/g of beads.

Following the method c in the preparation of polymer-attached bis(cyclopentadienyl)zirconium dichloride, the polymer-attached methylene-bridged Cp_2ZrCl_2 beads were prepared from the methylene bridged cyclopentadiene-substituted copolymer beads and $ZrCl_4$. The elemental analysis gave 0.81 mmol Zr/g of beads.

Reduction of Carbon Monoxide to Alcohols by Polymer-Attached Cp₂ZrCl₂ Catalysts

Typically, about 8 g of supported Cp₂ZrCl₂ beads (0.67 mmol Zr/ g of beads) in benzene in the presence of 3 equivalents of diisobutylaluminum hydride (DIBAH) was stirred in a 200 mL pressure bottle under 60 psi of CO atmosphere for 3 days. The reaction mixture was then hydrolyzed with dilute aqueous sulfuric acid. The product was analyzed by GLC on 10 ft x 1/8 in 19% FFAP/Chromosorb G and 12 ft x 1/8 in Carbowaz 1500/Chromosorb G columns.

ESR Studies

A sample of 0.3 g polymer-attached zirconocene dichloride (0.112 mmol Zr/g of beads) was charged into a reaction flask and the beads were suspended in 5 mL hexane. The supported zirconocene dichloride was then reduced by the addition of 1 mL 1.6 M butyllithium in hexane and the reaction mixture was stirred for 12 h under hydrogen. The solution was removed and the beads were washed several times with hexane. The beads were dried under vacuum and transferred into the ESR tube. The ESR spectrum of the reduction product was recorded. The same experiment was repeated under argon.

Preparation of Polymer-Attached Methylene-Bridged Cp_TiCl_

Method 1.

The procedures for the preparation of methylene-bridged cyclopentadiene-substituted copolymer beads is the same as those described in the preparation of polymer-attached methylene-bridged zirconocene dichloride.

Typically, 10 g of methylene-bridged cyclopentadiene-substituted copolymer beads (2.2 mmol Cp/g of beads) were suspended in 20 mL THF, and two fold excess of butyllithium in hexane was added. The beads

changed from yellow to dark red. After being stirred at room temperature for 2 days, the solution was removed and the beads were washed several times with benzene. To the dark red beads wuspended in 50 mL benzene, 9 g of CpTiCl₃ was then added and the reaction mixture was allowed to stir for 4 days. The solution was removed and the beads were washed with benzene in a soxhlet extractor. The product, red beads, was dried under a vacuum. Metal analysis was performed. Anal. Found for supported methylene-bridged Cp_2TiCl_2 : Ti, 0.700 mmol/g of beads (1st batch); 1.066 mmol/g of beads (2nd batch). Anal. Found for supported dimethylene-bridged Cp_2TiCl_2 : Ti, 0.859 mmol/g of beads. Anal. Found for supported trimethylene-bridged Cp_2TiCl_2 : Ti, 1.103 mmol/g of beads. Anal. Found for supported tetramethylene-bridged Cp_2TiCl_2 : Ti, 0.899 mmol/g of beads.

Method 2.

About 20 g of 2% cross-linked polystyrene-divinylbenzene copolymer beads was suspended in 60 mL of freshly distilled cyclohexane. The mixture was refluxed for 24 h, and then 80 mL of 1.6 M butyllithium in hexane and 25 mL of N,N,N',N'-tetramethylenediamine (TMEDA) (150 mL) were added by means of a syringe.¹¹³⁻¹¹⁵ The reaction mixture was heated for 3 days. After cooling, the polymer beads were washed several times with cyclohexane and THF.

To the dark brown lithiated polymer beads suspended in 60 mL of THF and cooled at 0° , 30 mL of CCl₄ was then added slowly. After being stirred at room temperature for 24 h, the solution was removed and the beads were washed with THF in a soxhlet extractor. The dried

beads gave 3.45 mmol Cl/g of beads.

The trichloromethylated beads were suspended in 80 mL of THF and 80 mmol of NaCp was added. After being stirred for 5 days, the beads were washed with THF. The dry beads contain 0.9 mmol Cl/g of beads. The beads were then suspended in 80 mL of THF and 35 mmol of Vitride in THF was added. The mixture was refluxed for 24 h. Then, 10 mL of MeOH/H₂O (1:1) was added slowly and the beads were washed with THF in a soxhlet extractor. The dried beads, methylene-bridged cyclopenta-diene-substituted copolymer, contain 0.014 mmol Cl/g of beads.

The procedures for the attachment of Cp_2TiCl_2 to the 2% cross-linked methylene-bridged cyclopentadiene-substituted copolymer beads are the same as those described in Method 1. Metal analysis gave 1.556 mmol Ti/g of beads.

Nitrogen Fixation Studies

van Tamelin Nitrogen Fixation.

Typically, 0.343 g of supported methylene-bridged Cp_2TiCl_2 beads (1.066 mmol Ti/g of beads) was suspended in 20 mL THF. The reaction flask was cooled at -40° and 3.7 mmol sodium naphthalide in THF was added slowly. Nitrogen was then bubbled through the solution into a gas washing tower filled with 60 mL 20% H₂SO₄ for one day. The ammonia produced was analyzed by Kjeldahl method. Nessler's Reagent¹¹⁶ was also used for the presence of ammonia. No ammonia was detected. Vol'pin-Shur Nitrogen Fixation

All fixations were done by using 1500 psi of nitrogen in an autoclave previously flushed with nitrogen, at ambient temperatures with continual stirring during the pressurized period of the reaction. In a typical reaction, 2.30 g of supported methylene-bridged Cp_2TiCl_2 beads (1.066 mmol Ti/g of beads) was transferred into an autoclave, 60 mmol of sodium naphthalide in THF and 100 mL of diethyl ether. The system was pressurized and stirred for 2 days, then depressurized and acidified with 20 mL of absolute methanol and 20 mL of 20% H₂SO₄. After stirring the resulting solution for 3 h in the autoclave, the solution was removed and ammonia was analyzed by Kjeldahl method.

Preparation of Polymer-Attached Cp₂Ti(CO)₂

About 1 g of polymer-attached Cp_2TiCl_2 beads (1.07 mmol Ti/g of beads) was treated with excess $LiBH_4$ in 20 mL of diethyl ether for 2 days. The color of beads changed from red to greyish blue. The beads were then washed with ether and dried under vacuum.

