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ABSTRACT

POLYMER-SUPPORTED TRANSITION METAL CATALYSTS

By

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Homogeneous catalysts have so far found only limited use, chiefly because of the difficulty of their separation from the reaction products. Making homogeneous transition metal catalysts insoluble by attachment to various polymers is a significant step in improving their industrial applicability. While the polymer-attachment technique obviously prevents the loss of possibly expensive materials and contamination of reaction products, 6-13 the method also offers the opportunity to prepare a new class of catalyst systems with other desirable properties. For instance, the polymer-supported catalysts have been demonstrated to have selectivity towards molecules of different bulk and polarity. 7,12 Also, the attachment of a saturated complex that is a potential catalyst to a rigid matrix, followed by reductive elimination of a ligand, should produce higher concentration of monomeric, coordinatively unsaturated species than is obtained in solution.^{6,10} This would be reflected in the increase in catalytic activity of that complex when compared to a similar non-attached complex under the same conditions and has been found to be true in the recent publications. 4,5

For the research discussed here, it was decided to use polystyrene-divinylbenzene copolymer beads as the supporting matrix. Beads ranging in size from 30 to 60 mesh and with a divinylbenzene content of two to twenty percent (600 Å pore) were used.

The reaction scheme used for the polymer-attachment was as follows:





Treatment of (A) with MCl_4 (where M = Ti, Zr, and Hf) in benzene results in the formation of mono cyclopentadienyl metal trichlorides.

The polymer-attached and non-attached species showed close resemblance in their colors. The polymer-attached species were identified by the metal and chloride analysis. The expected and the observed metal to chloride ratio agree reasonably well. Additional evidence to characterize the polymer-supported species was obtained from far infrared spectra. The spectra of the non-attached and polymer-attached species agreed closely.

The knowledge of the physical nature of the metal catalyst dispersion is useful in understanding the chemical properties of the polymer-attached compound. An electron microprobe was used to study the physical nature of the metal catalyst dispersion on the polymer support. Electron microprobe X-ray fluorescence analysis of the sectioned beads suggests a uniform distribution of metal and chloride.

The mono cyclopentadienyl titanium trichloride on reduction produces an active catalyst whose hydrogenation efficiency is about twenty times as great as the corresponding non-attached species. This was attributed to the ability of the rigid supporting matrix used (20% divinylbenzene) to keep the metal atoms apart, preventing dimerization and the accompanying loss in activity. The supported catalyst also has been shown to have selectivity towards molecules of different bulk. The general trend among the supported catalyst systems is toward slower rates for larger olefins as observed by Kroll.¹⁴ This behavior is substantially different from ordinary heterogeneous catalysts. Another area of interest with metallocenes (titanocene in particular) is the nitrogen fixation. Two titanocenes seem to be required for the formation of dinitrogen complex, $^{3,15-18}$ followed by its reduction to ammonia as shown by the following reaction:



But in the supported titanocene system, the titanium centers are too far apart to form the dinitrogen complex and so is not expected to be a nitrogen fixing catalyst. This was found to be true by Kroll,¹⁴ using both Van Tamelin¹⁵⁻¹⁷ and Vol'pin-Shur¹⁸ nitrogen fixation schemes. With this problem in view, attempt was made in this work to see whether by using a polymer with a lower degree of crosslinking, one can bring the titanium centers close enough (as the polymer matrix would be less rigid or more flexible) to form the dinitrogen complex.

The research work reported here consists of (A) the polymerattachment of cyclopentadienyl metal chlorides of titanium, zirconium, and hafnium to the polystyrene-divinylbenzene copolymer beads; (B) their characterizations using low frequency infrared spectroscopy in the solid state; (C) study of the physical nature of the metal catalyst dispersion on the polymer support by use of electron microprobe X-ray fluorescence studies; (D) the catalytic activity of the polymer-attached species towards hydrogenation of unsaturated organic molecules and towards nitrogen fixation.

POLYMER-SUPPORTED TRANSITION METAL CATALYSTS

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Chandrasekaran. E.S.

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

To my parents, for their understanding and moral support throughout the many years of my education; to my brothers and sister, whose encouragement has made these years good and worthwhile.

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INTRODUCTION

The unusual reactivity of systems involving titanocenes and other metallocenes of early transition metals towards normally rather inactive molecules such as hydrogen and nitrogen has been of great interest. This is illustrated by the figures 1 and 2 taken from Bercaw's thesis.¹



Figure 1. Reactions of $(n^5-C_5H_5)_2$ Ti $(CH_3)_2$ in which Titanocene Appears to Occur as an Intermediate





an Intermediate

These compounds have been shown to be particularly useful in the hydrogenation of unsaturated organic compounds and in the chemistry of nitrogen fixation. However, the complexes readily polymerize,² according to the following reaction, to form catalytically inactive materials.³



This dimerization could be prevented by attaching the metallocene precursor compounds to a rigid polymer support. Several ways to attach the transition metal compounds on to polystyrene-divinylbenzene copolymer resin^{4,5} have been demonstrated.

Homogeneous catalysts have so far found only limited use, chiefly because of the difficulty of their separation from the reaction products. Making homogeneous transition metal catalysts insoluble by attachment to various polymers is a significant step in improving their industrial applicability. While the polymer-attachment technique obviously prevents the loss of possibly expensive materials and contamination of reaction products, $^{6-13}$ the method also offers the opportunity to prepare a new class of catalyst systems with other desirable properties. For instance, the polymer-supported catalysts have been demonstrated to have selectivity towards molecules of different bulk and polarity.^{7,12} Also, the attachment of a saturated complex that is a potential catalyst to a rigid support, followed by reductive elimination of a ligand, should produce higher concentration of monomeric, coordinatively unsaturated species than is obtained in solution.^{6,10} This would be reflected in the increase in catalytic activity of that complex when compared to a similar non-attached complex under the same conditions as has been reported in recent publications from this laboratory.^{4,5}

For the research discussed here, it was decided to use polystyrenedivinylbenzene copolymer beads as the supporting matrix. Beads ranging in size from 30 to 60 mesh and with a divinylbenzene content of two to twenty percent (600 Å pore) were used.

CH,

The reaction scheme used for the polymer-attachment was as



(A)

4

Treatment of (A) with MCl_4 (where M = Ti, Zr and Hf) in benzene results in the formation of mono cyclopentadienyl metal trichlorides. In general treatment of (A) with a metal chloride of the formula MCl_n proceeds as shown in the following reaction scheme:



(M = Ti, Zr, Hf, Nb, Mo, W)

Initial studies with Nb, Mo, and W chlorides indicated the polymer-attachment of the cyclopentadienyl metal chloride. But the present work was directed mainly to Zr, Ti and Hf.

The mono cyclopentadienyl titanium trichloride, on reduction, produces an active catalyst whose hydrogenation efficiency is about twenty times as great as the corresponding non-attached species. This was attributed to the ability of the rigid supporting matrix used (20% divinylbenzene) to keep metal atoms apart, preventing dimerization and the accompanying loss in activity. The supported catalyst also has been shown to have selectivity towards molecules of different bulk. The general trend among the supported catalyst systems is toward slower rates for larger substrates as observed by Kroll.¹⁴ This behavior is substantially different from ordinary heterogeneous catalysts.

