POLYMER-SUPPORTED ORGANOMETALLIC COMPOUNDS OF TITANIUM AND NIOBIUM AND THEIR APPLICATIONS TO CATALYSIS

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ABSTRACT

POLYMER-SUPPORTED ORGANOMETALLIC COMPOUNDS OF TITANIUM AND NIOBIUM AND THEIR APPLICATIONS TO CATALYSIS

By

Chak-po Lau

Homogeneous catalytic reactions employing transition metal complexes have become increasingly important in recent years, as exemplified by the production of acetaldehyde from ethylene and air by the Wacker process.[1] However, the scope of practical application of homogeneously catalyzed reactions has been limited, chiefly by the difficult separation of the usually very expensive catalysts from the reaction products. Therefore, heterogenizing homogeneous catalysts is a significant step in improving their industrial applicability. While the heterogenization technique obviously prevents loss of possibly expensive catalytic materials and contamination of reaction products, this method also offers the opportunity to prepare new classes of catalyst systems with other desirable properties. For instance, selectivity towards molecules of different bulk[2] and polarity[3].

For the research discussed here, the organometallics of Ti and Nb were heterogenized by attachment to 20 % cross-linked (600 Å pore size) macroreticular polystyrene-divinylbenzene copolymer beads ranging in size from 30 to 60 meshes.

Recently, Grubbs, Brubaker and coworkers[4] demonstrated that the attachment of titanocene-related catalysts to polymers resulted in an

increase in activity for olefin hydrogenation. Since titanocene species undergo deactivation by polymerization process [5], it was proposed that this increase in activity resulted from site isolation on the polymer. Since this phenomenon has become a major concern with polymer attached reagents and catalysts, a study of site isolation as a function of loading of catalyst was carried out. A model has been developed to permit calculation of the extent of metal-metal interactions in polymer attached metallocene catalysts, such as $\vdash Cp_2Ti$ or its hydride. Caculations predict a maximum in the curve of hydrogenation rate (for olefins) vs polymer loading and that is observed. The corresponding homogeneous catalysts do not exhibit a maximum, but only show an ever-lessening increase in rate as concentrations of catalyst increase as would be expected for a monomer--dimer equilibrium involving the catalyst.

A hydrogenation catalyst can have other catalytic activities, such as isomerization, oligomerization, etc.. Since polymer attached titanocene and the reduction product of polymer attached $TiCpCl_3$ have been proved to be excellent catalysts for olefin hydrogenation, their activities in other catalytic reactions were studied.

Allylbenzene and 1,5-cyclooctadiene undergo isomerization in the presence of either one of the polymer attached Ti catalysts. Allylbenzene was converted a mixture of trans and cis-propenylbenzene and 1,5-cyclooctadiene to a mixture of 1,4-cyclooctadiene and 1,3-cyclooctadiene. Oligomerization of ethyl propiolate was effected by the same catalysts. The acetylenic derivative oligomerized to give a mixture of closed and open trimers.

Polymer attached $TiCp_2Cl_2$ and $TiCpCl_3$ can also be used directly, without going through the reduction process, to catalyze the epoxidation of cyclohexene and cyclooctene.

Polymer attached titanocene dicarbonyl, $TiCp_2(CO)_2$, was prepared by first reducing the attached $TiCp_2Cl_2$ with BuLi and carbon monoxide gas was added at 4 atm and was effective in the hydroformylation of olefins.

Resin bound $NbCpCl_3$ was prepared by reacting the cyclopentadienide anion substituted copolymer with benzene solution of $NbCl_5$. The polymer attached $NbCpCl_3$ was converted to $NbCp_4$ with excess NaCp; and then by treating the corresponding $NbCp_4$ with a saturated solution of dry hydrogen chloride in THF, polymer attached $NbCp_2Cl_2$ was formed. From the polymer attached $NbCp_2Cl_2$, it has been possible to prepare some of the polymer attached niobocene derivatives, such as $NbCp_2HCl$, $NbCp_2BH_4$ and $NbCp_2H$. Catalytic activities of these polymer attached organometallics of Nb have been examined, and it has been found that they are much poorer catalysts than the polymer attached titanocene complexes.

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By

Chak-po Lau

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To The Chinese And

Amercian Peoples

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INTRODUCTION

Catalysts are classified as "homogeneous" or "heterogeneous". The former commonly operate through the formation of "intermediate compounds", and the latter, by adsorption of the reactants on the catalyst surface. But the line between the two is not a sharp one, for the distinction between adsorption and compound formation is not at all clear. In recent years, several writers [1-5] have stressed that there is much overlap between homogeneous and heterogeneous catalysis. While it is incorrect to say that there is no distinction, it is beyond any doubt that many homogeneous catalysts can be converted into heterogeneous ones.

Homogeneous catalytic reactions employing transition metal complexes have become increasingly important in recent years, as exemplified by the production of acetaldehyde from ethylene and air by the Wacker process.[1] However, the scope of practical application of homogeneously catalyzed reactions has been limited, chiefly by the difficult separation of the usually very expensive catalysts from the reaction products. Therefore, heterogenizing homogeneous catalysts is a significant step in improving their industrial applicability. While the heterogenization technique obviously prevents loss of possibly expensive catalytic materials and contamination of reaction products, this method also offers the opportunity to prepare new classes of catalyst systems with other desirable properties, for example, selectivity towards

molecules of different bulk[6] and polarity.[7]

A homogeneous catalyst can be heterogenized in a variety of ways. The common method is to attach it to a solid support by adsorption or by an ionic or covalent chemical bond. Less common methods involve polymerizing the catalyst to such a high molecular weight that it becomes insoluble in the medium in which it is to be used, or by trapping it in a gel or other porous medium.

If the catalyst is heterogenized by linking it to a polymer, one may look upon the heterogenized catalyst as consisting of the insoluble, polymeric portion, which is the catalyst support, and the catalytic portion, which projects into the solution and is solvated and, in a sense, dissolved by it.

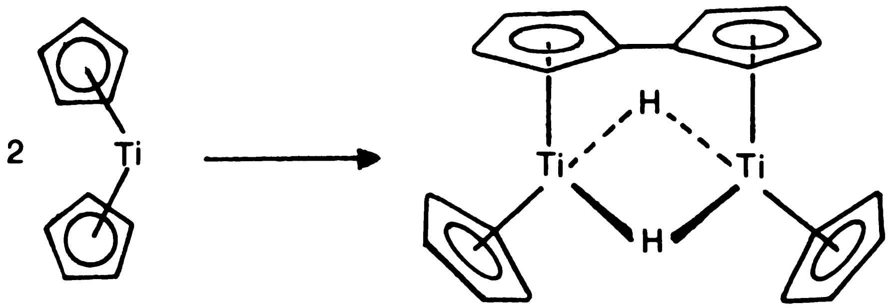
Haag and Whitehurst [8] have been pioneers in the field of heterogenizing homogeneous catalysts for industrial use. They attached $[Pt(NH_3)_4]^{2+}$ to sulfonate resins and used this material as catalyst for carbonylation. In another piece of work, these authors [9] prepared an active hydrogenation catalyst by coordinating rhodium trichloride to phosphine ligands bound to organic polymers. Manassen [10] captured rhodium, cobalt and other transition metals as coordination complexes bound to organic polymers, and then the polymer-attached complexes were used as heterogeneous catalysts for hydrogenation and hydroformylation. Capka [11] and coworkers have also worked with similar resin supported rhodium complexes.

Grubbs and Kroll [6] have attached Wilkinson's catalyst, tris-triphenylphosphine rhodium (I) chloride to the polystyrene-divinylbenzene resin through a triphenylphosphine function on the polymer. They have demonstrated that rates of hydrogenation of olefins have been enhanced and are dependent to a large extent upon the size and shape of the olefin molecules.

Bailar[12] has prepared polystyrene-divinylbenzene polymers with attached palladium(II) chloride and platinum(II) chloride, which they used in the selective hydrogenation of soybean oil methyl ester. Collman's group[13] has prepared complexes from the multinuclear $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. They attached these complexes to polystyrene-divinylbenzene-$P\phi_2$ polymers to form $\textcircled{P}\text{-}P\phi_2Rh_4(CO)_{11}$ and $\textcircled{P}\text{-}P\phi_2Rh_6(CO)_{15}$ respectively. Oxidation of these complexes by oxygen gave active metal species which would catalyze the hydrogenation of arenes at 25°.

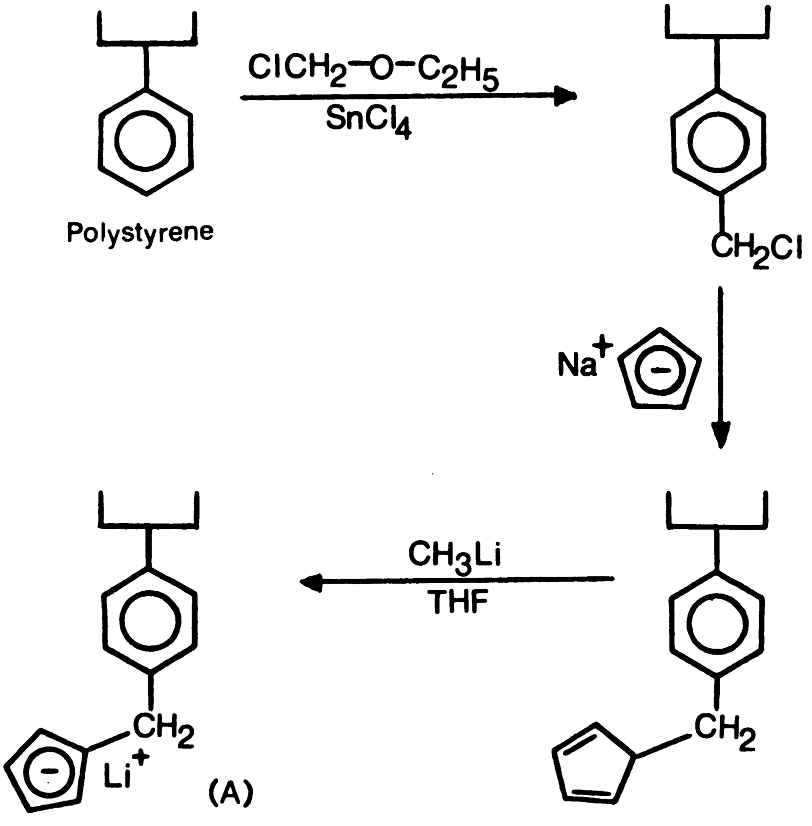
Pittman[14-17], et al., have synthesized a variety of polymer bound transition metal (Fe, Mo, Ni, Co) carbonyl catalysts. The catalyst center has been bound to the polystyrene and cross-linked polystyrene-divinylbenzene polymer by coordination to a phosphine. These materials that Pittman and coworkers have prepared have been employed in hydroformylation, oligomerization and isomerization of unsaturated hydrocarbons.

Titanocene dichloride has been a compound of interest for a long time. When reduced by a variety of reducing agents such as butyllithium, sodium naphalide, and aluminum alkyls, it has found considerable catalytic utility in the hydrogenation of olefins and fixation of nitrogen.[18-23] Breslow[24] had shown that it is also a good catalyst for the polymerization of ethylene. But some of the problems in the reduced, homogeneous titanocene material lie in their easy polymerization, according to the following reaction, to form catalytically inactive material.

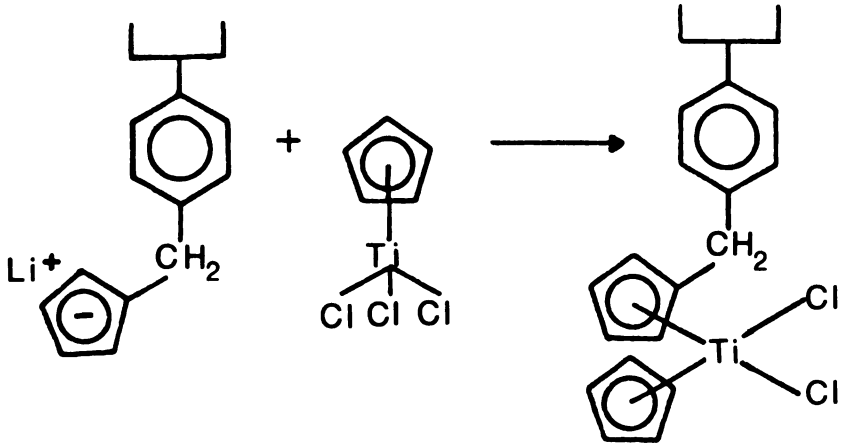


Grubbs, Brubaker, and coworkers [6,25-28] sought to prevent the dimerization reaction by attaching titanocene dichloride to a polystyrene-20% divinylbenzene copolymer. On reduction, a catalyst is produced whose hydrogenation efficiency is greater than that of a corresponding nonattached species.

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



The resin bound titanocene dichloride is prepared by treatment of (A) with cyclopentadienyl titanium trichloride.



The polymer-attached titanocene dichloride may be reduced by butyllithium to give the attached "titanocene" species which is an excellent catalyst for hydrogenation. This resin bound catalyst has been tested for a variety of olefins, and it has been found that the hydrogenation efficiency is six times greater than that of the correspondingly reduced nonattached titanocene dichloride or benzyltitanocene dichloride.

In addition to the compound just described, Brubaker and coworkers have also synthesized polymer-attached monocyclopentadienyls of the general formulation $M(C_5H_5)Cl_n$ from cyclopentadienyl attached copolymer and $TiCl_4$, $ZrCl_4$, $MoCl_5$ and WCl_6.[29]

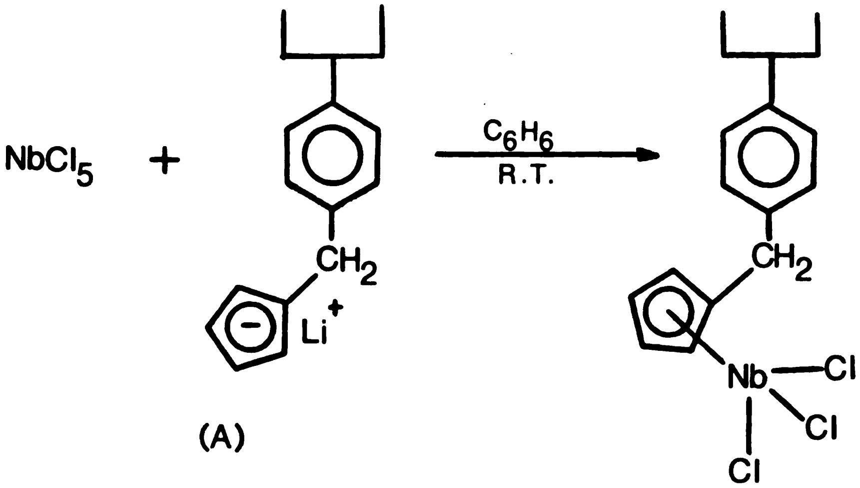
As has been mentioned above, titanocene species undergoes deactivation by polymerization process; and that the attachment of the titanocene species to the rigid polymer resulted in an increase in activity for olefin hydrogenation. It was proposed that this increase in activity resulted from site isolation on the polymer.

Since this phenomenon has become a major concern with polymer attached reagents and catalysts, one of the objectives of the research reported in this thesis was to study site isolation as a function of loading of catalyst. It has been found that the rate of hydrogenation of 1-hexene at room temperature as expressed in ml H_2/min-mmol Ti, increases as loading decreases. Also, the rate in ml H_2/min-g of polymer reaches a maximum at a loadings of 0.14 mmol Ti/g of polymer. Both of these observations are consistent with site isolation at low loading.[30]

In addition to using the reduced polymer-attached titanocene dichloride and monocyclopentadienyl titanium trichloride as hydrogenation catalysts, these materials have been employed in catalytic isomerization of allylbenzene and 1,5-cyclooctadiene. Allylbenzene was isomerized to trans and cis-propenylbenzene, while the 1,5-cyclooctadiene was converted into a mixture of 1,3-cyclooctadiene and 1,4-cyclooctadiene. The oligomerization of ethyl propiolate has also been carried out using the polymer-attached titanocene species, a mixture of both open and closed trimers of the acetylene derivative have been formed. It has been found that the attached titanocene dichloride and monocyclopentadienyl titanium trichloride can be used directly, without going through the reduction process, for the epoxidation of cyclohexene and cyclooctene, although the yields are not exceptionally good.

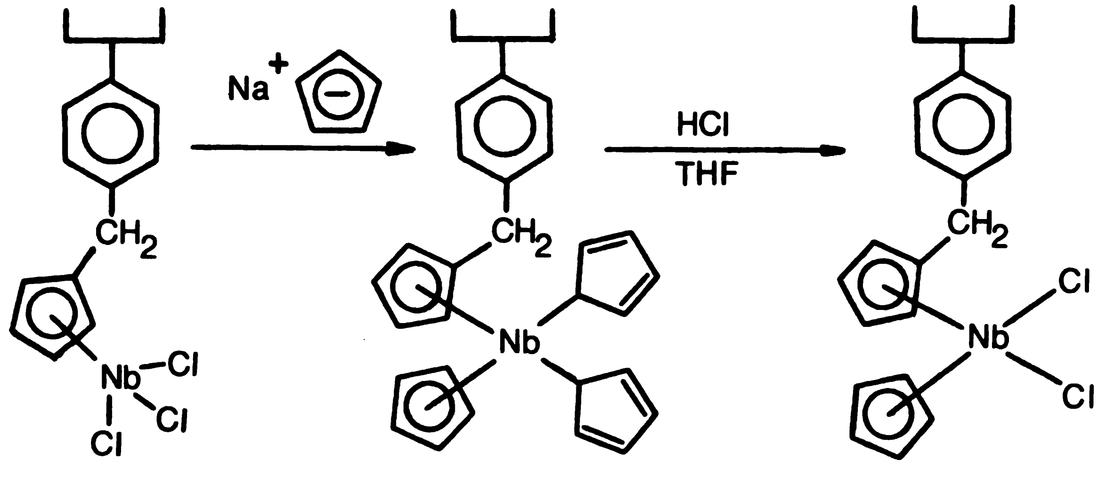
Another area of interest in the present research is the preparation of the polymer-attached titanocene dicarbonyl. This compound has been prepared by first reducing the attached titanocene dichloride with excess BuLi and then the introduction of 4 atm of carbon monoxide into the reduced species. The resin bound titanocene dicarbonyl is employed in the hydroformylation of olefins, giving a mixture of linear and branched aldehydes.

Polymer-attached monocyclopentadienyl niobium trichloride, $NbCpCl_3$ [31] has been prepared by treating (A) with niobium pentachloride solution in benzene.



(A)

When excess sodium cyclopentadienlide in THF was added to the polymer-attached monocyclopentadienyl niobium trichloride, it was converted into the very air and moisture sensitive niobium tetracyclopentadienyl. Finally, polymer-attached niobium dichloride was obtained by passing anhydrous hydrogen chloride gas into a suspension of polymer-attached niobium tetracyclopentadienyl in THF. The following figure shows the reaction scheme:



A very important reason for undertaking the study of the niobium compounds (in addition to evaluating the extent to which metals other than titanium can serve as catalysts on the resins), is that they generally give much better esr signals than titanium or zirconium. If hyperfine structure can be observed, spin densities can be determined and the residence of the electron on the metal can be demonstrated. This esr study has been undertaken by Neal Kilmer*.

