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CATALYSIS BY TITANOCENE DERIVATIVES

presented by

John D. Ray

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

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CATALYSIS BY TITANOCENE DERIVATIVES

,

Ву

John D. Ray

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirement

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

ABSTRACT

CATALYSIS BY TITANOCENE DERIVATIVES

By

John D. Ray

Titanocene dichloride has been used for Ziegler-Natta polymerization¹ and nitrogen fixation experiments² as a precursor to the active catalyst. A polymer attached titanocene dichloride can, after reduction with BuLi, catalyze hydrogenation of olefins, hydroformylation, and diene isomerization.^{3,4} Titanocene is a reactive, coordinatively unsaturated species that is predicted to have carbene-like activity.⁵ Singlet carbenes undergo facile insertion into C-H sigma bonds, addition to pi bonds of alkenes and alkynes, and addition to pi acceptors like CO and N_{2} .⁶ Besides accounting for the reactions of titanocene with other compounds, the titanocene carbene-like behavior leads to rearrangement within the molecule itself. Thus, titanocene deactivates to an inactive fulvalenide bridged dimer, $[(C_5H_5)TiH]_2(C_{10}H_8)$.⁷ Attachment of titanocene dichloride to 20% crosslinked poly-(divinylbenzene-styrene) prevents deactivation by

dimerization.

The research reported here attempts to further identify the polymer attached titanocene species by (1) an esr study of the titanocene derivatives and comparison to the polymer attached compounds, (2) a comparison of hydrogenation activity of homogeneous titanocene derivatives compared to the polymer attached compounds, (3) characterization of the active species by its reactions and by preparation using alternative routes. In addition, the activity of the reduced polymer attached species toward nitrogen was of interest because the homogeneous titanocene compounds that have been used for nitrogen fixation. It was thought that reaction of the carbene-like titanocene with nitrogen could lead to formation of ammonia if the dimerization to inactive "titanocene" could be prevented. Comparison reactions of titanocene species with the reduced polymer species led to the discovery of catalytic activity by some titanocene derivatives, especially the monohydride dimer (Cp₂TiH)₂.

A convenient method for the preparation of the monohydride dimer, $(Cp_2TiH)_2$, in high yields in a hydrocarbon solvent has now been developed. Titanocene dichloride may be reduced in hexane under one atmosphere of hydrogen to the purple monohydride dimer by use of two equivalents of butyl lithium (BuLi). The purple hydride dimer is an active catalyst for hydrogenations of olefins and isomerization of dienes. Hydrogenation rates obtained with the purple hydride and 1-hexene are approximately 30 times faster than the reduced titanocene dichloride beads and hundreds of times faster than the homogeneous Cp_2TiCl_2 reduced at room temperature. Isomerization of allylbenzene, 1,5-cyclooctadiene, and 1-octene occurs readily even at 0°. The purple hydride also reacts with N₂ and the complex formed may be hydrolyized to yield greater than 1 mmol NH₃/mmol Ti. The catalytic activity of $(Cp_2TiH)_2$ is compared to reduced polymer supported titanocene dichloride species, $Cp_2TiH_2^-$, Cp_2TiCl , $Cp_2Ti(CH_2Ph)$, and THF or PPh₃ derivatives.

The identity of the reduced polymer supported titanocene species is still unknown. ESR spectra of the species are consistent with either a Ti (II) or Ti (III) compound on the polymer. Treatment of the reduced polymer attached species indicates the presence of a hydride. The dihydride anion, $Cp_2TiH_2^-$, species can be ruled out on the basis of esr spectra and catalytic activity. Thus, the polymer attached species is probably the titanocene analog ($\bigcirc -Cp_2Ti$), the hydride derivative from ring hydrogen abstraction, or the titanocene monohydride derivative.

No nitrogen could be fixed for either the reduced polymer supported Cp_2TiCl_2 or for the polymer supported $Cp_2Ti(CH_2Ph)$. Neither high pressure nor lower temperatures were effective for improving the nitrogen fixation. A dimeric titanocene species is apparently required for binding the dinitrogen. Such dimeric binding cannot occur with the polymer supported titanocene compounds and a dinitrogen complex does not form.

BIBLIOGRAPHY

- 1. F. A. Eisch and R. B. King, "Organometallic Synthesis", Vol. 1, Academic Press, New York, NY, 1965.
- P. C. Wailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Ti, Zr, and Hf", Academic Press, New York, NY, 1974.
- 3. W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandresekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, Jr., J <u>Am. Chem. Soc.</u>, <u>97</u>, 2128 (1975).
- 4. C. P. Lau, Thesis, Michigan State University, 1977.
- 5. H. H. Brintzinger and L. S. Bartell, <u>J. Am. Chem. Soc.</u>, <u>92</u>, 1105 (1970).
- 6. W. Kirmse, "Carbene Chemistry", Academic Press, New York, NY, 1964.
- 7. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, <u>J. Am. Chem. Soc.</u>, <u>94</u>, 1219 (1972).

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INTRODUCTION

Transition metal complexes that are catalysts and are bonded to an insoluble polymer support lie somewhere between the usual classifications of heterogeneous or homogeneous species. Since the polymers are insoluble and filterable, the overall polymer as a catalyst must be considered to be a heterogeneous catalyst. Our usual understanding of a heterogeneous catalyst is a solid containing a reactive surface and may have several different active sites. The metal site on a homogeneous catalyst, however, has a defined steric and electronic environment. Only one type of identical active center is present, and so a high degree of substrate selectivity may occur. Organometallic complexes that behave as homogeneous catalysts may be made insoluble by attachment of a bulky ligand to the metal. The reactive site is changed very little when a bulky polymer is a side chain on the ligand. Thus the insoluble catalyst formed is more like a homogeneous catalyst in reactivity and selectivity.

Several authors have offered new definitions to avoid the homogeneous-heterogeneous classifications. Homogeneous catalysts attached to insoluble polymer supports have thus been referred to as "heterogenized" homogeneous catalysts,¹ "solid-phase" synthesis,² hybrid phase catalysts,³ or homoactive heterogeneous catalysts.⁴ The latter describes

the system well. Homoactive catalysts have only one type of active center and the words homogeneous and heterogeneous refer only to the number of phases present.

Homogeneous catalysts have found only limited use in industrial chemistry, Partly because of the difficulty in their separation from the reaction products. Limited temperature ranges of activity, loss of catalytic activity, and need for batch rather than flow systems are drawbacks. Polymer attachment of a homogeneous catalyst has the potential of significantly improving their industrial applicability. Insoluble bead polymers allow separation of the catalyst from the liquid phase components by filtration. Columns of supported catalyst could easily be used for flow systems. The homoactive catalyst retains the specificity, efficiency, and controllability inherent in homogeneous catalysis. The support, furthermore, allows use of compounds that might dimerize or otherwise be deactivated by interaction of metal sites.

There are some disadvantages to the polymer supported catalyst systems. Identification of the active catalyst "intermediate" is more difficult because of the surrounding polymer. In some cases reactions may be diffusion limited and only limited temperatures and pressures can be used. More than one species may be unintentionally attached to the polymer which makes separation nearly impossible. The effectiveness and selectivity then would be reduced.

Indications are that such is the case during the synthesis procedures, as each reaction is not 100% effective. Some catalysts are known to be leached from the polymer leading to a loss in activity and of the metal complex.⁵

Several methods of attaching a catalyst to a polymer have been developed. Ion exchange resins have been used with charged or polar species.⁶ Adsorption into nonfunctionalized polymer has been used to advantage with AlCl₃.⁷ Generally, covalent chemical bonding as pendant functional groups to the polymer is viewed as stronger, more desirable attachment. In some cases monomer units of the catalyst can be copolymerized so that the catalytic moieties are part of the polymer backbone.⁸

With covalent linkage to the polymer, one may consider the supported catalyst as an insoluble polymer framework with pendant catalyst projecting into the solvent and in a sense solvated. An alternate view would be to consider dilute solvated catalyst complexes as having attached a bulky insoluble ligand. Although the polymer may limit diffusion and control the size of incoming substrate, it neither appears to effect the electronic environment of the metal nor its reactivity significantly.

A number of metal complexes have now been attached to organic polymer supports.⁹ Haag and Whitehurst⁶ were pioneers in the field of polymer attachment of homogeneous complexes for industrial use. They attached

 $[Pt(NH_3)_4]^{2+}$ to sulfonate resins and used this material to catalyze the reaction of allyl chloride and carbon monoxide. In another patent,¹⁰ these authors disclosed a method to coordinate rhodium chloride to polystyrene polymer with pendant phosphine groups. The resultant polymer metal complex was an active catalyst for hydrogenation.

Grubbs and Kroll¹¹ have attached Wilkinson's catalyst, tristriphenylphosphine rhodium (I) chloride, to 2% crosslinked polystyrene divinylbenzene resin through a triphenylphosphine function on the polymer. The polymer was an active hydrogenation catalyst that could be "reused" repeatedly without loss of activity. In addition the polymer catalyst was capable of substrate size selectivity in the rate of hydrogenation of olefin molecules.

Pittman,¹² <u>et al</u>. have synthesized a variety of polymer bound transition metal (Mo, Fe, Mn, Ni, Co, Rh) carbonyl catalysts. The catalyst center could be bound to linear or crosslinked polystyrene by coordination to a phosphine or by copolymerization with an organometallic monomer containing a vinyl group. They found the metal resins to be useful hydroformylation, oligomerization, isomerization catalysts.

Grubbs, Brubaker, and coworkers¹³ were able to attach titanocene dichloride to a polystyrene-divinylbenzene copolymer. On reducing with butyl lithium (BuLi) a catalyst was obtained that had a hydrogenation efficiency several

times greater than that of the homogeneous species under similar conditions. Like the polymer attached Wilkinson's catalyst, the titanocene resin could be reused with only slight loss in activity. In addition, the attached titanocene dichloride could be regenerated from the active catalyst by treatment with HCl. The polymer attached titanocene catalyst has been shown to also promote isomerization, oligomerization, and hydroformylation.¹⁴

Organometallic compounds containing a cyclopentadienyl ligand are attached to macroreticular polystyrene-divinylbenzene copolymer beads by the following reaction scheme:



Treatment of the cyclopentadienyl substituted resin with a transition metal compound leads to attachment of the metal to the polymer through pi bonding to the cyclopentadienyl ring. The polymer bound titanocene is prepared by treatment of (A) with cyclopentadienyl titanium trichloride.



An alternate scheme for attaching metallocenes to the copolymer is based on the observation by J. Lee that $(h^5-c_5H_5)_2Ti(h^1-c_5H_5)Cl$ undergoes intermolecular sigmapi ring exchange. This ring exchange reaction has now been used to attach a variety of metals¹⁵ (Ti, Zr, Hf, Hb, Mo, W).



To avoid the use of chloromethylated polymer that requires handling the cancer suspect agent chloromethyl ethyl ether,¹⁶ a method developed by L. Kroll¹¹ can be used to attach titanocene dichloride. The amount of titanium attached to the polymer is generally less than when the other methods are used. No difference in activity is noted due to the slightly different linkage of the titanocene dichloride to the polymer backbone.



Since polymer attachment of the titanocene species by the methods above lead to metal center isolation because of the rigid support, dimerization of the reduced titanocene dichloride species is prevented. The homogeneous



titanocene undergoes a cyclopentadienyl sigma-hydrogen abstraction followed by dimerization to form a fulvalenide



bridged hydride, [(h⁵-C₅H₅)TiH]₂(C₁₀C₈).¹⁷ This is the

inactive green "titanocene" prepared by Watt and Drummond.¹⁸ The polymer supported titanocene species is prevented from undergoing this type of deactivation, that results in an increase in activity for olefin hydrogenation. Site isolation is further supported by observation of the rate of hydrogenation of 1-hexene compared to titanium loading on the polymer.¹⁴

Because of the difficulty in identifying compounds with the polymer, the exact nature of the titanocene species has not been specified.¹⁵ In addition to titanocene itself, several titanocene hydrides or alkyl complexes are also possibilities for being the active species on the polymer. Observation of an esr signal at g = 1.99is consistent with the active species being Ti (II) or Ti (III) but without hyperfine splitting further identification is difficult. That treatment of the reduced species regenerates polymer attached titanocene dichloride indicates that the bis- π -cyclopentadienyl integrity is retained throughout the reduction procedure.

The research work reported here attempts to further identify the polymer attached titanocene species by:

- An esr study of the titanocene derivatives and a comparison of those spectra to those for the polymer attached compounds;
- (2) A comparison of hydrogenation activity of homogeneous titanocene derivatives compared to the polymer attached compounds;
- (3) Characterization of the active species by its reactions and by preparation using alternate routes.

In addition, the activity of the reduced polymer attached species toward nitrogen was of interest because of the homogeneous titanocene compounds that have been used for nitrogen fixation. It was thought that reaction of the carbene-like titanocene with nitrogen could lead to formation of ammonia if the dimerization to inactive "titanocene" could be prevented. Comparison of reactions of titanocene species with the reduced polymer species led to the discovery of catalytic activity by some other titanocene derivatives, especially the monohydride dimer, $(Cp_2TiH)_2$.

EXPERIMENTAL

Manipulations involving air-sensitive materials were performed under argon or nitrogen in Schlink-type (airless ware) vessels. Transfers of air sensitive reagents and reaction solvents were often made by using glass syringes. For small amounts of polymer supported compounds, 50 ml septum capped erlenmeyer flasks were used. An inert-gas vacuum manifold fitted with syringe needles held the flasks during reaction. To transfer solids an argon filled glove box was used. Many preparations of moderately air-sensitive compounds were carried out in 100 ml round bottom flasks with stopcock sidearms fitted with rubber septums. Preparations of compounds for esr experiments were often carried out in septum capped 50 ml flasks with esr side-tubes (Figure 1).

Spectra were measured with samples prepared by grinding the polystyrene beads in a Wig-l-Bug under inert gas and then were mulled in dry Nujol. Far infrared spectra in the 100-500 cm⁻¹ region were obtained by use of a Digilab model FTS-16 Fourier transform spectrometer. Spectra were recorded with the sample in dry nitrogen atmosphere and mounted between polyethylene plates. Infrared spectra were obtained by means of a Perkin Elmer 457 or a 237B grating spectrophotometer in Nujol mulls. The esr spectra were recorded by use of a Varian E-4



Figure 1. Septum capped reaction flask with esr side tube.

.

esr spectrometer and the instrument calibrated against or by use of a pitch sample. Mass spectra were recorded by use of Hatachi-Perkin Elmer RMU-6 mass spectrometer.

Reagent grade diethyl ether, tetrahydrofuran (THF), hexane, benzene, and toluene were dried by being refluxed under argon with sodium-benzophenone or lithium aluminum hydride, and distilled under argon immediately before use. Argon and nitrogen gases were purified before use by passing through a column of activated copper catalyst (BTS catalyst) and subsequently through Aquasorb (phosphorous pentoxide on an inert support). Titanocene dichloride obtained from Alfa Products was extracted by use of a Soxhlet extractor and recrystallized from toluene.

The 20% crosslinked (600 Å pore size) and 2% crosslinked macroreticular polystyrene-divinylbenzene copolymer beads were gifts from the Dow Chemical Company. Before use the polymer beads were sieved to 40-60 mesh and washed to remove impurities. Organolithium reagents were obtained from Alfa Products or Aldrich Chemical Company. Chloromethyl ethyl ether was obtained from Aldrich and distilled carefully before use.¹⁶

Chloromethylation of Copolymer Beads 19

A batch of 20% crosslinked copolymer beads was sieved to obtain a 32-35 mesh size. These beads were then washed with 10% HCl, 10% NaOH, 1:1 $H_2O:CH_3OH$,

 CH_3OH , 1:1 $CH_3OH:CH_2Cl_2$, CH_2Cl_2 , and benzene to remove impurities, as recommended by Pittman.²⁰ They were then vacuum dried. Following the chloromethylation method of Pepper, et al.²¹ 50 g of washed and dried copolymer beads were placed into a one liter three-neck flask fitted with a drying tube, addition funnel, and overhead stirrer. After the addition of 300 mL of freshly distilled chloromethyl ethyl ether,¹⁶ the mixture was stirred for 15 hrs. The flask was cooled in an ice bath and then a cold solution of 8.1 mL of $SnCl_{\mu}$ in 100 mL of chloromethyl ethyl ether was introduced dropwise. The beads and solution turned a light pink as the $SnCl_4$ was added. After addition of the $SnCl_{\mu}$ solution was completed, the reaction mixture was allowed to warm to room temperature and stirred for 13 hrs. The chloromethyl ethyl ether solution was removed by suction through a fritted dispersion tube. The beads were washed with three 300 mL portions of 50% aqueous dioxane, two portions aqueous dioxane containing 10% HCl, and finally with dry dioxane until the washings were chloride free as determined with a test $AgNO_3$ solution. The beads were further washed with two 200 mL portions of benzene and then dried by evacuating for two days a flask placed in a warm water bath. Chloride analysis^{19,22} of the white beads indicated 0.79 mmol Cl/g of copolymer, which is equivalent to 8% chloromethylation of the styrene rings.