Study of the physical nature of the metal catalyst dispersion on the polymer support by using an electron microprobe X-ray fluorescence study indicates that the dispersion is uniform throughout the entire section of the bead. The diffusion of reagents into the interior of the beads was found to be slow and depended on the polarity of the solvent.¹² The samples of attached catalyst contain the catalytic sites surrounded by nonpolar-aromatic groups. Polar solvents tend to decrease the pore size and consequently decreases the rate of diffusion of the reagents. The reducing agent and the olefin used in the hydrogenations may not be able to diffuse into the interior of the polymer bead and reach all the catalytic sites. This could be avoided by grinding the beads prior to hydrogenation. The substrates would no longer have to diffuse through the pore structure of the polymer beads to reach the catalytic sites. This was observed to be very successful by Kroll.¹⁴ The ground beads in this research were found to be about eight times more active than the whole beads.

Another area of interest with metallocenes (titanocene in particular) is the nitrogen fixation. Two titanocenes seem to be required for the formation of dinitrogen complex, $^{3,15-18}$ followed by its reduction to ammonia as shown by the following reaction.



6

But in the supported titanocene system, the titanium centers are too far apart to form the dinitrogen complex and so is not expected to be a nitrogen fixing catalyst. This was found to be true by Kroll,¹⁴ using both Van Tamelin¹⁵⁻¹⁷ and Vol'pin-Shur¹⁸ nitrogen fixation schemes. With this problem in view, an attempt was made in this work to see whether using a lesser crosslinked polymer matrix, one can bring the titanium centers close enough (as the polymer would be less rigid or more flexible) to form the dinitrogen complex.

EXPERIMENTAL

Manipulations involving air-sensitive materials were performed under argon in Schlenk-type (airless ware) vessels. Small amounts of polymer supported complexes were routinely treated in 50 ml septum stoppered erlenmeyer flasks with reagents drawn from needle-tipped burets. Where necessary, the transfers were made in an argon filled glove box.

Far infrared spectra in the region 100-600 cm⁻¹ were obtained on a Digilab model FTS-16 Fourier Transform Spectrophotometer. 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 box. The spectra were recorded with the sample in a dry nitrogen atmosphere and mounted between polyethylene plates.

An ARL-EMX/SM Electron microprobe¹⁹ was used to study the physical nature of the metal catalyst dispersion on the polymer support. The polystyrene beads embedded in wax block were sliced by using a microtome and mounted on a quartz plate (1" X 1").

MATERIALS

The 20% crosslinked (600 Å pore size) and 2% crosslinked macroreticular polystyrene-divinylbenzene copolymer were gifts from the Dow Chemical Company and were washed before use to remove the impurities. Organolithium and organo aluminium reagents were obtained

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from Alfa, while TiCpCl₃ was prepared by previously published method²¹ with some modifications, as described in page 14. TiCl₄ was obtained from J. T. Baker Chemical Co., $ZrCl_4$ and $HfCl_4$ were obtained from Alfa and TiCl₃ was obtained from Research Organic/Inorganic Chemical Corp. Chloromethyl ethyl ether was obtained from Aldrich Chemical Co., and was distilled before use. Tetrahydrofuran (THF), hexane, benzene, and toluene were distilled over sodium-benzophenone complex under argon. Diethyl ether was refluxed over lithium aluminium hydride before distillation. Pyridine was stored over sodium hydroxide pellets before distillation over barium oxide under argon.

Preparation of Cyclopentadienyl-Substituted Copolymer

Two hundred grams of 20% crosslinked copolymer beads were washed with 10% HCl, 10% NaOH, H_2O , H_2O-CH_3OH , CH_3OH , $CH_3OH-CH_2Cl_2$ and CH_2Cl_2 as recommended by Pittman.²² They were then vacuum dried. Following the chloromethylation method of Pepper, <u>et al.</u>,²³ 1 ℓ of freshly distilled chloromethyl ethyl ether* was added to the beads in a 2 ℓ three-necked flask with a drying tube and an overhead stirrer. The flask was cooled in ice for 2 hours. A solution prepared by cautiously adding 35 ml SnCl₄ to 125 ml of ice-chilled chloromethyl ethyl ether was then introduced slowly. After vigorous stirring of the reaction mixture at room temperature for 30 hours, the ether was removed by filtration. The beads were washed with four 1 ℓ portions

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^{*}Caution is advised in chloromethylation and in the handling of chloromethyl ethyl ether because the related compound dichlorodimethyl ether is carcinogen as is the monochloro ether.

of 50% aqueous dioxane, aqueous dioxane containing 10% HCl (v/v), and, finally, with dry dioxane, until the washings were chloride free. Chloride analysis of the chloromethylated copolymer after it had been dried for two days <u>in vacuo</u> yielded 1.30 meq Cl⁻/g or a 14% chloromethylation of the styrene rings.

The above obtained chloromethylated beads were treated with 300 ml dry THF and 300 ml of 1.6 M sodium cyclopentadienide in THF. After the mixture was stirred for 5 days at room temperature, excess sodium cyclopentadienide and THF were removed by filtration and the product was washed with 1:1 dry, airfree ethanol: THF until the washings were chloride free. The product was washed with three one liter portions of THF and then dried in vacuo for several days and yielded beads containing 1.1 meq Cp $(C_5H_5)/g$ (by Cl⁻ difference).

Preparation of the cyclopentadienyl substituted, 2% crosslinked copolymer beads, were done by following the above described method for 20% crosslinked beads. Figure 3 summarizes the reaction scheme used.

Preparation of Copolymer-Attached TiCpCl₃

Cyclopentadiene substituted copolymer was converted to the cyclopentadienide anion by treatment with a two-fold excess of butyl lithium in benzene. After being stirred overnight under argon, the solution was removed, washed with benzene five times. The beads were then treated with a two-fold excess of TiCl_4 in benzene and were stirred for 2 days. The beads were then separated by filtration and washed with benzene in a soxhlet extractor until excess chloride had been removed. Extraction with THF converted the dark colored beads to



Reaction Scheme for Preparation of Cyclopentadienyl-Substituted Copolymer Figure 3.

yellowish beads. They were washed a few times with THF, and dried at room temperature <u>in vacuo</u> overnight. The flask containing the beads was covered with aluminium foil and cooled in ice bath, chlorine gas was added and bright yellow beads were formed. Figure 4 shows the reaction scheme.

Analysis: Ti = 0.282 mmol/g of beads Cl = 0.811 mmol/g of beads Ti:Cl ratio = 2.88 (found) = 3.00 (calcd)

<u>Far Infrared Spectrum</u>: (polymer-attached) 452, 422, 380, 333 cm⁻¹ (nujol mull): (non-attached) 450, 418, 381, 331, 295 cm⁻¹ (nujol mull).