Testing various kinds of catalytic activity of the attached niobocene dichloride and monocyclopentadienyl niobium trichloride has been done. Starting out with the resin bound niobocene dichloride, the preparation of some of the niobocene derivatives such $NbCp_2BH_4$, $NbCp_2H$, $NbCp_2(CO)_2$, etc., has been attempted.

The research work reported here consists of (1) study of site isolation as a function of catalyst loadings. The reaction of concern is the hydrogenation of 1-hexene with polymer-attached titanocene species; (2) the testing of catalytic activities of polymer-attached titanium complexes towards isomerization of allylbenzene and 1,5-cyclooctadiene, oligomerization of acetylene derivatives, and epoxidation of unsaturated hydrocarbons; (3) the preparation and characterization of polymer-attached titanocene dicarbonyl, and study of its application to catalytic hydroformylation of olefins; (4) the preparation and characterization of polymer-attached niobium complexes and examination of their catalytic activities.

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* Neal Kilmer is one of the members of Professor C. H. Brubaker's group

EXPERIMENTAL

General Techniques

In view of the air and moisture sensitivity of most of the materials described in this thesis, standard Schlenck-tube technique was employed. Sometimes, small amounts of polymer-supported complexes were routinely treated in 50 ml septum stoppered erlenmeyer flasks with reagents drawn from hypodermic needle-tipped burets. In addition, an argon filled glove box was frequently used for transfers.

Electron spin resonance (esr) spectra were obtained by use of a Varian E-4 spectrometer. NMR spectra were obtained by use of Varian T-60 and Varian A-56/70D spectrometer systems, tetramethyl siland (TMS) was used as reference at 0 ppm. Gas chromatography (glc) analyses were performed by use of a F & M model 810-19 analytical gas chromatograph and a Varian 1400 analytical gas chromatograph.

Far-infrared spectra in the 100-500 cm^{-1} region were obtained by use of a Digilab Model FTS-16 Fourier transform spectrophotomer. Samples were prepared by crushing the polystyrene beads in a ball mill under anaerobic conditions and mulling the powder with dry nujol in a dry glove box. The spectra were recorded with the sample in a dry nitrogen atmosphere and mounted between polyethylene plates. Infrared spectra were recorded on similarly prepared samples suspended between NaCl plates by use of a Perkin-Elmer 457 or 237B spectrophotometer.

Reagent grade tetrahydrofuran (THF), benzene, toluene and xylene were distilled over sodium-benzophenone under argon. Hexane, heptane, cyclohexane and diethyl ether were refluxed over lithium aluminum hydride before distillation. Argon, hydrogen, carbon monoxide, chlorine, and hydrogen chloride were Matheson purified grade. Organolithium reagents, 1-hexene, allylbenzene, 1,5-cyclooctadiene, ethyl propiolate, cyclohexene, cyclooctene, tert-butyl hydroperoxide and chloromethyl ethyl ether* were obtained from Aldrich Chemical Co. Titanocene dichloride and niobium pentachloride were obtained from Alfa Chemical Co., while monocyclopentadienyl titanium trichloride was prepared by a previously published method [32] with some modifications. 1-pentene was obtained from J. T. Baker Chemical Co.

The 20% cross-linked (600 Å pore size) macroreticular polystyrene-divinylbenzene copolymer beads were gifts from the Dow Chemical Company and were washed to remove impurities before use. They were washed with 10% HCl, 10% NaOH, H_2O, 1:1 H_2O-CH_3OH mixture, CH_3OH, 1:1 CH_3OH-CH_2Cl_2, CH_2Cl_2 and benzene as recommended by Pittman.[33] They were then vacuum dried.

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* Caution is advised in chloromethylation and in the handling of chloromethyl ethyl ether because the related compound dichlorodimethyl ether is a carcinogen as is the monochloro diethyl ether.[34]

Chloromethylation of copolymer beads

Following the chloromethylation method of Pepper [35], *et al.*, 50 g of washed and dried copolymer beads was taken into a 1 liter three-necked flask fitted with a drying tube and an overhead stirrer. 180 ml of chloromethyl ethyl ether was added, and the mixture was stirred for 2 hr. The flask was cooled in an ice bath for another hr. A solution prepared by cautiously adding 8.5 ml of $SnCl_4$ to 80 ml of ice-chilled chloromethyl ethyl ether was then introduced slowly through a dropping funnel. The beads and the solution turned pink as the $SnCl_4$ solution was added. After the addition of all the $SnCl_4$ solution and stirring the mixture for about an hr, the color changed to light brown. The reaction mixture was stirred at room temperature for 13 hr, the chloromethyl ethyl ether solution was removed by suction and a dispersion tube. The beads were washed with four 300 ml portions of 50% aqueous dioxane, aqueous dioxane containing 10% HCl (V:V), and finally with dry dioxane until the washings were chloride free. After drying the beads *in vacuo* for 2 days; chloride analysis yielded 1.10 mmol Cl/g of polymer, which is equivalent to 14.3% chloromethylation of the styrene rings.

In another experiment, 100 g of beads were chloromethylated as above. A batch of beads was taken out 3 hr after chloromethylation was started. A second batch was taken out 2 more hr later; the third, fourth, fifth and sixth batches were taken out at three hour intervals. Chloride analysis of the various batches yielded:

Batch	Chloride content mmol Cl/g of beads	Percent chloromethylation
1	0.33	4.27
2	0.36	4.69
3	0.45	5.90
4	0.54	6.97
5	0.61	7.95
6	0.79	10.33

Preparation of cyclopentadienyl-substituted copolymer

In a typical experiment, the chloromethylated beads were suspended in THF and two fold excess of sodium cyclopentadienide in THF was added. After the mixture was stirred for 3-4 days at room temperature, excess sodium cyclopentadienide and THF were removed by filtration and the beads were washed with 1:1 ethanol:THF (V:V) until the washings were chloride free. This washing was followed by washing three times with THF and then by drying *in vacuo* for several days.

Preparation of $TiCpCl_3$

A sample of 12 g (0.048 mol) of titanocene dichloride was charged into a 250 ml round-bottomed, side-armed flask. 90 ml of dry xylene was added, and was followed by the introduction of 15 ml (0.136 mol) of titanium tetrachloride through a syringe. The mixture was heated at the boiling point (140°) for 3 hr. The reaction mixture was then cooled to room temperature, and yellow crystals of the product was separated. The crystals were washed twice with dry hexane. A small batch of activated charcoal was added and the mixture was treated with a 50 ml portion of dry hexane, it was stirred at room temperature for half an hour. The hexane was then removed under vacuum. The mixture was placed in a soxhlet extractor and was extracted 15 times with 70 ml dry benzene. The benzene solution was allowed to cool to room temperature slowly and finally in an ice bath. Bright yellow crystals of monocyclopentadienyl titanium trichloride were collected. The crystals, after drying under vacuum, gave a melting point of 208-210°. (60% yield)

Preparation of polymer-attached $TiCp_2Cl_2$

In a typical experiment, 3-4 g of cyclopentadiene substituted copolymer beads was treated with two fold excess of methyllithium or butyllithium in THF and the mixture was stirred for two days under argon. The color of the beads changed from milky to deep purple-red. Excess methyllithium or butyllithium and THF were removed by using a syringe. The beads were washed three times with THF and three times with benzene. They were then suspended in benzene, and a solution containing 1.5-2.0 fold excess of monocyclopentadienyl titanium trichloride dissolved in benzene was introduced. The mixture was stirred for three days. Excess monocyclopentadienyl titanium trichloride and benzene were removed and the product was washed several times with benzene and then THF. The excess monocyclopentadienyl titanium trichloride was removed by extracting with THF in a soxhlet extractor. The product, which was pink to red, was dried *in vacuo* for two days. Metal analysis was performed and far infrared spectrum taken. The reaction scheme is shown in the following figure and Table 1 shows the titanium analyses.

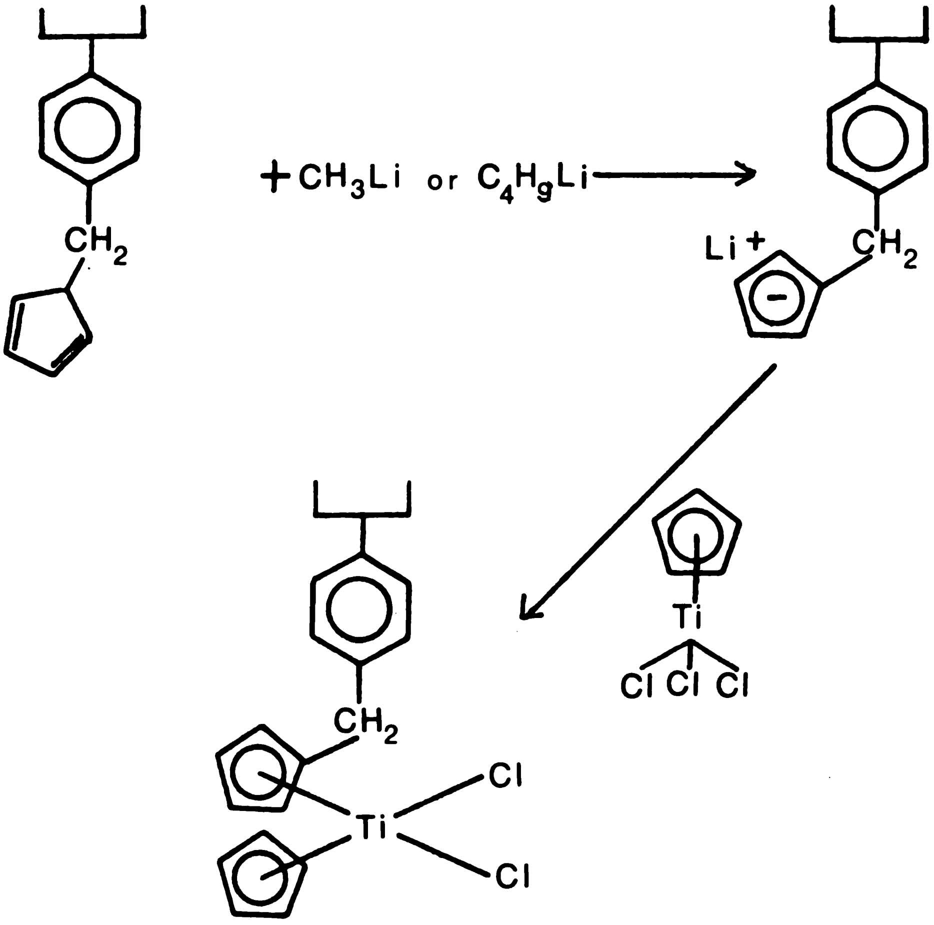


Table 1

Titanium contents of various batches of polymer-attached titanocene dichloride

Batch	Titanium content mmol Ti/g of beads
1	0.266
2	0.246
3	0.175
4	0.128
5	0.106
6	0.087
7	0.044

Far Infrared Spectra:

(polymer-attached) 402, 362, 307, 280, 256, 196 cm^{-1}

(non-attached) 400, 360, 303, 276, 247, 206 cm^{-1}

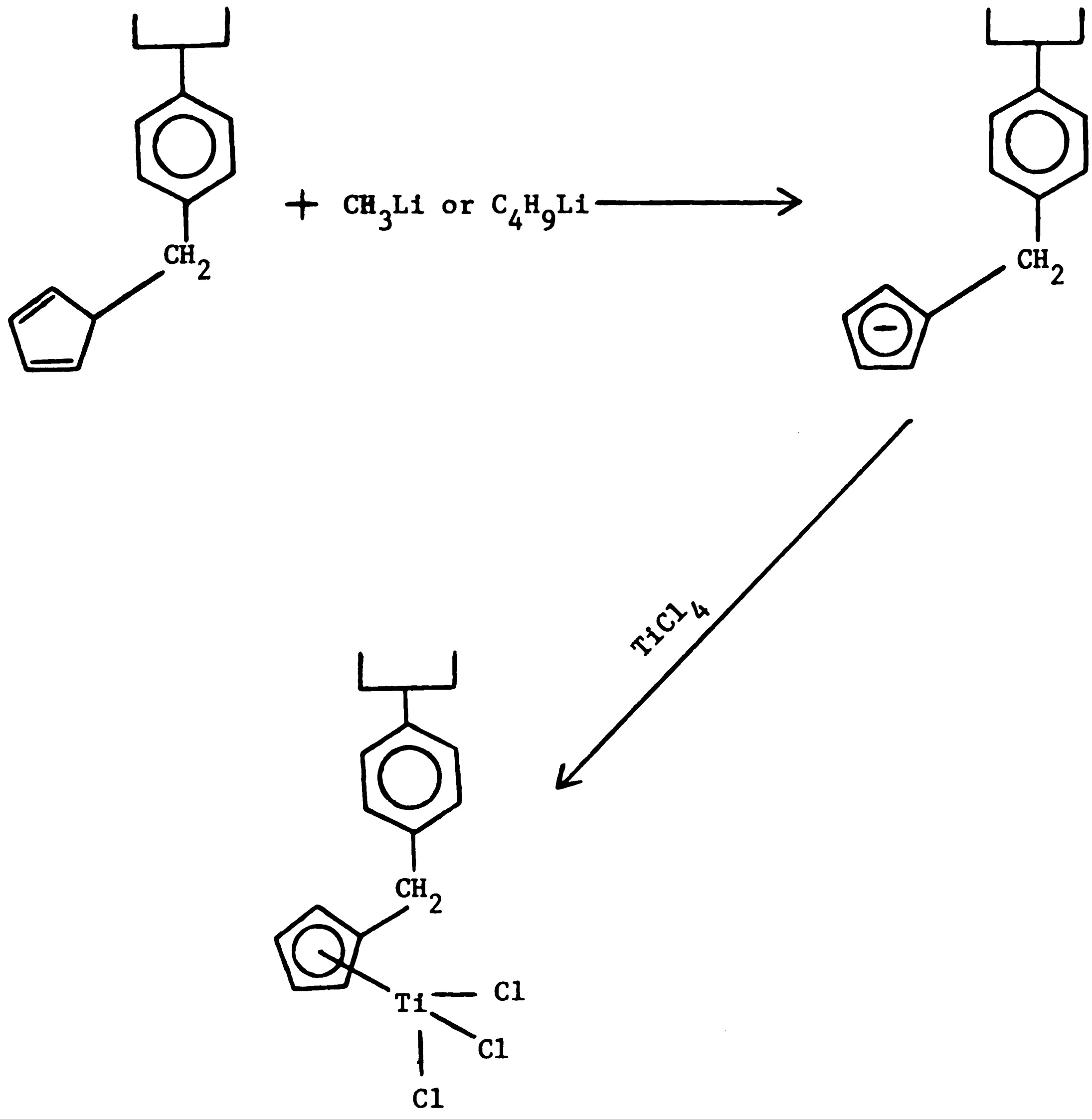
Preparation of polymer-attached $TiCpCl_3$

Cyclopentadiene substituted copolymer was converted to the supported cyclopentadienide anion by treatment with a two fold excess of methyllithium or butyllithium in THF under argon for 2 days. Solutions were removed and the beads were washed several times with THF and benzene. They were then suspended in benzene and a two fold excess of titanium tetrachloride was introduced. The reaction mixture was stirred for 2 days. Solutions were removed and the products were washed with THF in a soxhlet extractor for 3 days. A long washing time is required for complete removal of all the chloride. The chloride-free product, after being dried at room temperature *in vacuo*, was yellowish colored. The flask containing the product was covered with aluminum foil and cooled in an ice bath, chlorine gas was added and bright yellow colored product was formed. Metal analysis was performed and far infrared spectra were taken. The following figure shows the reaction scheme and Table 2 lists the titanium analyses.

Table 2

Titanium contents in the polymer-attached $TiCpCl_3$

Batch	Titanium content mmol Ti/g of beads
1	0.100
2	0.200
3	0.285



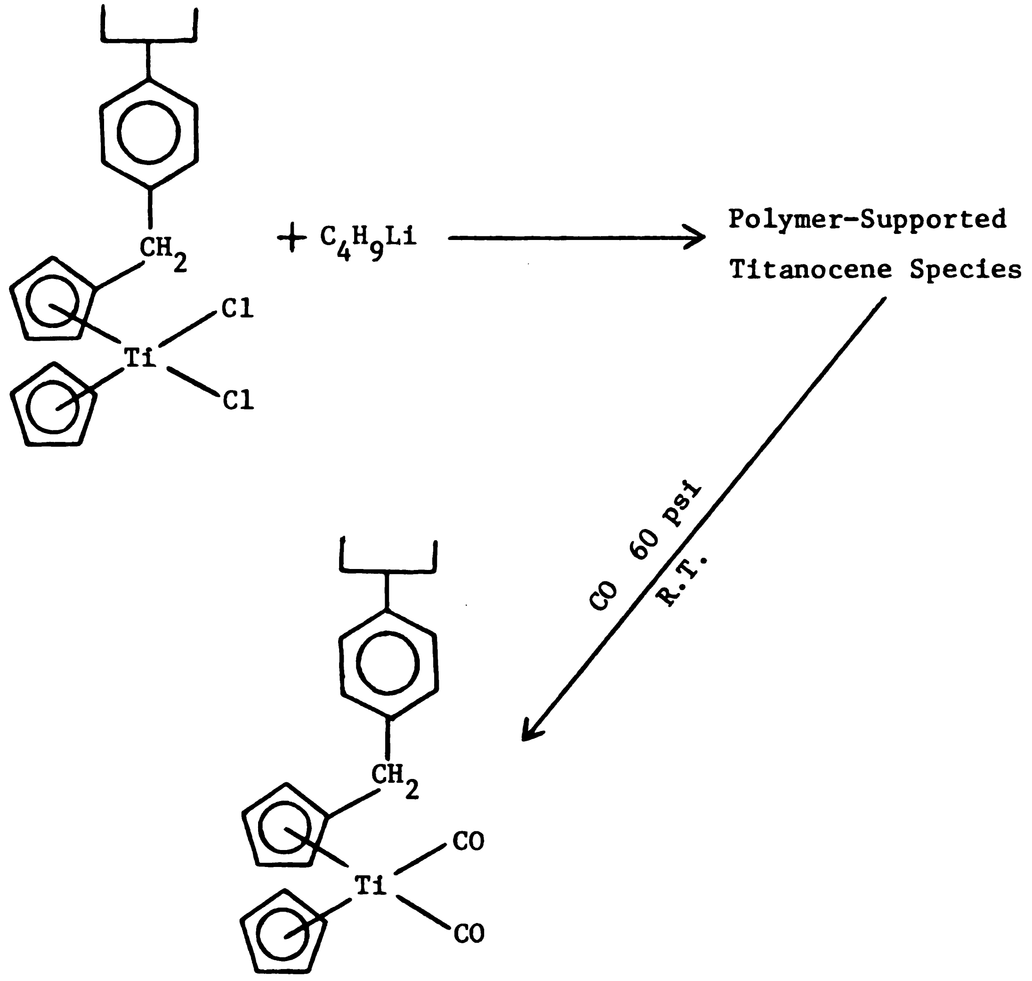
Far Infrared Spectra:

(polymer-attached) 452, 422, 380, 333 cm^{-1}

(non-attached) 450, 418, 381, 331, 295 cm^{-1}

Preparation of polymer-attached $TiCp_2(CO)_2$

About 3 g of polymer-attached $TiCp_2Cl_2$ (0.175 mmol Ti/g of beads) was charged into a pressure bottle. Excess butyllithium in heptane was added into the bottle in the glove box. After the addition of butyllithium, the bottle was carefully capped and taken out of the glove box. The reaction mixture was stirred under argon for 12 hr. It was then frozen in liquid nitrogen and the bottle was evacuated. Carbon monoxide was passed into the bottle until the pressure was ca. 60 psi. The reaction mixture was stirred for 10 hr at room temperature and a decrease in carbon monoxide pressure was observed. The product was transferred into a 100 ml side-armed flask in the glove box. The solution was removed and the beads were washed several times with heptane and then THF. The product was reddish brown, when suspended in solvent and greyish brown, when dried. Infrared spectra of the products were measured. The reaction scheme is:



Infrared Spectra:

(polymer-attached) 1965, 1878 cm^{-1}

(non-attached) 1965, 1882 cm^{-1} [36]

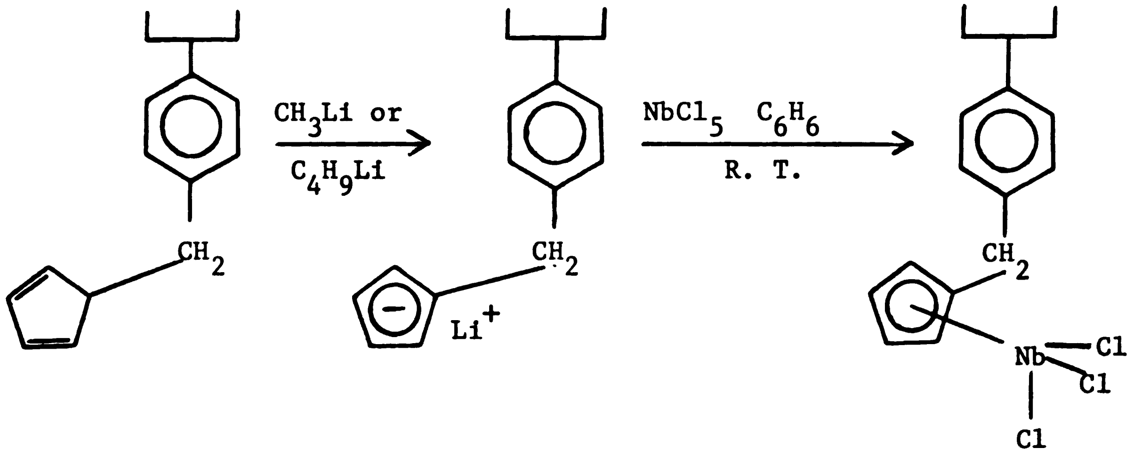
Preparation of polymer-attached $NbCpCl_3$

A sample of 6 g cyclopentadiene substituted copolymer was treated with a two fold excess of methyllithium or butyllithium in THF, and the reaction mixture was stirred for 2 days under argon. The polymer turned deep purple-red. The solution was removed and the beads were washed four times with THF and then four times with spectroscopic benzene. The flask was cooled in an ice bath and a ml portion of saturated niobium pentachloride solution in spectroscopic benzene was introduced by using a syringe. After the reaction mixture was stirred for about 20 minutes, the color of the solution disappeared. The solution was removed and a second 30 ml portion of saturated niobium pentachloride solution in benzene was injected. The solution was again decolorized after being stirred for half an hour. Several 30 ml portions of saturated niobium pentachloride solution were added until the solution was no longer decolorized. The solution was removed and the black colored beads were washed with benzene in a soxhlet extractor for 5 days. Metal and chloride analyses were performed and the esr spectrum was taken. The following illustrates the reaction scheme.

Analyses: Nb = 0.941 mmol/g polymer

Cl = 2.913 mmol/g polymer

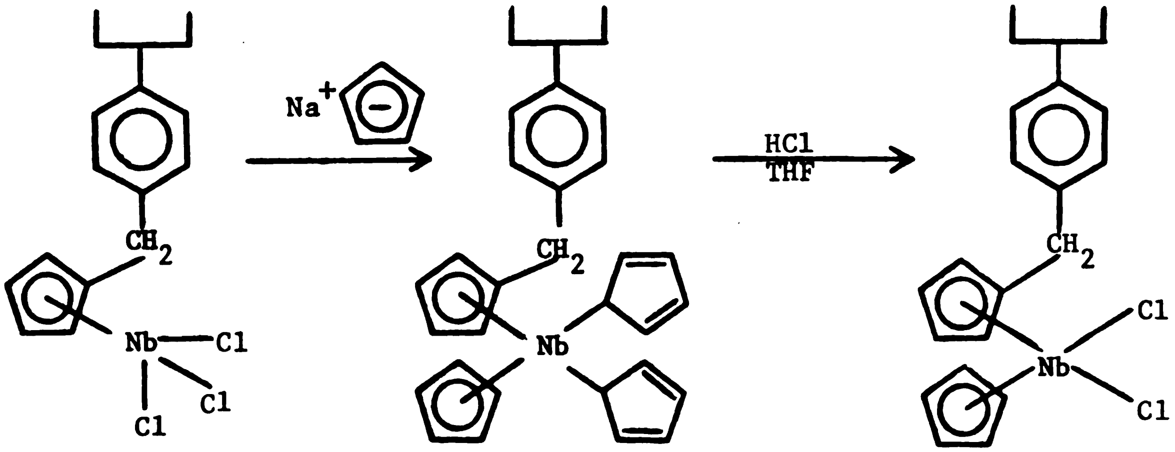
Cl/Nb = 3.10



Preparation of polymer-attached $NbCp_2Cl_2$

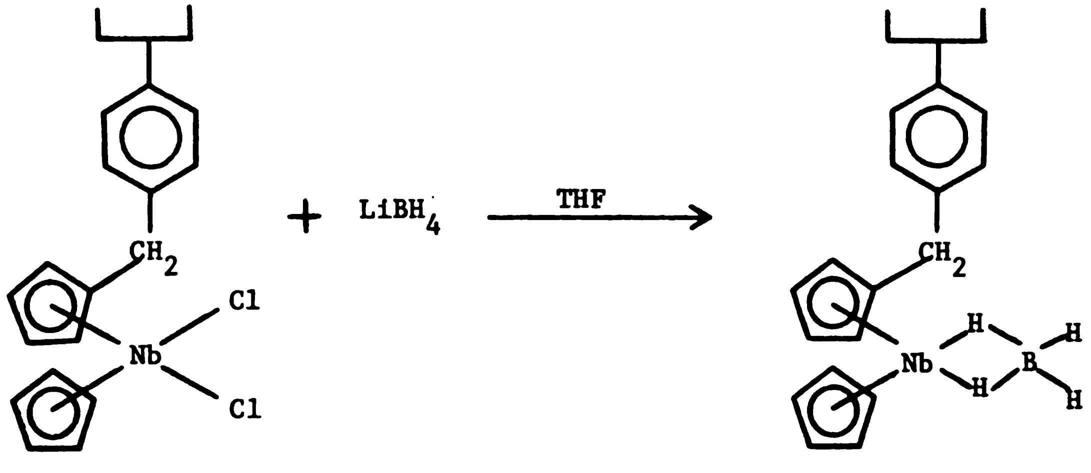
A sample of 3 g of polymer-supported $NbCpCl_3$ was treated with large excess of sodium cyclopentadienide solution in THF. The reaction mixture was stirred in darkness for 5 days. The solution, which had turned dark purple at the end of this period, was removed by using a syringe. The beads were washed several times with degassed THF. The brown beads, with attached niobium tetracyclopentadienyl, were suspended in THF and anhydrous hydrogen chloride was introduced. The beads turned black and after being washed with THF in a soxhlet extractor for 3 days, they were greyish brown. Metal and chloride analyses were performed and the esr spectrum of the beads was measured. The following shows the reaction scheme.

Analyses: Nb = 0.139 mmol/g of beads
Cl = 0.269 mmol/g of beads
Cl/Nb = 1.93



Preparation of polymer-attached $NbCp_2(BH_4)$

To 2 g of polymer-supported niobocene dichloride (0.139 mmol Nb/g of beads) was added excess lithium borohydride. 10 ml of degassed THF was injected and the reaction mixture was stirred under argon at room temperature for 12 hr. The color of the beads changed from greyish brown to dark green. Excess lithium borohydride was removed by washing the beads several times with THF. The product, which was very air and moisture sensitive, was stored in the argon filled glove box. The ir spectrum was recorded and it showed $\nu_{(B-H)}$ at 2380 cm^{-1}. The reaction scheme is shown below.

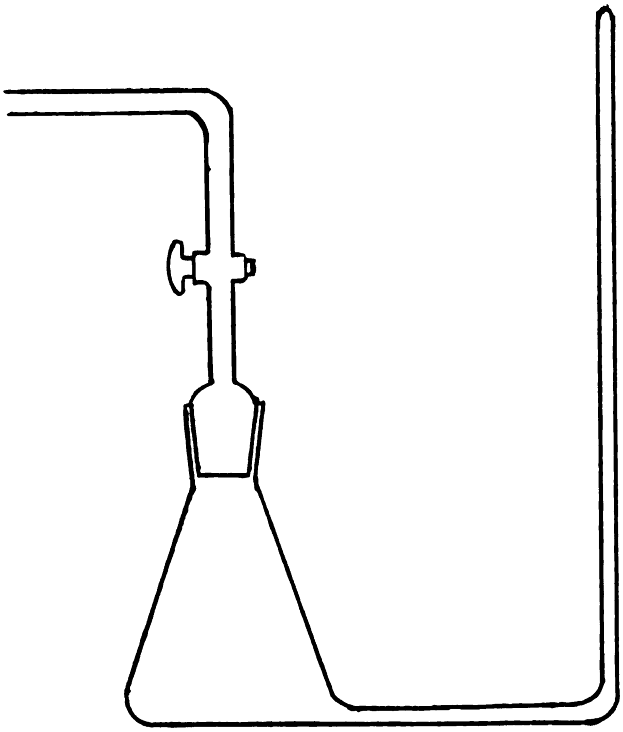


ESR studies of polymer-supported titanocene species

A sample of 0.2 g polymer-supported titanocene dichloride (0.044 mmol Ti/g beads) was charged into a specially designed 50 ml erlenmyer flask shown in Figure 1. Five ml of degassed hexane was injected into the flask. The supported titanocene dichloride was reduced by the addition of 0.5 ml 1.6 M butyllithium in hexane and the reaction mixture was stirred for 12 hr under hydrogen. Solution was removed and the beads were washed several times with hexane. The beads were dried *in vacuo* and were easily transferred into the esr tube by tilting the flask. The esr spectrum of the reduction product was recorded. The same experiment was repeated under argon.

Figure 1

Esr Study Apparatus



Analyses

Chloride (Volhart titration)[37]

Halide in the chloromethylated polymer was removed by heating and stirring approximately 0.3 g of beads at 100° for 3 days in 3 ml of pyridine in a test tube. The beads and the solution were then transferred to a 250 ml erlenmyer flask and 30 ml of 50% (by volume) acetic acid was added. An accurately measured aliquot of approximately 10 ml standardized $AgNO_3$ solution (0.044 N) was added followed by approximately 5 ml of concentrated nitric acid, a few drops of nitrobenzene, and about 10 drops of ferric alum indicator. The mixture, after standing in the dark for 10 minutes, was titrated with standardized NH_4CNS solution (0.037 N).

Chloride from the polymer-attached titanium or niobium compounds was removed by digestion of approximately 0.3 g of polymer sample in 25 ml 2N potassium hydroxide solution at 80° for 24 hr. Chloride was determined by the Volhard method as described above, following acidification of the aqueous supernatant.

Metal

Titanium and niobium contents in the beads were determined by digesting the polymer-supported titanium or niobium compound with a few drops of concentrated sulfuric acid, ashing with a micro burner, heating to 1000° for 12 hr, and weighing the TiO_2 or Nb_2O_5. Approximately 0.5 g of beads was used each time.

Catalysis Studies

Hydrogenation of olefins

Reagent grade n-hexane was used as the solvent. It was further purified and deoxygenated by refluxing with lithium aluminum hydride under argon before distillation. It was degassed before use. 1-hexene, cyclohexene and 1-octene were distilled under argon from barium oxide.

The hydrogenator (Figure 2) is a normal atmosphere pressure hydrogenation apparatus, with a 100 ml gas buret used for volume measurements. The leveling bulb was placed so that at any time the system is operating at a slight negative pressure, thereby preventing leaks from giving false hydrogen uptake data.

All reactions were carried out in a 100 ml round-bottomed flask with a side arm. The supported catalyst was weighed into the flask, suspended in 10 ml of hexane, and treated with 1 ml of 2.0 M butyllithium in hexane for 10 hr. The solution was removed and the catalyst was washed several times with hexane. 8.5 ml hexane was injected into the flask and 1.5 ml 1-hexene was added. The reaction mixture was stirred at a constant stirring rate, while the temperature was maintained at 20° by using a water bath. The rate of hydrogen uptake was measured by using the buret.

Polymer-attached $TiCp_2Cl_2$ hydrogenation of 1-hexene

About 0.1 g of polymer-attached $TiCp_2Cl_2$ was weighed into a 100 ml round-bottomed flask with a side arm. After attaching the flask to the hydrogenator, the hydrogenation apparatus was flushed with hydrogen by alternating evacuation and hydrogen addition, which was cycled several times to guarantee complete removal of oxygen from the system. The

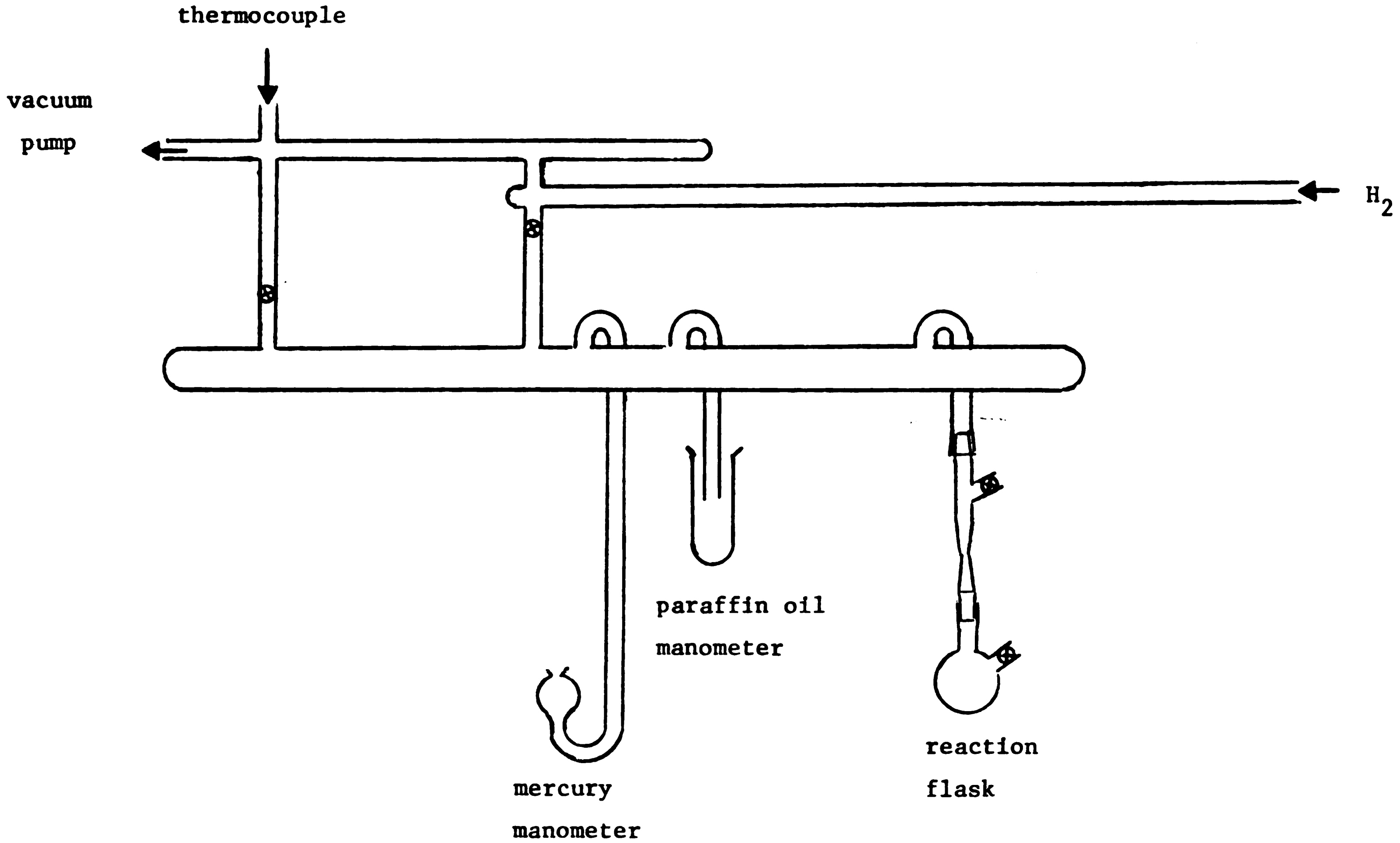


Figure 2. Sketch of Hydrogenation Apparatus.

beads were suspended in 10 ml hexane and 1 ml 2.0 M butyllithium in hexane was introduced. The reaction mixture was stirred at room temperature for 12 hr. Excess butyllithium was removed and the sample was washed several times with hexane. To the washed sample was added 8.5 ml of hexane, followed by the injection of 1.5 ml of 1-hexene. The reaction mixture was maintained at 20° by using a water bath. The stirrer was turned on and kept at a constant stirring rate. The rate of hydrogen uptake was measured by using the gas buret. The hydrogenation results are presented in Table 3 on page 39.

Homogeneous $TiCp_2Cl_2$ hydrogenation of 1-hexene

In a typical experiment, a $TiCp_2Cl_2$ sample ranging from 0.0010 to 0.0063 g was weighed into a 100 ml side-armed flask. After attachment to the hydrogenator and hydrogen flushing, the sample was treated with 8 ml of hexane and 0.5 ml of 2.0 M butyllithium in hexane. After being stirred for 8 hr, the solution turned cloudy and greyish. 1.5 ml of 1-hexene was injected into the flask, the flask was immersed into a water bath maintained at 20° and the reaction mixture was kept well stirred at a constant stirring rate. Rate of hydrogen uptake was measured. The hydrogenation results are presented in Table 4 on page 43.