Preparation of Cyclopentadienyl-Substituted Copolymer

The chloromethylated copolymer beads were suspended in 100 mL of THF in a one liter three-neck flask fitted with a gas inlet tube, a septum capped joint, and an overhead stirrer. A three-fold excess of freshly prepared sodium cyclopentadienide (NaCp) in THF was added using a double tipped needle. The mixture was stirred at room temperature for 2 days before removing the excess NaCp by filtration. The beads were washed with 3x 100 mL THF, once with 1:1 $C_{2}H_{5}OH$:THF, and finally with 3x 80 mL benzene. The yellow beads were then dried by evacuation of the flask. Chloride analysis indicates 0.06 mmol/g of polymer, which represents 0.73 mmol CpH/g of polymer.

Preparation of Polymer Attached Titanocene Dichloride

The 50 g batch of cyclopentadiene substituted copolymer beads was placed in a three-neck flask equipped as before. The beads were first suspended in 100 mL dry THF and then a three-fold excess of methyl lithium (or butyl lithium) in THF added. This mixture was stirred in the dark for two days at room temperature under an atmosphere of argon. Excess methyl lithium was removed by using a syringe. After being washed three times with THF and twice with benzene, the beads were suspended in 100 mL of benzene. A two-fold excess of CpTiCl₃ dissolved in benzene was added to the suspension of beads, and the mixture stirred another three days in the dark. Excess CpTiCl₃ was removed by first being washed 3x 80 mL with benzene and then by soxhlet extraction with benzene. The polymer supported titanocene dichloride beads were pink or light red after being dried in vacuo.

Analysis: 0.24 mmol Ti/g polymer

0.50 mmol Cl/g polymer

Cl:Ti ratio 2.08

Preparation of CpTiCl₂²³

A mixture of 12 g (0.048 mole) Cp_2TiCl_2 , 14.6 mL (0.136 mole) TiCl₄, and 90 mL of xylene was refluxed in a flask for 2.5 hours under a nitrogen atmosphere. After being cooled, the solution was filtered and dirty yellow crystals were obtained. The crude product and granular charcoal were placed in a glass soxhlet thimble and the CpTiCl₃ was extracted with dry benzene. Yellow crystals were collected by filtration of the extract and the product recrystallized from fresh benzene.

Bright yellow crystals mp.p. 208-210° far-ir - 290, 332, 415bd, 458 Cm⁻¹

Preparation of Polymer Attached Cp2Ti(CH3)24

Polymer attached titanocene dichloride beads, l.l g (0.25 mmol), and 10 mL of ether were stirred together in a 50 mL septum capped flask. After the mixture was cooled to -30° under argon, 0.48 mmol of CH₃Li in ether was added slowly and the mixture allowed to stir for 2 days. The yellow beads were extracted with several portions of THF and stored in the dark at -10° .

Preparation of Titanocene Monochloride

Although preparative methods using aluminum or $zinc^{25,26}$ for reduction of titanocene dichloride give good yields of the monochloride, they are unsuitable for use with the beads. Procedures using i-PrMgBr and 1,4-dioxane, or Et_2AlCl were modified slightly to be consistent with the syringe techniques used with the beads. The green-brown Cp_2TiCl was purified by recrystallization from toluene. An esr singlet at g = 1.979, width 3.56, gave a characteristic pattern in the frozen solution. Titanocene monochloride obtained by i-PrMgBr reduction was often used directly for further reactions.

Preparation of Benzyl Titanocene

The benzyl derivative was chosen for its thermal stability compared to the phenyl derivative. The procedure

of Teuben and Meijer²⁷ was followed. Brown crystalline product was obtained that had an esr singlet at g = 1.983, width 14G in ether. A frozen solution esr spectrum had a signal at g = 1.983 and a pattern similar to titanocene monochloride.

Nitrogen Fixation Using Benzyl Titanocene

The procedure used²⁸ was a model for attempted nitrogen fixation by using the polymer supported species. Α sample of 0.38 gm Cp₂TiCl (1.8 mmol) was placed in a flask with a septum side arm and 50 mL of dry ether added. Benzyl titanocene was prepared under nitrogen at -20°C by slow addition of 4.5 ml of PhCH₂MgBr in ether and 1.0 ml of 1,4-dioxane by use of a syringe. Reddish brown insoluble material formed, which, when cooled to -80° C under nitrogen, developed an intense blue color. Cold toluene was added, followed by 10 mL of 0.73 M NaNp in THF. The mixture was stirred and allowed to warm slowly over a 12 hour period. Hydrolysis of the mixture with methanol and aqueous hydrochloric acid was followed by separation of the aqueous layer and a Kjeldahl distillation into a 4% boric acid solution. Titration with standard HCl indicated a yield of ammonia of 0.21 mmol/mmol Ti.

Preparation of Polymer Supported Titanocene Monochloride

Polymer attached titanocene monochloride was prepared by two methods^{29,30} that were adapted to use with the bead polymer and syringe techniques.

Method A: A sample of 0.12 gm of polymer attached titanocene dichloride (0.03 mmol Ti) was placed in THF in a flask. At -70°C 0.03 mmol of i-PrMgBr was added dropwise. It was warmed to -20°C and stirred to obtain green beads.

esr g = 1.980 57G 4 peak pattern far-ir - 153, 191, 386, 438, 482 cm⁻¹

<u>Method B</u>: 1 g of polymer attached titanocene dichloride beads (0.24 mmol Ti) was placed in a 100 ml flask and stirred with 10 mL toluene under nitrogen. When 4 ml of 25% Et_2AlCl in hexane was added, the beads turned a brown. The solution was heated to boiling for one hour and stirred at room temperature overnight to obtain dark green beads. Excess reagent was removed by use of syringe and the beads were washed with 2x 10 mL toluene and 2x 10 mL of ether. Light green beads were obtained.

esr g = 1.980 4 peak pattern

Preparation of Polymer Attached Benzyl Titanocene

A sample of 0.53 g polymer attached titanocene monochloride (0.13 mmol Ti) was loaded in a glove box into a flask with septum side arm. After attaching the flask to an argon line, 10 mL of THF and 1.5 mL of 0.10 M PhCH₂MgBr in ether plus 0.11 mL of 1,4-dioxane was added. The solution was cooled to -60°C and stirred overnight before being used to wash the beads with 2 x 10 mL hexane. An esr of the brown beads indicated a change in the g (g = 1.983) value and the splitting between peaks from that of the titanocene monochloride beads.

Treatment of Polymer Attached Benzyl Titanocene with Nitrogen

The brown beads from the preparation above were placed in freshly distilled toluene in an esr flask containing one atmosphere of nitrogen. After being cooled to -80°C in a dry ice-acetone bath and being stirred under nitrogen for several hours, no color change in the beads occurred. The esr spectrum remained the same as for the benzyl titanocene. It was concluded that no nitrogen uptake occurred. No ammonia was obtained after the material was reduced with NaNp and hydrolyzed by methanol and hydrochloric acid.
Preparation of Titanocene Monohydride Dimer

Recrystallized titanocene dichloride was placed in a 100 mL flask and the system evacuated to remove residual moisture. After repeated purges with hydrogen gas, 10 ml of dry, degassed hexane was added to the flask by use of syringe. The insoluble titanocene dichloride was suspended in solution by vigorous stirring and 2 equivalents of n-BuLi in hexane were added slowly by syringe. A purple compound formed if the reaction was carried out under hydrogen gas at one atmosphere and at 20° to 0°. Temperatures above 0° cause a gray insoluble polymeric hydride to form. In most cases the purple hydride was used directly for reaction or catalysis because of the hydride's sensitivity to air and water. The dry solid could be isolated by careful filtration at temperatures below -20°. Decomposition to give the green "titanocene" and a yellow wolid occurred readily. The purple hydride dissolved with reaction in most other solvents than hexane. An ir peak at 1125 bd cm⁻¹ disappears when the purple solid is exposed to air.

The method above could be modified to yield the purple hydride when other alkyl lithium or Grignard reagents were used. Because of the product's instability in ether solvents, the alkylating reagents must be in hexane or the ether removed by evacuation from the unstirred reaction mixture at -40° .

Reactions of the Titanocene Monohydride Dimer

1. Reaction with Nitrogen

The purple hydride in hexane was cooled to -80° and the hydrogen gas removed by evacuation. Dry, degassed toluene at -80° was added and the purple slurry slowly turned an intense blue. The previously weak esr signal at g = 1.99 disappeared and the solution became diamagnetic. Isolation of the blue compound with nitrogen was not possible. Upon warming to room temperature the black color returns. Recooling the slurry to -80° gave the blue compound again. Under an atmosphere of argon the purple turned black in toluene but no blue compound was formed at low temperature.

2. Nitrogen Fixation

The blue complex obtained from the purple hydride cooled under nitrogen was treated with a ten-fold excess of NaNp in THF. The temperature was maintained at -80° for five hours and then allowed to rise to room temperature. The mixture was hydrolyzed by a solution of methanol and 0.5 M HCl. Organic and aqueous layers were separated by using a separatory funnel and the organic layer was washed with 3 x 25 ml acid solution. Ammonia yield was determined by Kjeldahl distillation into 4% boric acid solution and titration with 0.1 M standard HCl.

3. Reaction with Deuterium Chloride

The purple hydride, (Cp₂TiH)₂, was prepared under hydrogen by using BuLi to reduce titanocene dichloride. A flask containing the slurry of the purple material in hexane at -40° was evacuated and repeatedly purged with argon. After the solution was frozen at -196° the flask was evacuated and a measured quantity of deuterium chlcride The slurry was warmed to 0° and stirred. admitted. The purple slurry turned red as the insoluble titanocene dichloride formed. After the reaction was complete, the flask was immersed in liquid nitrogen to condense all volatile vapors and a sample of the hydrogen gases was collected in a tube designed to fit the mass spectrometer. Analysis of the hydrogen isotopes was achieved by comparison of the peaks in the mass spectrum or "spectra" if more than one.

4. Isomerization of Dienes

Allylbenzene and 1,5-cyclooctadiene were dried with barium oxide, distilled at reduced pressures, and stored under argon. Products from the isomerization reactions could be analyzed by integration of the nmr spectrum or by gas chromatography separation. A ten foot column of 10% SE-30 on Chromosorb P was used in a Varian model 920 gas chromatograph.

5. Isomerization of 1,5-cyclooctadiene

A sample of 0.14 mmol of the purple hydride, $(Cp_2TiH)_2$, in 10 mL of hexane was evacuated, flushed with hydrogen, and placed under an argon atmosphere. To the purple slurry at 0° was added two ml of 1,5-COD by use of a syringe. The mixture was stirred at 0° for 24 hours with periodic samples taken for analysis. Isomerization to 1,3-COD is essentially complete after seven hours.

6. Isomerization of Allylbenzene

A sample of 0.072 mmol of purple hydride in 10 mL hexane was evacuated and flushed with argon to remove hydrogen. To the purple slurry at 0° was added two mL allylbenzene and the mixture stirred for 24 hours with periodic sampling. Isomerization to cis-propenylbenzene and trans-propenylbenzene was complete within 13 hours.

7. Isomerization of 1-Octene

A sample of 0.09 mmol of purple hydride in ten mL hexane was evacuated and flushed with argon. Two mL of 1-octene was added and the mixture stirred at 0° overnight. After 12 hours the slurry was yellow and 5% isomerization to 2-octene had taken place.

Reaction with HCl

Hexane solutions of the purple hydride reacted with anhydrous HCl to form an insoluble red material that was identified as titanocene dichloride. Approximately 80%of the original amount of Cp_2TiCl_2 could be recovered by filtration of the red solid from the hexane solution followed by recrystallization from toluene.

Reaction with Carbon Monoxide

Hexane solutions of the purple hydride reacted at one atmosphere of CO to form a red-brown solid. The brown solid had ir peaks at 1985 and 1905 cm⁻¹. Under these mild conditions titanocene dicarbonyl, $Cp_2Ti(CO)_2$, was formed.

Reaction with Triphenylphosphine

A hexane solution of $(Cp_2TiH)_2$ was allowed to react with a 3-fold excess of PPh₃ dissolved in hexane at -80°. A translucent blue solution formed immediately. An esr spectrum at -80° indicates formation of $Cp_2Ti(PPh_3)H$ (Figure 21). When the temperature of the solution was increased, the blue faded to brown and an esr signal at g = 1.97 appeared.

<u>Preparation of Titanocene Monohydride From the Dimethyl</u> Derivative

<u>Method A</u>: Dimethyl titanocene was prepared by the method of Class and Bestian²⁴ as a yellow solid. When placed in hexane under one atmosphere of hydrogen gas at room temperature, the purple hydride was obtained after an induction period of several hours. The purple compound became gray-black after a few minutes, if the reaction temperature was maintained at 25°.

<u>Method B</u>: The purple hydride can be obtained more easily by combining the dimethyl preparation and the treatment with hydrogen. Titanocene dichloride was suspended in hexane at 0° under one atmosphere of hydrogen gas and 2 equivalents added of methyl lithium in hexane. A yellow compound formed immediately which yielded the purple hydride after an induction period of 1-3 hours. Catalysis by using the purple compound prepared by this method gave the same results as when BuLi was used as the reducing agent.

Hydrogenation by Using Titanocene Monohydride Dimer

The monohydride catalyst was prepared in the hydrogenator and used directly. A 0.0121 g sample (0.049 mmol Ti) was placed in a 100 ml round bottom flask with a stopcock side arm fitted with a septum. The reaction

flask was fitted to the hydrogenation apparatus evacuated, and flushed with hydrogen to remove air and water. To the flask was then added 20 mL of dry hexane and the solution was cooled to 0°. Slow addition of 0.1 mmol of BuLi in hexane by use of syringe initiates reaction. The red, insoluble titanocene dichloride darkened and a slightly soluble purple complex formed within an hour. This slurry of the purple monohydride is used directly for the hydrogenation by merely adding the desired olefin syringe.

Hydrogenation began immediately when 1.0 mL of 1hexene is added to the slurry of catalyst held at 0°. Gas uptake measured by using a mercury filled buret to balance the hydrogen pressure to atmospheric pressure. The reaction was complete within 5 minutes with an overall hydrogen uptake of 1 mmol hydrogen per mmol 1-hexane. Hydrogenation rates are taken as the maximum slope on the pseudo first order rate curve. A rate of 923 mL/min-mmol Ti was observed for the first addition of 1-hexene. Subsequent olefin additions led to progressively decreasing rates of hydrogenation.

Hydrogenation using Titanocene Dihydride Anion

A sample of 0.247 g titanocene monochloride (0.12 mmol Ti) was suspended in 20 ml of degassed THF under argon. By use of syringe 4.2 mL of 1.1 M i-PrMgBr in THF was added to the slurry at -80°. After being stirred for

two hours the black slurry was warmed to 0° and used for hydrogenation. A 1.0 mL sample of 1-hexene was added and the gas uptake observed. A rate of 8.5 mL/min-mmol Ti was obtained. An esr spectrum of the translucent black solution was a 1:2:1 triplet (g = 1.993, width - 7.2 G) which is characteristic of the $(Cp_2TiH_2)^{-.13}$

Hydrogenation with BuLi Reduced Homogeneous Titanocene Dichloride

A 0.0127 g (0.051 mmol) sample of Cp₂TiCl₂ was placed in a 100 mL flask attached to the hydrogenator. After the flask was evacuated and flushed with hydrogen, 10 mL of dry hexane and 1.0 mL of 1.6 M BuLi in hexane were added at room temperature (23°). A gray-black slurry develops within 30 minutes. Hydrogenation occurred when 0.5 mL of cyclohexene was added to the test solution at 25°. A hydrogen uptake rate of 0.12 mL/min was observed, which corresponds to an overall rate of 2.4 mL/min-mmol Ti. A similar experiment with 1-hexene yielded a rate of 160 mL/min-mmol Ti.