Figure 4. Reaction Scheme for Preparation of Polymer-Supported TiCpCl₃

Preparation of Copolymer Containing TiCpCl₂

Cyclopentadiene substituted copolymer was convered to the cyclopentadienide anion by treatment with a two-fold excess of methyl lithium in ether. After being stirred overnight under argon, the solution was removed and washed with THF five times. The beads were then treated with a two-fold excess of TiCl₃ dissolved in THF (was dissolved by using soxhlet extraction). The beads were separated by filtration and washed with THF in a soxhlet extractor until excess chloride had been removed. The violet blue beads were dried <u>in vacuo</u> and stored in a dry box.

Preparation of Copolymer-Attached $ZrCpCl_3$ and $HfCpCl_3$

 $ZrCl_4$ and $HfCl_4$ are solids (unlike TiCl_4 which is a liquid) and are sparingly soluble in most organic solvents. So following the procedure described for preparation of attached TiCpCl_3 (Page 10), only a very small amount (~ 0.06 mmol M/gm) of the species MCpCl_3 (where M = Zr, Hf) could be attached to the polymer support. The method was modified by using $ZrCl_4$, 2Py and $HfCl_4$. 2Py adducts. The pyridine adducts were prepared, following the procedure described by Ray and Westland.²⁴ $ZrCl_4$ was suspended in dry benzene and slightly more than a two-fold excess of dry pyridine was added. The reaction mixture was cooled in ice and vigorous stirring for two hours produced a white suspension, but the stirring was continued for a further 24 hours to ensure complete reaction, at room temperature.

The MCl₄. 2Py (M = Zr and Hf) adduct in benzene made above was then added to the polymer beads containing cyclopentadienide anion attached, in benzene and allowed to stir for 48 hours at room temperature. The cream colored beads were filtered, washed with dry benzene, followed by dry THF, in a soxhlet extractor until excess chloride had been removed. The cream colored beads were dried in vacuo. Figure 5 illustrates the reaction scheme:



Figure 5. Reaction Scheme for Preparation of Polymer-Attached ZrCpCl₃ and HfCpCl₃

Analysis:

Zr = 0.293 mmol/g	Hf = 0.250 mmol/g
C1 = 0.830 mmol/g	C1 = 0.700 mmol/g
Zr:Cl ratio = 2.83 (found)	Hf:Cl ratio = 2.80 (found)
= 3.00 (calcd)	= 3.00 (calcd)

Preparation of Cyclopentadienyl Titanium Trichloride

A mixture of 36.0 g (0.096 moles) of bis(cyclopentadienyl)titanium dichloride, 50.2 g (0.272 moles) of titanium tetrachloride, and 150 ml of dry xylene was heated at the boiling point of xylene (\sim 140°) for 2 1/2 hours. The reaction mixture was then cooled to room temperature, and yellow crystals of the product separated. These were filtered under dry nitrogen, washed with hexane, and dried briefly under nitrogen. The crude product was then dissolved in minimum amount of boiling benzene. Charcoal was then added to the solution and it was stirred for one hour. The solvent was removed by evaporation and the product was dried <u>in vacuo</u>. The crude product was transferred into a soxhlet extractor in a dry box under argon and extracted with 100 ml dry benzene. After a couple of hours the solution was cooled to room temperature and the yellow crystals of cyclopentadienyl titanium trichloride were separated by filtration under argon and vacuum dried (\sim 75% yield).

Preparation of 2% Crosslinked Copolymer Containing TiCp₂Cl₂

100 g cyclopentadiene substituted 2% crosslinked beads (\sim 2 meq C_5H_5 per gm. of beads) was treated with a two-fold excess of methyl lithium in ether and allowed to stir for two days. The beads were filtered, washed with dry THF. The product was suspended in dry THF and a solution containing 70 g TiCpCl₃ (0.32 moles) dissolved in dry benzene was introduced and the mixture stirred for three days. Excess TiCpCl₃ was removed by extracting with benzene in a soxhlet extractor, followed by a similar extraction with THF. The product, red colored beads, was dried <u>in vacuo</u> for two days. Figure 6 gives the reaction scheme:

Analysis: Ti = 0.788 mmol/g Cl = 1.499 mmol/g Ti:Cl ratio = 1.90 (found) = 2.00 (calcd) Far Infrared Spectrum:

(polymer-attached): 402, 362, 307, 280, 256 (broad) and 196 cm⁻¹ (nuiol mull)

(non-attached): 400, 360, 303, 276, 247, 206 cm⁻¹ (nujol mull)



Figure 6. Reaction Scheme for Preparation of Polymer-Attached TiCp_2Cl_2

 $\label{eq:preparation} \ensuremath{\mathsf{Preparation}}\xspace{0.5ex} \ensuremath{\mathsf{Opp}}\xspace{0.5ex} \ensure$

To 2 g (1.72 mmol Ti) of polymer-attached TiCp₂Cl₂ in a 50 ml septum stoppered vessel was added 10 ml tri-n-butyl aluminium.²⁵ The reaction mixture was stirred at 110° for three hours to produce the dark red-brown aluminium-titanium adduct. After the excess aluminium alkyl was removed, the beads were washed with diethyl ether to give a blue-grey species which became olive green when dried <u>in vacuo</u> for several hours. Analytical results are reported in Table 2, page 33.

Figure 7 shows the reaction scheme for the preparation of copolymer containing $TiCp_2Cl$.



Figure 7. Reaction Scheme for Preparation of Polymer-Attached TiCp₂Cl

Preparation of Copolymer Containing $\text{TiCp}_2(\text{CH}_3)_2$

Polymer-attached TiCp₂(CH₃)₂ was prepared by the method described by Clauss and Bestian²⁶ for monomeric TiCp₂(CH₃)₂ with appropriate modifications. To 2 g (1.6 mmol Ti/g) of polymer-attached (2% crosslinked) TiCp₂Cl₂ maintained at dry ice-acetone temperatures was added 20 ml diethylether and 10 ml of 1.64 M methyl lithium in ether. The mixture was stirred and allowed to warm slowly to room temperature. After four hours, the excess methyl lithium solution was removed by syringe and the copolymer was extracted with THF until the washings were chloride free. The yellow product was stored under argon at -10°; analytical results are reported in Table 2 and the far infrared spectrum discussed in page 35.

Analytical Methods

Halide from the chloromethyl groups was removed from the copolymer with hot pyridine and determined by the Volhard technique.²⁷ Titanium, zirconium and hafnium were determined²⁸ by ignition of the metal-containing polymer at 900° for eight hours and weighed as the oxide. Titanium was also analyzed by spectrophotometry of the titanium-peroxide complex. The two methods agree closely. Titanium complexed chloride was removed by digestion of the powdered polymer samples in 2N KOH solution at 80° for eight hours. Chloride was determined by the Volhard method following acidification of the aqueous supernant.

ELECTRON MICROPROBE STUDIES

Metal catalysts are often made in a high degree of dispersion on the surface of a high-area solid (polystyrene beads in this work). The knowledge of the metal catalyst dispersion on the polymer support surface will help understand the catalytic process taking place and the catalytic activity also.²⁹ The investigation was carried out by using an electron microprobe X-ray fluorescence study of titanium, zirconium and chlorine, supported on the copolymer beads as the cyclopentadienyl metal chlorides.