Polymer-attached $NbCpCl_3$ hydrogenation of olefins

A sample of ca. 0.1 g of polymer-supported $NbCpCl_3$ was charged into a 100 ml side-armed flask. After attachment of the flask to the hydrogenator and hydrogen flushing, 5 ml hexane was added, followed by large excess of butyllithium in hexane. The reaction mixture was stirred for 1 day, the solution turned cloudy at the end of this period. The beads were washed several times with hexane. 1.5 ml olefin (1-hexene, cyclohexene or 1-octene) was then added to a suspension of the beads in 8.5 ml hexane. The temperature was maintained at 20° by using a water bath. The reaction mixture was kept well stirred and the rate of hydrogen uptake was measured. The rate observed for 1-hexene was 1.49 ml H_2/min-mmol Ti, it was 1.11 ml H_2/minOmmol Ti for cyclohexene and was zero for 1-octene.

Polymer-attached $NbCp_2Cl_2$ hydrogenation of 1-hexene

The hydrogenation was carried out by following the above procedure for polymer-attached $NbCpCl_3$ hydrogenation. No hydrogen uptake was observed after prolonged stirring of the reaction mixture. In another experiment, 5 ml 1-hexene was used, but again no hydrogenation was observed after many hours of stirring. A glc study was carried out on the substrate, and it was found that there had been no isomerization of the 1-hexene either.

Catalytic isomerization of allylbenzene and 1,5-cyclooctadiene

Reagent grade hexane was used as the solvent. It was further purified and deoxygenated by refluxing and distillation under argon from lithium aluminum hydride. It was degassed before use. Allylbenzene and 1,5-cyclooctadiene were distilled from barium oxide under argon.

The product mixture from isomerization of allylbenzene was analyzed by gas chromatograph. A 6' x 1/8" column consisting of 15% SE-30 deposited on Chromosorb P, was used (carrier gas: He). Mixture of allylbenzene, trans-propenylbenzene and cis-propenylbenzene, which were effectively separated at 120° , were compared with authentic sample. The product mixture from isomerization of 1,5-cyclooctadiene was analyzed by an integrated nmr spectrum. The percentage of 1,3-isomer was calculated from integration of the peak at $\delta = 2.70$ ppm, and the 1,4-isomer from the peak at $\delta = 1.45$ ppm.

The isomerization results of allylbenzene is shown in Table 5 on page 46, and the isomerization results of 1,5-cyclooctadiene is shown in Table 6 on page 48.

Polymer-attached $TiCp_2Cl_2$ isomerization of allylbenzene

A sample of 0.193 g polymer-attached $TiCp_2Cl_2$ (0.246 mmol Ti/g of beads) was weighed into a 100 ml side-armed flask. After the flask was flushed several times with hydrogen, the beads were treated with 5 ml hexane and 1 ml 2.0 *M* butyllithium in hexane under hydrogen for 12 hr. The solution was removed and the beads were washed twice with hexane and dried *in vacuo* at room temperature. 4 ml allylbenzene was injected and the reaction mixture was stirred under argon at 145° for 13 hr. The flask was then cooled to room temperature. The substrate was removed by using a syringe and needle, and was analyzed by gas chromatography.

The beads were washed four times with hexane and dried *in vacuo* at room temperature. A fresh 4 ml portion of allylbenzene was introduced and the isomerization reaction was followed for 15 hr.

In another experiment, a sample of 0.872 g polymer-supported $TiCp_2Cl_2$ (0.044 mmol Ti/g of beads) was reduced with butyllithium solution under an atmosphere of argon. The isomerization procedures followed those described in the above paragraphs. (reaction time: 5.5 hr)

In a third experiment, the isomerization of allylbenzene was effected by using a different batch of polymer-attached $TiCp_2Cl_2$ (0.195 g; 0.195 mmol Ti/g beads). The reduction was again carried out under argon. (Reaction time: 15 hr)

Polymer-supported $TiCpCl_3$ isomerization of allylbenzene

A sample of 0.201 g polymer-supported $TiCpCl_3$ was charged into a 100 ml round-bottomed side-armed flask. After being flushed several times with hydrogen gas, 5 ml hexane and 1 ml of 2.0 M butyllithium in hexane were added. The reaction mixture was stirred under hydrogen at room temperature for a period of 12 hr. Then the excess butyllithium was removed and the beads were washed several times with hexane. After drying the catalyst in vacuo at room temperature, the flask was filled with argon and a 4 ml portion of allylbenzene was injected. The mixture was stirred at 145° for 5 hr. The substrate was separated from the catalyst by syringe technique and it was analysed by gas chromatography. The beads were washed several times with hexane and dried. Another aliquot of 4 ml allylbenzene was introduced and the isomerization reaction was carried out for 15 hr.

Polymer-supported $NbCp_2Cl_2$ isomerization of allylbenzene

A sample of 0.183 g polymer-supported $NbCp_2Cl_2$ (0.139 mmol Nb/g beads) was suspended in 5 ml hexane under hydrogen. 1 ml 2.0 M butyllithium in hexane was added. The reaction mixture was stirred for 36 hr. At the end of this period, the solution had become very cloudy. The cloudy solution was removed; the beads were washed several times with hexane and then dried in vacuo. After the flask was filled with argon, 4 ml allylbenzene was injected. The mixture was stirred at 145° for 15 hr.

The substrate was removed and analysed by gas chromatography. A total of 87% isomerization was achieved. (73% trans-propenylbenzene and 14% cis-propenylbenzene)

Polymer-supported $NbCpCl_3$ isomerization of allylbenzene

The isomerization was carried out, following the above described procedure for the polymer-supported $NbCp_2Cl_2$. It was found that only 7.4% of the original amount of allylbenzene had undergone isomerization (2% to cis-propenylbenzene and 5.4% to trans-propenylbenzene) after 15 hr of stirring at 145° under argon.

Polymer-supported $TiCp_2Cl_2$ isomerization of 1,5-cyclooctadiene

In a typical reaction, the polymer-supported $TiCp_2Cl_2$ (0.2-0.3 g) was weighed into a 100 ml round-bottomed side-armed flask. The flask was flushed several times with hydrogen or argon, depending on the gas under which the reduction is to be performed. The beads were then treated with 5 ml hexane and 1 ml 2.0 M butyllithium in hexane. The reaction mixture was stirred at room temperature under argon or hydrogen for 12 hr. Excess butyllithium was removed and the beads washed several times with hexane. After the beads were dried in vacuo and the flask was filled with argon, 4 ml 1,5-cyclooctadiene was introduced and the reaction mixture was stirred at 145° for a certain period of time (ranging from 10 to 13.5 hr). The flask was allowed to cool to room temperature and the substrate was separated from the catalyst by using a syringe. The product mixture was analysed by NMR integration.

Regeneration of catalyst

After removal of the substrate, the beads were washed several times with hexane and then two times with THF. To a suspension of beads in THF, anhydrous hydrogen chloride was added, the beads turned from dark, greenish brown to pinkish brown immediately, thus regenerating the polymer-supported $TiCp_2Cl_2$. The regenerated catalyst was reduced with butyllithium and was reused for the isomerization of a fresh 4 ml portion of 1,5-cyclooctadiene. The isomerization time was extended to 1.5 days.

Recycling the catalyst

The beads, after the first use in isomerization, were recycled by removing the substrate and then washing them thoroughly with hexane. The recycled catalyst was used to catalyse the isomerization of a second 4 ml portion of 1,5-cyclooctadiene. Isomerization time was usually approximately one day.

Polymer-supported $TiCpCl_3$ isomerization of 1,5-cyclooctadiene

Isomerization of 1,5-cyclooctadiene by use of polymer-supported $TiCpCl_3$ was carried out. Experimental procedures followed those of polymer-supported $TiCp_2Cl_2$ isomerization. Regeneration and recycling procedures were also identical to those described in above paragraphs.

Polymer-supported $TiCp_2Cl_2$ oligomerization of ethyl propiolate

Hexane was distilled from lithium aluminum hydride, THF was distilled over the sodium-benzophenone complex under argon. Ethyl propiolate was purified by vacuum distillation over molecular sieves.

Reagent grade carbon tetrachloride and petroleum ether were used without further purification.

The product mixture was analysed by gas chromatography. A 5' x 1/4" Porapak Q column was used, and the column temperature was 150°. (Carrier gas: He)

A sample of 0.2 g polymer-supported $TiCp_2Cl_2$ (0.087 mmol Ti/g beads) was weighed into a 100 ml round-bottomed flask with side arm. After the flask was flushed several times with hydrogen, the beads were treated with 5 ml hexane and 1 ml 2.0 M butyllithium in hexane. The reaction mixture was stirred at room temperature for 15 hr. Excess butyllithium was removed and the reduction product was washed several times with hexane, After the beads were dried in vacuo, they were suspended in 5 ml THF under an atmosphere of argon. 2.0 g ethyl propiolate was introduced, and the reaction mixture was stirred at 60°. The solution first turned yellow, gradually turned brown and finally very dark brown. The reaction was stopped after 6 hr. The dark brown solution was taken out by using a syringe. The beads were washed a few times with 10 ml portions THF and the washings were mixed with the dark brown solution. The solution mixture was filtered, and the filtrate was concentrated under vacuum to give a viscous dark brown oily material. This dark brown oily material was then extracted with 150 ml of refluxing CCl_4/pet. ether (1/4 by volume) mixture. The yellow extract was filtered. The extraction solvents were removed in vacuo, and a mixture of oily material was obtained. The total weight was 0.76 g. A Mass spectrum of the oil was obtained. It indicated a parent peak at 294.

The product materials, after dilution with diethyl ether, were chromatographed, the glc spectrum showed 5 well separated peaks, although one of them was relatively broad. The proton NMR spectrum was also taken; it showed a multiplet at δ= 7.6-8.1 ppm and a singlet at δ= 8.5 ppm. No acetylenic proton peak was observed.

Polymer-supported $TiCp_2(CO)_2$ hydroformylation of olefins

Reagent grade benzene was distilled from sodium-benzophenone under argon. 1-pentene and 1-hexene were distilled over barium oxide under argon before use.

Products were analysed by gas chromatography. The column was a 32' x 1/8" 10% Carbowax on Chromosorb W.

Carbon monoxide was Matheson purified grade, and was used directly without further purification.

Hydroformylation of olefins were carried out in an autoclave. Typically, about 0.2 g of polymer-supported $TiCp_2(CO)_2$ (0.175 mmol Ti/g beads) and a solution of 3.5 ml olefin in 10 ml benzene were charged into the autoclave. The reaction mixture was frozen immediately by pouring in liquid nitrogen. While the mixture was still frozen, the system was flushed several times with nitrogen gas. Rapid freezing of the reaction mixture is neccessary to prevent deactivation of the titanocene dicarbonyl by air. The autoclave was then filled with a 1:1 or 3:1 mixture of $CO:H_2$ gases until the total pressure reached 1500 psi. Carbon monoxide was added before hydrogen, otherwise hydrogenation of the olefin would result. The mixture was heated at 100° and kept well stirred for 9 hr. After being cooled to room temperature, the vessel was vented, and the substrate was removed as fast as possible by using a syringe and needle. A fresh sample of 3.5 ml olefin in 10 ml benzene was added to the beads immediately. The freezing and flushing procedures were carried out as described before and the hydroformylation reaction was repeated.

A sample of the product was injected into the gas chromatograph apparatus with column temperature at 130°. The hydroformylation results are listed in Table 7 on page 64.

Catalytic epoxidation of unsaturated hydrocarbon

Cyclohexane was distilled from lithium aluminum hydride under argon and THF was refluxed and distilled over the sodium-benzophenone complex. Tert-butyl hydroperoxide was purified by vacuum distillation over molecular sieves. Cyclohexene and cyclooctene were refluxed and distilled from barium oxide under argon.

Epoxides were determined by gas chromatography. The column was a 10' x 1/8" 10% Carbowax on Chromosorb W. Chlorobenzene was used as an internal standard in the analysis for cyclohexene oxide, whereas p-dichlorobenzene was used in the analysis for cyclooctene oxide. Cyclohexene oxide analysis was carried out with oven temperature at 110°, cyclooctene oxide analysis at 140°.

Polymer-supported $TiCpCl_3$ epoxidation of cyclohexene

A sample of polymer-supported $TiCpCl_3$ (0.2-0.5 g) was weighed into a 100 ml round-bottomed side-armed flask. The flask was flushed several times with argon. 5 ml (50 mmol) of tert-butyl hydroperoxide was added to the beads. The mixture was stirred for 20 minutes at room temperature. The beads gradually turned light yellow. Five ml (50 mmol) of cyclohexene was then introduced, and the reaction mixture was stirred at 80°. Different time interval samples were taken out for analyses of the epoxide.

Polymer-supported $TiCp_2Cl_2$ epoxidation of cyclohexene

Experimental procedure was same as that of the supported $TiCpCl_3$ epoxidation of cyclohexene.

Polymer-supported $TiCpCl_3$ epoxidation of cyclooctene

Five ml (50 mmol) tert-butyl hydroperoxide was added to a sample of polymer-supported $TiCpCl_3$ suspended in a solution of ca. 3 g of p-dichlorobenzene (internal standard) in 8.5 ml cyclohexane. The mixture was stirred for 20 minutes at room temperature. The beads gradually turned light yellow. 6.5 ml (50 mmol) cyclooctene was added into the flask and the reaction mixture was stirred at 80°. At several times, samples were taken out for epoxide analyses.

Polymer-supported $TiCp_2Cl_2$ epoxidation of cyclooctene

Experimental procedures described in above paragraph was followed for the polymer-supported $TiCp_2Cl_2$ epoxidation of cyclooctene.

Regeneration of catalysts

After epoxidation of cyclooctene, the light yellow beads were washed several times with THF. They were then suspended in THF and anhydrous hydrogen chloride gas was introduced. The polymer-supported $TiCp_2Cl_2$ or $TiCpCl_3$ was regenerated. The regenerated catalysts were reused for the epoxidation of cyclooctene.

The epoxidation results are shown in Table 8 on page 67.

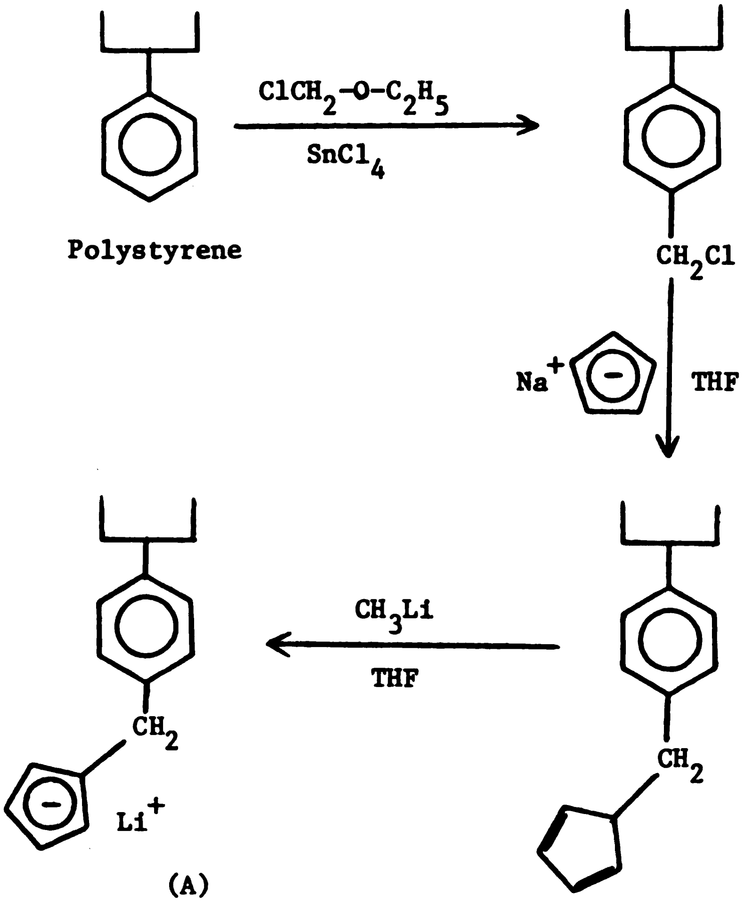
RESULTS AND DISCUSSION

Homogeneous catalysts have found only limited use, because of the difficulty of the separation from the reaction products. Recently, the utility and versitility of homogeneous catalysts has been greatly expanded by attachment to polymer supports. By heterogenizing the homogeneous catalysts, their advantages of great activity and selectivity inherent in homogeneity are retained; and ready recovery, which is an advantage of heterogenity, is assumed.

If the catalyst is heterogenized by linking it to a polymer, one may look upon the heterogenized catalyst as consisting of the insoluble, polymeric portion, which is the catalyst support, and the catalyst portion, which projects into the solution and is solvated and, in a sense, dissolved by it. The polymer support must be inert to the reagents that are in contact with it and must withstand the temperatures and pressures that are required for the reaction under consideration. Polystyrene-divinylbenzene copolymer meets all these requirements and is therefore a satisfactory support for homogeneous catalysts.

For the research discussed here, 20% cross-linked (600 Å pore size) macroreticular polystyrene-divinylbenzene copolymer beads, ranging in size from 30 to 60 mesh were used. The highly cross-linked polymer is very rigid, totally insoluble, and has a very large surface area to volume ratio, due to its porous nature.

Cyclopentadienide ion has provided a remarkedly effective means of binding transition metal to the polystyrene-divinylbenzene copolymer. Penta-hapto bonding to the metal ensures the formation of a strong bond between the polymer and the metal. The cyclopentadiene is bonded to the polymer by chloromethylating the benzene rings of the polystyrene-divinylbenzene copolymer and then treating it with sodium cyclopentadienide. The cyclopentadiene is converted to the cyclopentadienide anion by methyllithium or butyllithium. The resin-bound anion is treated with monocyclopentadienyl titanium trichloride and polymer-attached $TiCp_2Cl_2$ is formed. Polymer-attached monocyclopentadienyls of the general formulation $MCpCl_n$ have been synthesized from cyclopentadienyl attached polymer and $TiCl_4$ and $NbCl_5$.



Scheme of Cyclopentadienide Ion Attachment

Hydrogenation Studies

It has been possible to effect the reduction of titanocene dichloride by one or two electrons/titanium, producing an active titanocene species. However, this titanocene species readily forms dimers or oligomers that have no catalytic activity. It has recently been reported that the polymerization of active titanocene species can be prevented or at least minimized by attaching the titanocene precursor, $TiCp_2Cl_2$ to the 20% cross-linked polystyrene-divinylbenzene copolymer resin, resulting in an enhancement of activity for olefin hydrogenation.[27] In view of the rigidity of the copolymer, it is proposed that this increase in activity resulted from site isolation on the polymer. Since this phenomenon has become a major concern with polymer-attached reagents and catalysts, site isolation as a function of loading of catalyst, titanocene dichloride, has been studied.

Loading was controlled to give values between 0.044 and 0.266 mmol Ti/g polymer (Table 3). Each sample was reduced with butyllithium in hexane and then used for the catalytic hydrogenation of 1-hexene. The rate expressed in ml H_2/min-mmol Ti, increases as the loading decreases. The rate in ml H_2/min-g polymer reaches a maximum at a loading of 0.14 mmol Ti/g polymer. These observations are consistent with site isolation at low loading.