Treatment of the greyish blue beads, in 10 mL of Et_3N with CO at atmospheric pressure for 2 weeks, gave brown beads. The beads were washed with hexane and dried under vacuum. The IR spectrum of brown beads showed two strong CO stretching bands of similar intensity at 1880 and 1965 cm⁻¹.

The synthesis of polymer-attached $Cp_2Zr(CO)_2$ was not successful when a similar reaction in Et_3N with polymer-attached $Cp_2Zr(BH_4)_2$ under 150 atm of CO for a week was carried out.

Photolysis of Polymer-Attached Cp₂Ti(CO)₂

About 0.2 g of polymer-attached $Cp_2Ti(CO)_2$ beads suspended in 5 mL hexane or toluene was irradiated under argon. The color of beads changed from brown to greyish brown. The IR spectrum of greyish brown beads shows no CO stretching bands. After stirred under 1 atm of CO for 2 days, the greyish brown beads gave two very weak CO stretching bands at 1880 and 1965 cm⁻¹.

Hydrogenation of Carbon Monoxide by Polymer-Attached $Cp_2Ti(CO)_2$

About 5 g of polymer-attached $Cp_2Ti(CO)_2$ beads (0.7 mmol Ti/g of beads) in 20 mL of toluene was treated with 200 psi of H₂ and CO mixture (3:1 molar ratio) at 160° . No methane was observed after the reaction mixture was stirred for 5 days. Trace of methane was observed for another reaction in which 8.5 g of 2% polymer-attached methylene-bridged $Cp_2Ti(CO)_2$ beads (1.5 mmol Ti/g of beads) was used. Methane was analyzed by GLC on a 20 ft x 1/8 in Durak column and a 6 ft x 1/4 in Molecular Sieve 5A column.

Preparation of Polymer-Attached CpMCl₄ (M=Nb and Ta)

In a typical reaction, 1 g of cyclopentadiene-substituted copolymer beads (1.41 mmol Cp/g of beads) was treated with excess n-BuLi in THF for 2 days under argon. The excess n-BuLi was removed and the beads were washed with THF, then dried under vacuum. The dried beads were suspended in benzene and R_3SnC1 (R=n-Bu, or Me) was added. The reaction mixture was stirred for 3 days. The color of beads changed from red to pale yellow. The beads were then washed with benzene and dried. Treatment of pale yellow beads in toluene with MCl_5 (M=Nb, or Ta) gave red supported CpNbCl₄ beads and yellow supported CpTaCl₄ beads, respectively. Anal. Calcd for supported CpNbCl₄: Cl/Nb, 4.00. Found: Nb, 0.810 mmol/g of beads; Cl, 3.081 mmol/g of beads; Cl/Nb, 3.80. Anal. Calcd for supported CpTaCl₄: Cl/Ta, 4.00. Found: Ta, 0.792 mmol/g of beads; Cl, 3.052 mmol/g of beads; Cl/Ta, 3.85.

Preparation of Polymer-Attached (PhCH₂)MCl₄ (M=Nb and Ta)

Typically, 2 g of chloromethylated polystyrene beads (1.57 mmol Cl/g of beads) were suspended in 10 mL of THF and the reaction flask was cooled in an ice bath. A two-fold excess of trimethylstannyllithium in THF, which was prepared by treatment of a tetrahydrofuran solution of hexamethyldistannane with methyllithium, was added slowly. After being stirred at room temperature for 36 h, the solution was removed and the beads were washed several times with THF, then dried. The polymer-attached benzyltrimethyltin beads were suspended in 20 mL toluene and treated with excess TaCl₅. After being stirred for 5 days, the beads were washed in a soxhlet extractor with toluene for 3 days. The product, cream beads, was then dried under vacuum and gave chloride contents of 3.61 mmol/g of beads.

Olefin Dimerization Catalyzed by Polymer-Attached Tantalum Complexes

Typically, 0.50 g polymer-attached $CpTaCl_4$ beads (0.792 mmol/g of beads) was placed into a pressure bottle and suspended in 15 mL pentane. Two equivalents of neopentyl lithium in pentane (0.80 mmol) was added slowly. The beads changed from yellow to brown. After being stirred for 2 days, the brown beads were washed several times with pentane. The brown beads were then suspended in 15 mL pentane. The pressure bottle was pressurized with 60 psi ethylene and the reaction mixture was stirred for 2 h. The brown color of the beads lightens to pale yellow. The solvent and ethylene were removed and the beads were dried under vacuum. After being st rred at 100° under 80 psi of ethylene for 24 h; the gas sample was analyzed on a 20 ft x 1/8 in Durapak column.

When the pale yellow beads suspended in ether were treated with 90 psi of CO for 30 h, a supported dicarbonyl complex was formed. The IR spectrum shows two CO stretching bands at 2020 and 1940 cm^{-1} .

Hydrogenation of Olefins and Diphenylacetylene Catalyzed by Polymer-Attached Niobium and Tantalum Complexes

The procedures carried out for hydrogenation of olefins and diphenylacetylene are the same as those for the hydrogenations catalyzed by polymer-attached zirconocene and hafnocene catalysts.

Isomerization of Allylbenzene Catalyzed by Polymer-Attached Niobium and Tantalum Complexes

In a typical reaction, 0.25 g polymer-supported $CpTaCl_4$ beads (0.21 mmol Ta/g of beads) was treated with excess BuLi in hexane under atmospheric pressure of hydrogen for 36 h. The beads changed from light yellow to brown. The brown beads were washed several times with hexane and dried in a vacuum. Allylbenzene (1 mL) was then injected into the reaction flask and allowed to stir under argon at 145° . A small amount of reaction mixture was drawn out periodically and chromatographed by GLC on a 8 ft x 1/8 in 15% SE-30/Chromosorb P column. The relative amounts of allylbenzene, cis-propenylbenzene and trans-propenylbenzene were measured by integration.

Preparation of Polymer-Attached CpCo(CO),

Photochemical Reaction.

A mixture of 3 g $\text{Co}_2(\text{CO})_8$ in 30 mL benzene and 5 g cyclopentadienesubstituted copolymer beads (1.41 mmol $\text{C}_5\text{H}_5/\text{g}$ of beads) in a quartz apparatus was irradiated under argon for 2 days with a 140 W Hanovia type 30620 UV lamp. The excess $\text{Co}_2(\text{CO})_8$ and benzene were then removed and the beads were washed with benzene until the washings were clear. The product, greyish brown $\text{CpCo}(\text{CO})_2$ -substituted copolymer beads, was then dried under vacuum and yielded a substance containing 0.26 mmol Co/g of beads.
Thermal Reaction.¹¹⁹

Five g of cyclopentadiene-substituted copolymer beads (1.41 mmol C_5H_5/g of beads), 50 mL dried methylene chloride and 3 g $Co_2(CO)_8$ were placed in a 100 mL flask, which was fitted with a reflux condenser. The system was flushed with argon and was covered with aluminum foil to exclude light. The contents were heated to reflux on a steam bath for 3 days, then the methylene chloride was removed and the beads were washed with methylene chloride until the washings were clear. The greyish green beads were then dried under vacuum and stored under argon. The cobalt content was 0.32 mmol Co/g of beads.