Experimental

The polymer-supported $TiCpCl_3$, $TiCp_2Cl_2$, and $ZrCpCl_3$ were prepared according to the procedures described in pages 10-15. The beads were sliced by using a microtome. Since the beads were fragile, they had to be coated with wax before slicing them. This was done by adding some beads to molten wax in a metal container and allowing it to cool, to solidify. The wax block containing the beads was mounted on a microtome and sliced. The sliced sections were about 10 microns in thickness. Selected thin sections of the beads were then placed on a 1" X 1" quartz plate and most of the wax was removed by careful melting. The rest of the wax was removed by careful rinsing with xylene. The sections were then mounted on the quartz plate by using a contact cement, "Zipbond". A thin evaporated carbon coating was

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applied to give good surface conductance. Analyses were done with three or four beads of each sample, selected at random.

Radial profiles of Ti, Zr, and Cl in the sample were determined from the traverses of sectioned beads with the ARL-EMX/SM electron microprobe* at the Horticulture Department of Michigan State University.¹⁹

The microprobe conditions were the following:

25 KV accelerating voltage

.01 µa sample current

1 µm beam width

 K_{α} X-ray lines were used for titanium and chlorine. L_{α} X-ray line was used for zirconium. The crystal used for titanium was LiF and $(NH_{\Delta})_{2}HPO_{\Delta}$ crystal for zirconium and chlorine.

Results

Electron microprobe X-ray fluorescence analysis of the sectioned beads gave radial distributions of the metal and chloride as exemplified by the results of figures 14 and 15 (pages 40 and 41). The metal and chloride distributions on the polymer bead support is uniform through the entire section of the bead. Similar results were obtained for the other polymer-supported cyclopentadienyl metal chlorides of zirconium and hafnium. Figure 16 shows the K_{α} X-ray micrographs of polystyrene-supported TiCpCl₃ for titanium and chlorine. This also corresponds to a uniform distribution of the metal and chloride on the beads.

^{*}Technical assistance of Vivian E. Shull, Department of Horticulture is appreciated.

INFRARED STUDIES

The vibrational spectra of tetrahedral cyclopentadienyl halogeno complexes of Ti(IV) and Zr(IV), in the low frequency region of 100-600 cm⁻¹ have been reported in two recent publications.^{30,31} The spectra of these complexes in the high frequency region (600-5000 cm⁻¹) are relatively simple to interpret, as they are not complicated and are similar to those of Cp₂Ru and Cp₂Fe, for which the theoretical bands assignments are available.³² But, in the low frequency region their spectra are difficult to interpret because the metal-ring and the metal-halogen stretching frequencies lie in the same region.

In this investigation, the low frequency infrared spectra in the region 50-600 cm⁻¹, of the polymer-supported compounds in the solid state was studied. The spectra obtained were substantially in agreement with those reported in the literature.

The infrared spectra were measured on a Digilab model FTS-16 Fourier Transform Spectrophotometer. Samples prepared by crushing the polystyrene beads in a ball mill under argon in a dry box and their nujol mulls sandwiched between polyethylene plates. The spectra were recorded in a dry nitrogen atmosphere. The spectral resolution was approximately 4 cm⁻¹, with an accuracy of ± 1 cm⁻¹.

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Use of the Reduced Copolymer-Attached Complexes as Catalyst

(1) Olefin Reduction

All solvents used were reagent grade, further purified and deoxygenated by refluxing and distilling under nitrogen with the sodium (or potassium)benzophenone complex. n-Hexane was distilled over CaH₂. All the liquid substrates were distilled from sodium under argon.

The hydrogenations were carried out by using gas burets of 100 ml volume. The hydrogen uptake was measured at normal atmospheric pressure and at $20^{\circ} \pm 0.5^{\circ}$ C.

Alkenes were obtained from Aldrich Chemical Co., and from Chemical Samples Co.

All reductions were carried out in a 100 ml round-bottomed flask, with a side arm. The catalyst was weighed into this flask, suspended in 10 ml of hexane, and treated with 1 ml of 2.0 M BuLi in hexane for two hours. The excess BuLi was removed and the sample washed few times with hexane by using a syringe and a needle. The reduced catalyst was then taken in 9 ml hexane and the appropriate olefin was then added by means of a syringe. The rate of hydrogen uptake was measured by using the gas buret as mentioned earlier.

Homogeneous CpTiCl₃ Hydrogenations

A 0.071 g sample of TiCpCl₃ (0.3238 mole) was weighed into a 100 ml sidearm round-bottomed flask under argon, attached to the hydrogenation unit. The line was flushed with hydrogen by alternate vacuum and hydrogen addition, cycled a few times to remove the oxygen from the system before solvent addition. BuLi (0.97 mmol) was then added and allowed to stir for two hours. The appropriate olefin was then added and hydrogen uptake rate was measured, with the reaction vessel immersed in a 20° water bath. The results are presented in Table 8 on page 52.

Polymer-Supported TiCpCl₃ Hydrogenations

A 0.0354 g sample of polymer-attached TiCpCl₃ (0.0085 mmol Ti) was weighed into a 100 ml sidearm round-bottomed flask under argon. After attachment to the hydrogenator and hydrogen flushing, the beads were treated with 10 ml of hexane and 1 ml of BuLi in hexane. After two hours of stirring, the excess of BuLi was removed and the reduced beads were rinsed with two 10 ml portions of hexane. Then the beads were placed in 9 ml of hexane, the appropriate olefin substrate was added and the hydrogen uptake rate was measured. The substrates tested were cyclohexene, 1-hexene and cyclooctene. The rate observed for cyclohexene was 30 ml/min- mmol Ti, for 1-hexene it was 42 ml/min-mmol Ti and 7.6 ml/min-mmol Ti, for cyclooctene.

One sample of the polymer-attached TiCpCl₃ was tested with sodium naphthalene as the reducing agent. For this experiment, the same procedure as above was used, except that 1 ml of 0.3 M NaNp in THF was added to the beads in 10 ml of THF. After being stirred for three hours, the excess NaNp was removed and the beads were rinsed with three 10 ml portions of hexane. Then the beads were placed in 9 ml of hexane, the substrate was injected and the hydrogen uptake was measured. The rate observed for cyclohexene was 20 ml/min-mmol Ti and 32 ml/min-mmol Ti, for l-hexene.

In the above hydrogenations using BuLi and NaNp as the reducing agents, the sample was used for more than one substrate hydrogenation experiment. After completing the hydrogenation of one substrate, the solvent was removed, the beads were rinsed with three 10 ml portions of hexane and the hydrogenation was repeated with the same substrate or another substrate. The results were reproducible.

The same reduction procedure was repeated using the beads which were thoroughly ground in a ball mill under argon, before use. The ground beads were about eight times more active than the whole beads towards hydrogenation. The initial rate observed was 194 ml/min-mmol Ti, for cyclohexene, 390 ml/min-mmol Ti, for l-hexene and 60.5 ml/min-mmol Ti, for cyclooctene.