Reduction of (P-Cp₂TiCl₂ and Treatment with DCl

Polymer supported titanocene dichloride beads (2.0 g) were weighed out in the reaction flask. After evacuation and purging with argon, the flask was charged with freshly

distilled hexane (10 mL) and BuLi (2mL of 2.4 M in hexane). The beads changed from red to black within 10 minutes at room temperature. The mixture was stirred overnight to ensure complete reaction, then the beads were washed with hexane (2 x 10 mL) and with THF (3 x 10 mL). THF (4 mL) was added and the contents of the flask frozen in a liquid nitrogen bath. The sample tube was attached and the system evacuated. DCl was added quickly to the frozen system to ca. 1 atm and the reaction flask closed off. The contents were then warmed to the desired reaction temperature. Bubbling could be observed and a slow change in color from black to pink beads occurred. After an interval of 1 to 14 hours the contents were once again frozen and the sample tube closed off. Analysis of the gases within the tube was made by use of a mass spectrometer. Values are given in Table in the Results section.

High Pressure Nitrogen Fixation

The Volpin and Shur method³¹ for nitrogen fixation, which uses a mixture of Cp_2TiCl_2 and PhLi in ether under 100-200 atm of pressure was followed. All reactions were carried out using 1200-1500 psi of nitrogen in an autoclave at ambient temperatures and with continual stirring during the reaction period. After the Cp_2TiCl_2 or \bigcirc - $CpTiCpCl_2$ was loaded into the autoclave, it was flushed

with nitrogen and then twice pressurized to 1000 psi and the pressure released before the reaction was begun.

Nitrogen Fixation by Use of Homogeneous Cp2TiCl2

A 0.651 g sample of recrystallized Cp₂TiCl₂ (2.61 mmol) was loaded into a glass liner and placed into the autoclave. After purging the autoclave of air, 100 mL of diethyl ether and 8 mL of 1.7 M PhLi in ether were introduced using syringes. A slight positive pressure of nitrogen was maintained during the loading procedure. The mixture was stirred at ca. one atmosphere pressure for one hour and then the autoclave pressurized to 1500 psi. After 15 hours the system was depressurized and the mixture acidified with 20 mL of CH_3OH and 20 mL of 20% Following a reaction period of 30 minutes, the H₂SO₁₁. glass liner was removed and the volume of solution reduced by evaporation. The solution was made basic and was ammonia steam distilled into a 4% boric acid solution. Titration with 0.1032 \underline{M} HCl by use of bromocresol green as an indicator indicated the amount of ammonia. A total of 1.80 mmol NH_3 was found for a yield of 0.69 mmol/mmol Ti.

Nitrogen Fixation by Use of Polymer Supported Cp2TiCl2³²

The reaction was repeated by using 3 g (1.8 mmol Ti) of polymer attached Cp_2TiCl_2 . The beads were loaded in the glass liner, the system purged with nitrogen, and 5 mL of 1.8 M PhLi in 50 mL of ether introduced using a syringe. After one hour of stirring at atmospheric pressure, the system was pressurized to 1200 psi for 16 hours, then depressurized and acidified with 20 mL of CH_3OH and 20 mL of 20% H_2SO_4 . Powdered beads were removed by filtration, the solution volume reduced by evaporation, and a Kjeldahl distillation into 4% boric acid performed. Titration with standard HCl indicated that no ammonia had been formed. Table in the Result section summarizes the results of several attempts at nitrogen fixation.

Polymer supported titanocene dichloride originally prepared by C. Gibbons, ¹⁹ has been shown to be an active catalyst for hydrogenation, ¹⁵ isomerization, and other catalytic reactions.¹⁴ Before use the supported titanocene dichloride must be reduced to form the gray or graygreen beads which contain the active catalyst. The exact nature of the active catalyst is still unknown. When alkyl lithium, sodium napthalide, or Grignard reagents are used, an air sensitive, paramagnetic species is formed on the polymer. The reaction conditions and the g value of the esr signal are consistent³ with the active species being a Ti(II) or Ti(III) compound. Although several possible compounds could be formed, the reactive compound is predicted to be the titanocene analog, I,



Like titanocene, the analog would be expected to exhibit carbene like behavior 3^{4} , 3^{5} toward nucleophilic molecules.

Titanocene is reported to undergo a large variety of reactions.³⁶ The reaction of nitrogen gas with titanocene or titanocene derivatives is especially interesting. Only a few metal compounds 37 react with the normally inert nitrogen molecule, but in several instances titanium complexes have reacted with nitrogen to form ammonia.³⁸ Generally the titanium-nitrogen-fixation systems have not, with a few exceptions, 39,40 been catalytic, however. At first, several forms of "titanocene" were reported, not all of which reacted with nitrogen. The inactive form has now been identified 17 as a dimeric molecule with a fulvalenide bridge between the titanium centers. The active form is generally presumed to be Cp₂Ti or the dimer $(Cp_2Ti)_2$. A number of researchers^{37,41,42} favor the dimer form as the species that actually binds the dinitrogen. Bercaw⁴³ recently published a crystal structure for $\{[C_5(CH_3)_5]_2 TiN_2\}_2 N_2$ and indicates that a dimeric titanocene is probably the species which binds with nitrogen.



Formation of the fulvalenide bridged "titanocene" is a deactivation mode for homogeneous $(h^5-c_5H_5)_2Ti$ that is not possible with the polymer supported species due to separation of the metal sites by the polymer. Titanocene is predicted to be an unstable species with a carbenelike reactivity^{44,35} unlike the reactivity of the other 3d metallocenes. Singlet carbenes are known⁴⁵ to undergo facile insertion into C-H σ bonds, addition to π bonds of alkenes and alkynes, and addition to π acceptors like CO and even N₂.⁴⁶ Besides accounting for reactions of titanocene with other compounds, the titanocene carbenelike behavior leads to rearrangements within the molecule itself. Thus a σ -hydrogen abstraction from a cyclopentadienyl ring may occur to form a $(h^1-c_5H_4)(h^5-c_5H_5)TiH$



structure III.³⁶ Intermediate III then could dimerize with

a second titanocene molecule to form the inactive fulvalenide bridged dimer, II. Even the more stable bis(pentamethylcyclopentadienyl) titanium (II) undergoes a related reaction by abstraction of a hydrogen from a ring methyl group.



Because of its carbene-like reactivity, titanocene is best considered an intermediate. Besides the hydrogen abstraction reaction, which leads to an inactive dimer, another dimerization process is possible to form $[(h^5-c_5H_5)_2Ti]_2$.³⁶ The presence of normal $h^5-c_5H_5$ rings is supported by its chemical behavior. When exposed to HCl gas, solutions of $(Cp_2Ti)_2$ rapidly form Cp_2TiCl_2 or if $(Cp_2Ti)_2$ is exposed to CO, the dicarbonyl complex, $Ti_2Ti(CO)_2$, is formed. By contrast, the green $[(c_5H_5)TiH]_2(c_{10}H_8)$ reacted with HCl to form the magenta fulvalenide bridged monochloride dimer, $[(c_5H_5)TiCl]_2$ - $(c_{10}H_8)$.^{47,48} Also, unlike the inactive dimer, $(Cp_2Ti)_2$ is in equilibrium with the titanocene monomer as indicated



by paramagnetism of toluene solutions of the dimer. Two especially significant reactions of $(Cp_2Ti)_2$ solutions are the reaction with D_2 and the reaction with nitrogen. Under D_2 gas a complete exchange of deuterium between the gas phase and all positions on the cyclopentadienyl rings occurs. This exchange implies a ring hydrogen abstraction process to form a hydride intermediate. Under N_2 the dimer reacts to form $(Cp_2Ti)_2N_2$. This compound can produce ammonia and suggests that a dimer is required for the nitrogen fixation reaction.

$$2(h^5-C_5H_5)_2Ti \longrightarrow (Cp_2Ti)_2 \xrightarrow{N_2} (Cp_2Ti)_2N_2$$

By reacting solid dimethyl titanocene, $Cp_2Ti(CH_3)_2$, with hydrogen Bercaw⁴⁹ succeeded in isolating a violet compound which he identified as the titanocene monohydride

dimer, $[(h^5-C_5H_5)_2TiH]_2$. A diborane-like double hydrogen bridge between the two metal centers has been postulated. This postulate is supported by infrared and mass spectrometry. The reactions of the monohydride dimer are very similar to those of titanocene (Figure 2 and Figure 3).



Titanocene monohydride dimer

Since the monohydride dimer can form the titanocene dimer, $(Cp_2Ti)_2$, by loss of hydrogen, titanocene is probably an intermediate in the reactions of the monohydride dimer. The hydride bridged dimer may also polymerize to form a gray-green hydride, $(Cp_2TiH)_x$, which is a convenient source of the reactive form of titanocene. The ir band at 1450 cm^{-1} , which is associated with the diborane-like hydride bridge, shifts to 1140 cm^{-1} for the gray-green polymer, $(Cp_2TiH)_x$. It is significant that the hydride dimer and polymer retain the π bonding to the rings and therefore undergo the reactions characteristic of $(h^5-C_5H_5)_2Ti$ rather than the inactive fulvalenide bridged structure,



Figure 2. Reactions of titanocene.



Figure 3. Reactions of titanocene monohydride dimer.

[(h⁵-C₅H₅)TiH]₂(C₁₀H₈).

Hydrogenation Studies

Butyl lithium reduced polymer supported titanocene dichloride have been tested for catalytic activity towards hydrogenation of unsaturated organic compounds.¹³ With the olefins cyclohexene and l-hexene, the rates of hydrogenation were several times greater for the polymer supported titanocene species than a homogeneous titanocene species prepared under similar reaction conditions. The active catalyst is the gray copolymer beads that are paramagnetic and air sensitive. Repeated additions of olefins can be made without significant reduction in hydrogenation activity. When hydrogenation is completed, the polymer attached titanocene dichloride may be regenerated by treatment with HCl. Therefore, it is concluded that the bis- π -cyclopentadienyl integrity is retained throughout the reduction procedure.

The active titanocene species can only be surmised from such indirect evidence. It has been observed that l or 2 electron reductions are possible and that when an excess of reducing agent is used, no difference in either esr signal or hydrogenation rates is noted. Reduction of titanocene dichloride with alkyl lithium reagents would be expected to follow the sequence below:



Scheme (1)

$$Cp_2TiCl_2 \xrightarrow{RLi} Cp_2TiCl \longrightarrow Cp_2Ti-R \longrightarrow Cp_2Ti-H$$

Scheme (2)

The concentration of reducing agent, solvent, temperature, and type of inert gas used are all factors that determine which of the several possible products are obtained. Hydrocarbon solvents would tend to favor scheme (1) whereas ether solvents would favor formation of Ti III compounds, Cp_2Ti-R or $Cp_2Ti(H)_2^{-}$. Unstable sigma bonded alkyls with β -hydrogens or the unstable dihydride are known to decompose with loss of an alkane, alkene, or hydrogen gas.⁵⁰ Thus, the catalytically active species on the polymer might be the titanocene analog, (I), or might be a hydride (VI) or (VII).

The effect on the hydrogenation rate was determined when the polymer supported catalyst was prepared by use of other reducing agents: i-PrMgBr, NaNp, CH₃Li, C₂H₅MgBr. Little difference in the hydrogenation rates was observed when BuLi was used for reduction. This result implies



that the same catalytically active species is being formed on the polymer in each case.

When polymer attached titanocene derivatives, Cp_2TiCl , $Cp_2Ti(CH_2)$, are reduced with an excess of reagent, the hydrogenation rates are also nearly the same as when reduction is of the polymer attached titanocene dichloride. Although beads reduced under hydrogen generally have higher hydrogenation rates, it is not known whether the problem is due to handling technique or a difference in the species formed. Experience with the titanocene hydride derivatives leads one to suspect the former explanation. In all cases the esr signal of the reduced species is the same.

Comparison of the Beads with (Cp₂TiH₂)⁻

Reaction conditions known to lead to specific titanocene derivatives were used to compare hydrogenation rates of the polymer catalyst with the homogeneous catalyst. When a 40-60 fold excess of an alkyl lithium or Grignard reagent is used in an ether solvent at less than room temperatures, the Ti (III) alkyl or dihydride anion compounds are formed. The process can be observed by esr. The dihydride anion, $(Cp_2TiH_2)^-$, is stable for days at room temperature. For

 $Cp_2TiCl_2 + xs i - PrMgBr \longrightarrow (Cp_2TiR_2)^- \longrightarrow (Cp_2TiH_2)^-$

the homogeneous species a hydrogenation rate for 1-hexene was 8.5 mL/min-mmol Ti whereas the polymer attached species under similar conditions had the same hydrogenation rate observed before, 38 mL/min-mmol Ti. Since the dihydride anion is not believed to undergo a deactivating dimerization reaction, the higher hydrogenation rate by the bead catalyst indicates a different species than the dihydride anion is formed on the polymer.

- Preparative methods for the dihydride anion specify an ether solvent.^{50,51} The polar solvent is undoubtedly involved in solvation and stabilization of the anion. Another titanocene alkyl anion, $(Cp_2TiC_2H_5)_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_20$

prepared by Marvich⁴⁷ under similar conditions requires an ether solvent. Thus, when a 40 fold excess of i-PrMgBr is added to Cp_2TiCl_2 in a large excess of hexane, the mixture turns brown instead of black and the dihydride anion does not form as indicated by the lack of its triplet esr signal. Since the titanocene dichloride beads are normally reduced in hexane and the esr signal of the beads does not resemble the frozen glass spectrum⁵² of $(Cp_2TiH_2)^-$, one would not expect the polymer supported species to be the dihydride anion.

Another possibility is that the supported titanocene species is the monohydride reported by Bercaw.⁴⁹ The monohydride is normally a hydride bridged dimer, but a weak esr signal and the compound's reactivity indicate a



monomer-dimer equilibrium. Preparation of the monohydride dimer is effected by the reaction of the solid dimethyl titanocene with hydrogen gas.⁴⁹ This same reaction, if carried out in a hydrocarbon solvent, leads

$$Cp_2Ti(CH_3)_2 + 3/2 H_2 \rightarrow 1/2(Cp_2TiH)_2 + 2CH_4$$

to green "titanocene", $(CpTiH)_2(C_{10}H_8)$. Although not isolated, the dimer $(Cp_2TiH)_2$ was probably formed as an intermediate in the reactions reported by two authors.^{47,53}

Preparation of Titanocene Monohydride Dimer

A convenient method for the preparation of the monohydride dimer, $(Cp_2TiH)_2$, in high yields in a hydrocarbon solvent has now been developed. Titanocene dichloride may be reduced in hexane under one atmosphere of hydrogen to the purple monohydride dimer by use of two equivalents of BuLi. Care must be taken to maintain the reaction temperature between -20° and 0°. The insoluble red titanocene dichloride is observed to darken slowly and a

 $Cp_2TiCl_2 + 2BuLi + H_2 \xrightarrow{hexane} (Cp_2TiH)_2 +$

 $2C_4H_{10} + 2LiCl$

slurry of slightly soluble purple $(Cp_2TiH)_2$ to form, as the reaction mixture is stirred. Reaction is complete in one-half to one hour of stirring of the mixture at 0°. The purple solid may be isolated by filtration with Schlenkware followed by washing the solid with cold hexane or pentane. Non-hydrocarbon solvents or temperatures above 0° cause the purple hydride to turn green and eventually yellow. The preparative reaction may follow one of the reaction schemes below.

$$Cp_2TiCl_2 + 2BuLi \rightarrow Cp_2Ti(Bu)_2 \xrightarrow{H_2} 1/2(Cp_2TiH)_2 +$$

204H10

Scheme (3)

$$Cp_2TiCl_2 + BuLi \longrightarrow Cp_2TiCl \longrightarrow CpTi-Bu \xrightarrow{H_2}$$

$$1/2(Cp_2TiH)_2 + C_4H_{10}$$

Scheme (4)

Reaction scheme (3) follows that of the dimethyl titanocene, except that the butyl groups have β -hydrogens that may transfer to the Ti by β -hydrogen elimination. Only titanocene alkyl groups without β -hydrogens are reasonably stable at room temperature. Thus the less stable dibutyl derivative reacts at low temperature in much the same way as the dimethyl derivative and forms the same product, $(Cp_2TiH)_2$.

Reaction scheme (4) is also possible. Titanocene monochloride can be prepared by slow addition of an equivalent of i-PrMgBr or BuLi to the dichloride. Mono alkyl compounds can be prepared from the monochloride, although only alkyl groups without β -hydrogens are stable at room temperature.⁵⁴ The possibility of this reaction sequence was demonstrated in the lab by reaction of solid Cp₂TiCl with one equivalent of BuLi in hexane under a hydrogen atmosphere. The purple monohydride dimer is formed if the temperature is 0° or below.

Other reducing agents may be used to prepare the purple hydride if the agents have β -hydrogens. Thus i-PrMgBr and $C_{2}H_{5}MgBr$ can also be used to make the purple dimer. Because the dimer reacts with most solvents other than hydrocarbons, the Grignard reagents must be placed in hexane before addition to the titanocene dichloride. The monohydride dimer did not form when NaNp was used. Other reducing agents that operate by alkylation followed by elimination should also be useful for this reaction.