Preparation of Polymer-Attached $CpRh(CO)_2^{120}$

In a typical reaction, 3 g cyclopentadiene-substituted copolymer beads (0.36 mmol C_5H_5/g of beads) was treated with a two-fold excess of butyllithium in THF or hexane and the mixture was stirred for 3 days under argon. The excess n-BuLi and THF or hexane were removed and the beads were washed with THF. They were suspended in THF, the reaction flask was cooled in an ice bath, and a solution containing 0.5 mmol of $(Rh(CO)_2Cl)_2$ dissolved in THF was then introduced. The orange color of the solution disappeared within 20 min. The mixture was stirred for 2 days at room temperature. The color of beads changed from deep purple-red to dark brown. The solvent was removed and the beads were washed with THF and then dried under vacuum. The rhodium content was 0.29 mmol Rh/g of beads. Other solvents, petroleum ether and hexane, were also used. It was found that THF was the most appropriate solvent.

Hydrogenation of Olefins

The hydrogenations were carried out by using gas burets of 100 mL volume. The hydrogen uptake was measured at normal atmospheric pressure and at $25^{\circ} \pm 0.5^{\circ}$.

All reactions were carried out in a 100 mL of round-bottomed flask with a side arm. The catalyst (0.29 mmol Rh/g of beads) was weighed into the reaction flask, placed under an atmosphere of hydrogen and suspended in 8-9 mL hexane. The appropriate olefin (1-2 mL) was then added. The rate of hydrogen uptake was measured by using the buret.

Hydrogenation of Ketones and Aldehydes

A mixture of 0.1-0.3 g of catalyst (0.29 mmol Rh/g of beads), 1 mL aldehyde or ketone and 5 mL benzene were placed in a 100 mL of pressure bottle. The bottle was flushed with hydrogen, pressurized to 7.8 atm with H_2 and heated and stirred at 100⁰ for 7-48 h. After being cooled to room temperature, the reaction mixture was analyzed by GLC and NMR.

Isomerization and Disproportionation

About 2-4 mL substrates and 0.05-0.2 g catalyst (0.29 mmol Rh/g of beads) were placed in a 5 mL pressure bottle under argon. The vessel was then heated to 145° . A small amount of reaction mixture was drawn out periodically and then chromatographed by GLC. The

relative amounts of reaction products were measured by GLC and NMR integration.

Cyclotrimerization of Ethyl Propiolate

Typically, 0.3 g of polymer-attached $CpRh(CO)_2$ (0.10 mmol Rh/g of beads) beads was introduced into a side-armed flask containing 5 mL benzene under argon. After the mixture was stirred for about 10 min, 2.0 mL ethyl propiolate (1.91 g; 19.5 mmol) was injected and the reaction mixture was then heated at 80° for 32 h. The color of solution gradually turned dark brown. After it was cooled to room temperature, 50 mL benzene was introduced into the flask and after being stirred for several minutes, the solution was drawn out by means of a syringe. The viscous oil, obtained by concentrating the brown solution under vacuum, was then extracted with 200 mL of a refluxing $CCl_4/petroleum$ ether (1/4) mixture. The yellow extract was filtered and the solvents were removed under vacuum to give 70% products based on the weight of ethyl propiolate used. The relative amounts of 1,3,5-tricarbethoxybenzene and 1,2,4-tricarbethoxybenzene were measured by NMR integration.

Hydroformylation

In a typical reaction, 0.1 g polymer-attached $CpRh(CO)_2$ catalyst (0.39 mmol Rh/g of beads) and 10 mL dry benzene were introduced into a 250 mL stainless steel autoclave. Following the addition of 2.0 mL 1-pentene (18.3 mmol) and the attachment of the head, the system was

flushed three times with hydrogen and twice with carbon monoxide. The system was then pressurized to 14.6 atm with CO and heated to 110° in an oil bath. After 40 min., during which the system achieved physical equilibrium, carbon monoxide and then hydrogen (1:1) were rapidly added to 69 atm and the autoclave was heated and stirred at 110° for 3 h. During this period there was a 6.1 atm pressure drop. After being cooled to room temperature, the vessel was vented and the clear golden solution was drawn out by using a syringe.

A sample of the product was injected into the gas chromatograph with the column temperature at 40° in order to separate the pentane reduction product from any unreacted 1-pentene. The column temperature was then increased to 90° and the linear and branched hydroformylation products were separated. A column temperature of 130° was used to verify that no higher boiling products-alcohols were obtained.

PART II

THERMAL DECOMPOSITION OF TRANSITION METAL ALKYLS

INTRODUCTION

Since Frankland's discovery¹²¹ in 1849 of the first organometallic compound, the spontaneously inflammable ZnEt₂, metal alkyls have been of considerable interest. Attempts to synthesize transition metal alkyls were not successful until the isolation of the trimethylplatinum iodide tetramer, $\{(CH_3)_3PtI\}_4$, a stable product obtained by Pope and Peachy¹²² in 1907. Unsuccessful attempts to prepare simple transition metal derivatives led to the generalization that they are much less stable than their main group element analogues¹²³ and that transition metal-carbon bonds are weak, a view supported by calculations.¹²⁴ The scope of relevant problems is immense, ranging from theoretical or structural studies to organic or biological chemistry. Many metal alkyls have a key role as synthetic reagents, notably the Grignard reagents and alkyls of Li, Zr, Hg, Al, Sn and Cu. Some main group metal alkyls feature as important materials for industrial use: $PbEt_4$ as an antiknock gasoline additive; Sn^{IV} compounds as stabilizers for poly(vinyl chloride) and as fungicides or germicides; Al derivatives in the manufacture of isoprene or long chain alcohols; and Me_2SiCl_2 in silicones as rubbers, resins, or paper finishes. Vitamin B_{12} coenzyme provides a metal alkyl as an essential biological material. Transition metal alkyls are key intermediates in many catalytic reactions of olefins or acetylenes, e.g., carbonylation, dimerization,

polymerization, isomerization and hydrogenation. These intermediates are well characterized in homogeneous catalysis but only recently has it become apparent that similar alkyl species exist on the surfaces of heterogeneous catalysts. Some transition metal alkyls are important in petrochemical, polymer, or heavy organic chemical industry, e.g., alkyls of Ti in Ziegler-Natta polymerizations and of Co in hydroformylation by $Co_2(CO)_8$.