Polymer-Supported TiCpCl₂ Hydrogenations

A 0.1 g sample of polymer-attached TiCpCl₂ (0.011 mmol Tì) was weighed into a 100 ml sidearm round-bottomed flask under argon. After attachment to the hydrogenator and hydrogen flushing, the beads were treated with 10 ml hexane and 1 ml of BuLi in hexane. After two hours of stirring, the excess BuLi was removed and the beads were rinsed with two 10 ml portions of hexane. Then the beads were taken in 9 ml of hexane, the substrate was injected and the hydrogen uptake measured. The substrates used were 1-hexene, cyclohexene and cyclooctene. The rate observed for 1-hexene was 36.5 ml/min-mmol Ti, 22.7 ml/min-mmol Ti, for cyclohexene and 13.6 ml/min-mmol Ti, for cyclooctene.

Polymer-Supported ZrCpCl₃ and HfCpCl₃

The hydrogenations were carried out, following the above described procedure for polymer-attached TiCpCl₃. The substrates used were 1-hexene, and cyclohexene. The rates of hydrogenation was about 2 ml/min-mmol of metal in both cases.
RESULTS AND DISCUSSION

Homogeneous transition metal catalysts have so far found only limited industrial use, mainly because of their difficulty of separation from the reaction products. Heterogeneous catalysts have been widely used in industry for many years, and a great deal has been learned about them. A homogeneous catalyst can be heterogenized in a variety of ways, as discussed in recently published review articles.^{8,33,34} The common method is to attach it to a solid support by adsorption or by an ionic or covalent chemical bond. Less common methods involve polymerizing the catalyst so that it becomes insoluble in the medium in which it is to be used, or by trapping it in a gel or other porous medium.

The catalyst heterogenized by linking it to a polymer consists of the insoluble, polymeric portion, which is the catalyst support, and the catalytic portion, which projects into the solution and is solvated and, in a sense, dissolved in it. The polymer support must be inert to the reagents that are to be in contact with it and it must withstand the temperatures and pressures that are required reaction conditions. Polystyrene-divinylbenzene seems to meet all these requirements and offers a convenient method to support the cyclopentadienyl metal chlorides.

The main difficulty in the field of polymer-supported catalysts, is the determination of the structure and the exact nature of the active

catalyst. Elemental analysis of the complexes gives the amount of the elements that are present, but this information is of only limited use. Detailed information about the environment of the metal atom and how it changes when chemical reactions occur is generally not known. Attempts have been made in this work to get some information of the nature of the complex by using far infrared and electron microprobe X-ray fluorescence studies.

A copolymer of 80 percent styrene and 20 percent divinylbenzene in the form of reticulated beads with a pore size of about 600 Å was chosen. This highly crosslinked polymer is quite rigid, totally insoluble, and has a very high surface area to volume ratio, due to its porous nature. The first step in the polymer support scheme is the attachment of chloromethyl (-CH₂Cl) group to the aromatic rings in the polystyrene-divinylbenzene copolymer beads. The chloromethylation procedure was discussed in pages 9 and 10. The chloromethylated beads were found to have 1.30 mmol of chloride/g of beads by analysis. The analytical method used was to reflux the polymer in pyridine and then determine the chlorine content of the pyridine using standard Volhard analysis.³⁵ The following reaction illustrates the chloromethylation step

 $C1CH_2 - 0 - C_2H_5/SnC1_4$ 1) dioxane H₂O wash 2) anhy. dioxane Polystyrene/DVB ΗͻϹΙ

1.30 meg/g Cl; ∿14.0% phenyl rings chloromethylated

(Pepper, <u>ct al.</u>)

Substitution of the chloride of the chloromethyl groups attached to the polymer support, with cyclopentadienide ion was done by using sodium cyclopentadienide. The procedure is outlined in page 9. Analysis of the washed, dried beads indicated that the substitution was very good (about 80%). The following reaction illustrates this substitution.



1.10 meg/g

Cyclopentadiene substituted copolymer was then converted to the cyclopentadienide anion by treatment with alkyl lithium as described in page 10. This step eliminates the unreacted chloromethyl groups and completes the substitution reaction. Because the procedure completely eliminates - CH_2Cl , the halogen analyses reported in tables 2 and 3 do not reflect the presence of chloromethyl chloride after the conversion of cyclopentadiene to cyclopentadienide by treatment with methyl lithium. The treatment of cyclopentadienide anion attached to the polymer with MCl_n results in the formation of polymer-attached

 $MCpCl_{n-1}$ (where M = Ti, Zr and Hf), as described in pages 10-14. The preparation of other metal cyclopentadienyl derivatives attached to the polymer were also described in pages 14-18.

Optical Properties

The optical properties of these cyclopentadienyl metal chlorides (especially Ti compounds) are striking. For example, titanocene dichloride is dark red in color, monocyclopentadienyl titanium trichloride is bright yellow, titanocene is dark grey, bis cyclopentadienyl titanium dimethyl is yellow, bis cyclopentadienyl titanium mono chloride is green, mono cyclopentadienyl titanium dichloride is purple, mono cyclopentadienyl zirconium and hafnium trichlorides are cream colored. So one would expect, to some extent the polymerattached species involving the above described compounds to be similar in color, and they were found to be so. The following table summarizes the colors of the non-attached and polymer-attached species.

Table 1

Colors of Non-Attached and Polymer-Attached Metal Cyclopentadienyl Compounds

Species	Non-Attached	Polymer-Attached
TiCp ₂ Cl ₂	Dark red	Salmon to red (depending on the Ti concentration)
TiCp ₂ (CH ₃) ₂	Yellow	Yellow
TiCpCl ₃	Bright yellow	Bright yellow
TiCpCl ₂	Purple	Violet-blue
TiCp ₂ Cl	Green	Olive Green
ZrCpC1 ₃	Cream	Cream
HfCpC1 ₃	Cream	Cream



Colors of Polymer-Attached and Non-Attached Titanium Species Figure 8.







The colors of the polymer-attached species are illustrated in Figures 8, 9 and 10. A close resemblance in color of the non-attached and polymer-attached species is observed. Also the intensity of the color of the polymer-attached species was found to be approximately proportional to the concentration of the attached species, as expected.

Analytical Results

The next step in the identification of the polymer-attached species was the metal and chloride analysis. Metals titanium, zirconium and hafnium were determined²⁸ by ignition of the metal containing polymer at 900° for eight hours and weighed as the oxide. Titanium was also analyzed as peroxide complex spectrophotometrically, after the polymer matrix was decomposed and the sample taken in acid solution. The two methods agree closely. Metal complexed chloride was removed by digestion of the powdered polymer samples in 2N KOH solution at 80° for eight hours. Chloride was determined by the Volhard method following acidification of the aqueous supernant. The results of the analysis are summarized in Tables 2 and 3. The expected and the observed metal to chloride ratio agree reasonably well.