When dimethyl titanocene is stirred in hexane under hydrogen the slurry turns purple, but within several minutes the green fulvalenide bridged dimer forms.²⁴ Bercaw, therefore, isolated $(Cp_2TiH)_2$ by reaction of the solid $Cp_2Ti(CH_3)_2$ with hydrogen.³⁶ It was found that titanocene dichloride will react with 2 equivalents of CH_3Li under hydrogen to give the purple hydride in hexane. This procedure simplifies preparation because the dimethyl intermediate need not be isolated. Upon addition of CH_3Li

After 2-5 hours of stirring, the yellow slurry will turn completely purple within 2-5 minutes of the first faint sign of purple. The purple slurry of $(Cp_2TiH)_2$ is then as stable as the dimer when prepared from BuLi. If the yellow $Cp_2Ti(CH_3)_2$ slurry is stirred in the dark under hydrogen, the purple compound is not obtained. A photochemical reaction mechanism is implied by this observation and is consistent with literature reports.^{54,55}

The monomeric titanocene monohydride is also a possibility for the structure of the reduced polymer supported catalyst (Structure VI). Originally, $(Cp_2TiH)_2$ was prepared by reaction of $Cp_2Ti(CH_3)_2$ with hydrogen,⁴⁹ but can be prepared more easily by BuLi reduction of Cp_2TiCl_2 under hydrogen. The purple hydride, $(Cp_2TiH)_2$, was tested as a hydrogenation catalyst so that hydrogen uptake rates could be compared with those of the reduced polymer supported catalyst.

Hydrogenation by (Cp₂TiH)₂

Hydrogenation rates obtained with the purple hydride and 1-hexene are approximately 30 times faster than the reduced beads and hundreds of times faster than the homogeneous Cp_2TiCl_2 reduced at room temperature, the species used for previous comparisons with the bead catalyst.

The purple hydride, $(Cp_2TiH)_2$ was prepared in a flask

attached to the hydrogenation apparatus and olefin added by syringe to initiate hydrogenation. Results of testing several olefins for hydrogenation rate are given in Tables 1 and 2. Generally 0° was found to give the highest reproducible rates without the gray insoluble polymer (Cp₂TiH), being formed. Selectivity for primary alkenes over those with internal was large bonds. Table (3) compares hydrogenation rates of olefins at two different concentrations. Doubling the total amount of olefin at the same concentration gives comparable results, but more reproducible rates were obtained when 1.0 mL of olefin was added to 20 mL of solvent and catalyst. Rates of hydrogenation obtained with (Cp₂TiH)₂ were greatly in excess of any obtained with either the bead system or any homogeneous titanocene systems tested before in these Even with vigorous stirring the systems were labs. hydrogen diffusion limited. The rates are affected by stirring rate and by Ti concentration (Table (4)). The rates in Table (1) are, therefore, not maximum rates, but rather rates obtained under conditions comparable to those used when the reduced titanocene beads were used.

Effect of Temperature on Hydrogenation Rates

Figure (4) shows a plot of reaction temperature <u>vs</u>. rate of hydrogenation of 1-hexene and cyclohexene with

Hydrogenation Ra	ates ^C
Polymer Attached ^a Titanocene Species	(Cp ₂ TiH) ^b 2
213.0	970
	950
	170
243.0	70
90.3	20
1.0	
0.0	
216.0	
183.0	7 05
	60
(polymer)	
149.0	
40.6	210
	Hydrogenation Ra Polymer Attached ^a Titanocene Species 213.0 243.0 90.3 1.0 0.0 216.0 183.0 (polymer) 149.0 40.6

T	able	l.	Hydrogen	ation	Rates	Compared	d: H	Polymer	Attached
			Species	and (Cp ₂ TiH) ₂ .			

^aAt 25°.

^bAt 0°.

^c(mL H₂/min-mmol Ti).

		Rates (mL H2/min-mmol)		
Catalyst Precursor	mmol-Ti	Initial	Maximum	
titanocene dichloride	0.05	5.6	28	
attached Cp ₂ TiCl ₂	0.03	88.7		
Attached Cp ₂ TiCl ₂ ground before reduction	0.034	105.6		
Benzyltitanocene dichloride	0.2	9.5		
titanocene dichloride	0.2	10		

.

Table 2. Hydrogenation Rates¹³ at 25 °C for Cyclohexene.

 mmol Ti	Temp.	Olefin ^a	Rate (mL/min-mmol)	
 0.049	0°	l-hexene	920	
0.057	0 °	cyclohexene	10	
0.047	0°	l-octene	970	
0.047	0°	2-octene	20	
		Olefin ^b		
0.056	0°	l-hexene	970	
0.049	0°	l-octene	770	
0.133	0°	cyclohexene	20	

Table 3. Effect of Olefin Concentration on Hydrogenation Rates.

^al.0 mL olefin in 20 mL hexane solvent.

 b 0.5 mL olefin in 10 mL hexane solvent.

mmol T	i ^a Temp	Rate (mL/mmol-min)	
0.102	0 0°C	600	
0.031	3 0°	775	
0.012	9 0°	780	
0.010	8 0°	150	

Table 4. Effect of Ti Concentration on Hydrogenation Rates.

^aIn 20 mL hexane.



Figure 4. Graph of hydrogenation temperature versus rate.

the purple hydride catalyst. Projection to room temperature gives rates that might be compared with those of the bead catalyst. For the purple hydride, the rate would be in excess of 1,100 mL/min-mmol Ti compared with a hydrogenation rate on the same apparatus for the titanocene beads of only 37 mL/min-mmol. This difference amounts to a 30 fold rate increase for primary olefins. For cyclohexene even the projected room temperature rate for the (Cp₂TiH)₂ catalyst is lower than the rate with the bead catalyst. The effective temperature range for hydrogenation by the reduced titanocene beads has not been determined at temperatures above 20° because of polymerization to (Cp₂TiH), or deactivation by formation of a yellow solid from which Cp2TiCl2 cannot be regenerated by HCl treatment.

Effect of Incremental Olefin Addition

With each incremental addition of olefin the hydrogenation rate decreases when the purple hydride is used as the catalyst. After each 1 mL addition of olefin has been hydrogenated another 1 mL addition is made. The olefin concentration decreases only 4% per addition whereas the hydrogenation rates decreased by 10-40% per increment. Deactivation of the catalyst rather than dilution is the cause of the rate decrease. The rate decrease probably

Temp.	Olefin	# of Additions	Olefin Conc.	Rate (mL/min-mmol)
0°C	l-hexene	1	0.381 M	920
		2	0.364	845
		3	0.348	690
0°C	l-octene	1	0.305	97 0
		2	0.291	670
		3	0.278	400
		4	0.267	260

Table 5.	Effect of Incremental Olefin Additions o:	n
	Hydrogenation by (Cp ₂ TiH) ₂ .	

is due to impurities from each olefin addition that react with the monohydride dimer.

Effect of Adding PPh3 or THF

Either solvents of triphenylphosphine will react with $(Cp_2TiH)_2$ to cleave the dimeric hydride and give monomic hydrides. The reaction is examined in more detail in the esr section. The monomic hydrides plus coordinated THF or PPh₃ were tested for catalytic activity. The results of hydrogenation of 1-hexene are shown below (Table 6). The species $Cp_2Ti(PPh_3)H$ is produced by adding PPh₃ in cold hexane directly to the cold solution of purple hydride. A translucent purple solution formed immediately. Catalytic activity of the purple hydride solution at -20° was greatly diminished by both PPh₃ and THF. The beads show a similar, though less drastic, effect when treated with THF or PPh₃.

Comparison of Hydrogenation Rates with the Bead Species

Since excess reducing agents can lead to different species than can 2 equivalents, the beads were tested for hydrogenation ability after reduction by 2 equivalents of BuLi. Unreacted cyclopentadiene groups on the polymer may react with BuLi, so 2 equivalents BuLi/Ti and 1 equivalent per unreacted (P) -CpH was added. Conditions similar to those that lead to the homogeneous purple
mmol Ti	Temp.	Olefin	Rate (ml/min-mmol)
0.065 ^a	-20°C	l-hexene	600
Added PPh ₃ /hexane		11	80
Added THF		"	20
0.074 ^a	-20°C	l-hexene	620
Added PPh3		11	80
Added THF (brown)		11	0
0.056 ^a	0°C	l-hexene	360
Added THF	0°C	"	185
0.045 (beads) ^b	0°C	l-hexene	4 O
Added PPh3	0°C	"	20
Added THF	0°C	11	25

Table 6. Effect of THF or PPh3 on Hydrogenation Rates.

^a(Cp₂TiH)₂ in hexane.

^bBuLi reduced **P**-Cp₂TiCl₂.

hydride were used. As Table (7) shows, 2 equivalents of reduction are enough to give the beads full activity. The rate is the same as was obtained with beads reduced

Table 7. Hydrogenation with Beads^a Treated with 2 Equivalents of BuLi.

		Prep. Conditions	Hydro	ogenatic	n
Temp.	Gas	Equivalent of Reduction	Olefin	Temp.	Rate ^b
0°C	^Н 2	2 eq. BuLi/Ti	l-hexene	0°C	37
0°	^H 2	2 eq. BuLi/Ti+P-CpH	l-hexene	0°	30
0°	^H 2	2 eq. BuLi/Ti+P-CpH	l-hexene	0°	36

^a P-Cp₂TiCd₂ copolymer beads.

^b(mL/min-mmol Ti)

with an excess of BuLi, but much less than the homogeneous $(Cp_2TiH)_2$. The bead color was gray-green, just as was obtained previously.

When equal amounts of homogeneous Cp_2TiCl_2 and polymer supported $\bigcirc -Cp_2TiCl_2$ are reduced by 2 equivalents of BuLi in hexane, combined hydrogenation rates are far below what would be expected if all the Ti were the catalyst $(Cp_2TiH)_2$. When the beads are washed with hexane several times, the rate decreases to a value on the order of the expected rate for the polymer supported Ti only.

		Temp.	Rate ^b (mL/min-mmo)
Homogeneous Cp ₂ TiCl ₂ plus P -Cp ₂ TiCl ₂	0.0281 mmol 0.0277 mmol	0°C	112 lst ru	ın
beads only (washed with hexane)	0.028	0 °	25 2nd ru	ın

Table 8. Hydrogenation with Beads^a Plus Homogeneous Cp₂TiCl₂.

^a (P-Cp₂TiCl₂ copolymer beads.

^bl.0 mL l-hexene.

There are two reasonable explainations of this experiment: (1) polymer supported titanocene dichloride and homogeneous Cp_2TiCl_2 yield different species when reduced by BuLi, or (2) the hydride monomer cannot dimerize in the polymer supported Ti.

Comparison of Catalyst Rates

A comparison of hydrogenation rates of 1-hexene by $(Cp_2TiH)_2$ and by reduced titanocene beads demonstrates a significant difference in reactivity. Tables 1 and 2 list rates of hydrogenation obtained by other researchers in these labs. A number of variables make direct comparison of rates difficult. Bead size, Ti concentration on

the polymer, rate of stirring during reaction, temperature, total amount of catalyst used, concentration of olefin, and purity of reagents used have all been observed to effect the measured hydrogenation rates. The largest difference is size of the polymer beads; ground beads have the higher rates of hydrogenation. In Figure 5 the rates are compared for $(Cp_2TiH)_2$ and for reduced beads. Except for cyclohexene, $(Cp_2TiH)_2$ has rates significantly better than those rates obtained with the bead catalyst. Both catalysts hydrogenate primary double bonds better than internal double bonds, but the difference is more dramatic for the $(Cp_2TiH)_2$.

Dienes and alkynes are hydrogenated by $(Cp_2TiH)_2$ all the way to alkanes. With cyclooctadiene the internal double bonds so not seem to diminish the rates as much as observed in cyclohexene. Diphenyl acetylene has a lower rate than for the non-conjugated diene. Figure 6 compare hydrogenation rates when the same conditions (except for temperature) are used for $(Cp_2TiH)_2$ and for reduced beads with 1hexene. As before, $(Cp_2TiH)_2$ has higher rates than the whole beads. The effect of PPh₃ and THF on each of these catalysts is to decrease the rate but the relative decrease is greater for $(Cp_2TiH)_2$.

Titanium concentration is also seen to effect (Figure 6) the rates for $(Cp_2TiH)_2$. Figure 7 illustrates this effect more clearly. At higher Ti concentration the



Figure 5. Relative hydrogenation rates for bead catalyst and $(Cp_2TiH)_2$.

.



Figure 6. Relative hydrogenation rates after THF or PPh_3 addition.

•



overall rate tapers off. At low Ti concentration there is an abrupt drop in rates. This drop is probably because of limits in purity of reagents and in the ability to exclude air and water from the system used for hydrogenation. Because of the Ti concentration effect on observed rates, most of the $(Cp_2TiH)_2$ rates are not maximum rates for the olefins tested.

The reduced titanocene beads have been compared to the homogeneous system for hydrogenation of olefins.¹³ The bead catalyst was found to be several times more active than the homogeneous species. This difference is probably due to decomposition of the homogeneous species; the inactive dimer, $(CpTiH)_2C_{10}H_8$, is one of the decomposition products. Increased catalytic activity was then observed for the bead species that could not deactivate by dimerization. No attempt was made to maximize the rates in the homogeneous system. Room temperature is detrimental toward formation of active titanocene species, thus the conditions used assure formation of inactive species. At lower temperatures a gray material identified as $(Cp_2TiH)_x$ forms instead of the inactive brown solution obtained at 25°. The polymeric hydride, $(Cp_2TiH)_x$, is an active catalyst, although not as active as the purple dimer, (Cp₂TiH)₂. The gray polymeric hydride can be used for hydrogenation at 25°, at which its rate of hydrogenation is greater than the bead species. Small

changes in the reaction conditions and concentrations of reagents used can change the titanocene species being formed. It is therefore difficult to make comparisons of the bead system to a homogeneous system unless the active intermediate can be identified in each case.

Figure 8 compares the reduced polymer attached titanocene dichloride beads to several catalysts that have been identified in the solutions used for the hydrogenation. The rates of hydrogenation of 1-hexene by the purple hydride catalyst are much greater than any of the other catalysts tested. The purple hydride is not as easy to handle (although easier to prepare) as the reduced beads.

The difference in hydrogenation rates and olefin selectivity between the purple hydride and the reduced beads indicates either that the catalysts are different species or that some severe limitation is being imposed on the polymer bound species by its polymer attachment. The most reasonable possibilities for the polymer bound catalytic species is then polymer attached analogs of titanocene (I), titanocene monohydride (VI), or fulvalenide bridged hydride (II). Reasonable mechanisms can be drawn for each of the possibilities (Figure 9). If both the titanocene and the fulvalenide bridged hydride are present, it would account for the mixed results when reduced beads were treated with DC1. In a D₂ atmosphere one would expect deuterium to be incorporated into the ring positions

by the titanocene ring hydrogen abstraction mechanism.⁴⁹ The change in symmetry of the titanocene as hydrogen abstraction occurs should lead to a second esr signal superimposed on the titanocene signal. When these species are bound to the polymer, esr detail would be lost and an unsymmetrical singlet would be reasonable as the observed signal.



Figure 8. Comparison of hydrogenation rates for titanocene catalysts.



Mechanisms for hydrogenation by titanocene derivatives. Figure 9.

Reactions of (Cp₂TiH)₂

Catalytic Isomerization of Allylbenzene

The purple hydride was tested for activity as an isomerization catalyst. Allylbenzene, ALB, which has a terminal double bond, can be isomerized to form the more stable system - cis- and trans- propenylbenzene. The products were identified by gas chromatography or by integration of NMR peaks. The purple hydride was prepared under hydrogen as before, then the hydrogen removed and argon substituted. Two mL of dry ALB was added to the hexane slurry and the mixture stirred overnight at 0°. After 13 hours, 100% isomerization to predominately transpropenylbenzene had occurred. By comparison, the polymer supported titanocene catalyst had isomerized only 90% of the ALB after 13 hours at 145°.¹⁴ Unlike the active bead catalyst, homogeneous (Cp₂TiH)₂ often turns yellow during a test and is then inactive.

Isomerization of 1,5-Cyclooctadiene

In a similar manner to allylbenzene, 1,5-cyclooctadiene (1,5-COD) can be isomerized to the more stable conjugated 1,3-COD. A slurry of $(Cp_2TiH)_2$ in 10 mL of hexane was

treated with 1.0 mL of 1,5-COD under an argon atmosphere. At a reaction temperature of 0°, 80% isomerization to 1,3-COD was obtained in 3.5 hours or 100% isomerization in 7 hours. No 1,4-COD was obtained, as indicated by gas chromatography. By comparison, Lau reported¹⁴ that the titanocene dichloride beads gave 90% isomerization to 1,3-COD after 10 hours at 145°.