The rate in ml H_2/min-mmol Ti gives a measure of the percentage of metal centers that are active. As the loading increases, the metal centers close enough to interact increases. Consequently the rate per potential active site decreases.

Consideration of the data, expressed in terms of ml H_2/min-g polymer is revealing. A model for this system can be considered that is made up of a rigid surface (the surface of the polymer) with the metal sites in a completely random fashion. The sites can be assumed not to overlap completely and that if two complexes touch, i.e. are within reaction distance, the center is inactive. If each complex is also assumed to occupy a constant surface area, the the equation for such a model is:

$$\mathrm{Rate}_{\mathrm{obsvd.}} = k\ (1-\rho)^{n}$$

where k = monomer rate constant

$$\rho = \frac{\text{number of sites occupied}}{\text{maximum possible sites}}$$

$$= \frac{(\text{moles loaded})\ (6.023 \times 10^{23})\ (\text{area of each complex})}{\text{total surface area of polymer}}$$

n = 4 or 6 for square sites or circular sites

This equation gives a maximum value for R/k at $\rho = 0.2$ for n = 4. In Figure 3, this equation is plotted as a function of R/k vs. ρ. The shape of the curve is reasonable, if it is considered that without any site-site destruction, the rate should increase smoothly with increased loading. However, when sites do interact, the rate decreases. Site interaction should increase with loading, so the rate-loading relationship should be a sum of two curves with opposite shapes and results in a curve with a maximum, as is observed. Figure 3 shows the experimental data plotted on a best-fit calculated curve. The fit is amazingly good considering the sensitivity of the catalyst system to poisoning. From this curve it is easily determined that the maximum rate for hydrogenation is at a loading of 0.14 mmol Ti/g polymer. From the calculated ρ at the maximum rate (0.2), the loading of Ti at the

Table 3

Hydrogenation of 1-Hexene by Polymer-Supported $TiCp_2Cl_2$ at Room Temperature

Loading	Rate of H_2 Uptake	
Mmol Ti/g polymer	Ml/min-mmol Ti	Ml/min-g polymer
0.266	23.49	6.24
0.246	27.13	6.65
0.175	49.00	8.55
0.128	67.38	8.65
0.106	68.90	7.25
0.087	76.24	6.63
0.044	103.46	4.60

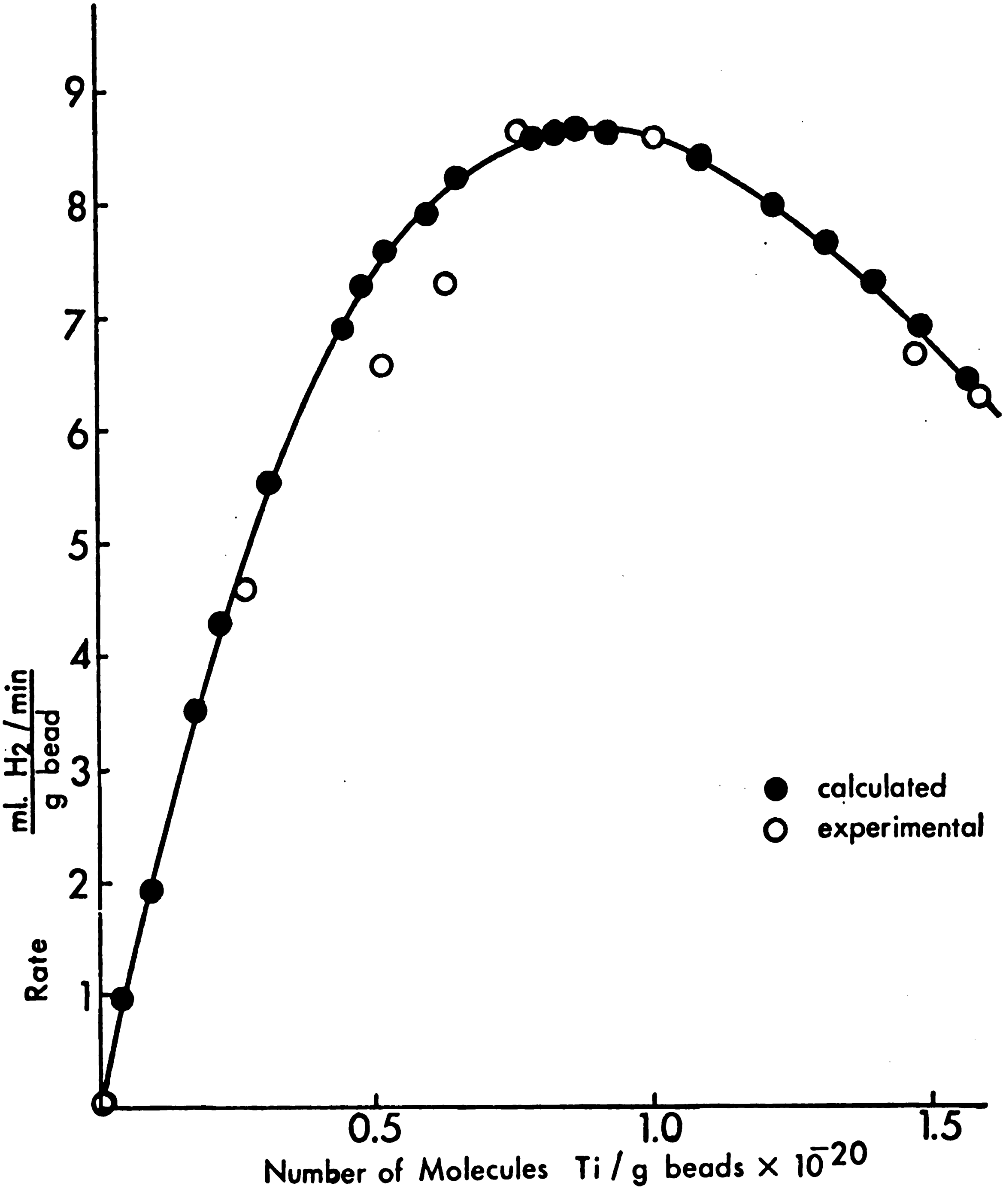


Figure 3. Rate of Hydrogenation vs $TiCp_2Cl_2$ Loading on Polymer.

maximum rate (0.14 mmol Ti/g polymer) and the surface area of the polymer used (90 m^2/g) [38], an area for each site can then be calculated. The value for this is 22 $Å^2$. Although this value is smaller than expected, the difference could be accounted for by recognizing that the dimerization reaction requires a very specific relative orientation of the two adjacent molecules [19,39] and that the normal surface area measurements may not truly reflect the solution reaction area.

A series of parallel experiments with homogeneous hexane solutions of $TiCp_2Cl_2$ was carried out. The concentrations of the solutions were carefully controlled to give 0.402×10^{-3} $\underline{M}$ to 2.57×10^{-3} $\underline{M}$. The results (Table 4) show an ever lessening increase in hydrogenation rate with increasing catalyst concentration.

In homogeneous solution, the active titanocene monomer is in equilibrium with the inactive dimer:

$$2 \text{ Monomer} \xrightleftharpoons{K} \text{Dimer}$$

$$K = \frac{[Ti_2]}{[Ti]^2} \qquad \text{and so} \qquad [Ti_2] = K[Ti]^2$$

where [Ti] = monomer concentration

$[Ti_2]$ = dimer concentration

Since the dimer is more stable than the monomer, the dimer concentration increases more rapidly than that of the monomer as the concentration of the precursor--titanocene dichloride increases. Qualitatively, a plot of percent monomer $\underline{vs}$ $TiCp_2Cl_2$ concentration should resemble diagram (A):

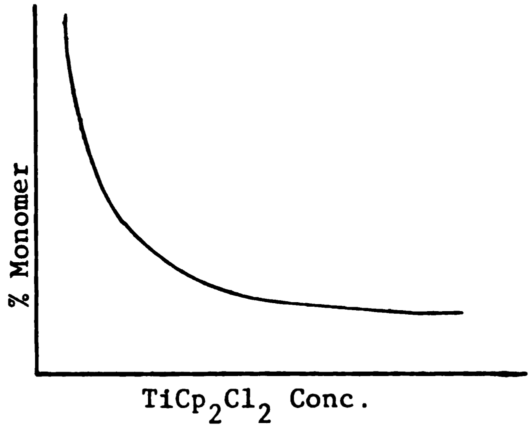


Diagram (A)

On the other hand, if we assume there is no dimerization of the titanocene species, the rate of hydrogenation should increase smoothly with increased $TiCp_2Cl_2$ concentration, as shown in diagram (B):

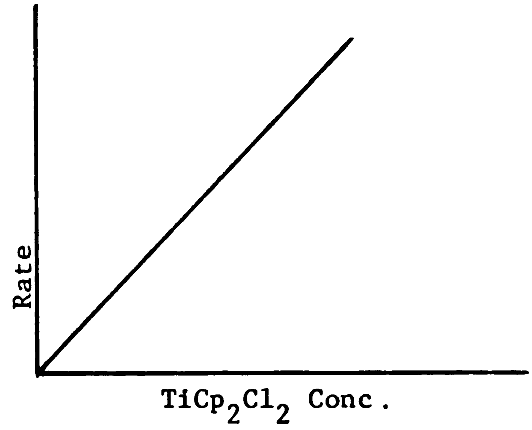


Diagram (B)

The rate-concentration relationship as shown in Figure 4 is a sum of the two curves in diagrams (A) and (B). The plot (Figure 4) exhibits no maximum as in Figure 3 for the polymer-supported catalyst.

Table 4

Hydrogenation of 1-Hexene by Homogeneous Hexane Solution

of $TiCp_2Cl_2$ at Room Temperature

$[TiCp_2Cl_2]$ M x 10^3	# of molecules/ml solution x 10^{-18}	Rate of hydrogenation ml H_2/min-ml solution	Rate of hydrogenation ml H_2/min-mmol Ti
0.402	0.242	0.030	74.63
0.722	0.435	0.044	60.94
1.287	0.775	0.049	38.07
1.850	1.114	0.058	31.35
2.530	1.524	0.063	24.90

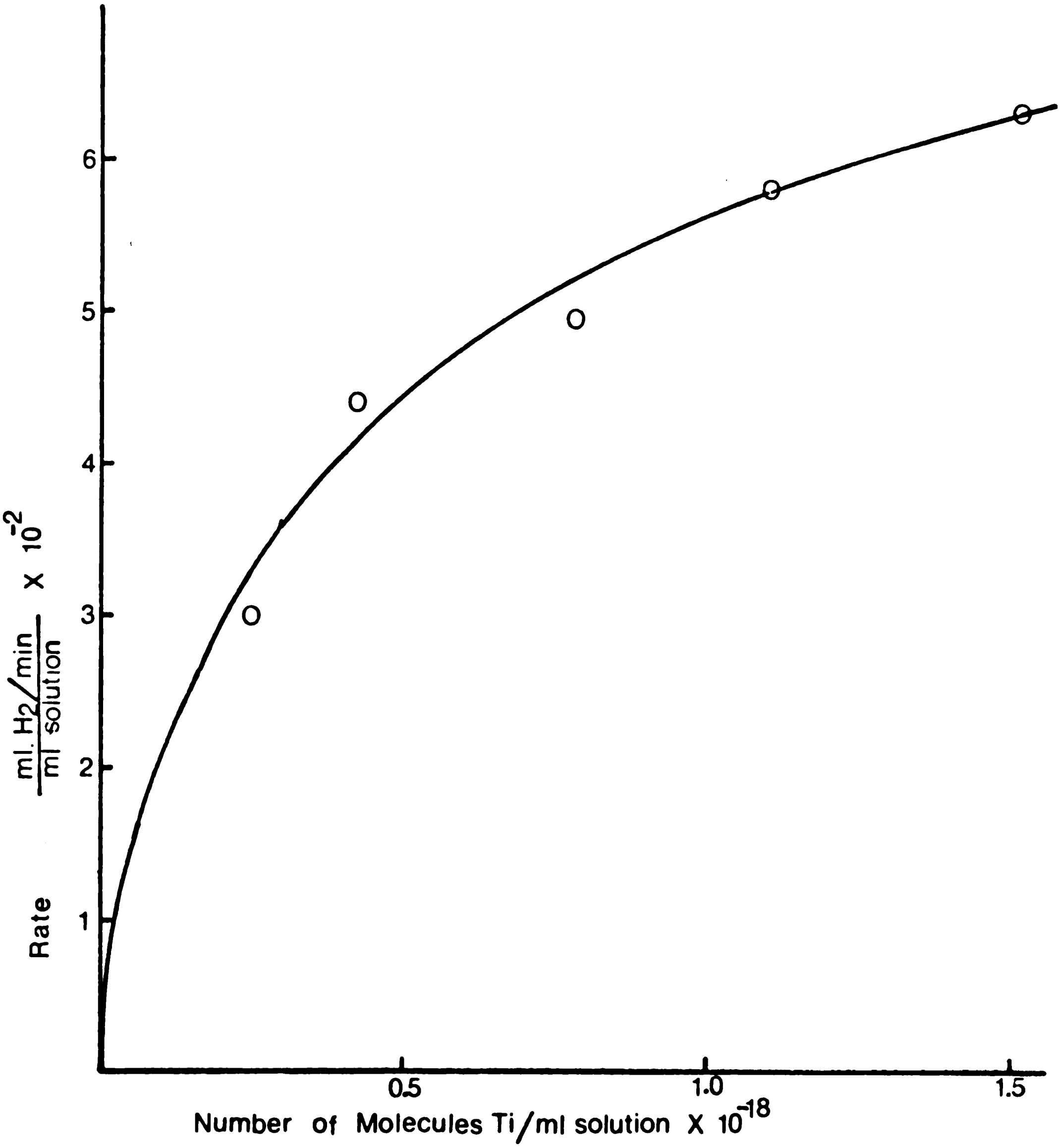


Figure 4. Rate of Hydrogenation *vs* $TiCp_2Cl_2$ Concentration.

Polymer-supported $TiCp_2Cl_2$ and $TiCpCl_3$ isomerization

Similary to the reduction of olefins, the isomerization of unsaturated organic compounds, catalyzed by transition metal complexes, generally requires the presence of an open coordination site or sites, on the metal. Polymer-attachment circumvents the formation of the inactive dimer of the titanocene species and results in the enhancement of the rate of hydrogenation of olefins. Therefore, it is not unexpected that the polymer-supported titanocene species can be a good catalyst for isomerization of unsaturated organic compounds.

Isomerization of allylbenzene

Allylbenzene, which has a terminal double bond, can be isomerized to form the more stable conjugated system — cis and trans-propenylbenzene. Table 5 shows the results of isomerization of allylbenzene by using polymer-supported catalysts. Comparison of reactions (A) and (B) in Table 5 shows that 0.2 g polymer-supported $TiCpCl_3$ (0.24 mmol Ti/g beads), when reduced, can effect the isomerization of 4 ml allylbenzene in 5 hr; while approximately the same amount of supported $TiCp_2Cl_2$ (0.25 mmol Ti/g beads) requires 13 hr. That is to say, the reduced species of polymer-supported $TiCpCl_3$ is more than two times as effective than that of the supported $TiCp_2Cl_2$ in catalyzing the isomerization of allylbenzene. A survey of reactions (C) and (D) reveals that although the absolute amount of catalysts used and the substrate/catalyst ratios are about the same in both reactions, the beads with the smaller loading of titanocene dichloride had higher activity than those with higher loading — a reiteration of increased activity due to site isolation on the polymer.

Table 5

Results of the isomerization of allylbenzene with polymer-attached catalysts

Catalyst	Substrate (ml)	Substrate / Catalyst	Time (h)	Temp	Products[d]		
					Allyl-benzene	Trans-propenyl benzene	Cis-propenyl benzene
(A) Ⓟ-$TiCpCl_3$[a] 0.201 g (0.24 mmol Ti/g)	4	625	5	145°	9.0	81.0	10.0
Recycled[b]	4	625	15	145°	82.0	13.5	4.5
(B) Ⓟ-$TiCp_2Cl_2$[a] 0.192 g (0.25 mmol Ti/g)	4	625	13	145°	10.5	81.4	8.1
Recycled[b]	4	625	15	145°	85.0	11.8	2.2
(C) Ⓟ-$TiCp_2Cl_2$[c] 0.872 g (0.044 mmol Ti/g)	4	780	5.5	145°	1.5	86.5	12.0
(D) Ⓟ-$TiCp_2Cl_2$[c] 0.195 g (0.195 mmol Ti/g)	4	795	15	145°	3.9	87.5	8.6

a Catalyst reduced with excess BuLi under H_2; b Catalyst used was recycled from previous reaction;
c Catalyst reduced with excess BuLi under Ar; d Mole per cent

Isomerization of 1,5-cyclooctadiene

Similar to allylbenzene, 1,5-cyclooctadiene would tend to isomerize to the more stable conjugated 1,3-cyclooctadiene, with the 1,4-cyclooctadiene as the intermediate product. Although in all the reactions shown in Table 6, 1,4-cyclooctadiene is present as the minor product; prolonged stirring of the substrate with the catalyst eventually brings the 1,4-cyclooctadiene content down to 1 or 2 %. In constrast with the isomerization of allylbenzene, it can be seen from reactions (I) to (IV) in Table 6 that the catalytic activity of polymer-attached $TiCp_2Cl_2$ for isomerization of 1,5-cyclooctadiene is about the same as that of the $TiCpCl_3$. The catalyst produced, by reducing the supported $TiCpCl_3$ under argon, can only effect about 80% isomerization in 13 hr (Reaction V), while the reduced species obtained, by reduction of the supported $TiCpCl_3$ under hydrogen, brings the isomerization nearly to completion in the same period of time, as shown in Reaction IV in Table 6. Although little is known about the reduced species of the polymer-supported $TiCpCl_3$, the different isomerization activities as demonstrated in Reaction IV and V is a good indication that the reduced species produced under hydrogen is different from that produced under argon. Comparison of Reactions VI and VII indicates that the titanocene species formed by reduction under hydrogen is more effective than that generated under argon.