Infrared Studies

Additional evidence to characterize the polymer-supported species was obtained using a Digilab model FTS-16 Fourier Transform Spectrophotometer (far infrared spectra). The experimental portion of this work was discussed in page 21. Comparison was made between the spectra of non-attached and polymer-attached species. Figure 12 shows the far infrared spectra of non-attached TiCp₂Cl₂ and polymer-attached

Table 2

Analytical Results

Substituent	Chloride (mmol/g)	Titanium (mmol/g)	Calcd	Cl:Ti Ratio Found
-сн ₂ с1	1.20			
-СН ₂ СрН	0.17			
-CH ₂ CpTiCpCl ₂	0.543	0.281	2	1.93
-CH ₂ CpTiCp(CH ₃) ₂	0.00	0.233		
-CH ₂ CpTiCp				
-CH ₂ CpTiCpCl	0.285	0.274	1	1.04
CH ₂ CpTiCl ₃	0.811	0.282	3	2.88
-CpTiCpCl ₂	0.115	0.058	2	1.93

Table 3

Analytical Results

Substituent	Chloride (mmol/g)	Metal M (mmol/g)	C Ra	I:M atio
		(Calcd	Found
-CH ₂ C1	1.30			
-СН ₂ СрН	0.20			
-CH ₂ CpTiCl ₃	0.811	0.282	3	2.88
-CH ₂ CpTiCl ₂	0.209	0.110	2	1.90
-CH ₂ CpZrCl ₃	0.830	0.293	3	2.83
-CH ₂ CpHfC1 ₃	0.700	0.250	3	2.80
-CH ₂ CpTiCpCl ₂	1.499	0.788	2	1.90
(2% cross linked)				

TiCp₂Cl₂. The bands agree closely. These bands are also in substantial agreement with the reported data in the literature.^{30,31} The band assignments were deduced from these reported data. The spectral data are summarized in Table 4.

Table 4

Far Infrared Bands of Polymer-Supported TiCp_2Cl_2 and Non-Attached TiCp_2Cl_2 (Nujol Mull) in cm⁻¹

Non-Attached TiCp ₂ C1 ₂	Polymer-Attached TiCp ₂ Cl ₂	Assignments
400	402	ν (M-C1)
360	362	ν (M-Cp)
303	307	ring tilt
276	280	na
247	broad	ring tilt
206	196	δ (Cl-M-Cl) bending

na - not assigned

The assignments were made by comparison with those reported by Edward Maslowsky, Jr., <u>et al.</u>,³¹ and E. Samuel <u>et al</u>.³⁰

Figure ¹¹ illustrates the far-infrared spectra of non-attached $TiCp_2Cl_2$ and polymer-supported $TiCp_2Cl_2$.

The infrared spectrum of polymer-supported $\text{TiCp}_2(\text{CH}_3)_2$ showed the absence of the intense (Ti-Cl) stretching frequency and the presence of a strong v(Ti-me) band at 475 cm⁻¹ as expected. The observed bands are at 265, 368, 410, and 475 cm⁻¹.





The far infrared spectra of non-attached and attached TiCpCl₃ also agree well.

The Table 5, summarizes the spectral data obtained for non-attached TiCpCl₃ and polymer-attached TiCpCl₃. The assignments were deduced from the reported data. 30,31

Table 5

Far Infrared Bands of Non-Attached TiCpCl₃ and Polymer-Attached TiCpCl₃ in cm^{-1} (Nujol Mull)

Non-Attached TiCpCl ₃	Polymer-Attached TiCpCl ₃	Assignments
450	452	v(Ti-Cl)
418	422	v(Ti-Cp)
381	380	na
331	333	ν(Ti-Cp)
295		ring tilt

na - not assigned

Figure 12 illustrates the far-infrared spectra of non-attached $TiCpCl_3$ and polymer-attached $TiCpCl_3$.

The bands for polymer-attached $ZrCpCl_3$ and $HfCpCl_3$ are broad compared to the analogous titanium compound bands. The bands lie in the region 300-400 cm⁻¹ as expected, but there are no reported data for comparison (mainly because of the low yield and difficulty of purification), for the non-attached $ZrCpCl_3$ and $HfCpCl_3$. The observed bands for these polymer-supported compounds are 468, 410, and 324 cm⁻¹. The interpretation and comparison in going from titanium to zirconium





will depend on the definite assignments of these bands. One would expect the metal-chloride stretching frequency to decrease in progression from titanium to zirconium to hafnium on the basis of mass consideration. It has been observed that the (M-Cp) bands show little dependence on the nature of the metal and take values between 300 and 360 cm⁻¹. This is attributed to the closely related structures and same oxidation state of the metals. Also from the reported data for ZrCp_2Cl_2 and HfCp_2Cl_2 , one could observe that there is little difference between the (M-Cl) and (M-Cp) bands for these compounds. This probably is the reason why the polymer-supported ZrCpCl_3 and HfCpCl_3 far-infrared bands lie in the same region.

Electron Microprobe Studies

The knowledge of the physical nature of the metal catalyst dispersion is useful in understanding the chemical properties of the polymer-attached compound. The electron microprobe X-ray fluorescence study would indicate whether the metal catalyst is dispersed mainly on the surface of the polymer bead or distributed uniformly within the entire section of the bead. The experimental part of this work was described in page 19. Electron microprobe X-ray fluorescence analysis of the sectioned beads gave radial distributions of the metal and chloride as exemplified by the results of the Figures 13 and 14. Figure 13 gives the K_{α} X-radiation counts per second of titanium and chloride in the polymer-supported TiCpCl₃, as a function of the radial distance of the section in microns.









Supported TiCp₂Cl₂



Most of the sections studied were thin sections of about 10 microns in thickness and about 500 microns in length, as illustrated by the above diagram. The analyses were carried out for three or four beads of each sample, selected at random.

The metal and chloride distributions on the polymer bead support were uniform through the entire section of the bead. Similar results were obtained for the other polymer-supported metal cyclopentadienyl chlorides of titanium and zirconium. Figure 14 shows the radial distribution of titanium and chlorine in polymer-supported TiCp₂Cl₂. Figure 15 shows the K_{α} X-ray micrographs for titanium and chlorine in polymer-attached TiCpCl₃, which also corresponds to a uniform distribution of the metal and chloride on the polymer bead.

Chemical Reactions

The polymer-attached compounds undergo chemical reactions analogous to its non-attached counterpart. Following are some of such reactions.





Polymer-attached TiCp_2Cl_2 on 2% crosslinked copolymer, when treated with CH_3Li in ether, underwent reaction similar to non-attached TiCp_2Cl_2 , forming $\text{TiCp}_2(\text{CH}_3)_2$ on the polymer. The experimental procedure was discussed in page 17. The reaction scheme is as follows:



(Stable at R.T.)