Isomerization of 1-Octene

Unlike the other substrates tested, 1-octene does not have the driving force for rearrangement to a conjugated diene. The 2-octene is only slightly more stable than 1octene. When a slurry of $(Cp_2TiH)_2$ was treated with 1.0 mL of 1-octene at 0° under argon, 5% isomerization to 2octene occurred after 12 hours. Although longer reaction times might lead to more complete isomerization, the purple hydride is unstable under argon and decomposes readily to give an inactive yellow species.

Isomerization reactions of the purple hydride, $(Cp_2TiH)_2$, could proceed by the mechanism below if the dimer is in equilibrium with the coordinatively unsaturated monomer. The alkene first may bind to the Ti followed by a hydrogen transfer to an alkene carbon. Two possible β -hydrogen abstraction reactions could occur. One reaction returns to the original alkene but the other β -hydrogen abstraction leads to the isomerization product.



When the homogeneous $(Cp_2TiH)_2$ catalyst is compared to the reduced species on the polymer beads, the purple hydride is a more active isomerization catalyst than the beads. The stability of the homogeneous compound is not very stable under argon or at temperatures above 0°. In most cases the isomerization yield was limited by decomposition of the purple hydride. By comparison, the bead species were active even at 145°, which is high for a titanocene species. Furthermore, the beads could be reused or regenerated by treatment with HCl. Regeneration of $\bigcirc -Cp_2TiCl_2$ from the reduced beads, which had been at 145°, indicates the π -cyclopentadienyl integrity had been maintained. If the polymer supported species were the monohydride monomer, **P**CpTi-H it is not clear why the monomer should have such high thermal stability when polymer supported.

Nitrogen Fixation

Volpin and Shur High Pressure Method

The Volpin and Shur method³¹ for nitrogen fixation uses a mixture of titanocene dichloride and phenyl lithium (PhLi) in ether under 100-200 atm of nitrogen pressure. Homogeneous and polymer attached Cp_2TiCl_2 were compared for nitrogen fixation at 150 atm of N₂ and ambient temperatures. The ammonia yields for several different experimental runs are listed in Table 9. Homogeneous nitrogen fixation gave ammonia yields comparable to those reported by Volpin and Shur.³¹ When polymer attached Cp_2TiCl_2 was used, however, no ammonia was detected.

In cases where the titanocene-nitrogen intermediates have been identified, dimeric titanocene species with bridging nitrogen molecules were the intermediates that led to ammonia after hydrolysis.^{37,42,43} The titanocene sites on the polymer are physically separated and formation of a dimeric titanocene that could react with nitrogen is unlikely. Since no nitrogen was fixed by the monomeric titanocene species on the polymer, the conclusion that a dimer is required for nitrogen fixation by titanocene is

			NH ₃ Yield
	mmol Ti	mmol PhLi	mmol Ti
Homogeneous Cp ₂ TiCl ₂	2.41	13.6	0.73
	2.44	13.6	0.51
	2.43	13.6	0.60
	2.61	13.6	0.69
	2.47	13.6	0.67
Polymer Attached			
P -Cp ₂ TiCl ₂	1.11	6.5	0.0
	1.08	6.5	0.0
	1.80	9.0	0.0

Table	9.	Nitrogen	Fixation	Results:	Volpin	and	Shur
		Method.					

supported.

Fixation of N2 by Cp2Ti(arene) Compounds

A number of Ti (III) compounds of the general formula Cp_2TiR are known to react with nitrogen to form a dimeric species, $(Cp_2TiR)_2N_2$.^{56,27,30} Thermal stability of the Cp_2TiR compounds is dependent on the alkyl group. Generally, substituted aromatic groups give compounds with the greatest stability.⁵⁷ Teuben has found that a number of compounds can react with nitrogen to form blue diamagnetic complex, $(Cp_2TiR)_2N_2$, which can be reduced by NaNp, RLi or RMgX to form ammonia and hydrazine.²⁸

The benzyl derivative, $Cp_2Ti(CH_2C_6H_5)$, is thermally stable enough for convenient use in nitrogen fixation. Preparation results from treatment of Cp_2TiCl with one equivalent of benzyl magnesium bromide and an equimolar amount of 1,4-dioxane. A brown solid of $Cp_2Ti(CH_2C_6H_5)$ can be isolated from an ether solution under argon if a temperature of -20° or below is maintained. In toluene or hexane the brown compound reacts with nitrogen at -80° to form $[Cp_2Ti(CH_2C_6H_5)]_2N_2$, an intensely blue complex. Formation of the blue nitrogen complex corresponds with the disappearance of an esr singlet at g = 1.983 and the mixture becomes diamagnetic. When the blue nitrogen complex was treated with an excess of NaNp followed by hydrolysis, 0.205 mmol of ammonia per mmol Ti was obtained.

The polymer attached compound, $\mathbb{P} - Cp_2Ti(CH_2C_6H_5)$, was prepared by the above method. Brown beads were obtained that had an esr signal consisting of a four peak pattern, g = 1.983. The brown beads were treated with NaNp under one atm $\rm N_{\odot}.~$ After hydrolysis of the mixture, no ammonia was detected. When the brown beads were cooled to -80° in toluene under nitrogen, there was no color change. The esr signal remained the same. Physical separation of the Ti sites by the polymer must prevent formation of the required dimer, (Cp₂TiR)₂N₂, and nitrogen does not bind to the monomeric compound. This experiment confirms the conclusion of the Volpin and Shur nitrogen fixation experiments with the beads. A dimeric titanium is required for formation of the nitrogen complex and the polymer support prevents formation of such nitrogen bridged titanium dimers.

Fixation of N₂ by (Cp₂TiH)₂

Bercaw⁴⁹ had found that $(Cp_2TiH)_2$ could be used to fix nitrogen. The hydride dimer was treated with NaNp under 150 atm of nitrogen to obtain a maximum yield of 0.99 mmol NH₃ per mmol Ti. It was found in this work that $(Cp_2TiH)_2$ fixes nitrogen at one atm N₂. The purple hydride was suspended in toluene under nitrogen, the reaction cooled to -80° to obtain an intense blue solution, and then a 10 fold excess of NaNp in THF added. After being stirred for 12 hours and being warmed to room temperature, the mixture was hydrolyzed with CH_3OH and aqueous HCl. The aqueous layer was separated and ammonia determined by standard HCl titration of the Kjeldahl distillate. Ammonia yields were the highest when NaNp was used to reduce the N₂ complex. Since the yields were greater than one, there was the possibility that the reaction would be catalytic if the reduced nitrogen could be transferred to a second complex. Lewis acids have performed this function in one titanium nitrogen fixation system.⁴⁰ The Lewis acid Et₂AlCl was added to the nitrogen complex with NaNp reducing agent, but the yield of ammonia was lower than before. Other Lewis acids may function better.

Polymer supported titanocene dichloride was tested for nitrogen fixation under conditions under which the monohydride titanocene may have formed. The beads were treated with 2 equivalents of BuLi under hydrogen in hexane at 0°. The hydrogen gas was replaced by nitrogen gas, toluene added, and the mixture cooled to -80°. As before, the beads remained gray. Sodium naphthalide was added and, after 12 hours of stirring, the mixture was hydrolyzed. No ammonia was detected in the aqueous layer. This experiment confirms that the reduced polymer supported species does not fix nitrogen. The identity of the reduced species on the beads in this experiment is not known.

mmol Ti	Reducing Agent	NH ₃ Yield (<u>mmol</u>)
0.24	NaNp	1.20
0.21	NaNp	1.27
0.25	NaNp	0.94
0.16	NaNp + Et ₂ AlCl	0.81
0.38	i-PrMgBr	0.0
0.37	i-PrMgBr	0.0
0.36	n-BuLi	0.35

Table 10. Nitrogen Fixation Yield by Use of (Cp₂TiH)₂.

DC1 Treatment of the Polymer Supported Titanocene Species

An attempt was made to identify whether the reduced titanocene species on the polymer was a hydride or not by analysis of the hydrogen gases liberated when the beads were treated with DC1. Four runs were made at different temperatures and the gases analyzed by mass spectrometry. Table 11 summarizes the reaction conditions and results. A graph of gas composition <u>vs</u>. temperature shows a straight line relationship for each of the hydrogen isotopes.

The results of treating the reduced species with DCl indicates the presence of a hydride, but that not all Ti centers involve a hydride. There are several ways in which a hydride could have formed. Bercaw⁴⁹ has shown that ring hydrogen exchange does occur. Brintzinger⁵⁰ obtained a Ti (III) dihydride when alkyl lithium reagents were used where the hydride is from the β position on the alkyl group. The DCl treatment experiment does not answer the question of the origin of the hydrogen, the oxidation state of the metal, or the nature of the other ligands.

Presuming that the hydrogen comes from the cyclopentadienyl rings, one can make inferences based on the reaction temperature <u>vs</u>. percent hydrogen isotope (Figure 10). There are two possible ways in which to obtain hydrogen: an exchange route which leads to HD or H_2 : or a nonexchange route where no hydride is involved, leading to D_2 .

	% Isotope			
D ₂	HD	H ₂	Re	eaction Conditions
47	35	18	+24°C	BuLi-hexane-Ar
35	41.5	23.4	-78°	"
40.7	39.5	19.2	0°	11
37.9	39.4	22.7	0 °	BuLi-hexane-H ₂
57.0	39.2	4.1	0°	i-PrMgBr-ether-Ar

Table 11. Composition of Liberated Gas From DC1 Treated Reduced P-Cp2TiC12.







Consider the rates of reaction with DCl that would be affected by the temperature of reaction. If the hydride is formed initially, the exchange process would give mostly H_2 and some D_2 . These two species would have the same temperature relationship, i.e., the same slope, for the graph of percent species <u>vs</u>. temperature. For the non-exchange process, only HD is formed; this process would result in a slope differing from that for H_2 and D_2 . If a hydride is not the initial species, then the exchange route would give both HD and H_2 with the same slope, and the non-exchange route would lead to formation of D_2 , with a different slope. The observed graph fits the latter

Exchange route:

case, implying a titanocene species that is not initially a hydride. The β -hydrogen abstraction from a cyclopentadienyl ring by the metal to form a hydride is then a reasonable explanation of the data. The data suggest that both titanocene and the hydride obtained by rearrangement are present as the polymer attached species.

A titanocene dihydride which is formed by β -hydrogen abstraction from the titanocene dialkyl is another possibility.



Treatment of the homogeneous dihydride with D_2O was reported to give evolution of a gas mixture of H_2 , HD, and D_2 in a ratio of 1:2:1 (Brintzinger⁵⁰) and 1/2:2:2 (Volpin and Shur⁵⁸). These values for the isotopic mixture of gases are reasonably close to the results obtained from the reaction of the titanocene species beads and DCl, but do not match the theoretical yields for a dihydride. ESR evidence and observation of reactions indicate that dihydride formation occurs in ether solvents but not hydrocarbon solvents. Furthermore, the esr of the reduced polymer supported species does not match the frozen glass spectrum of the homogeneous $(Cp_2TiH_2)^-$. The results for the isotope mixture do not match the theoretical yields well enough to presume that $(Cp_2TiH_2)^-$ is the species on the polymer and other evidence suggests that the dihydride is not present.

In hexane BuLi treatment of $\bigcirc -Cp_2TiCl_2$ might give the monohydride, $\bigcirc -Cp_2Ti-H$. Bercaw³⁶ treated the homogeneous monohydride with DCl (91.5% isotopic purity) to obtain hydrogen gas of the composition 12% H₂, 83% HD, and 60% D₂. The overall equation for the reaction indicates the % D₂ should be 1/2 that of the percent HD.

$$Cp_{2}Ti-H + 2DC1 \longrightarrow Cp_{2}TiCl_{2} + HD + 1/2D_{2}$$

Treatment of the polymer attached reduced species gave roughly equal amounts of HD and D_2 (an approximate average ratio, H₂:HD:D₂, was 1:2:2). Results for the bead species do not correspond well to either the predicted or the actual isotope yields obtained by Bercaw for (Cp₂TiH)₂.

The DCl treatment results indicate that some hydride intermediate is available, but the identity of the hydride

or the mechanism by which it is formed are as yet unknown. Ring hydrogen abstraction to form a hydride intermediate seems to fit the data reasonably well. Other types of evidence, however, are needed to identify the species on the beads.

ESR of the Copolymer Bead Species

Electron Spin Resonance (esr) spectra of the titanocene species attached to the copolymer beads gives some clues as to the identify of the reduced species. Reduction of $\bigcirc -Cp_2TiCl_2$ with excess BuLi, NaNp, or RMgBr leads to gray beads that have an esr signal consisting of a slightly distorted singlet (Figure 11). The g values obtained for most samples in the temperature span of $\pm 40^{\circ}$ to $\pm 150^{\circ}$ are in the range g = 1.990 ± 0.002 with an average signal width of 28 gauss. The lack of detailed hyperfine splitting precludes a positive identification of the reduced species on the beads. Since both Ti (II) and Ti (III) compounds are known that have g values in the range of g = 1.975 through g = 1.998, even the oxidation state of the titanium cannot be exactly determined.

Either BuLi in hexane or NaNp in THF reduce the titanocene dichloride beads to the same species, as indicated by the esr signal. The g values are the same when reduction is under argon or under nitrogen at room temperature. Although Lau¹⁴ has reported that a doublet can be obtained



by BuLi reduction of very low Ti content beads under a hydrogen atmosphere, experiments with beads containing 10 times more Ti have not given the multiple peaks observed by Lau. Reductions in pure THF lead to beads with an esr signal that is more distorted but has a g value in the same range as before. It would appear that, perhaps, with the exception of reduction under hydrogen, the same titanocene species is generated within the polymer beads under a wide variety of conditions and reducing agents.

Controlled addition of reducing agents can lead to a stepwise reaction. Addition of one equivalent of NaNp or i-PrMgBr to \mathbb{P} -Cp₂TiCl₂ gives beads with a 4 peak pattern in the esr spectrum, g = 1.979 (Figure 12). When 1 more equivalent or an excess of reducing agent is then added, the distorted singlet signal, g = 1.990, appears. The species with the 4 peak pattern is probably P-Cp₂TiCl. Homogeneous titanocene monochloride has a g value of 1.980 which corresponds well to the g value of the species on the polymer. If the homogeneous Cp2TiCl solution is frozen at -110°, a distortion of its singlet occurs and a 4 peak pattern at g = 1.980 appears (Figure 13). The splitting between peaks matches well the splittings in the bead esr spectra. Polymer attached Cp₂TiCl can be prepared by reaction of Et_2AlCl with \mathbb{P} - Cp_2TiCl_2 and the esr spectrum matches both the homogeneous Cp_2TiCl and the 1 equivalent reduced bead species.



Figure 12. ESR spectrum of (P)-Cp₂TiCl.



Figure 13. Frozen solution esr spectrum of Cp₂TiCl.

It is possible then to identify some titanocene derivatives attached to the polymer beads if the esr spectrum patterns are compared to the patterns of the frozen solutions spectra of the homogeneous compounds. Another compound, $\bigcirc -Cp_2Ti(CH_2Ph)$, was identified by this method. The symmetry and oxidation state of the $Cp_2Ti(CH_2Ph)$ is similar to that of Cp_2TiCl . Thus, the esr signal of $\bigcirc -Cp_2Ti(CH_2Ph)$ is a 4 peak pattern like that of the polymer attached monochloride but with different splitting between peaks and with a g value of 1.983, (Figure 14). These values matched the frozen solution spectra for homogeneous $Cp_2Ti(CH_2Ph)$.

A number of homogeneous titanocene derivatives were prepared and their esr spectra obtained for comparison to the reduced species on the beads. The temperature, solvent, and amount of reducing agent added have significant effects on what reduced titanocene species is obtained. In ether solvents or benzene at temperatures below -40° , Ti (III) dialkyl derivatives are obtained. Brintzinger⁵⁹ had prepared and recorded esr spectra for a number of these compounds. At Ti concentration of 10^{-2} M when a large excess (40-60 fold) of reducing agent, RLi or RMgBr (R=Me-, Et-, i-Pr-, Bu-), is added to a cold solution of Cp₂TiCl, the titanocene dialkyl anion can be detected by esr. By BuLi reduction the anion [Cp₂Ti(Bu)₂]⁻ was obtained; its esr spectrum consisted of a quintriplet,



Figure 14. ESR spectrum of \mathbb{P} - Cp₂Ti(CH₂Ph).

g = 1.989 (Figure 15). The hyperfine splitting is due to interaction of the Ti (III) (d^{1}) with the 4 α -hydrogens on the two butyl ligands. The number of hyperfine lines can be determined by the (2n(I)1/2 + 1) rule (I = 1/2). When the cold solution was warmed slowly an intermediate [Cp₂Ti(Bu)H]⁻ (Figure 16) was obtained which was formed by β -hydrogen abstraction from a butyl ligand. The esr spectrum consists of a doublet (7.4 G splitting), due to the Ti (III)-hydride interaction, which is split into triplets (2.5 G) by the α -hydrogens on the butyl group. Further warming to room temperature of this solution yielded [Cp₂TiH₂]⁻. The esr spectrum (Figure 17) is a triplet (7.5 G) due to the two hydride ligands. Under certain conditions the associated cation can cause further splitting of the triplet as in Figure 18 where the dihydride anion was prepared with i-PrMgBr; a septet (0.4 G splitting) due to Mg (I = 3/2) is obtained.