Metallacycles are also of current interest due to the potential importance of metallacyclic intermediates. Small-ring metallacycles have been implicated as intermediates in a large number of transition metal catalyzed reactions of olefins and acetylenes. Thus, metallacyclobutanes are postulated to play a key role in the catalysis of the olefin metathesis reactions.¹²⁵⁻¹³³ Metallacycles are also implicated in various ring openings and rearrangements, ¹³⁴⁻¹³⁶ (2 + 2) cycloadditions and cyclooligomerization of olefins, ¹³⁷⁻¹⁴¹ and polymerization of silacyclobutanes.¹⁴²⁻¹⁴³

Transition metal alkyls are often thermally unstable and their thermal instability is frequently the characteristic that makes them catalytically important. Metal-carbon bond breaking may formally be uni- or bimolecular. A unimolecular process involves either (a) migration of a substituent from the alkyl group to the metal (α , β , etc., elimination) or (b) homolytic cleavage of metal-carbon bond. The pathways of higher molecularity result in disproportionation or formation of clusters. Much mechanistic information derives from studies of platinum alkyls, which are experimentally convenient because of stability to air, but the results probably apply equally well to early transition metal alkyls. The most important pathways for the decomposition of transition metal alkyls will now be discussed.

Beta-hydrogen elimination dominates the thermal decomposition of metal alkyls and may be represented by the equation as follows:

LNM-CH2-CH2R - LNM-H + CH2=CHR

The migration of a β -hydrogen from carbon to the metal (M) with formation of an alkene probably proceeds through a concerted reaction. The olefin may remain within the coordination sphere of the metal. The best-studied example is the thermal decomposition of di-n-butylbis(triphenylphosphine)platinum(II).¹⁴⁴ The products on thermolysis are n-butane, l-butene and a complex of platinum(0). The decomposition has been proposed to take place by intramolecular β -hydrogen elimination process (Figure 38).

Beta-hydrogen elimination is reversible, and indeed both metalcarbon bond-making and bond-breaking by this route are involved in many catalytic reactions such as olefin or acetylene hydrogenation, hydroformylation, hydroboration, hydrosilylation, isomerization and olefin oligomerization and polymerization.¹⁴⁵ A β -hydrogen may also be abstracted from an aryl ligand, ¹⁴⁶⁻¹⁴⁸ where evidence for the formation of a coordinated benzyne, Cp₂Ti(C₆H₄), was provided and confirmed by deuterium-labeling experiments.¹⁴⁹⁻¹⁵¹ Finally, intermolecular abstraction of hydrogen is also possible in β -hydrogen elimination.



Figure 38. Decomposition of di-n-butylbis(triphenylphosphine)platinum(II).

Alpha-hydrogen elimination involves migration of a hydrogen from the α -carbon to the metal with formation of a carbenic fragment which may remain coordinated to the metal. A substantial amount of information indicates this is also a significant decomposition pathway.

 $L_NM-CHR'R'' \longrightarrow L_NM(H)(CR'R')$

The above process is more likely to occur in complexes with less than 18 valence electrons since the number must increase by two; the relationship to formal metal oxidation state is less clear. Alpha-hydrogen elimination is generally less well established than β -hydrogen elimination. The best example of α -hydrogen elimination is neopentyl tantalum complex (Figure 39). The neopentylidene ligand forms by abstraction of a neopentyl α -proton by a neighboring neopentyl group in the sterically crowded penta(neopentyl) intermediate.



Figure 39. Formation of the tantalum neopentylidene complex.

Reductive elimination is the reverse of oxidative addition and provides a route to cleavage of metal-carbon bonds. The process is shown below. Both the coordination number and the oxidation state

 $\longrightarrow L_NM + X-Y$

of the metal are reduced by two. This mode of thermal decomposition plays a role in several organic syntheses where transition metal species are involved in the formation of carbon-carbon bonds.

Decomposition by homolytic metal-carbon bond cleavage often gives a complex mixture of products, the composition of which is dependent on reaction conditions. This pathway formally involves oxidation of the ligand ($R^- + R^-$) with corresponding decrease in the oxidation state of the metal. Other modes for thermal decomposition such as ligand hydrogen abstraction, binuclear elimination, etc., have also been discussed recently.¹⁵³⁻¹⁵⁵

In addition to β -hydrogen elimination and reductive elimination, a different elimination which involves carbon-carbon bond cleavage is observed in the thermal decomposition of metallacycles. 1,4-Tetramethylenebis(cyclopentadienyl)titanium(IV) has been reported to decompose to produce ethylene in good yield¹⁵⁶⁻¹⁵⁹ (Figure 40). No reductive elimination (formation of cyclobutane) was reported while β -hydrogen elimination (formation of l-butene) occurred to only eight percent.

$$\begin{array}{ccc} C_{P} & & \Delta \\ & & T_{1} & \longrightarrow & H_{2}C = CH_{2} + / & & & C_{P_{2}}T_{1}'' \\ C_{P} & & & 92\% & 8\% \end{array}$$

Figure 40. Decomposition of 1,4-tetramethylenebis(cyclopentadienyl)titanium(IV).

It is believed that titanacyclopentane decomposes by reversible carboncarbon bond cleavage to produce an intermediate bis(ethylene) complex. That is, when bis(cyclopentadienyl)titanium dichloride is reduced to titanocene in the presence of ethylene, a titanacyclopentane is formed. Carbonylation of the titanacycle with carbon monoxide yields cyclopentanone in 17% yield (Figure 41).



Figure 41. Conversion of olefins to cyclopentanones by reaction with titanocene equivalents.

The thermal decomposition of Pt(IV) metallacyclopentanes was investigated by Puddephatt <u>et al</u>¹⁶⁰ The decomposition of 1,4-tetramethylenebis(dimethylphosphine)diiodoplatinum(IV) gives exclusively 1-butene generated by β -hydrogen elimination. It is interesting to note that no cyclobutane is formed in the decomposition of any platinum(IV) metallacyclopentanes. Puddephatt and coworkers believe the lack of cyclobutane production from a reductive elimination process is due to the higher activation energy needed to close the strained cyclobutane ring.