A similar reaction has been observed earlier by Bonds⁵ and by Gibbons,³⁶ by using 20% crosslinked copolymer-supported TiCp₂Cl₂. Bercaw <u>et al.</u>,³ have studied the reaction of homogeneous TiCp₂Cl₂ with CH₃Li. Polymer-supported dimethyl titanocene, TiCp₂(CH₃)₂, is significantly less reactive than free TiCp₂(CH₃)₂ in solution. Attempts to decompose the yellow colored beads in a hydrogen atmosphere thermally were unsuccessful. But treatment of a mixture of polymer-supported TiCp₂(CH₃)₂ and free TiCp₂(CH₃)₂ by using the slurry technique described by Bercaw and Marrich,³ resulted in the formation of CH₄. Treatment of polymer-attached TiCp₂(CH₃)₂ with anhydrous HCl produces TiCp₂Cl₂ on the polymer, as shown in the above reaction scheme. Similar results were observed⁵

earlier in this laboratory, when polymer-attached (20% crosslinked copolymer) $\text{TiCp}_2(\text{CH}_3)_2$, $(\text{TiCp}_2\text{H})_x$ and butyllithium reduced TiCp_2Cl_2 were treated with anhydrous HCl results in the formation of TiCp_2Cl_2 . This is particularly encouraging, because this observation is different from its homogeneous analogue. Homogeneous titanocene and its hydrides readily undergo a thermally induced rearrangement to form a dimer containing both σ - and π -bonded cyclopentadienyl residues.^{2,3} This complex is not converted to TiCp_2Cl_2 , when exposed to HCl, but rather forms a green chloride containing dimer. Therefore, it is concluded that these polymer-attached species retain their bis- π -cyclopentadienyl integrity throughout the reduction procedure.

The formation of polymer-supported $\text{TiCp}_2(\text{CH}_3)_2$ by treatment of polymer-attached TiCp_2Cl_2 and CH_3Li has been supported by the chemical analysis and by the far infrared spectrum. The chemical analysis showed the absence of chloride as reported in Table 2, page 33. The far infrared spectrum showed the disappearance of Ti-Cl stretching frequency and the appearance of a strong Ti-CH₃ stretching frequency around 475 cm⁻¹.

Treatment of polymer-attached TiCp_2Cl_2 with tri-n-butyl aluminum proceeded according to the reaction reported²⁵ for homogeneous titanocene dichloride. The experimental procedure is outlined in page 16. The reaction scheme is as follows:



The olive green polymer-attached complex was identified by its color and chemical analysis. The product is very air-sensitive and it was not possible to obtain the far infrared spectrum. The analytical results are reported in Table 2, page 33.

Treatment of the above product with anhydrous HCl at room temperature produced polymer-attached TiCp_2Cl_2 , as shown in the following reaction:



Reduction of polymer-supported TiCp_2Cl_2 with BuLi in hexane has been observed by Gibbons.³⁶ The BuLi reduced species forms an active hydrogenation catalyst under hydrogen at room temperature. The above observations may be due to the following reaction scheme:



Polymer-attached TiCpCl₃ also was observed to be similar in its chemical behavior to non-attached TiCpCl₃. Treatment of the polymer-attached TiCpCl₃ with CH₃Li in ether, produced the methyl derivative, as shown by the Ti-CH₃ stretching frequency around 480 cm⁻¹. Both TiCpCl₃ and TiCp(CH₃)₃ are yellow and so the reactions could not be followed by color changes. One would expect the polymer-attached TiCp(CH₃)₃ to form TiCpCl₃, on treatment with anhydrous HCl, as observed earlier in the case of TiCp₂(CH₃)₂.

Treatment of polymer-attached TiCpCl₃ with BuLi produces a dark green product, similar to that observed for homogeneous TiCpCl₃. Treatment of this polymer bound complex with anhydrous HCl results

in the formation of bright yellow colored TiCpCl₃. The BuLi reduced polymer-bound complex under hydrogen at room temperature produces an active hydrogenation catalyst. The polymer-attached complex on treatment with anhydrous HCl results in the formation of TiCpCl₃.

Hydrogenation Studies

The polymer-attached cyclopentadienyl metal catalysts were then tested for their catalytic activity towards hydrogenation of unsaturated organic compounds and in the nitrogen fixation process. The reduction of olefins catalyzed by transition metal complexes generally requires the presence of an open coordination site on the metal. 38 The experimental evidence to date suggests that this is also true in the case of alkyl lithium reduced titanocene derivatives. Only monomeric titanocene species contains such a site. If this is the case, any increase in monomeric species concentration associated with attaching these catalysts to a polymer support should be reflected in an increase in catalytic activity of that complex when compared to a similar non-attached complex under the same conditions. Gibbons³⁶ has studied the hydrogenation ability of polymer-attached titanocene dichloride and found it to be more active than the non-attached titanocene dichloride. The final results of the hydrogenation studies using polymer-supported TiCp₂Cl₂ reduced beads are reported recently.⁵ The results are summarized in Tables 6 and 7.

From the electron microprobe study, it was seen that the catalyst is distributed uniformly within the bead. During the reduction process it was observed that some of the catalyst sites, which are within the bead, were unreduced. It was suggested by Kroll to be due

Catalyst Precursor	mmol-Ti	Olefin	Concen.	Rates, ml H ₂ /m Initial	in-mmol T [.] Maximum
Non-attached TiCp ₂ Cl ₂	0.05	cyclohexene	1.16	5.6 ^a	28
Attached-TiCp ₂ Cl ₂ - Method A	Q 031	cyclohexene	1.16	88.7	same ^C
Non-Ground Method B	0 002	cyc lohexene	0.25	105.6	same
Attached-TiCp ₂ Cl2 ^b ground before reduction	Q 034	cyclohexene	1.16	714	same ^c
Benzyltitanocene dichloride Non-Attached	Ω2	cyclohexene	!	9.5	same
Benzyltitanocene dichloride Non-Attached	Ω2	l-methyl-	1	less than 10 ⁻	4
Titanocene dichloride Non-Attached	Q 2	cyclohexene	;	10	same

^aRepeated runs verify that an induction period is present; bead systems show no such effect.

^bThe dry beads were ground to a fine powder before activation.

^CFor the bead cases, no sign of an induction period is seen.

^dTotal pressure = 760 torr

Table 6

Hydrogenation Rates at 25° with Polymer-Attached and Non-Attached Titanocene Species^d

Table 7

Hydrogenation Rates at 25° with Polymer-Attached Titanocene Species

Olefin	Hydrogenation Rate
(0.5 M in hexane)	(ml H ₂ /min-mmol Ti)
l-hexene	213.0
styrene	243.0
cyclohexene	90.3
l-methylcyclohexene	1.0
l,2-dimethylcyclohexene	0.0
l,3-cyclooctadiene	216.0
l,5-cyclooctadiene	183.0
l-hexyne	(polymer)
3-hexyne	149.0
diphenylacetylene	40.6
cholestenone	0.0
vinylacetate	0.0

to the diffusion problem.¹⁴ If the bead structure is destroyed (by grinding), however, a great increase in rate should be observed, because diffusion through the pores to get to the catalytic sites is then unnecessary. It was observed by Kroll that the rate of hydrogenation measured by using reduced polymer-supported titanocene dichloride is increased by a factor 8 to 10 by grinding the beads prior to hydrogenation. The results are seen in Table 6.