The dihydride anion is stable at room temperature for several days. Preparative reactions performed at room temperature yield the dihydride anion rapidly. No difference in the sequence of esr signals was observed at any temperature when nitrogen was substituted for argon as the inert gas during the reaction. Although initial reports⁵⁹⁻⁶¹ concerning $[Cp_2TiH_2]^-$ attributed nitrogen fixation to the dihydride anion, subsequent conclusions are that the dihydride anion is an inactive side product with regard to



i.

Figure 15. ESR spectra of Cp₂Ti(Bu)₂⁻.


Figure 16. ESR spectrum of (Cp₂Ti(Bu)H⁻.

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Figure 17. ESR spectrum of (Cp₂TiH₂)⁻.



Figure 18. ESR spectrum of (Cp₂TiH₂)⁻ with Mg hyperfine splitting.

reaction with nitrogen. 43,62,63 No nitrogen fixation would be expected then by the reduced polymer beads if the species on the polymer was $[P-Cp_2TiH_2]^-$.

When BuLi in hexane is used to reduce the titanocene dichloride beads, chemical and esr observations indicate that a species other than $(\mathbb{P} - Cp_2 TiH_2)^-$ is being formed. Formation of the dihydride anion is not observed for homogeneous reactions in hexane. Apparently a more polar ether solvent is needed to help stabilize the anion. Frozen homogeneous solutions of the dihydride anion give esr spectra that are different from the distorted singlet observed for the reduced species on the polymer (Figure 19). By contrast, the dialkyl anions, that had detailed hyperfine in solution, when frozen were merely broad singlets (Figure 20). Table 12 compares the esr signals observed for a number of compounds. Signals containing hyperfine with splittings lose all detail when the solution is frozen. Signal width often changes also but the g value remains nearly the same. The thermal instability of the dialkyl anions, however, suggests that they are not reasonable possibilities as the reduced polymer supported species obtained at ambient temperatures. Thus, neither the alkyl nor dihydride anions are the polymer supported titanocene species.

The polymer attached $(P - Cp_2Ti(CH_2Ph))$ was prepared by treatment of $(P - Cp_2TiCl)$ beads with one equivalent of



Figure 19. Frozen solution esr spectrum of $(Cp_2TiH_2)^-$.

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Effect on an esr quintruplet of freezing the solution. Figure 20.

Species		g Value	Width	Split
Cp ₂ TiMe ₂	septet	1.987	24.5	4.5
Cp ₂ TiBu ₂	Quintuplet	1.989	7.0	2.0
Cp ₂ TiEt ₂	Quintuplet	1.989		2.0
Cp ₂ TiPr ₂	Triplet	1.982	6.0	2.3
Cp ₂ TiH ₂	Triplet	1.993	14.5	7.5
Cp ₂ TiCl	Singlet	1.980		
	Frozen Solu	tion Spectra		
Cp ₂ TiMe ₂	Singlet	1.982	18.0	
Cp ₂ TiBu ₂	Singlet	1.988	7.0	
Cp ₂ TiEt ₂	Singlet	1.986	12.0	
Cp ₂ TiPr ₂	Singlet	1.982	8.0	
Cp ₂ TiH ₂	brd signal	cl.993	22.0	
Cp ₂ TiCl	Pattern	1.980		
Beads				g
BuLi + P-Cp	TiCpCl ₂	THF disto:	rted singlet	1.
i-PrMgBr + (P)-CpTiCpCl ₂	THF disto:	rted singlet	1.

Table 12. Summary of esr Results for Titanocene Derivatives.

PhCH₂MgBr and an equimolar amount of 1,4-dioxane. The brown beads that were obtained had an esr signal consisting of a four peak pattern, g = 1.983 (Figure 14). The splitting between peaks and the g value match those of the frozen homogeneous solution spectrum for Cp₂Ti(CH₂Ph). When the brown beads were treated with nitrogen at -80° no color change was observed and the esr signal remained the same. Had nitrogen been taken up by the complex the esr signal and the bead color should have changed. Since no nitrogen could be fixed using these beads, the conclusion is that the required dimeric complex with bridging nitrogen cannot be formed with the titanocene derivative that is attached to the polymer.

Solutions of the purple hydride, $(Cp_2TiH)_2$, in hexane have an esr signal at g = 1.989 (28 G width). Bercaw³⁶ reported that the solid was diamagnetic, as would be expected for the dimer complex, but that solutions showed a weak singlet signal. By analogy to solutions of $(Cp_2Ti)_2$ and $C_5(CH_3)_5$]Ti, in solution a monomer-dimer equilibrium appears to exist which would account for the observed esr signal.

Addition of triphenylphosphine (PPh_3) to a solution of $(Cp_2TiH)_2$ in cold hexane causes symmetrical cleavage of the dimer to form $Cp_2Ti(PPh_3)H$. The esr signal consists of two doublets with spacings of 9.9 and 23.0 G (Figure 21). The larger split is due to ³¹P hyperfine interaction and



Figure 21. ESR spectrum of Cp₂Ti(PPh₃)H.

the smaller split is due to the hydride. Each peak is further split by 0.6 G into a quintet. Although no positive explanation of the quintet can be made, it is probably due to association of a THF molecule. A peak at higher field, g = 1.968, corresponds to a decomposition product obtained in greater yield at higher temperatures.

When THF is added to a hexane solution of $(Cp_2TiH)_2$, a fleeting doublet is observed followed by the 12 line spectrum shown in Figure 22. The basic pattern is a 1:2:1 triplet (8.5 G splitting) each line of which is split into a quartet (2.0 G splitting). Olivé and Olivé have observed similar spectra.⁶¹ The quartet is probably due to 7 Li (I = 3/2) which is reported to have hyperfine splitting of approximately 2 G. The rest of the spectrum is harder to explain when the experimental conditions are considered. A dihydride would, however, explain the triplet splitting. One of the structures below might explain the spectrum.⁶¹ Since the Ti concentration $(10^{-2}M)$ is so low in the esr experiments an excess of 2 equivalents of BuLi was added in the initial reaction to form the purple hydride dimer. Formation of an anion species may be aided by the more polar THF. Bercaw³⁶ did not observe this esr spectrum but BuLi was not present in the solution in his experiment.



Figure 22. ESR spectrum of (Cp₂TiH)₂ in THF.

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APPENDIX A

ATTEMPTED PREPARATION OF POLYMER SUPPORTED MOLYBDENOCENE DICHLORIDE THROUGH THE P-CpMoCl_L INTERMEDIATE

Since titanocene species were obtainable that were active catalysts when coordinated to a polymer support, it was suggested that other compounds that were coordinatively unsaturated and electron deficient might also prove to be active catalysts, when attached to the copolymer beads. Molybdenocene is a sixteen electron system that has been predicted to undergo carbene like reactions⁶⁴ and a variety of basic addition and insertion steps that are of interest for homogeneous catalysis. Although chromocene is stable and readily prepared,⁶⁵ neither molybdenocene nor tungstenocene have been isolated. Inert bis(pentaphenylcyclopentadienyl)molybdenum (II) has been reported⁶⁶ and the metallocenes have been postulated as intermediates in a number of reactions.

Tungstenocene intermediates were postulated in the insertion reactions of olefin and acetylene complexes with $(C_5H_5)_2WH_2^{67}$ and in formation of aryl hydrides and addition to dienes.⁶⁸ Thomas reported⁶⁹ generation of the metallocenes from the dichloride and Na(Hg) which undergo addition and insecrion reactions typical of organic

carbones. The metallocene intermediates can also be photogenerated from $(C_5H_5)_2M(CO)^{70}$ or from $(C_5H_5)_2MH_2$.⁷¹ Thus, polymer supported molybdenocene would be expected to be highly reactive and possibily useful for catalysis, just as was the polymer attached titanocene species.

In a manner similar to titanocene, molybdenocene polymerizes readily with itself⁶⁹ to form less reactive compounds. Attachment to a polystyrene backbone would prevent molybdenocene dimerization and could lead to a useful hydrogenation or nitrogen fixation catalyst. When generated as an intermediate, molybdenocene has been shown to add across the triple bonds of dinitrogen, acetylenes, and carbon monoxide.⁶⁹ Tungstenocene is capable of inserting into C-H bonds of aromatic hydrocarbons⁶⁴ and would be expected to deactivate quickly by reaction with the polystyrene support. Molybdenocene species generated on the polymer support would be expected to show greater reactivity because of metal center isolation just as was achieved with the titanocene species.

A synthesis scheme similar to the preparation of polymer attached titanocene dichloride was initially envisioned for attached molybdenocene dichloride (Figure 23). Unlike CpTiCl₃ the compound CpMoCl₄ (I) is unstable and difficult to obtain. The compound <u>I</u> is prepared in low yield by reaction of hydrogen chloride with oxoor oxochloro- complexes.⁷² While anhydrous the red









crystalline \underline{I} is stable at room temperature, but is very sensitive to hydrolysis, and either is insoluble or reacts with common organic solvents.^{73,74} A communication outlining a preparation using TlCp which reports a yield of 40% \underline{I} has since appeared.⁷⁵ Preparation of polymer supported molybdenocene dichloride via the method in Figure 23 has not been successful because of the unsuitable properties of compound I.

An alternate preparative method (Figure 24) was undertaken where the compound <u>I</u> need only be an intermediate attached to the polymer support. Bonds et al.¹³ had reported this method for the attachment of Nb, Mo, and W to the polymer. Only bead color changes and a Cl:Mo ratio of 4:1 support the supposition that \bigcirc -CpMoCl₄ (<u>III</u>) formed on the polymer. Bonds offered the equations below to explain the color change of the beads from black in benzene to yellow in THF.¹³

$$MCl_{n} + Cp^{-}Li^{+} \xrightarrow{C_{6}H_{6}} CpMCl_{n}^{-}Li^{+}$$
(1)

$$CpMCl_{n}Li^{+} \xrightarrow{THF} CpMCl_{n-1} + LiCl$$
(2)

The free compound <u>I</u> is reported to be red and paramagnetic with an esr singlet at g = 1.990, width 52 G.⁷² Beads obtained by my preparative method for <u>III</u> do not match the free compound for those two properties. Reactions (1)

and (2) seem unlikely in that the polar THF would be more suitable for stabilizing the polar, charged $CpMoCl_5^{-Li}^+$ than would benzene. There are several other compounds which could account for the observed data, especially considering the conditions used for reaction.

The procedure to prepare \mathbb{P} -CpMoCl_l used was to stir the \mathbb{P} -Cp⁻Li⁺ beads in a solution of MoCl₅ in benzene under a dinitrogen atmosphere. Slightly different results were obtained depending upon the reaction temperature. Intensely colored, black or brown, paramagnetic beads were obtained that had Cl:Mo ratios of approximately 4:1. Reactions performed at room temperature yield beads that have an esr singlet at g = 1.96, width 20 G. When the reaction is performed by reflux extraction of the MoCl₅ from a Soxhlet thimble (the procedure also used by Bonds and Chrandrasekaran⁷⁶) the yellow-brown beads, after THF extraction, have multiple esr signals; the predominate peak was at g = 1.95, width 58 G. Variations in temperature during preparation obviously led to different results even though the beads had a similar appearance.

There are several factors that bear against the success of the synthesis of <u>III</u>. Molybdenum pentachloride is only slightly soluble in benzene and is known to form adducts with most common solvents.⁷⁷ Adduct formation is easily observed by the different colors obtained when $MoCl_5$ is added to a variety of solvents. That it is not just the $MoCl_5$ adducts absorbed in the beads is clearly

		esr si	gnal
MoCl ₅ in	Color	g value	width
Benzene	black/brown	1.944	25 G
THF	green	1.944	12
ether	purple	1.944	14 1
hexane	red	1.944	12
powdered MoCl ₅	black	1.956	55
MoCl ₅ + beads	gray	1.955	44

Table 13. ESR spectral Values for MoCl₅.

indicated by the esr results and the green rather than yellow color of the THF adduct. Furthermore, hot benzene reacts with $MoCl_5$ to form insoluble $MoCl_4$ readily.^{77,78} Absorption of the tetrachloride by the beads would give a paramagnetic compound of the right color and Cl:Mo ratio to match the black beads obtained in the attempted synthesis of compound <u>III</u>. Adduct formation by the tetrachloride⁷⁷ would then account for the color change in the beads when extracted with THF.

 $2MoCl_5 + C_6H_6 \longrightarrow 2MoCl_4 + C_6H_5Cl + HCl$

 $MoCl_4 + THF \longrightarrow MoCl_4 \cdot (THF)_n$ Considering the low stability of <u>I</u> reported by Green^{72,73} and by Shive⁷⁴ coupled with the fact that <u>I</u> reacts with most common solvents, formation of a stable polymer supported species <u>III</u> at reflux temperatures in benzene or THF is highly unlikely. If <u>III</u> were formed, the beads should be red after the MoCl₅ adduct is washed out; instead the beads remain black. It may be concluded that <u>III</u> is not obtained by the preparative procedures used, and that insoluble $MoCl_4$ is deposited within the polymer. Molybdenum tetrachloride, its adducts, and oxo-decomposition products then account for the polymer bound species obtained by this method and not compound <u>III</u>.

Experimental

Attempted Preparation of (P) -CpMoCl₄ by Use of MoCl₅

<u>Method A</u>: Dry cyclopentadient substituted copolymer beads (5 g) were suspended in THF for two hours before treatment with 10.3 mL of 1.7M CH_3Li in ether. After two days the red beads were extracted with 3x20 mL of THF and with 3x20 mL benzene. The beads were suspended in benzene and the reaction flask fitted with a Soxhlet extractor charged with 1.8 g MoCl₅. The benzene was boiled to extract the MoCl₅ into the reaction flask. Violent bubbling and white fumes were observed as the hot benzene contacted the MoCl₅ in the Soxhlet thimble. The brown slurry obtained by this procedure was stirred with the beads for three days. Excess solvent was removed, the beads dried, and the beads extracted with benzene. Afterwards, the black beads had an esr spectrum of a distorted singlet, g = 1.950, width 48 G. Further extraction of the beads with THF caused an immediate color change to yellow-brown beads. These beads had a complex esr spectrum with four major peaks, the largest being at g = 1.946, 58 G width.

Method B: Into a flask was placed 3 g of cyclopentadiene substituted copolymer beads, 20 mL of THF, and a three-fold excess of CH₃Li in ether. After two days of being stirred, the beads were extracted with 3x20 mL of THF and with 3x20 mL benzene. Into a 50 mL septum flask was placed 1.1 g $MoCl_5$ and dry benzene at room temperature added to dissolve the solid. An ink black solution of MoCl₅ in benzene was transferred using a syringe into the flask containing the red P-CpLi beads. After the mixture was stirred a few minutes the black solution turned a translucent green. More MoCl₅ in benzene was added until the color change to green no longer occurred. All solvent was removed after three days and the beads extracted at room temperature with benzene until no color was observed in the washings. The black beads had a distorted singlet with g = 1.948 (45 G width) in its esr spectrum. After treatment with THF at room temperature, the beads were rust and had an esr singlet at g = 1.958, 19 G width.

<u>Method C</u>: The procedure above was followed except that the P-CpLi beads were treated with a two-fold excess of MoCl₅ in THF at room temperature. When wet the beads were a green color but when vacuum dried turned to tan. The esr was similar to that above and 0.18 mmol of Mo/g of copolymer was found.