Whitesides <u>et al</u>¹⁶¹⁻¹⁶³ reported the thermal decomposition of a series of platinum(II) metallacycles and compared rates of decomposition to their corresponding alicyclic platinum complexes. It was found that the thermal decomposition of 1,4-tetramethylenebis(tri-n-butylphosphine)platinum(II) dichloromethane and dibromomethane solutions generated both cyclobutane and butenes derived from the metallacyclic moiety and cyclopentane and pentenes formed by incorporation of a solvent-derived methylene group. Thermal decomposition of platinacyclopentane in hydrocarbon or ethereal solutions yielded only butenes having the same number of carbon as the metallacyclic group (Figure 42).



Figure 42. Decomposition of 1,4-tetramethylenebis(tri-n-butylphosphine)platinum(II).

However, Grubbs, Miyashita and coworkers¹⁵⁸, 159, 164-166 reported that thermolysis of phosphine nickelmetallacyclopentanes produced ethylene, cyclobutane and butenes and the coordination number of the nickel played an important role on the decomposition pathway. Three coordinated nickelacyclopentanes decompose by β -hydrogen elimination to give l-butene. Four coordinated nickelacyclopentanes decomposed by reductive elimination to give cyclobutane while five coordinated nickelacyclopentanes decomposed by reversible carbon-carbon bond cleavage to give ethylene. Figure 43 summarizes the effects of added phosphine on the decomposition modes of nickelacyclopentanes.



L: TRIALKYL OR ARYL PHOSPHINE.

Figure 43. Decomposition of nickelacyclopentanes.

Thermal decomposition of metal alkyls often affords a complex mixture of products. It is not always possible to ascertain all the product-forming reactions. Although a number of thermal decomposition modes have been discussed and studied specifically, 153-155 no unified theory of decomposition has resulted. Knowledge of the detailed mechanisms of thermal decompositions is important both in the application of known catalytic reactions and in the development of new ones. In this research, new decomposition pathways, γ - and δ -hydrogen elimination, are proposed and discussed for the thermal decomposition of transition metal alkyls.

RESULTS AND DISCUSSIONS

Alkyllithium, -magnesium and -aluminum reagents¹⁶⁷⁻¹⁷² have been reported to react rapidly with transition metal salts, yielding complex mixtures of hydrocarbons which are believed to be derived from the thermal decomposition of intermediate transition metal alkyls. A number of mechanisms for the thermal decomposition of transition metal alkyls have been mentioned, but the detailed ones have not been well established. Similarly, the detailed mechanisms for the thermal decomposition of alkyl- and aryl-bis(cyclopentadienyl)titanium compounds are still uncertain. Razuvaev <u>et al</u> 173 proposed a homolytic cleavage of the Ti-C σ -bond as the main pathway in the thermal decomposition of Cp_2TiR_2 (R= alkyl and aryl) in various solvents. Dvorak et al¹⁴⁹ suggested that benzene was formed by abstracting a hydrogen atom from another phenyl group with formation of a phenylenetitanium complex in the decomposition of $Cp_2Ti(C_6H_5)_2$. Teuben <u>et al</u>¹⁵¹ found that the compounds, Cp_2TiR_2 (R= aryl and benzyl), decomposed with quantitative formation of R-H via intramolecular abstraction of a hydrogen atom either from a cyclopentadienyl ring or from the other coordinated group R.

In our study, some unexpected hydrocarbons such as methane and ethylene from the reaction of dichlorobis(cyclopentadienyl)titanium and n-butyllithium were observed. The results outlined above prompted us to prepare dialkyltitanocene complexes and investigate their detailed mechanisms of thermal decomposition.

<u>Preparation and Thermal Decomposition of Di-n-butyl-bis(cyclopentadi-</u> <u>enyl)titanium(IV)</u>

The preparation of di-n-butylbis(cyclopentadienyl)titanium (Cp_2TiBu_2) can be achieved by the reaction of a suspension of dichlorobis(cyclopentadienyl)titanium (Cp_2TiCl_2) with n-butyllighium in diethyl ether at -78° . The orange product, Cp_2TiBu_2 , was purified by column chromatography over alumina at -78° under argon by using n-pentane as eluent. Since its thermal instability precluded traditional analytical procedures, it was characterized by some chemical reactions. Treatment of orange solution with hydrogen chloride gas in pentane gave Cp_2TiCl_2 and n-butane in molar ratio of 1:1.98; treatment with concentrated D_2SO_4 or gaseous DCl in n-pentane gave Cp_2TiBr_2 and l-bromobutane in molar ratio of 1:1.88. Di-n-butylbis(cyclopentadienyl)titanium decomposes at -40° , therefore it is stored at -78° or below.

Whitesides $\underline{et al}^{157}$ reported that thermal decomposition of Cp_2TiBu_2 at 250° by injecting samples directly into the gas chromatograph gave the 1:1 mixture of n-butane and butenes. In this research, the thermal decomposition was carried out by stirring a toluene solution of Cp_2TiBu_2 at -60° to -78° for 5 h, then warming up to 60°. Interestingly, small amounts (~1%) of methane and ethylene were generated besides the major products of n-butane and butenes produced from initial β -hydrogen elimination followed by reductive elimination of n-butane. The production of light hydrocarbons other than β -hydrogen elimination products was also observed in the thermal decomposition of some early transition metal n-alkyls. The results are given in Table 13. The formation of methane and ethylene is apparently not consistent with the frequently discussed mechanisms of thermal decomposition for transition metal alkyls and will be discussed first.

Table 13. Minor products from thermal decomposition of n-alkyl transition metals.

Compounds	Decomposition Products(%)	Products	other than β -Hydrogen Elimination
	CH ₄	C2H4	Other Hydrocarbons
Cp ₂ TiPr ₂	1.9	1.1	C ₆ (5.2%)
Cp ₂ TiBu ₂	0.2	0.6	C ₃ (0.1%), C ₈ (not examined)
Cp ₂ TiAm ₂	0.8	0.6	C ₃ (0.9%), C ₄ (0.3%) C ₁₀ (not examined)
Cp ₂ ZrBu ₂	trace	trace	
Cp ₂ HfBu ₂	trace	trace	
Cp ₂ NbBu ₂	trace	trace	
Cp ₂ TaBu ₂	0.6	0.2	

Grubbs and Miyashita¹⁷⁴ have reported that the carbenoid intermediate is formed and provides a route to the formation of methane in the thermal decomposition of nickel and titanium metallacyclohexanes. The metal-carbene complexes have also been found to dimerize¹⁷⁵ to produce ethylene. Therefore, di-n-alkylbis(cyclopentadienyl)titanium was allowed to decompose in the presence of cyclohexene. Indeed, about 1-3% yields of norcarane were isolated. The results are given in Table 14. The generation of metal carbene is not certain in these thermal decompositions, but the methane and ethylene may be formed by metal-carbene complexes according to the following equations.