We have repeatedly stated that the resin bound titanocene dichloride is reduced by butyllithium to give the polymer-supported "titanocene species". But we have only vaguely stated that the "titanocene species" may either be titanium(II) or titanium(III), not to mention the possibility of forming different products when the

Table 6

Results of the isomerization of 1,5-cyclooctadiene with polymer-attached catalysts

Catalyst	Substrate (ml)	Substrate / Catalyst	Time (h)	Temp	Products[f]		
					1,3-cyclooctadiene	1,4-cyclooctadiene	1,5-cyclooctadiene
(I) Ⓟ-$TiCpCl_3$[a] 0.322 g (0.1008 mmol Ti/g)	4	1006	9.5	145°	90.0	10.0	0.0
Regenerated [b,c]	4	1006	35	145°	80.0	20.0	0.0
(II) Ⓟ-$TiCp_2Cl_2$[a] 0.320 g (0.1055 mmol Ti/g)	4	968	10	145°	90.0	5.0	5.0
Regenerated [b,c]	4	968	36	145°	17.1	19.7	63.2
(III) Ⓟ-$TiCp_2Cl_2$[a] 0.231 g (0.1055 mmol Ti/g)	4	1340	13.5	145°	87.5	12.5	0.0
Recycled [d]	4	1340	22	145°	33.8	15.2	51.0
(IV) Ⓟ-$TiCpCl_3$[a] 0.237 g (0.1008 mmol Ti/g)	4	1367	13	145°	76.5	19.0	4.5
Recycled [d]	4	1367	20	145°	15.1	11.0	73.9
(V) Ⓟ-$TiCpCl_3$[e] 0.246 g (0.1008 mmol Ti/g)	4	1314	13	145°	54.5	24.1	21.4
Recycled [d]	4	1314	20	145°	13.9	13.0	73.1
(VI) Ⓟ-$TiCp_2Cl_2$[e] 0.235 g (0.195 mmol Ti/g)	4	714	13	145°	79.9	12.5	7.6
Recycled [d]	4	714	20	145°	26.9	32.3	40.8
(VII) Ⓟ-$TiCp_2Cl_2$[a] 0.229 g (0.195 mmol Ti/g)	4	733	10	145°	87.3	11.1	1.6
Recycled [d]	4	733	20	145°	28.6	10.3	61.1

a Catalyst reduced with excess BuLi under; b Catalyst regenerated by addition of HCl gas; c Regenerated catalyst reduced with excess BuLi under H_2; d Catalyst recycled from preceding reaction; e Catalyst reduced with excess BuLi under Ar; f Mole percent.

supported titanocene dichloride is reduced under different gaseous atmospheres. (Hydrogen or Argon)

Bercaw [40] was able to isolate and identify the elusive "titanocene", $(\eta^5\text{-}C_5H_5)_2Ti$ in a dimeric form by reacting freshly powdered $TiCp_2Cl_2$ with Na under argon. Titanocene dichloride was first reduced by 2 electrons/Ti to form the monomeric $(\eta^5\text{-}C_5H_5)_2Ti$. Monomeric $(\eta^5\text{-}C_5H_5)_2Ti$ is an unstable species with a carbene-like reactivity. It is well known that a carbene rearranges most frequently by abstraction of an α-hydrogen and formation of olefin. Analogously, the titanium center in $(\eta^5\text{-}C_5H_5)_2Ti$ is prone to abstract, possibly <u>via</u> a $(\eta^1\text{-}C_5H_5)_2Ti$ derivative, one of the ring hydrogens to form titanofulvene, indicated in Figure 5.

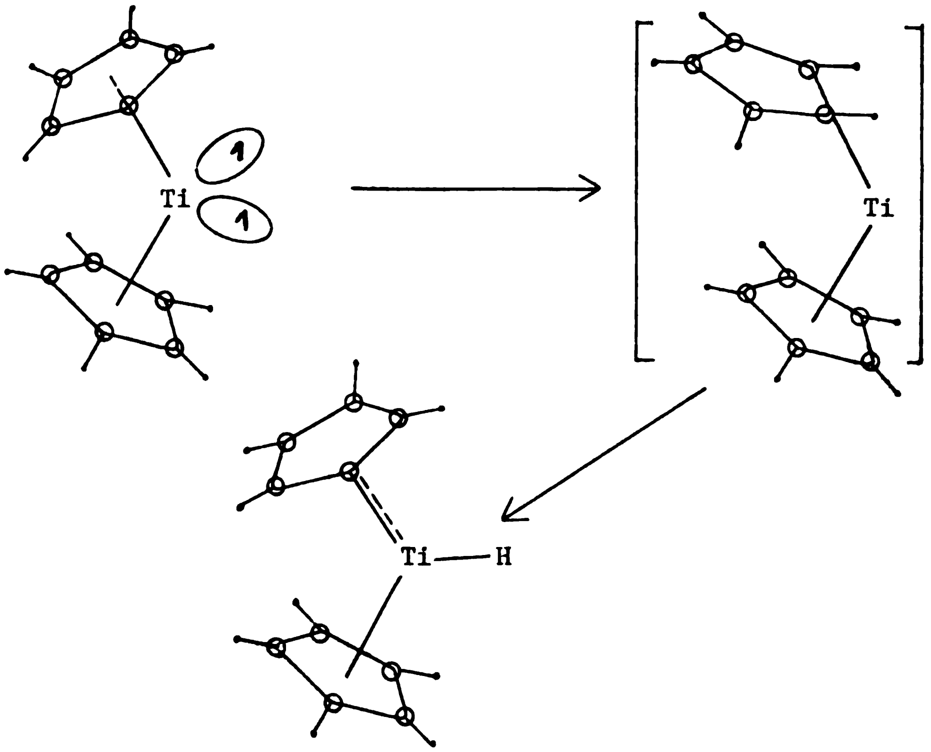
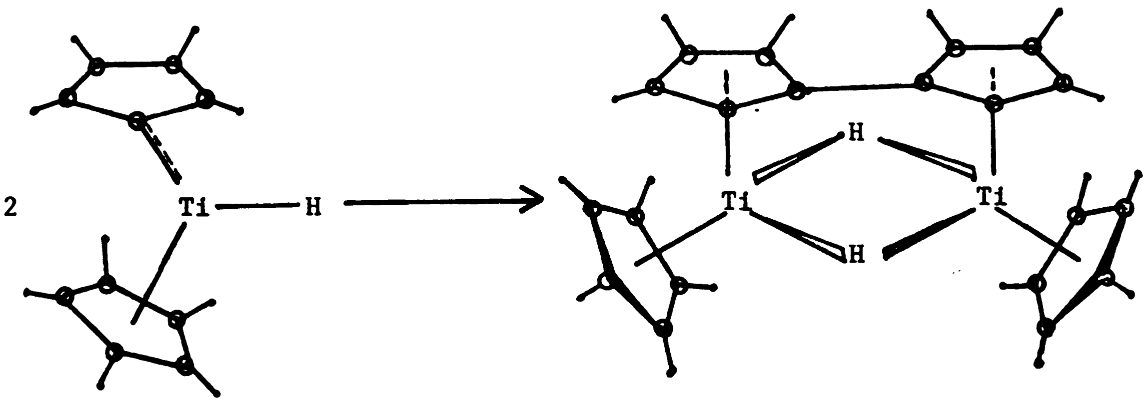
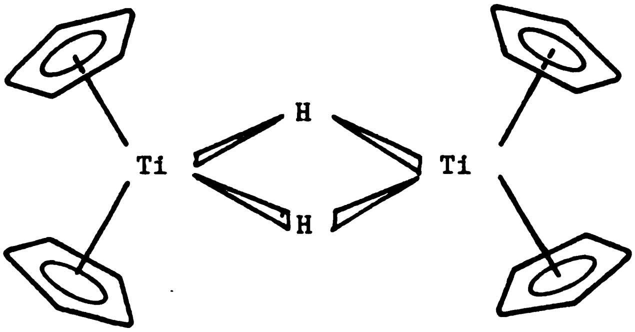


Figure 5. Postulated rearrangement of di-η^5-cyclopentadienyltitanium to η^5-cyclopentadienyl-η^1-cyclopentadienylidenetitanium hydride.

The n^5-cyclopentadienyl-n^1-cyclopentadienylidenetitanium hydride then dimerizes:



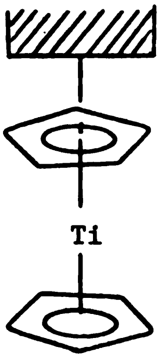
By reacting dimethyl titanocene, $TiCp_2(CH_3)_2$, with hydrogen gas, Bercaw [40] succeeded in isolating a violet compound which he characterized as the titanocene monohydride dimer, $[(\eta^5-C_5H_5)_2TiH]_2$. A diborane-like double hydrogen bridge between the two metal centers has been postulated. This postulate is supported by infrared and mass spectrometry.



Titanocene monohydride dimer

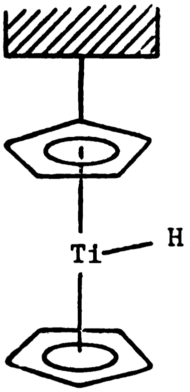
In view of the difference in rates of isomerization by resin bound titanocene species produced under hydrogen and argon, esr studies of the two different reduced species have been carried out. The esr spectrum of the "under-argon reduction" product gives a broad singlet with g = 1.988 (Figure 6), while the "under-hydrogen reduction" product shows a doublet with g = 1.991 and a splitting of 7.7 gauss. (Figure 7)

With Bercaw's titanocene and titanocene monohydride in mind, buttressed with the different rates of isomerization and different esr spectra, one is tempted to speculate that the species formed by reduction of polymer-supported $TiCp_2Cl_2$ under argon is the supported titanocene (Structure I), while that generated under hydrogen is the supported titanocene monohydride. (Structure II)



Structure I

Polymer-supported titanocene



Structure II

Polymer-supported titanocene monohydride

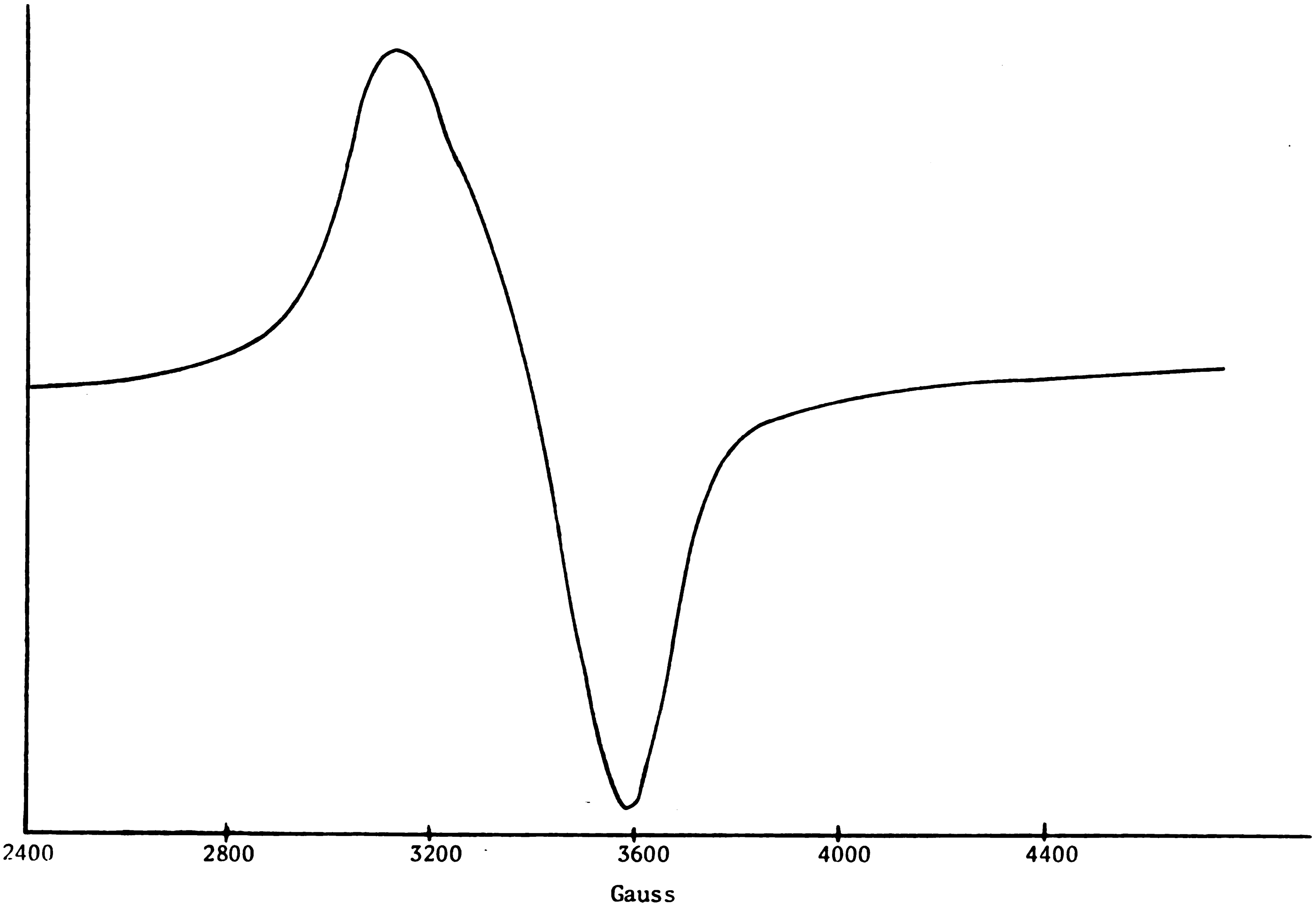


Figure 6. ESR Spectrum of Polymer-Supported Titanocene.

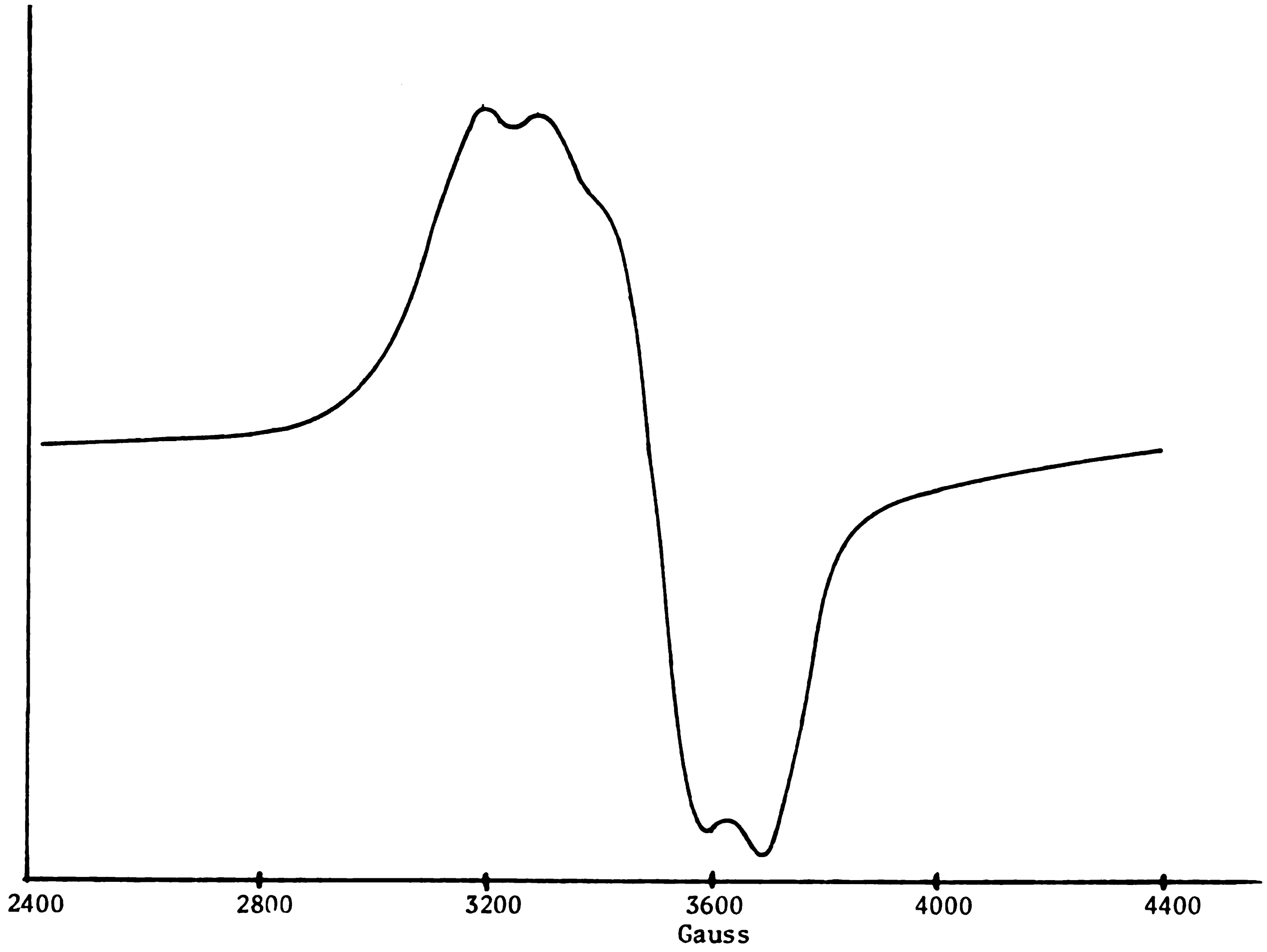


Figure 7. ESR Spectrum of Polymer-Supported Titanocene Hydride.

The esr spectrum of the "under-argon reduction" product does not show any splitting; it can rationalized in the following manner:

The driving force for rearrangement of "titanocene" to the η^5-cyclopentadienyl-η^1-cyclopentadienylidenetitanium hydride is the easy dimerization of the latter to form the stable species, $(C_5H_5TiH)_2C_{10}H_8$. Since dimerization is largely prevented on the polymer, such a driving force is lacking, and the supported "titanocene" abstraction of an α-hydrogen from one of the cyclopentadiene rings is not spontaneous.

Comparison of reactions (VI) and (VII) in Table 6 shows that the catalyzed isomerization of 1,5-cyclooctadiene by the "under-hydrogen reduction" product is faster than that formed under argon. The difference in rates may be attributed to the neccessity of the initially π-bonded substrate to abstract a hydrogen from one of the cyclopentadiene rings of the "under-argon reduction" product, (Figure 8) this process has a higher energy barrier than that of the "under-hydrogen reduction", in which the hydride shift does not cause any symmetry change in the metal center. (Figure 9)

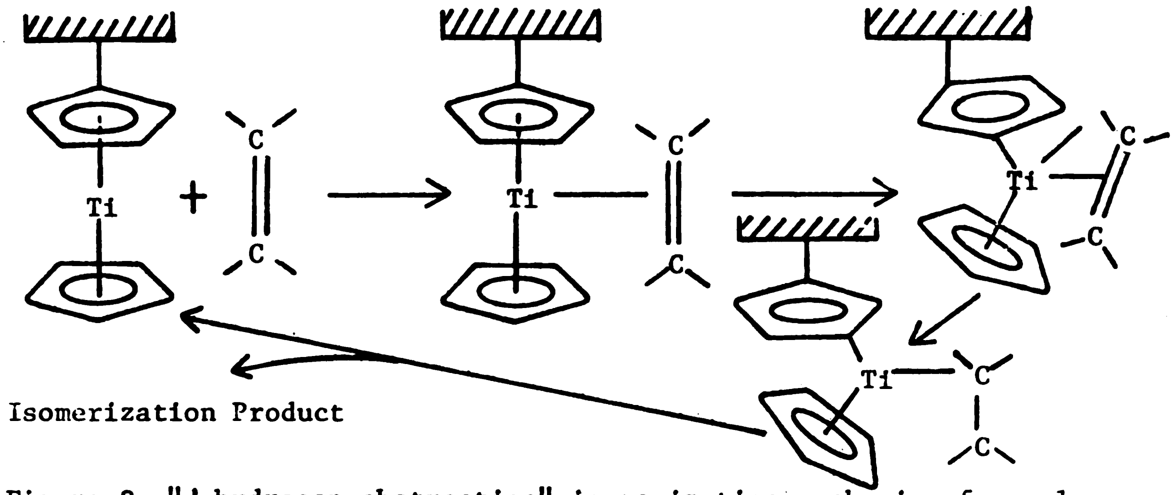


Figure 8. "α-hydrogen abstraction" isomerization mechanism for polymer-supported titanocene.