APPENDIX B

PREPARATION AND ATTEMPTS TO REDUCE POLYMER ATTACHED MOLYBDENOCENE DICHLORIDE

Discussion

The procedure developed by John Lee¹⁵ for attachment of metallocenes to a polymer support was followed with minor modifications. Cyclopentadiene substituted beads were treated with $CH_{3}Li$ and then with molybdenocene dichloride. Sigma-pi ring exchange led to attachment (Figure 25) and treatment with HCl generates polymer attached (P) -Cp₂MoCl₂. The dry beads were air stable, green-brown, and paramagnetic. Since free Cp₂MoCl₂ is diamagnetic, either an impurity was present or $(\mathbf{P} - Cp_2 MoCl_2)^+$ was formed. The esr spectrum of the bead species (Figure 26) was similar to the reported frozen glass spectrum of $(Cp_{2}MoCl_{2})^{+}$.^{79,80} Analysis indicated a Mo concentration of 0.66 mmol/g beads and a Mo:Cl ratio of 1:2.16. Farir spectra of Cp_2MoCl_2 and polymer attached $\bigcirc -Cp_2MoCl_2$ have been obtained (Table 14). The spectrum of the ground bead species is a reasonable match if the molybdenocene dichloride anion is also present.

Reduction of molybdenocene dichloride with Na/Hg or BuLi has been reported to give molybdenocene as an



Figure 25. Scheme for the Preparation of polymer supported molybdenocene dichloride.¹⁵



Figure 26. ESR spectrum of beads obtained from $(P - Cp_2MoCl_2)$ synthesis.

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P-CpMoCpCl ₂	Cp ₂ MoCl ₂	Literature ⁷⁹	
460			
412	417w	412w	
369	392	388	
342	356	346	
316			
295m	292s	293vs	
27 Om	262s	262s	
217w	212s	208s	

Table 14. Far-ir Spectral Data of Cp2MoCl2 Compounds.

intermediate. Molybdenocene undergoes carbene like reactions with CO, N₂, and HC=CH.⁶⁹ Several attempts were made to produce the molybdenocene analog on the polymer from the dichloride. After addition of a reducing agent to the beads in hexane or THF, the beads were washed and a second reagent added. The $\bigcirc -Cp_2MoCl_2$, after reduction, was tested for insertion reaction and for catalytic activity. Listed below is a summary of the reactions attempted and the results (Table 15). Only two reactions worked: (1) LiBH₄ treatment produced the dihydride, $\bigcirc -Cp_2MoH_2$, and (2) allyl benzene was isomerized by LiNp reduced beads.

M. L. H. Green⁸¹ has reported a number of unusual products when Cp_2MoH_2 is treated with RLi or RMgBr. An anionic species, $(Cp_2MoH)^{-}M^{+}$ (M = Li, MgBr), is produced that is capable of a wide variety of reactions. These Mo compounds show reactivity similar to R⁻ in RLi. The co-valent Mo-Li bond is formed by alkane elimination in reverse of the usual β -hydrogen transfer and elimination reaction.

The dihydride is not normally a hydrogenation catalyst. Olefins and acetylenes with activating groups react with Cp_2MoH_2 to form stable insertion compounds instead.⁸² Whereas titanocene dihydride has an empty orbital available for bonding with the π system of an olefin, the molybdenocene dihydride has a filled orbital and is a

Mo Species	Reducing Agent	Reagent	Reaction	Product/Description
PcpMoCpC12	BuL1/hexane			brown beads, para-
green	BuLi or LiNp	CO	No	No v _(CO) in i.r.
	BuL1 or L1Np	CO	No	No V(CO) in 1.r.
	BuL1	PhC≡CPh	No	No V(C≡C)
	BuL1 or LINp	H ₂ /1-hexene	No	No H ₂ uptake
	LINP	1,5-COD/120°C	No	No isomerization
		L1BH4/reflux THF	Yes	Yellow beads
	1	NaBH4	No	remained green
	L1Np/THF	allyl benzene	Yes	Isomerization
	L1Np/THF	l-hexene	No	
	Vitride	-	No	
		с ₄ н ₉ ѕн(с ₂ н ₅) ₃ и	Yes	$\mathbb{P} - c_{p_2Mo}(sc_{\mu}H_g)_2$

Summary of Attempted Reactions with (P)-Cp₂MoCl₂. Table 15.

)-Cp ₂ MoH ₂ .
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Table

Mo Species	Reducing Agent	Reagent	Reaction	Product/Description
DramoraH		enerned [w[[c	CN N	
Zurdooudo C	But 1 /heven	allyl benzene		isomerivation
	Buli	H ₂ /1-hexene	NO	No H ₂ uptake
	BuL1	PHc≡CPh	No	No v _{C≡C} in IR
	BuL1	CO	No	No v _(CO) in IR
Brown beads from LINP re	ductio			
reauction	8	ТОИ	Ies	green peads
B cpwcpc1 ₂	Et ₂ AlCl		Yes	black beads
	Et ₂ AlCl	allyl benzene	No	

fairly stable 18 electron system. The $\bigcirc -Cp_2MoH_2$ was tested for its ability to undergo insertion reactions or to form the anionic complex reported by Green.⁸¹ Isomerization of allylbenzene was the only reaction that gave positive results. In all other cases the bead compound was unreactive.

The lack of reactivity of the molybdenocene dichloride and dihydride is certainly puzzling. It could be that the molybdenocene intermediate is not generated by the reducing agents used. Another possibility is that the very reactive molybdenocene reacts with the polymer or reacts to deactivate in some way soon after it is generated. Whatever the reaction, the molybdenocene dichloride when reduced with BuLi or LiNp does not produce a catalyst or an intermediate capable of insertion reactions.

Experimental

Preparation of Polymer Attached Chromocene

To 20% crosslinked polystyrene beads containing pendent cyclopentadiene was added an excess of BuLi and THF. The red beads were washed 3 x 20 ml with THF by using syringe techniques. Dissolved $CrCl_3(THF)_3$ in THF was added to the reaction flask containing the beads along with some powdered zinc. After being refluxed for two hours, the solution was cooled and excess reagent removed

by extraction with THF to yield green beads. These beads were then treated with excess NaCp in THF overnight. After extraction of the beads with THF, deep red beads were obtained. The beads were diamagnetic and mildly air sensitive.

A sample of free chromocene was prepared for comparison by reaction of $CrCl_3$ with excess NaCp.⁸³ Scarlet red crystals were obtained upon sublimation. A THF solution of the red crystals was also diamagnetic.

Preparation of Polymer Attached Molybdenocene Dichloride

The procedure of John Lee¹⁵ was followed with minor modifications (Figure 25). To 15 g of polymer attached cyclopentadiene beads (34 mmol) was added 43 ml of $1.4\underline{M}$ methyl lithium in ether and 75 ml freshly distilled THF. This mixture was stirred for three days under nitrogen and then the excess methyl lithium removed by syringe. The red beads were washed with THF 4 x 20 ml and 9.95 g (33.5 mmol) of molybdenocene dichloride was added along with 75 ml of THF. After being stirred for seven days, excess reagent was removed by syringe and anhydrous HCl bubbled into the mixture. Uniform green colored beads were obtained after Soxhlet extraction with THF.

Analysis: Mo 0.66 mmol/g Cl:Mo ratio 2.16 Cl 1.43 mmol/g far-ir 412, 295, 270, 217w cm⁻¹

Preparation of Polymer Attached Molybdenocene Dihydride

Polymer attached molybdenocene dichloride and an excess of LiBH_4 was loaded into a flask in the dry box. To this mixture, under a nitrogen atmosphere, was added dry THF. A vigorous reaction occurred immediately as the beads become a dirty yellow. Excess LiBH_4 was removed by withdrawal of the suspension by a syringe and needle. After several washings with THF, the beads were used directly for other reactions.

Preparation of Polymer Attached Dibutanethiol Molybdenocene

Special care in handling techniques was exercised because of the foul smell of the thiol compounds. All reactions were carried out under inert gas in enclosed glassware. Stock solutions were stored in septum capped flasks and transferred as required by use of a syringe and needle. All reactions were carried out in a fume hood and unreacted thiols were treated with an ethanolpotassium hydroxide solution to decompose them.

Into a 100 mL sidearm flask with a condenser was placed 2.0 g of (P) -Cp₂MoCl₂ beads and 9.0 mmol of BuSH (from a stock solution of 1:1 Et₃N:BuSH). Benzene, toluene, or THF was added (20 mL) and the mixture heated to reflux and stirred for 1-3 days. The beads were washed with solvent to remove excess reagent and vacuum dried.

Red-brown beads were obtained that contained 0.11 mmol Mo/g and 0.10 mmol S/g. Analysis of the remaining chloride on the beads indicates incomplete reaction of the polymer attached Cp_2MoCl_2 .

APPENDIX C

PREPARATION OF POLYMER ATTACHED GROUP VI CpM(CO)₃H COMPOUNDS

Discussion

A variety of group VI metal carbonyl compounds were attached to the polymer support for the following reasons:

- 1. As intermediates to other compounds;
- 2. To demonstrate the physical separation of compounds that dimerize readily when homogeneous;
- 3. To test for catalytic activity;
- 4. To attach compounds that could easily be identified by spectral means;
- 5. To demonstrate the variety of compounds that could be supported on the polymer.

The compounds $CpM(CO)_{3}H$ (M = Cr, Mo, W) are useful intermediates easily identified by strong carbonyl stretches in the ir,^{83,84} and are known reagents for the hydrogenation of dienes.⁸⁵ A dimer, $(CpM(CO)_{3})_{2}$, forms readily when the hydride is exposed to air or heated. The dimer is also the by-product of diene hydrogenation; the chromium dimer being capable of being reduced by hydrogen back to the hydride, whereas the molybdenum

and tungsten compounds cannot.^{85,86} These carbonyl hydrides were thought to fit the criteria above and thus to be able to take advantage of polymer support.

Synthesis of $(\mathbb{P}-CpM(CO)_{3}H$ (Cr, Mo, W) was achieved by a modified procedure used for the preparation of the homogeneous compounds.⁸⁷ Direct reaction of molybdenum hexacarbonyl in THF with the $(\mathbb{P}-CpLi)$ beads leads to yellow beads with weak carbonyl peaks in the infrared. Yields were improved by reaction of $(CH_{3}CN)_{3}M(CO)_{3}$ with the $(\mathbb{P}-CpLi)$ beads in THF under a nitrogen atmosphere.⁸⁸

$$\mathbb{P} - CpLi + (CH_3CN)_3 \stackrel{\text{THF}}{\longrightarrow} \mathbb{P} - CpM(CO)_3 \xrightarrow{\text{HOAc}} \mathbb{P} - CpM(CO)_3^{\text{HOAc}}$$

The reaction is easily observed by color change of the red (P)-CpLi beads to yellow beads and by the release of carbon monoxide or acetonirtile.

Formation of the $(\mathbb{P}-CpM(CO)_{3}H$ compounds was confirmed by observation of the carbonyl stretch in the ir. Normally the polystyrene absorptions obscure the infrared spectra of attached compounds but a window between 1700-2100 cm⁻¹ is available for observation of carbonyl stretching modes. The number of peaks and their position can be used to identify the attached compounds. Although the metal hydride stretch is also in this region, it is too weak to be observed for polymer attached species. Below is a table comparing the observed infrared spectra for the supported and for the homogeneous compounds.

Since the time these polymer attached compounds were prepared, a report has appeared⁸⁹ for the synthesis of these compounds in dimethyl formamide on 18% crosslinked polystyrene copolymer. A similar compound has also been prepared⁹⁰ by sigma bond attachment, $\mathbf{P}-\mathbf{C}_{6}\mathbf{H}_{4}-\mathbf{W}(\mathbf{CO})_{3}(\mathbf{Cp})$. This compound has been shown to catalyze olefin metathesis.

The polymer supported $Cp_2M(CO)_3H$ compounds have greater stability in air or when heated than the non-attached compounds. Since the dimer $[Cp_2M(CO)_3]_2$ would normally be formed by decomposition of the hydride, the greater stability of the polymer supported compounds is because dimerization is prevented. That the dimer is not formed is demonstrated by bead color and by the supported compound's ir spectrum. When (P)-CpMO(CO)H was tested for hydrogenation of conjugated dienes, no hydrogen addition could be detected by gas chromatography of the solution. Apparently a mechanism is not available for hydrogenation by use of the monomer hydride under a hydrogen atmosphere.

Experimental

Preparation of (P)-CpW(CO)₃H^{91,92}

To 0.4 g of beads containing ca. 0.4 meq of \bigcirc -CpH was added an excess of n-BuLi in hexane and 15 ml of THF. The beads turn from light yellow to dark red. After being stirred for 15 minutes, the excess BuLi was washed out by using two 12 ml portions of THF. Solid tungsten hexa-carbonyl (0.29 g) was added and the deep red color of the beads changed to yellow. The mixture was refluxed for five hours, washed with two 10 ml portions of THF, and the beads treated with glaical acetic acid. After being washed three times with 15 ml portions of THF, the beads were vacuum dried. Pale yellow beads were obtained.

tungsten analysis 0.042 mmol/gm beadsinfrared $(O)_{3H}$ 1975, 1900 cm⁻¹

<u>Method B</u>: Improved yields were achieved by using the soluble $(CH_3CN)_3Mo(CO)_3$ instead of $Mo(CO)_6$ to treat the beads. Molybdenum hexacarbonyl was refluxed in dry

acetonitrile for five hours and the solvent removed by evacuation to obtain $(CH_3CN)_3Mo(CO)_3$.

To 0.5 g of the beads was added 2.0 ml 1.6M n-BuLi and 20 ml THF. After being stirred for 30 minutes, the beads were washed with THF by using syringe techniques. Solid $(CH_3CN)_3MO(CO)_3$ was dissolved in 20 ml of THF and the solution added to the flask with the beads. The mixture was stirred for 0.5 hour at 50°. The solvent was then removed, the beads transferred to a Soxhlet extractor, and the beads extracted well with THF. Yellow beads were obtained.

Infrared (P-CpMo(CO)₃H 2025w, 1995s, 1925-55bd cm⁻¹

<u>Preparation of (P) - CpMo(CO)₃Cl⁸⁷</u>

The $(\mathbb{P} - CpMo(CO)_3H$ beads were placed in a septum capped 50 ml flask which was filled with argon. Ten ml CCl_4 and ten ml THF were added by syringe. The beads, which float on top of the carbon tetrachloride layer, were stirred vigorously to insure contact. A faint red color developed and remained as the beads were washed with THF and vacuum dried.

infrared 2010, 1950 and 1915 cm^{-1} far-infrared 530sh, 560sh, 180bd cm^{-1}
APPENDIX D

PREPARATION OF POLYMER ATTACHED GROUP IV ARENE METAL TRICARBONYL COMPOUNDS

Discussion

The known synthesis procedures 93 for ArM(CO)₃ (M = Cr, Mo, W) are very similar to the conditions used in making $CpM(CO)_{3}H$. Since benzene rings of the polystyrene are more numerous than the (P) -CpH the possibility of obtaining a mixture of compounds or only polymer attached $ArM(CO)_3$ suggested that a direct synthesis should be attempted. Pittman⁹⁴ has reported preparing $(\mathbb{P} - \operatorname{ArCr}(CO)_3)$ on linear and 2% crosslinked polystyrene by using the direct method of refluxing the polymer with chromium hexacarbonyl. Recently, Farona⁹⁵ has reported that preparation is possible on 2% crosslinked polymer by direct refluxing with the chromium hexacarbonyl in heptane. The polymer supported species could be used as a catalyst for Friedel-Crafts reactions. A number of other catalysis uses have been reported including Friedel-Crafts reactions, 95,96 hydrogenations, 97,98 carbon tetrachloride addition to olefins,⁹⁹ dehydrohalogenations,¹⁰⁰ and polymerization of acetylene.¹⁰¹

Direct reaction of molybdenum hexacarbonyl with plain

20% crosslinked polystyrene beads was attempted using THF or hexane as solvent. After prolonged refluxing, no apparent reaction had occurred as indicated by bead color and lack of $v_{(CO)}$ in the infrared. If dimethoxyethane (DME) or heptane are used as solvents, refluxing for several hours yields yellow beads that have infrared peaks at 1970 and 1885 cm⁻¹.

		<u>i.r. spectra</u>
P-ArMo(CO) ₃	2% beads	1975, 1890 cm ⁻¹
P-ArMo(CO)3	20% beads	1970 , 1885
(toluene)Mo(CO) ₃	homogeneous	1985 , 1915
(xylene)Mo(CO) ₃	homogeneous	1975, 1910

Both 2% and 20% crosslinked beads reacted in this manner with molybdenum hexacarbonyl, however, the tungsten derivatives could not be obtained even after prolonged refluxing in heptane. If DME is used, which has a higher boiling point, and ethyl cyanide added, light yellow beads can be obtained after three days of refluxing. The <u>in</u> <u>situ</u> formation of (EtCN)₃W(CO)₃ and higher reaction temperature allows preparation of the polymer supported arene tungsten tricarbonyl.