The hydrogenation studies using polymer-attached TiCpCl₃ are summarized in Table 8. The experimental part is discussed in page 22. The hydrogenation rate with the use of homogeneous TiCpCl₃ reduced with BuLi was only 2.0 ml per minute per millimole of titanium for cyclohexene and 2.9 ml/min-mmol Ti for 1-hexene. The hydrogenation rate with the polymer-attached TiCpCl_3 reduced with BuLi was 30 ml/min-mmol Ti for cyclohexene and 42 ml/min-mmol Ti for l-hexene. There is a rate increase of about 15 times with polymer-supported TiCpCl₃ compared to homogeneous TiCpCl₃. The ground beads containing TiCpCl₃ gave a hydrogenation rate of 194 ml/min-mmol Ti for cyclohexene and 390 ml/min-mmol Ti for 1-hexene. This is an increase in rate of about 7 to 10 times compared to the whole beads. This observation is similar to the earlier results found for polymer-attached TiCp₂Cl₂ and attributed to the ease of diffusion of the substrates. So the increase in activation factor for polymer attachment is about 100 times compared to non-attached species. Also, on an operational basis, the non-attached catalyst required more than 40 hours to complete the reduction of cyclohexene, where as the attached catalyst completed the reduction in about 100 minutes. The attached catalyst shows good pseudo-first-order kinetics under a variety of conditions. Figure 16 shows the hydrogenation

Hydrogenation Rates at	20° with Polymer-	Attached TiCpCl ₃ a	ind Non-Attach	hed TiCpCl ₃
Catalyst Precursor	mmol Ti	Olefin	Concen. mole/l	Rates ml/min- mmol Ti Initial
Non-attached TiCpCl ₃	0.36	cyclohexene	1.15	2.00
Polymer-attached TiCpCl ₃	0.0138	cyclohexene	1.15	30.00
Polymer-attached ground TiCpCl ₃	0.0085	cyclohexene	1.15	194.00
Non-attached TiCpCl ₃	0.2937]-hexene	1.15	2.90
Polymer-attached TiCpCl ₃	0.0118]-hexene	1.15	42.00
Polymer-attached ground TiCpCl ₃	0.0085	1-hexene	1.15	390.00
Non-attached TiCpCl ₃	0.32	cyclooctene	1.15	0.5
Polymer attached TiCpCl ₃	0.014	cyclooctene	1.15	7.60
Polymer-attached ground TiCpCl ₃	0.012	cyclooctene	1.15	60.5

Table 8



Figure 16. Hydrogenation Curve for Polymer-Attached TiCpCl₃ (ground beads)

curve for polymer-attached TiCpCl₃. The major determinant in the rates of reduction with the attached catalysts was their size of the copolymer beads. Grinding the beads to a fine powder increased their activity. Another observation that can be made from the Table 8, is that the hydrogenation rate depends on the size of the substrate. The rate decreases as the size of the substrate increases. The order of decreasing rates of hydrogenation through the use of polymer-attached TiCpCl₃ is 1-hexene > cyclohexene > cyclooctene. Figure 17 shows the plot of relative reduction rates observed and the results are summarized in Table 9. This observation is in accordance with the results obtained by Kroll, ¹⁴ using Wilkinson's catalyst.

The hydrogenation rates for polymer-attached $TiCpCl_2$ are summarized in Table 10. The results agree with the earlier observations.

Attempts to use the polymer-bound $ZrCpCl_3$ and $HfCpCl_3$ were not very successful. Only about 3 ml of hydrogen uptake per minute per milliequivalent of the metal was observed. At present, the reason for this observation is not clear. In the past the hydrogenations reported with cyclopentadienyl zirconium catalysts were carried out at high temperature and high hydrogen pressures. The absence of reported rates may be attributed to synthetic problems and probably also to very low hydrogenation rates. Recently some work has been reported on hydrozirconation.^{39,40} The reactivity of $(n^5-c_5H_5)_2ZrCl(R)$ with olefins have been studied. The alkyl zirconium(IV) complexes formed were treated with electrophiles like H^+ , Br_2 , I_2 etc. The yields of the products formed were determined by vapor phase chromatography and were based on $(n^5-c_5H_5)_2Zr(R)Cl$ species, and were between 90 and 100 percent. A similar experiment should be attempted with polymer-bound metal cyclopentadienyl species of zirconium and hafnium.

Table 9

Relative Hydrogenation Rates at 20°

Substrate Used	Hydrogenation Rate ^a	Relative Rate
1-Hexene	42.0	1.00
Cyclohexene	30.0	0.71
Cyclooctene	7.6	0.18

^aIn ml of hydrogen per minute \pm 0.05 ml of hydrogen per min.

Table 10

Hydrogenation Rates	at 20°	with Polymer-	Attached	TiCpCl ₂	
Catalyst Precursor	mmol Ti	Olefin	Concen. M ml	Rates /min-mmol	Ti
Polymer-attached TiCpCl ₂	.011	l-hexene	1.15	36.5	
Polymer-attached TiCpCl ₂	.011	cyclohexene	1.15	22.7	
Polymer-attached TiCpCl ₂	.014	cyclooctene	1.15	13.6	



Figure 17. Relative Reduction Rates

Nitrogen Fixation Studies

The study of the catalytic activity of the polymer-attached species towards nitrogen fixation was attempted. Homogeneous titanocene has been used for nitrogen fixation by several workers. Van Tamelin's method $^{15-17}$ uses sodium-napthalene as the reducing agent and nitrogen is continuously bubbled through the solution. The effluent ammonia may be trapped in an acid trap and quantitatively estimated. In the method of Vol'pin and Shur, 18 the catalyst is treated with organolithium or Grignard reagent in diethyl ether under 100 to 200 atmospheres of nitrogen. Ammonia was quantitatively estimated after the reaction mixture was hydrolyzed.

Attempts were made by Kroll¹⁴ using 20% crosslinked copolymersupported TiCp₂Cl₂ following Van Tamelin's and Vol'pin-Shur's methods. No significant amounts of ammonia were produced by the polymer-supported titanocene beads. This was not very surprising, since researchers in titanocene nitrogen fixation believe that a dinuclear titanium complex is involved in the process, as shown in Figure ¹⁸.



Figure 18. Reaction Scheme for Nitrogen Fixation

This leads to the expectation, that if the supporting matrix in the polymer-supported titanocene system is rigid enough to prevent the

association of the supported titanocene (titanium centers being far apart), then no ammonia formation should be observed in the nitrogen fixation attempts with the beads. The polymer-attached ligands should be mobile enough to have two titanocene centers for the formation of dinitrogen complex. Lower crosslinked (2% crosslinked) copolymer beads may have more mobile polymer matrices compared to the rigid 20% crosslinked copolymer support. Attaching the titanocene species to this 2% crosslinked beads, one would expect the titanium centers to be somewhat closer in distance, to aid the formation of dinitrogen complex. 2% crosslinked polymer-supported titanocenedichloride was prepared as described in page 15. The dark red colored beads looked very much like homogeneous titanocene dichloride (as seen in Figure 11) and the titanium content was 0.78 mmol per gram of the beads. An initial attempt by Van Tamelin's method, by using about 3.9 mmol of titanium gave about 10% ammonia and was very encouraging.
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