Table 14. Metal-carbenes trapped by cyclohexene.

Compounds	ProductNorcarane
	(yield)
Cp ₂ TiPr ₂	2.93%
Cp ₂ TiBu ₂	1.51%
Cp ₂ TiAm ₂	1.10%

However, the production of ethylene in the decomposition of Cp_2TiBu_2 possibly results from β -carbon-carbon bond cleavage of titanacyclopentane formed by δ -hydrogen elimination with reductive elimination of one molecule of n-butane as shown below (Figure 44).



Figure 44. Possible scheme for the formation of ethylene via 6-hydrogen elimination in the decomposition of Cp₂TiBu₂.

Delta-elimination as well as γ -elimination are not well established in organometallic chemistry. In principle, they are similar to β -elimination. Two good examples¹⁵³ involving γ -elimination are found in organoaluminum and silicon compounds and illustrated in Figure 45. Diisobutyl(3-ethoxypropyl)aluminum, derived from diisobutylaluminum hydride and allyl ethyl ether, decompose to give cyclopropane and diisobutylaluminum ethoxide. Similarly, diethylmethyl(chloropropyl)silane thermally decomposes to give cyclopropane and diethylmethylsilyl chloride.





Figure 45. Scheme for γ -elimination in organoaluminum and silicon compounds.

Recently, Grubbs and Miyashita¹⁷⁶ prepared nickelacyclobutane compounds from di-neopentylbis(triphenylphosphine)nickel. The formation of nickelacyclobutane involves γ -hydrogen elimination with loss of one molecule of neopentane. The nickelacyclobutane complex containing odd number of carbons decomposes by cleavage of an α , β -carboncarbon bond to produce carbenoid complexes which dimerize to give ethylene complexes or react with olefins to produce substituted cyclopropanes. The scheme for the decomposition of dineopentylbis-(triphenylphosphine)nickel is illustrated in Figure 46.

To further examine γ - and δ -hydrogen elimination, the complexes of dineopentyl- and dineohexylbis(cyclopentadienyl)titanium were prepared and their thermal decompositions were studied.



Figure 46. Decomposition of di-neopentylbis(triphenylphosphine)nickel(II).

Preparation and Thermal Decomposition of Dineopentyl- and Dineohexylbis(cyclopentadienyl)titanium

Dineopentylbis(cyclopentadienyl)titanium was prepared by the reaction of Cp_2TiCl_2 and two equivalents of neopentyllithium in diethyl ether or pentane at -78° . After the solvent was removed, the residue was chromatographed on an alumina column at -78° under argon using n-pentane as eluent. The product was characterized by treatment of the orange pentane solution with hydrogen chloride gas and bromine. Similarly, the dineohexyl compound was prepared by the reaction of Cp_2TiCl_2 and two equivalents of neohexyllithium and characterized by the same methods as those for dineopentylbis(cyclopentadienyl)titanium.

Transition metal alkyls in which the alkyl contains β -hydrogen atoms often decompose fairly readily by β -hydrogen elimination as seen in the decomposition of dibutylbis(cyclopentadienyl)titanium. This decomposition pathway is blocked if no β -hydrogen atoms are available. For example, the high stability associated with methyl, neopentyl, benzyl and aryl derivatives of transition metals is thus attributable to the absence of β -hydrogens which can be eliminated as metal hydride. The thermal decomposition of Cp₂TiR₂ (R= neohexyl) gave mostly neohexane and small amounts (1.3%) of ethylene and isobutylene. The neohexane is probably produced from initial α -hydrogen elimination followed by reductive elimination of neohexane or from intramolecular abstraction of a hydrogen atom from a cyclopentadienyl ring formulated as in the following equation.

Thermal decomposition of $Cp_2Ti(CH_3)_2$ has shown that some methane arises from an intramolecular α-hydrogen elimination and some abstraction of hydrogen atoms from the cyclopentadienyl ring.¹⁷⁹ These two processes in the decomposition of Cp_2TiR_2 (R= neohexyl) could be distinguished by experiments with a deuterated compound such as $(C_5D_5)_2$ TiR₂ (R= neohexyl), but were not examined in this research. We are most interested in the formation of ethylene and isobutylene. Norcarane was also produced with 1.84% yield when thermal decomposition of dineohexylbis(cyclopentadienyl)titanium was carried out in the presence of cyclohexane. The production of a carbenoid complex probably resulted from the α , β -carbon-carbon bond cleavage¹⁷⁴ of intermediate dimethylsubstituted metallacyclopentane, which is formed by initial b-hydrogen elimination followed by reductive elimination of neohexane. Therefore, the formation of ethylene can occur either by dimerization of metal-carbone complexes or by β , γ -carbon-carbon bond cleavage of resulting intermediate substituted metallacyclopentane. Similarly, the isobutylene also probably resulted from β_{M} -carbon-carbon bond cleavage of intermediate substituted metallacyclopentane or from further α , β -carbon-carbon bond cleavage of intermediate carbenoid metallacyclobutane. The organometallic product of thermal decomposition of Cp_2TiR_2 (R= neohexyl) was possibly an unstable compound, "titanocene", which gave a dimeric titanium hydride at decomposition temperature. The proposed mechanism is shown in Figure 47 (Reaction b).

Similarly, the neopentyl complex, Cp_2TiR_2 (R= neopentyl), decomposes to give small amount of isobutylene (1.2%) possibly produced from α , β -carbon-carbon bond cleavage of intermediate dimethyl-substituted metallacyclobutane which formed by y-hydrogen elimination with reductive elimination of neopentane. A small amount of ethylene (0.98%) was also found besides the major product, neopentane, in the decomposition of Cp_2TiR_2 (R= neopentyl). The formation of ethylene probably resulted from the dimerization of carbenoid complexes which are produced from α .B-carbon-carbon bond cleavage of intermediate metallacyclobutane and have been trapped to give norcarane (1.71%), when the dineopentyl complex was allowed to decompose in the presence of cyclohexene. A ¹³C NMR signal at 359.07 ppm was observed for dineopentylbis(cyclopentadienyl)titanium in toluene at -50° . This signal is probably due to resonance, characteristic of carbene-type a-carbon atom bound to transition metal absorbing at the low field. The mechanism for the formation of ethylene and isobutylene in the thermal decomposition of dineopentyl titanium complex is proposed as shown in Figure 47 (Reaction c).