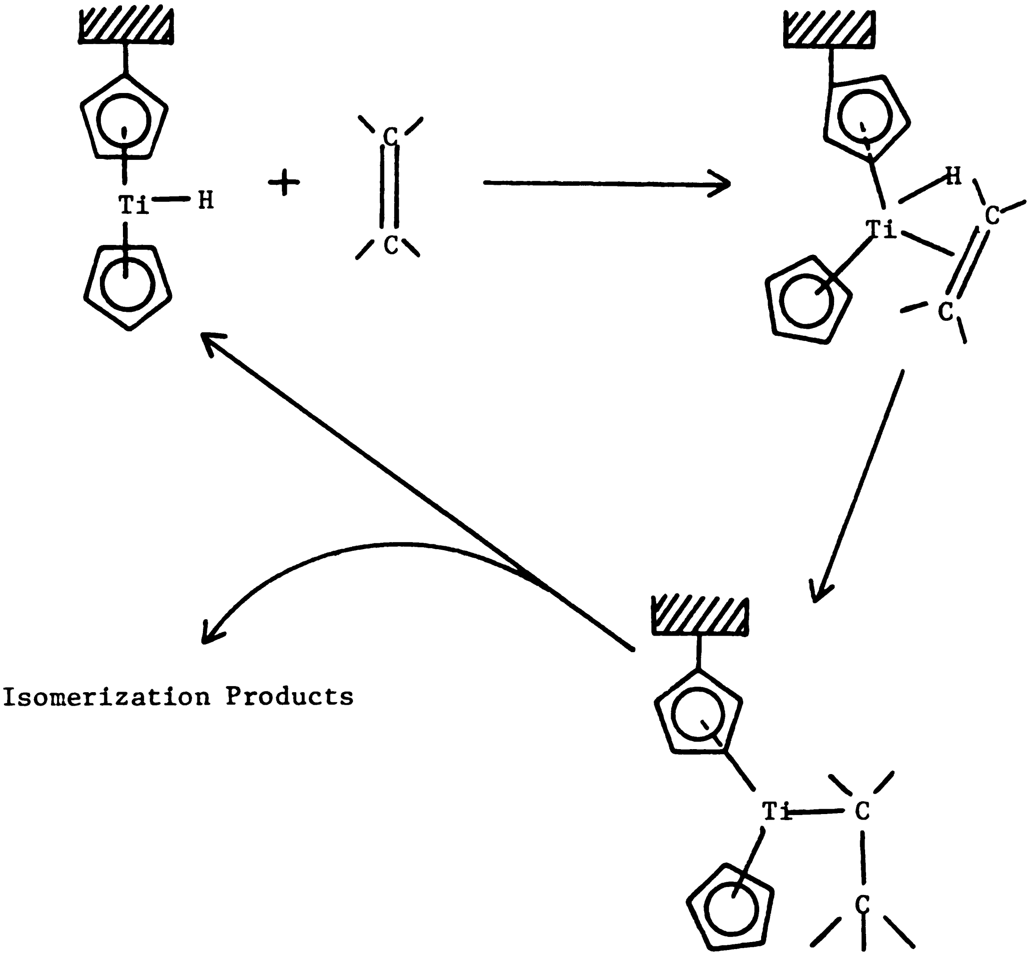


Figure 9. "Hydrogen abstraction" isomerization mechanism for polymer-supported titanocene monohydride.

So far, the metal-hydride mechanism for isomerization has been assumed; but one has to bear in mind that if polymer-supported "titanocene" is indeed the product in the "under-argon reduction", isomerization by other michanisms cannot be ruled out. The π-allyl complex intermediate mechanism is schematized in Figure 10.

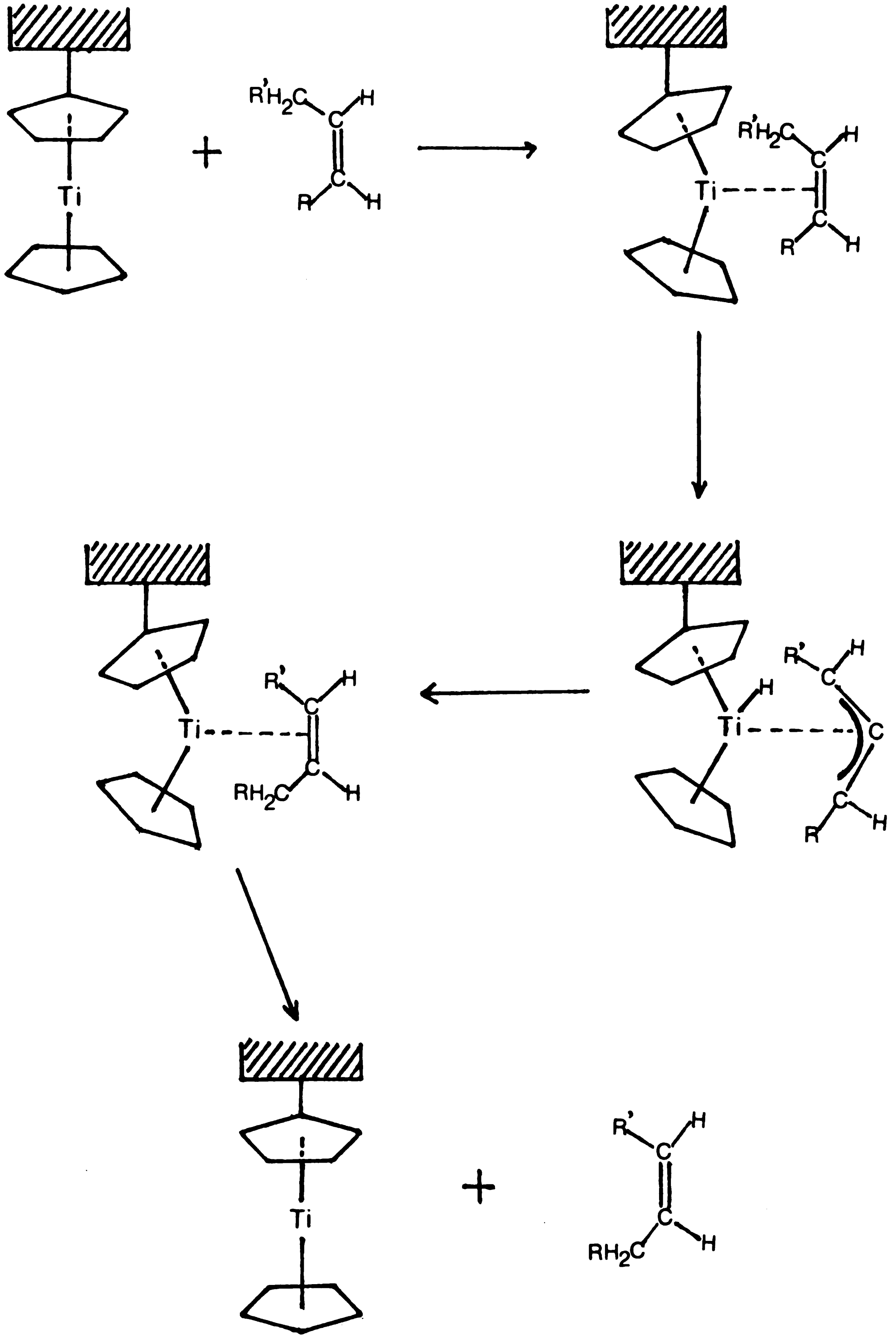
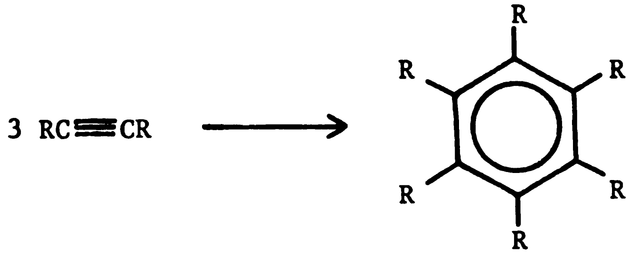


Figure 10. The π-allyl complex intermediate mechanism for isomerization.

Polymer-supported $TiCp_2Cl_2$ oligomerization of acetylenic derivatives

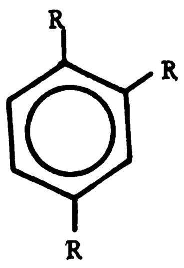
The catalytic cyclotrimerization of acetylenes to form benzene derivatives (Equation 1) has been investigated.[41,42]

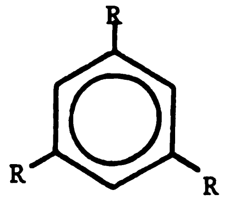

(1)

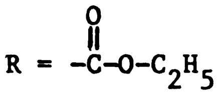
Pittman[17] has examined the oligomerization of ethyl propiolate in the presence of resin bound $Ni(CO)_2(PR_3)_2$ (R = alkyl or aryl) and has found a yield of 5.8% 1,3,5-tricarbethoxybenzene and 74.5% of the 1,2,4-tricarbethoxybenzene, by weight, based on the amount of ethyl propiolate used.

The reduction product of polymer-supported titanocene dichloride, being coordinately unsaturated, has vacancies in the valency shell and is a potential catalyst for oligomerization of acetylene compounds.

In our experiments, supported $TiCp_2Cl_2$ was reduced by excess BuLi under hydrogen, and oligomerization of ethyl propiolate was studied in the presence of this reduction product. It was found that 0.2 g resin bound catalyst (0.087 mmol Ti/g beads) had effected a total of 38% oligomerization (based on 2 g ethyl propiolate used). The product is a mixture of trimers of ethyl propiolate. Mass spectra indicated a parent peak at 294, due to the trimers. NMR spectra showed 2 peaks at δ= 7.6-8.1 ppm and 8.5 ppm. These two peaks indicated that the two closed trimers (T-1) and (T-2) were present in the product mixture.



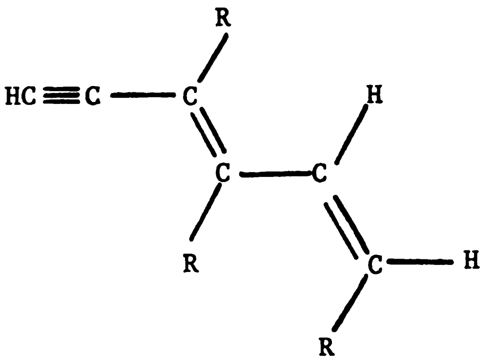


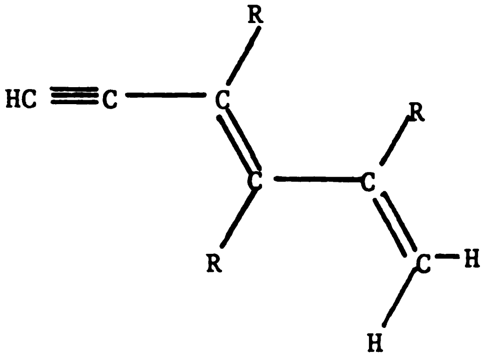


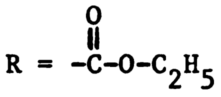
$$R = -\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

(T-1) 1,2,4-tricarbethoxybenzene (T-2) 1,3,5-tricarbethoxybenzene

No acetylenic proton peaks were observed. Thus the two open trimers can be ruled out.

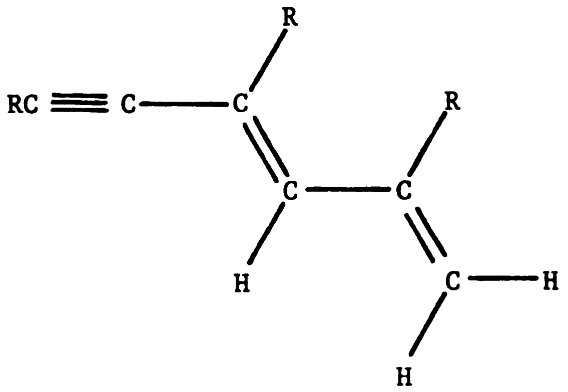




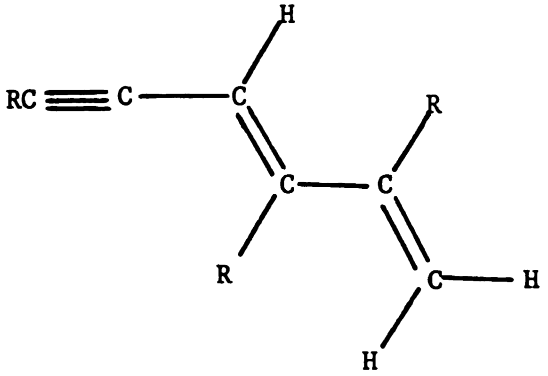


$$R = -\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

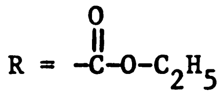
Glc analysis, using a Porapak Q column, gave 4 well resolved peaks and a relatively broad one. Although no further attempt had been made to identify each of the components in the product mixture, a conclusion that the oligomerization product is a mixture of two closed trimers (T-1) and (T-2), and some or all of the 4 open trimers (T-3, T-4, T-5 and T-6) can be drawn.



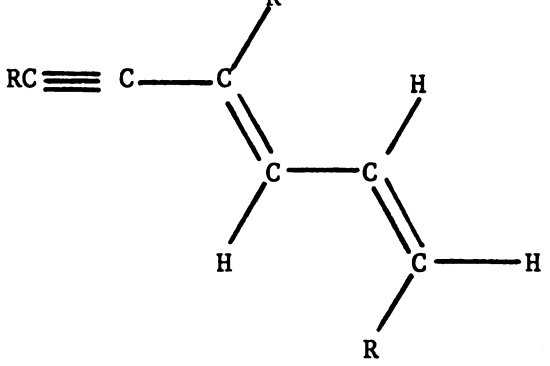
T-3



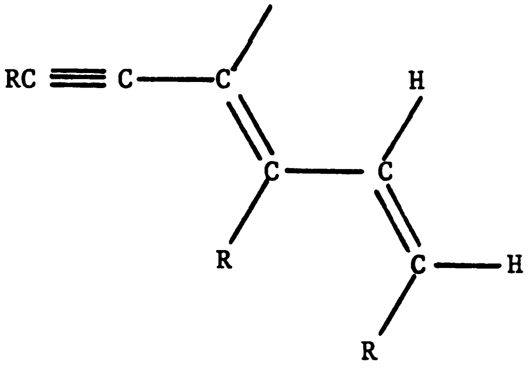
T-4



$R = -\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5$



T-5



T-6

The reduced polymer-supported $TiCp_2Cl_2$ differs from resin bound $Ni(CO)_2(PR_3)_2$ [17], by producing open trimers in addition to the closed ones. Such a variety of components in the product mixture makes separation nearly impossible.

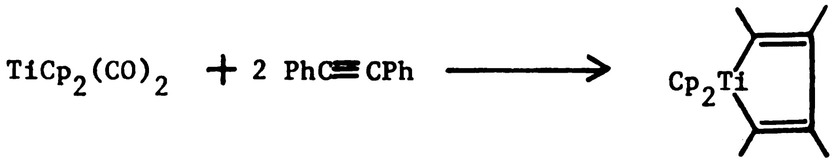
In addition to ethyl propiolate, polymer-supported $TiCp_2Cl_2$ oligomerization of phenylacetylene has also been examined, the result was far from satisfactary since only traces of oligomers were isolated.

Preparation of polymer-attached titanocene dicarbonyl, $TiCp_2(CO)_2$

There are a number of ways of preparing homogeneous titanocene dicarbonyl.[36,43,44] One of the methods is to mix titanocene dichloride with BuLi solution and stir the mixture under 240 atmospheres of carbon monoxide at 150°. One can rationalize the neccessity for such a drastic reaction condition by considering that titanocene dichloride is reduced by BuLi to form "titanocene" which dimerizes easily to give the very stable $(C_5H_5TiH)_2C_{10}H_8$; therefore it is not surprising that a high carbon monoxide pressure and temperature are required to regenerate the "titanocene" monomer from the dimer before carbon monoxide attachment can occur.

Since polymer-attachment circumvents dimerization of "titanocene", one would expect the preparation of polymer-attached titanocene dicarbonyl to be carried out under much milder reaction conditions. This is exactly the case. Polymer-attached titanocene dichloride, a after reduction by BuLi under argon, was converted exclusively to the attached titanocene dicarbonyl by stirring the reduction product under carbon monoxide at 60 psi. Figure 11 shows the very $\nu_{C\equiv O}$ peaks at 1965 cm^{-1} and 1878 cm^{-1}. The peak at 1878 cm^{-1} overlaps one of the peaks of the polystyrene-divinylbenzene copolymer, as a result, there i is a marked increase in intensity compared to the other polystyrene peak at 1945 cm^{-1}. In another experiment, one atmosphere of carbon monoxide was used instead of 60 psi, only partial carbonylation of the supported "titanocene" was observed. It can be seen from Figure 12 that the $\nu_{C\equiv O}$'s at 1965 cm^{-1} and 1878 cm^{-1} have much lower intensities than those in Figure 11.