The poor yields obtained when THF or hexane were used to prepare (P)-ArM(CO)₃ is attributed to the lower solvent boiling points. Yields are increased by using

 $(EtCN)_{3}M(CO)_{3}$ because of its increased solubility, but the higher reaction temperature is still required. When the functionalized $(P-Cp^{-}Li^{+})$ beads are used in THF or hexane the predominate reaction is expected to yield $(P-CpM(CO)_{3}H)$ rather than the arene metal tricarbonyl. Thus either type of compound can be prepared selectively on the beads by proper choice of reaction conditions.

Experimental

Attempted Preparation of (P-ArM(CO)3

<u>Method A</u>: When plain 20% crosslinked beads and an excess of metal hexacarbonyl (M = Mo, W) were refluxed in THF or hexane, no bead color change was noted. Prolonged refluxing eventually led to a gray solution with black particles. The gray beads obtained by this method were extracted with THF or hexane to remove excess hexacarbonyl. No $v_{(CO)}$ was observed for the beads, but they did contain a trace of metal. Prolonged heating in the presence of light was found to decompose the metal hexacarbonyl in THF solutions to gray insoluble material. Thus $(P-ArM(CO)_3)$ was not prepared under these conditions.

<u>Method B</u>: Plain beads and $(EtCN)_3M(CO)_3$ were refluxed in THF or hexane in the dark. They remain white and have no $v_{(CO)}$ peaks in the ir.

Preparation of (P) -ArMo(CO)₃

Plain beads (either 2% or 20% crosslinked) were placed in a flask with excess molybdenum hexacarbonyl and 30 ml of heptane or DME. Refluxing and stirring for 4-8 hours gave yellow beads. After Soxhlet extraction, the beads were vacuum dried. The yellow beads slowly darken over a period of several days in air or upon heating.

infrared (P-ArMo(CO)₃ 2% crosslinked 1975, 1890 cm⁻¹ spectra: 20% crosslinked 1970, 1885 cm⁻¹

The tungsten compound could not be prepared under these conditions.

Preparation of (P)-ArW(CO)3

Plain beads were mixed with tungsten hexacarbonyl and 30 ml DME plus 5 ml dry propionitrile added. The mixture was refluxed under nitrogen for three days. Initially the white tungsten hexacarbonyl dissolved and a yellow solution formed during the heating. The beads slowly turned yellow during the reflux period. Yellow beads were obtained after Soxhlet extraction that had peaks in the ir at 1995, 1920 cm⁻¹. BIBLIOGRAPHY

BIBLIOGRAPHY

- 1. J. C. Bailar, Jr., <u>Cat. Rev.-Sci. Eng.</u>, 10, 17 (1974).
- 2. J. I. Crowley and H. Rappoport, <u>Accts</u>. <u>Chem</u>. <u>Res</u>., <u>9</u>, 135 (1976).
- 3. R. H. Grubbs, Michigan State University, private communication.
- 4. A. Bjorkman, Chem. and Eng. News, Dec. 15, 1975, p. 5.
- 5. W. H. Lang, A. T. Jurewicz, W. O. Haag, D. Whitehurst, and L. D. Rollman, <u>J. Organometal</u>. <u>Chem</u>., <u>134</u>, 85 (1977).
- 6. W. Haag and D. D. Whitehurst, Belgian Patent 721,686 (1968).
- 7. D. C. Neckers, D. A. Kooistra, and G. W. Green, <u>J. Am.</u> <u>Chem. Soc.</u>, <u>94</u>, 9285 (1972).
- 8. C. U. Pittman, Jr., Chem. Tech., 1, 416 (1971).
- 9. (a) F. R. Hartley and P. N. Vezey, <u>Adv. Organometal</u>. <u>Chem.</u>, <u>17</u>, 189 (1977).

(b) Zofia, M. Michalska, and D. E. Webster, <u>Platinum</u> <u>Metal Rev.</u>, <u>18</u>, 65 (1974).

- 10. W. Haag and D. D. Whitehurst, German Offen. 1,800,379 (1969).
- 11. R. H. Grubbs and L. C. Kroll, <u>J. Am. Chem. Soc.</u>, <u>93</u>, 3062 (1971).
- 12. C. U. Pittman, Jr., and G. O. Evans, <u>Chem. Tech.</u>, <u>3</u>, 560 (1973).
- W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, J. <u>Amer. Chem. Soc.</u>, <u>97</u>, 2128 (1975).
- 14. C. P. Lau, Thesis, Michigan State University, 1977.
- 15. J. G. Lee and C. H. Brubaker, Jr., <u>J. Organometal Chem.</u>, <u>135</u>, 115 (1977).
- 16. "The Federal Register", Vol. 39, No. 20, Part III, Occupational Safety and Health Administration, "Carcinogens".

- 17. (a) A. Davison and S. S. Wreford, <u>J. Am. Chem. Soc.</u>, <u>96</u>, 3017 (1974).
 - (b) H. H. Brintzinger and J. E. Bercaw, <u>J. Am. Chem.</u> <u>Soc.</u>, <u>92</u>, 6182 (1970).
- 18. G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., J. <u>Am. Chem. Soc.</u>, <u>88</u>, 1138 (1966).
- 19. C. L. Gibbons, Thesis, Michigan State University, 1973.
- 20. C. U. Pittman, Jr., and R. M. Hanes, University of Alabama, Private Communication.
- 21. K. W. Pepper, H. M. Parsley, and M. A. Young, <u>J</u>. <u>Chem. Soc.</u>, <u>4097</u> (1953).
- 22. D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry", 2nd Edition, Holt, Rinehart, and Winston, New York, NY, 1963, p. 233.
- 23. R. D. Gorsich, <u>J. Am. Chem. Soc.</u>, <u>80</u>, 4744 (1960).
- 24. K. Claus and H. Bestian, Justus Liebigs <u>Ann. Chem.</u>, <u>654</u>, 8 (1962).
- 25. R. S. P. Coutts, P. C. Wailes, and R. L. Martin, J. Organomet. Chem., <u>47</u>, 375 (1973).
- 26. M. L. H. Green and C. R. Lucas, <u>J. Chem. Soc.</u>, <u>Dalton</u> <u>Trans.</u>, 1000 (1972).
- 27. J. H. Teuben and H. J. De Liefde Meijer, <u>J. Organo-</u> metal. <u>Chem.</u>, <u>46</u>, 313 (1972).
- 28. F. W. Van Der Weij and J. H. Teuben, <u>J. Organometal</u>. <u>Chem.</u>, <u>105</u>, 203 (1976).
- 29. D. G. Breslow and N. R. Newburg, <u>J. Am. Chem. Soc.</u>, <u>81</u>, 81 (1959).
- 30. J. H. Teuben, J. Organometal. Chem., 57, 159 (1973).
- 31. M. E. Volpin and V. B. Shur, "Organometallic Reactions", Vol. I, E. I. Becker and M. Tsutsui, Eds., Wiley-Interscience, New York, NY, 1970, p. 102.
- 32. L. Kroll Thesis, Michigan State University, 1976.

- 33. (a) H. H. Brintzinger, J. Am. Chem. Soc., 89, 6871 (1967).
 (b) G. H. Olive' and S. Olive', Angew, Chem., Int. Ed., 8, 650 (1969).
- 34. M. E. Volpin, V. A. Dubovitskii, O. V. Nogina, and D. N. Kursanov, <u>Dokl. Akad. Nauk</u> <u>SSSR</u>, <u>151</u>, 1100 (1963).
- 35. H. H. Brintzinger and L. S. Bartell, <u>J. Am. Chem. Soc.</u>, <u>92</u>, 1105 (1970).
- 36. J. E. Bercaw, Thesis, University of Michigan, 1971.
- 37. I. N. Ivleva, A. K. Shilova, S. I. Salienko, and Y. G. Borad'ko, <u>Dokl. Akad. Nauk. SSSR</u>, <u>213</u>, 116 (1973).
- 38. P. C. Nailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Ti, Zr and Hf", Academic Press, Inc., New York, NY, 1974, p. 249.
- 39. E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, J. Am. Chem. Soc., 91, 1551 (1969).
- 40. M. E. Volpin and M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, J. Chem. Soc., Chem. Comm., 1074 (1968).
- 41. G. P. Pez, and S. C. Kwan, <u>J. Am. Chem. Soc.</u>, <u>98</u>, 8079 (1976).
- 42. A. E. Shilov, <u>Russian Chem. Rev.</u>, <u>43</u>, 378 (1974).
- 43. J. E. Bercaw, et al., <u>J. Am. Chem. Soc.</u>, <u>98</u>, 8358 (1976).
- 44. M. E. Volpin, V. A. Duovitskii, O. V. Nogina, and D.
 N. Kursanov, <u>Dokl</u>, <u>Akad</u>. <u>Nauk</u>. <u>SSSR</u>, <u>151</u>, 1100 (1963).
- 45. W. Kirmse, "Carbene Chemistry", Academic Press, New York, NY, 1964.
- 46. Y. G. Borod'ko, A. E. Shilov, and A. A. Shteinman, Dokl, Akad. Nauk. SSSR, 168, 581 (1966).
- 47. R. H. Marvich, Thesis, University of Michigan, 1971.
- 48. G. J. Olthof, <u>J. Organometal</u>. <u>Chem</u>., <u>128</u>, 367 (1977).

- 49. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. <u>Am. Chem. Soc.</u>, <u>94</u>, 1219 (1972).
- 50. H. H. Brintzinger, J. Am. Chem. Soc., 89, 6871 (1967).
- 51. M. E. Volpin, V. B. Shur, <u>et al.</u>, <u>Dokl</u>, <u>Akad</u>. <u>Nauk</u>. <u>SSSR</u>, <u>194</u>, 577 (1970).
- 52. J. S. Kenworthy, J. Myatt, and M. C. R. Symons, <u>J.</u> Chem. <u>Soc</u>. (A), 1020 (1971).
- 53. J. X. McDermott, M. E. Wilson, and G. M. Whitesides, J. <u>Am. Chem. Soc.</u>, <u>98</u>, 6529 (1976).
- 54. M. H. Peng, Thesis, Michigan State University, 1977.
- 55. M. D. Rausch, W. H. Boon and H. G. Alt, <u>J. Organometal.</u> Chem., <u>141</u>, 299 (1977).
- 56. Y.G. Borodko, I. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and O. E. Shilov, J. Chem. Soc. Comm., <u>1178</u> (1972).
- 57. J. H. Teuben, J. Organometal. Chem., 69, 241 (1974).
- 58. M. E. Volpin, V. B. Shur, <u>et al.</u>, <u>J. Organometal</u>. <u>Chem</u>. <u>27</u>, C5 (1971).
- 59. H. H. Brintzinger, <u>J. Am. Chem. Soc.</u>, <u>88</u>, 4307 (1966).
- 60. V. B. Panov, Y. M. Shul'ga, E. F. Kvashina, and Y. G. Borod'ko, <u>Kinetika</u> <u>1</u>. <u>Kataliz</u>., <u>15</u>, 518 (1974).
- 61. G. H. Olive and S. Olive, <u>Angew</u>. <u>Chem.</u>, <u>Int.</u> <u>Ed.</u>, <u>1</u> 386 (1968).
- 62. E. Bayer and V. Schurig, Chem. Ber., 102, 3378 (1969).
- 63. C. Ungnienasu and E. Streba, <u>J. Inorg. Nucl. Chem.</u>, <u>43</u>, 3753 (1972).
- 64. K. L. T. Wong and H. H. Brintzinger, <u>J. Am. Chem. Soc.</u> <u>97</u>, 5143 (1975).
- 65. G. Wilkinson, F. A. Cotton, and J. M. Birmingham, <u>J.</u> <u>Inorg. Nucl. Chem.</u>, <u>2</u>, 95 (1956).
- 66. W. Hubel and R. Merenyl, <u>J. Organometal.</u>, <u>Chem.</u>, <u>2</u>, 213 (1964).
- 67. B. R. Francis, M. L. H. Green, and G. G. Roberts, <u>Chem. Commun.</u>, 1290 (1971).

- 68. M. L. H. Green and P. R. Knowles, <u>J. Chem</u>. <u>Soc</u>., 1508 (1971).
- 69. J. L. Thomas, J. Am. Chem. Soc., <u>95</u>, 1838 (1973).
- 70. K. L. T. Wong, J. L. Thomas, and H. H. Brintzinger, <u>J</u>. <u>Am. Chem. Soc.</u>, <u>96</u>, 3694 (1974).
- 71. G. L. Geoffroy and M. G. Bradley, <u>J. Organometal Chem.</u>, <u>134</u>, C27 (1977).
- 72. M. Cousins and M. L. H. Green, <u>J. Am. Chem. Soc.</u>, <u>1567</u> (1964).
- 73. M. Cousins and M. L. H. Green, <u>J. Am. Chem. Soc.</u>, 16 (1969).
- 74. L. Shive, Michigan State University, private communication, 1977.
- 75. M. J. Bunker, A. DeCian, and M. L. H. Green, <u>Chem</u>. <u>Commun.</u>, 59 (1977).
- 76. W. D. Bonds and E. S. Chandrasekaran, Michigan State University, Private communication, 1973.
- 77. M. L. Larson and F. W. Moore, <u>Inorg</u>. <u>Chem</u>., <u>3</u>, 285 (1964).
- 78. T. M. Brown and E. L. McCann, III, <u>Inorg</u>. <u>Chem</u>., <u>7</u>, 1227 (1968).
- 79. R. L. Cooper and M. L. H. Green, <u>J. Am. Chem. Soc.</u>, 1155 (1967).
- 80. W. M. E. Lindsell, J. Chem. Soc., (D), 2548 (1975).
- 81. F. W. Benfield, B. R. Francis, M. L. H. Green. N. T. Luoug-Thi, G. Moser, J. S. Poland, and D. M. Roe, J. Less-Comm. Metals., 36, 187 (1974).
- 82. A. Nakamura and S. Otsuka, <u>J. Am. Chem. Soc.</u>, <u>94</u>, 1886 (1972).
- 83. J. J. Eisch and R. B. King, "Organometallic Synthesis," Vol. 1., Academic Press, New York, NY 1965.
- 84. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, New York, NY, 1972.
- 85. A. Miyake and H. Kondo, <u>Angew</u>. <u>Chem</u>., <u>Int</u>. <u>Ed</u>., <u>7</u>, 880 (1968).

- 86. A. Miyake, H. Kondo, and M. Aoyama, <u>Angew</u>, <u>Chem</u>., <u>Int. Ed.</u>, <u>8</u>, 520 (1969).
- 87. T. S. Piper and G. Wilkinson, <u>J. Inorg. Nucl. Chem.</u>, <u>3</u>, 104 (1956).
- 88. R. B. King and A. Fronzaglia, <u>Inorg. Chem., 5</u>, 1837 (1966).
- 89. G. Gubitosa and H. H. Brintzinger, <u>J. Organometal</u>. <u>Chem.</u>, <u>140</u>, 187 (1977).
- 90. S. Warwel and P. Bushmeyer, <u>Angew. Chem.</u>, <u>Int. Ed.</u> <u>17</u>, 131 (1978).
- 91. D. P. Tate, W. R. Knipple, and J. M. Angel, <u>Inorg</u>. <u>Chem.</u>, <u>1</u>, 433 (1962).
- 92. S. A. Keppie and M. F. Lappert, <u>J. Organometal</u>. <u>Chem</u>. <u>19</u>, P5 (1969).

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- 93. B. Nicholls and M. C. Whiting, <u>J. Chem. Soc.</u>, <u>551</u> (1951).
- 94. (a) C. U. Pittman, <u>et al.</u>, <u>J. Poly</u>. <u>Sci.</u>, <u>10</u>, 379 (1972).

(b) C. U. Pittman, <u>J. Organometal</u>. <u>Chem.</u>, <u>67</u>, 295 (1974).

- 95. C. P. Tsonis and M. F. Farnoa, <u>J. Organometal</u>. <u>Chem</u>., 114, 293 (1976).
- 96. M. F. Farona and J. F. White, <u>J. Am. Chem. Soc.</u>, <u>93</u>, 2826 (1971).
- 97. E. N. Frankel, E. Selke, and C. A. Glass, <u>J. Am. Chem.</u> <u>Soc.</u>, <u>90</u>, 2446 (1968).
- 98. C. U. Pittman, Jr., B. T. Kim, and W. M. Douglas, <u>J.</u> <u>Org. Chem.</u>, <u>40</u>, 590 (1975).
- 99. O. Gandolfi and M. Cais, <u>J. Organometal</u>. <u>Chem.</u>, <u>125</u>, 141 (1977).
- 100. J. F. White and M. F. Farona, <u>J. Organometal</u>. <u>Chem</u>., <u>63</u>, 329 (1973).
- 101. P. S. Woon and M. F. Farona, <u>J. Poly. Sci.</u>, <u>12</u>, 1749 (1974).