At present, the production of isobutylene in the thermal decomposition of Cp_2TiR_2 (R= neohexyl and neopentyl) can only be increased to 2.3% by stirring a toluene solution of Cp_2TiR_2 at -60° to -78° for a week, then allowing it to decompose at 80° . No significant amount of ethylene and isobutylene was observed when a toluene solution of Cp_2TiR_2 (R=neohexyl and neopentyl) was irradiated with UV light at -78° . When the thermal decomposition of Cp_2TiR_2 was carried out in toluene-d₈, no significant amount of deuterium was found in the products, ethylene and isobutylene, and so participation of the solvent in the decomposition was unlikely. Similarly, a preliminary examination showed that the reaction of some metallocene chlorides with neohexyllithium in toluene yielded methane, ethylene and isobutylene. The results are given in Table 15. Possibly, the methane is formed by hydrogen abstraction of metal-carbene complexes and the formation of ethylene and isobutylene resulted from the same pathway as in the thermal decomposition of dineohexyl titanium complex. The C_4 compounds (1-2%) such as butane and butenes are probably formed by dimerization of ethylene.¹⁵⁷ In an experiment, the amount of C_4 was doubled, when Cp_2TiR_2 (R= neohexyl) decomposed in an atmosphere of ethylene and argon. An attempt to isolate intermediate metallacycles was not successful due to their instability and low yields.

Although there have been several studies of the thermal decomposition of transition metal alkyl complexes, there still is uncertainty concerning the mechanism of the thermolysis. From this research, it appears that the mechanisms proposed (Figure 47), γ - and δ -hydrogen eliminations, are one type of process for thermal decomposition of transition metal alkyls and at least can serve as a starting point for further experiments and discussions. This new mechanism can also provide models for a number of homogeneous and heterogeneous reactions of hydrocarbons.



Figure 47. The scheme for the proposed new mechanisms of thermal decomposition of transition metal alkyls.

Table 15.	Decompo	sition pr	oducts of	neohexyl me	etal compl	exes other	than α-hydrogen elimination	
Neohexyl	Complexes	(lomm)	Products	of Thermal	Decompos	ition other	than a-Hydrogen Elimination (1
(R= Neohe	(ľyx		CH ₄	c ₂ H ₄	ۍ ت	C4	H ₂ C=C ^{CH3}	
Cp2T1R2	(0.82)		3.09	1.24	0.12	1.11	1.27	
Cp ₂ TiR ₂ *	(0.87)		0.97	2.65	0.34	1.66	2.31	
ср ₂ VR	(0.45)		2.59	1.20	0.30	0.87	1.36	
CP2TaC1R2	(0.31)		1.39	1.29	0.10	2.34	1.87	
Cp ₂ MoR ₂	(0.31)		3.28	2.05	0.10	2.69	2.23	
Cp ₂ WR ₂	(0.31)		3.03	2.14	0.20	2.36	2.02	

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Decomposition was at 80⁰ after stirring in toluene at -60⁰ to -78⁰ for a week.

*

EXPERIMENTAL

All reactions and manipulations were performed under weldinggrade argon purified before use by a BASF deoxygenation catalyst and molecular sieves (Linde 4A). All solvents were purified as described in the EXPERIMENTAL section of Part I. Neopentyl chloride and neohexanol (t-amyl carbinol) were obtained from ICN pharmaceuticals, Inc. Toluene-d_R (>99%) was purchased from Aldrich Chemical Co.

Analytical GLC was performed on a Varian series 1400 FID chromatograph with a 20 ft x 1/8 in Durapak column or a 13 ft Paraffin wax/ 5% AgNO₃ on Al₂O₃ column. Product yields were determined by response relative to an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 mass spectrometer and Finnigan 4000 GC mass spectrometer. ¹³C NMR spectra were measured on a Varian CFT-20 spectrometer with TMSas internal standard.

Preparation of Alkyllithium Reagents

Except for the solution of n-butyllithium in hexane which is commercially available, the solutions of n-alkyllithium reagents in n-pentane or diethyl ether were prepared from the corresponding chlorides or bromides by previously reported procedures.¹⁷⁸

Neopentyllithium in n-pentane was prepared from neopentyl chloride. A mixture of 30 g neopentyl chloride and a two-fold excess of finely chopped lithium wire in 500 mL n-pentane was stirred and refluxed under argon for 10 days. The excess Li metal and LiCl were removed by filtration and the neopentyllithium was isolated from the

filtrate by cooling and reducing the volume <u>in vacuo</u> and yielded 90% of white, crystalline $LiCH_2CMe_3$. The white solid was then dissolved in freshly distilled n-pentane, diethyl ether or toluene ane store at -10° .

Neohexyllithium (LiCH₂CMe₂Et) was prepared from neohexyl bromide which was obtained from the reaction of neohexyl alcohol and $P(n-C_4H_9)_3Br_2$.¹⁸¹ A sample of 16 g (0.16 mole) dry neohexyl alcohol (t-amylcarbinol) was mixed with 43 mL (0.17 mole) of freshly distilled tri-n-butylphosphine in 85 mL of dry DMF in an argon atmosphere. About 8 mL of bromine was added slowly while the reaction flask was cooled in an ice bath. After being stirred for 6 h, all volatile material was then removed by vacuum distillation into a receiver cooled in a dry ice bath. Cold water was added and neohexyl bromide was separated. Neohexyl bromide (yield 90%) was then dried and distilled at 55⁰/40 torr. A 12 g neohexylbromide and a two-fold excess of Li wire were placed in 150 mL n-pentane under argon and refluxed for 12 days. The mixture was filtered and the neohexyllithium (>80%) was isolated from the filtrate. It was dissolved in n-pentane, diethyl ether or toluene and stored at -10⁰.

Preparation of Di-n-butylbis(cyclopentadienyl)titanium

A sample of 2 g (8 mmol) Cp_2TiCl_2 was suspended and stirred in 25 mL diethyl ether at -78° . An ethereal solution of n-butyllithium (16 mmol) was added slowly by a syringe. The reaction mixture was stirred at -78° for 36 h. During this period, the mixture turned dark red. About 100 µL methanol was then injected to destroy any

unreacted n-butyllithium. The solvent was removed at -78° to give orange-red residue. The residue was chromatographed on an alumina column which has been thoroughly dried and flushed with argon. This column was provided with a cooling jacket, and maintained at -78° . The column was eluted with n-pentane and an orange band was collected as it eluted. The orange pentane solution was then concentrated at -78° in vacuo and the product was stored below -78° .

Di-n-butylbis(cyclopentadienyl)titanium was characterized by its chemical reactions. Treatment of orange pentane solution with anhydrous HCl gas yielded n-butane and Cp_2TiCl_2 in a molar ratio of 1.98 : 1. Similar treatment with DCl gas or concentrated D_2SO_4 gave 1-deuterobutane with isotopic yield >99%. When the orange solution was treated with bromine, the dark red Cp_2TiCl_2 and 1-bromobutane were formed. GLC analysis of 1-bromobutane and weighing Cp_2TiBr_2 showed that the molar ratio of Cp_2TiBr_2 to 1-bromobutane was 1 to 1.88.

Thermal Decomposition of Di-n-alkylbis(cyclopentadienyl)titanium

A pentane or toluene solution of Cp_2TiBu_2 was stirred at -60° to -78° for 5 h, then warmed up to 60° . The gases produced were injected into the GC for analysis, cyclopropane was the internal standard. Subsequent analyses gave the same results, indicating complete decomposition. After complete decomposition, the products produced were collected by distillation into a liquid nitrogen trap. On being warmed to room temperature, the product gases were analyzed by GLC in the vapor phase as well as the liquid phase and their composition was determined.

Other thermal decompositions of di-n-alkylbis(cyclopentadienyl)titanium were carried out as follows: A sample of Cp_2TiCl_2 was suspended in n-pentane or diethyl ether at -78° . Two equivalents of alkyllithium in n-pentane or diethyl ether were added slowly. After the reaction mixture was stirred at -78° for 36 h, small amount of methanol was injected into the flask to destroy the excess alkyllithium reagent. The solvent was removed in vacuo at -78° and toluene was added. After being stirred at -78° for 5 h, the toluene solution was warmed to 60° . The products were analyzed by GLC as above. The composition of products was unaffected by chromatographing the solution through alumina.

Preparation and Decomposition of Di-n-neohexyl and Di-neopentylbis-(cyclopentadienyl)titanium

A sample of 1 g (4 mmol) Cp_2TiCl_2 was reacted with neohexyl- or neopentyllithium (8 mmol) in 30 mL diethyl ether or n-pentane at -78° for 2 days. About 100 µL of methanol was injected to destroy any unreacted lithium reagent. Removal of the solvent at -78° left an orange sludge. The product was chromatographed by a procedure analogous to that used for di-n-butylbis(cyclopentadienyl)titanium with n-pentane as the eluting solvent. A clear orange pentane solution was obtained and concentrated.

Treatment of the orange pentane solution with anhydrous HCl gave neohexane or neopentane and Cp_2TiCl_2 with the molar ratio of 1.93 to 1. Similar treatment with bromine yielded neohexyl bromide

and Cp_2TiBr_2 . The molar ratio of neohexyl bromide to Cp_2TiBr_2 was 1.90 to 1. The characterization of di-neopentylbis(cyclopentadienyl)titanium was the same as that used for Cp_2TiR_2 (R=neohexyl).

The procedures for the thermal decompositions at 80° are similar to those used for Cp_2TiR_2 (R=n-butyl). When the decomposition was carried out in deuterated solvent toluene-d₈, no significant amounts of deuterated products was found. When a toluene solution of Cp_2TiR_2 (R=neohexyl) (1 mmol) and 20 mL of ethylene was stirred at -78° for 5 h, then decomposition at 80° gave 2.5% butenes and butane.

Metal-Carbene Trapping Experiment

Typically, a toluene solution of Cp_2TiBu_2 (1.5 mmol) and 1 mL of freshly distilled cyclohexene were stirred at -78° for 3 h, then warmed to 60° . After being stirred at 60° for 36 h, the product was collected by distillation into a liquid nitrogen trap. On being warmed to room temperature, the product was analyzed by GLC on a 32 ft x 1/8 in 10% Carbowax 20M/Chromosorb W column and a 13 ft x1/8 in Parafin wax 15% AgNO₃ on Al₂O₃ column, compared with authentic sample and the yield of norcarane was 1.51%.

Preparation of Metallocene Chlorides

Vanadocene monochloride¹⁸⁰ and the metallocene dichlorides¹⁸¹⁻¹⁸³ of Nb, Ta, Mo and W were prepared as previously reported.

The new compound of trichlorobis(cyclopentadienyl)tantalum (Cp_2TaCl_3) was prepared and characterized as follows: A sample of 5.4 g (15 mmol) tantalum pentachloride $(TaCl_5)$ was reacted with 15 mmol of Mg $(C_5H_5)_2$ in 100 mL of toluene. After being stirred at room temperature for 24 h, the toluene was removed <u>in vacuo</u> and the yellow residue remained. A yellow crystalline compound, Cp_2TaCl_3 , was obtained by sublimation of the yellow residue at $260^{\circ}/0.01$ mmHg. Characterization was made by IR spectroscopy that showed a band pattern characteristic of biscyclopentadienyl complexes⁷⁹ (Figure 48) and by mass spectrometry. The characteristic IR peaks are 1440 (s), 1340 (m), 1125 (vw), 1015 (m) and 855 (s) cm⁻¹. The principal ions in mass spectra are Cp_2TaCl_3 (M⁺, m/e 417-421), Cp_2TaCl_2 (m/e 381-385) and $CpTaCl_2$ (m/e 316-320).

Preparation and Thermal Decomposition of Neohexyl Metallocene Derivatives

A sample of metallocene chloride was treated with the required amount of newhexyllithium reagent in diethyl ether or n-pentane at -78° for 2 days. Methanol (100 µL) was injected to destroy any unreacted lithium reagent. The solvent was removed at -78° and toluene was then added to dissolve the residue. After being stirred at -78° for 5 h, the toluene solution was warmed to 80° . The produce gases were injected into the GC for analysis. Subsequent analyses gave the same results, indicating complete decomposition. Some results are given in Table 15. The decomposition of Cp_2ZrR_2 , Cp_2HfR_2 and Cp_2NbR_2 (R=neohexyl) only 128

gave trace amounts (<0.01%) of ethylene and isobutylene.




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