The reaction of polymer-attached titanocene dicarbonyl with a benzene solution of diphenylacetylene yielded greenish-brown colored beads. The ir spectrum shows no $\nu_{C\equiv O}$, as is consistent with the formation of a titanium heterocycle in the reaction between titanocene dicarbonyl and diphenylacetylene. (Equation 2)



(2)

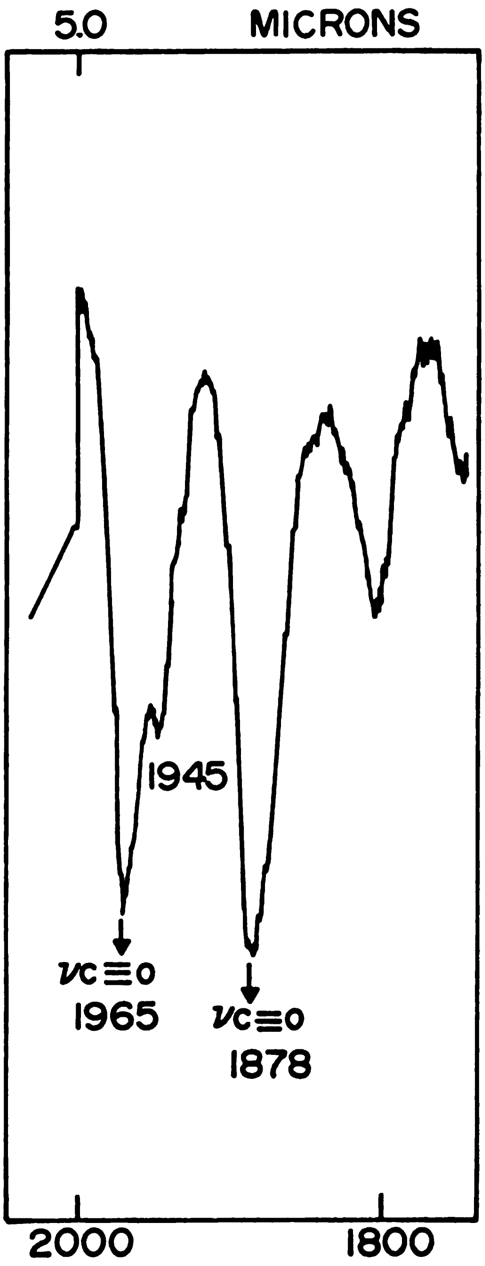


Figure 11. IR Spectrum of Polymer-Supported $TiCp_2(CO)_2$

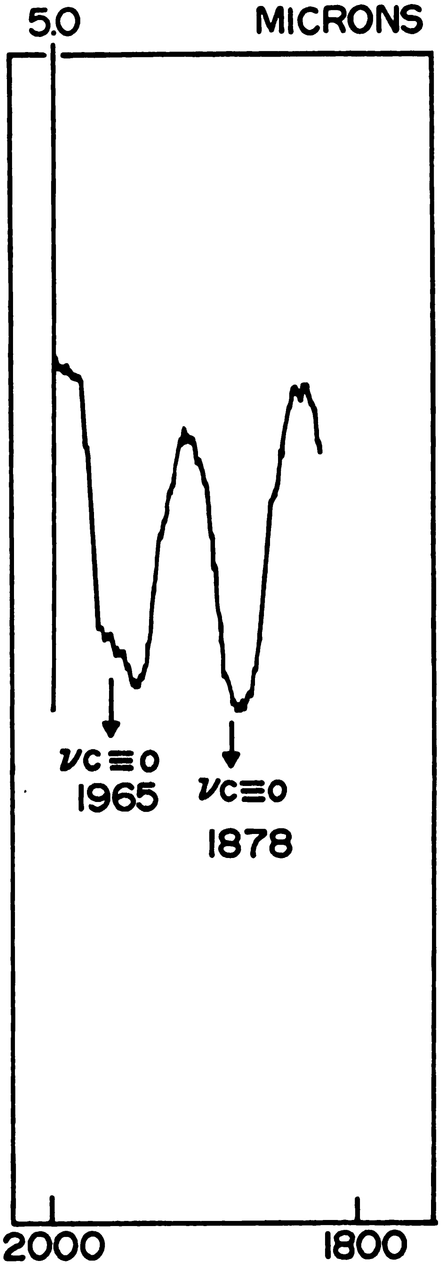


Figure 12. IR Spectrum of Partially Carbonylated Polymer-Supported Titanocene

Polymer-supported $TiCp_2(CO)_2$ hydroformylation of olefins

It has been well known that Group VIII transition metal complexes, such as those of Rh and Co, are good catalysts for hydroformylation of olefins. But the use of early transition metal complexes, such as those of Ti, as hydroformylation catalyst has rarely been reported. One of our endeavors has been to examine the hydroformylation ability of polymer-supported titanocene compounds. As has been described in a previous section, polymer-supported $TiCp_2(CO)_2$ can be easily synthesized. With this compound at our disposal, hydroformylation of olefins by using the polymer-supported catalyst has been studied.

The reaction was typically carried out at a total pressure of 1500 psi, for about 9 hr at 100°. The hydroformylation results are presented in Table 7. It can be seen from the Table that in the hydroformylation of 1-pentene, the linear/branched ratio was about 1 when the CO/H_2 ratio was 1 and the reaction time was 9 hr. Reducing the reaction time to 3 hr gave a linear/branched ratio of more than 2. Changing the CO/H_2 ratio from 1 to 3 only increased the linear/branched ratio slightly. But the recycled catalyst gave a ratio of a little over 2, although the total hydroformylation was lowered considerably. During the recycling process, it was unavoidable that the catalyst would contact with air, and since titanocene dicarbonyl is rather air sensitive, part of the catalyst may have been deactivatived.

Catalytic hydroformylation of 1-hexene gave only about 10% hydroformylation. (Table 7)

During hydroformylation, no hydrogenation or isomerization of 1-pentene was observed. With prolonged reaction times, hydrogenation of the resulting aldehydes to give the corresponding alcohols becomes

Table 7

Catalytic Hydroformylation of Olefins with Polymer-Attached $TiCp_2(CO)_2$

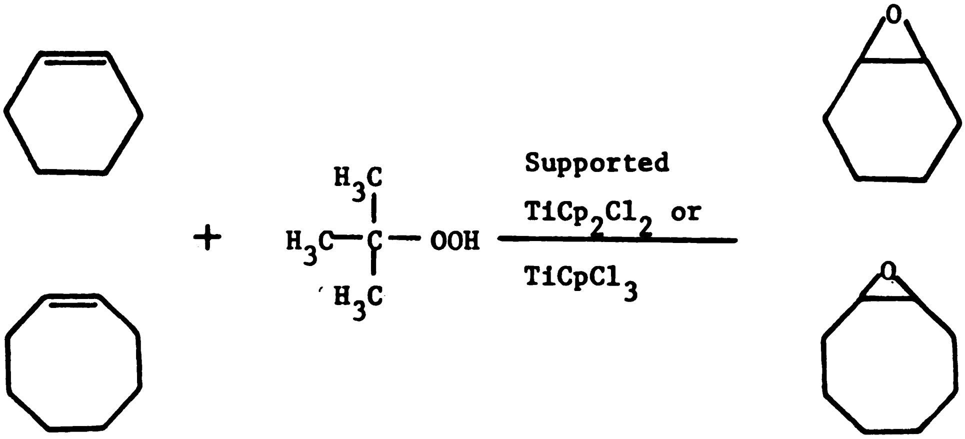
Catalyst	Substrate (ml)	Solvent (ml)	$\frac{\text{Substrate}}{\text{Catalyst}}$	Pressure (psi)	Temp	Time (h)	Products[b]: Aldehydes	
							Linear	Branched
0.2290 g (0.1746 mmol Ti/g)	1-pentene (3.5)	Benzene (10)	763	1500[a]	100°	9	42.3	38.2
Recycled [c]	1-pentene (3.5)	Benzene (10)	763	1500[a]	100°	9	34.4	15.4
0.2214 g (0.1746 mmol Ti/g)	1-pentene (3.5)	Benzene (10)	788	1500[a]	100°	3	36.2	16.3
0.2353 g (0.1746 mmol Ti/g)	1-pentene (3.5)	Benzene (10)	744	1500[a]	25°	9	16.8	15.5
0.2340 g (0.1746 mmol Ti/g)	1-pentene (3.5)	Benzene (10)	746	1500[d]	100°	9	46.5	31.5
0.2570 g (0.1746 mmol Ti/g)	1-hexene (3.5)	Benzene (10)	624	1500[a]	100°	9	5.2	4.7

a $CO/H_2 = 1/1$; b mol per cent based on olefin used;
c Catalyst recycled from preceding reaction; d $CO/H_2 = 3/1$

significant.

Catalytic epoxidation of cyclohexene and cyclooctene

Tert-butyl hydroperoxide reacts with cyclohexene or cyclooctene, in the presence of polymer-supported $TiCp_2Cl_2$ or $TiCpCl_3$, to yield the corresponding epoxycycloalkanes.



The epoxidation results are shown in Table 8. Comparison of reactions (1) and (3), reactions (5) and (7) in Table 8 shows that the polymer-supported $TiCpCl_3$ is a better catalyst than the supported $TiCp_2Cl_2$. In the polymer-supported $TiCpCl_3$ epoxidation of cyclohexene, the percent epoxidation (based on the initial amount of cyclohexene used) has been raised from 48% to 88%, when the amount of catalyst was increased from 0.123 g to 0.310 g. In the case of supported $TiCp_2Cl_2$ epoxidation, the percent epoxidation only increased from 20% to 40%, although the amount of catalyst was quadrupled.

Epoxidation of cyclooctene preceeds to a comparatively smaller extend. With 0.201 g supported $TiCpCl_3$ (0.285 mmol Ti/g beads), only 34% epoxidation was achieved. When the amount of supported $TiCpCl_3$ was increased to 0.419 g, the epoxidation remained almost unchanged, but the time of reaction was reduced from 18 to 12 hr.

Both the supported $TiCpCl_3$ and $TiCp_2Cl_2$ were regenerated after epoxidation of cyclooctene. The regenerations were carried out by passing anhydrous hydrogen chloride into the beads suspended in THF. The regenerated catalysts were reused for epoxidation studies of cyclooctene. It was found that the supported $TiCpCl_3$ retained ca. 75% of its catalytic activity while the supported $TiCp_2Cl_2$ lost ca. 35%.

Polymer-supported niobocene dichloride was used for epoxidation studies. But experimental results showed that the supported $NbCp_2Cl_2$ did not catalyze epoxidation of olefins.

Failure of the supported $NbCp_2Cl_2$ to catalyze epoxidation of olefins might be an indication that the acidity of the metal center does affect epoxidation activity. The lack of a d electron and the relatively small size of Ti(IV) makes it more acidic than the large d^1 Nb(IV). In addition, a steric effect also seems to play an important role in epoxidation, since it has been learned that the bulkier cyclooctene can only be epoxidated to a smaller extent than the cyclohexene.

Table 8

Catalytic Epoxidation Olefins with Polymer-Supported $TiCpCl_3$ and $TiCp_2Cl_2$

Catalyst	Substrate [a]	Time(h)	Temp	Products[b]	
				Cyclohexene oxide	Cyclooctene oxide
(1) Ⓟ-$TiCpCl_3$ 0.133 g (0.200 mmol Ti/g)	cyclohexene	18	80°	46	
(2) Ⓟ-$TiCpCl_3$ 0.310 g (0.200 mmol Ti/g)	cyclohexene	18	80°	88	
(3) Ⓟ-$TiCp_2Cl_2$ 0.130 g (0.195 mmol Ti/g)	cyclohexene	18	80°	26	
(4) Ⓟ-$TiCp_2Cl_2$ 0.516 g (0.195 mmol Ti/g)	cyclohexene	18	80°	40	
(5) Ⓟ-$TiCpCl_3$ 0.210 g (0.200 mmol Ti/g)	cyclooctene	18	80°		34
(6) Ⓟ-$TiCpCl_3$ 0.419 g (0.200 mmol Ti/g)	cyclooctene	13	80°		37
(7) Ⓟ-$TiCp_2Cl_2$ 0.213 g (0.195 mmol Ti/g)	cyclooctene	20	80°		25

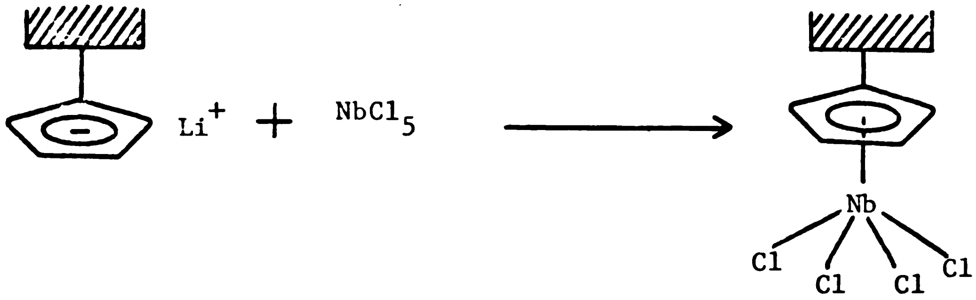
[a] 50 mmol olefin + 50 mmol tert-butyl hydroperoxide

[b] mol per cent based upon the amount of olefin used

Preparation of polymer-supported niobium complexes

(I) Polymer-supported $NbCpCl_3$

It has been our initial intention to prepare the polymer-supported $NbCpCl_4$ by treating cyclopentadienide substituted copolymer with $NbCl_5$, according to the following reaction:



Instead of $NbCpCl_4$, polymer-supported $NbCpCl_3$ is formed. The formation of supported $NbCpCl_3$ is not unexpected since the cyclopentadienide ion is a good reducing agent. During its reaction with $NbCl_5$, polymer-supported $NbCpCl_3$ is formed by reduction of Nb(V) to Nb(IV).

The polymer-supported $NbCpCl_3$ has been confirmed by metal and chloride analyses, which gave a Cl/Nb ratio of 3.1. The esr spectrum is shown in Figure 13. Since homogeneous $NbCpCl_3$ has never been reported, there is no way to compare the esr spectrum of the supported $NbCpCl_3$ with any known one. However, Neal Kilmer has plotted a computer simulated esr spectrum of this compound (Figure 14). Comparison of the experimental spectrum with the simulated one indicates that the two match very well.

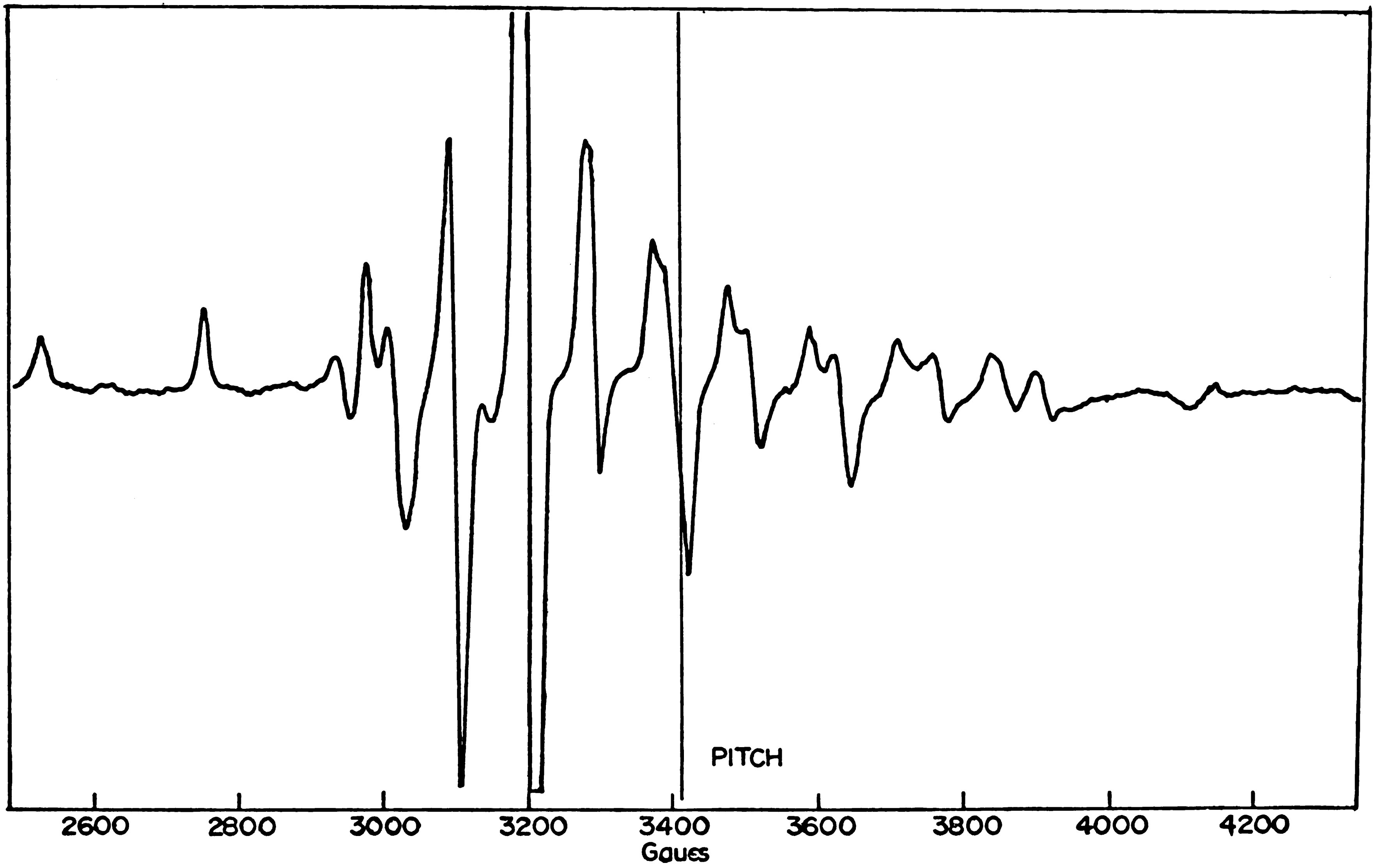


Figure 13. ESR Spectrum of Polymer-Supported $NbCpCl_3$.

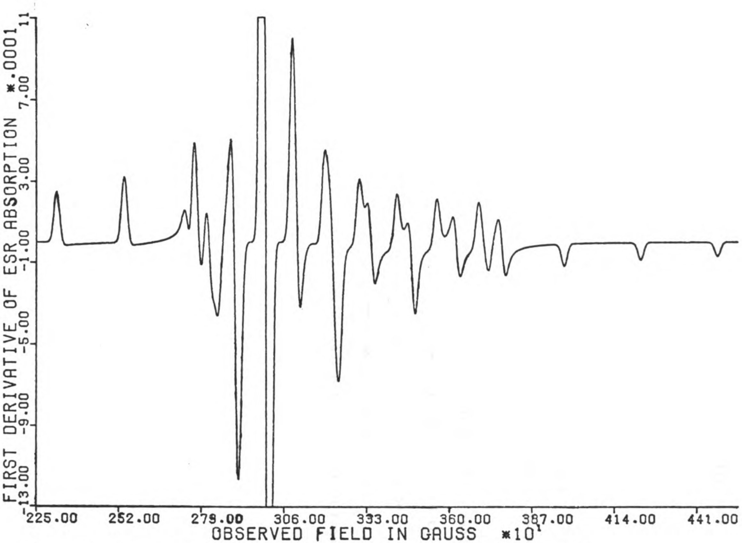


Figure 14. Computer Simulated ESR Spectrum of Polymer-Supported $NbCpCl_3$.

(II) Polymer-supported $NbCp_2Cl_2$

Polymer-supported $NbCp_2Cl_2$ was prepared by converting the correspinding $NbCpCl_3$ to $NbCp_4$ with excess NaCp solution in THF, and then by treating the supported $NbCp_4$ with a saturated solution of dry hydrogen chloride in THF. The resin bound $NbCp_2Cl_2$ is confirmed by metal and chloride analyses:

Cl/Nb	(experimental)	1.93
Cl/Nb	(theoretical)	2.00

Esr spectrum of the supported $NbCp_2Cl_2$ is shown in Figure 15. It is very similar to the frozen glass spectrum of the homogeneous $NbCp_2Cl_2$ reported in literature.[45]

Loading in the polymer-supported $NbCpCl_3$ is 0.94 mmol Nb/g beads, but in subsequent $NbCp_2Cl_2$ substituted polymer, it has decreased to 0.14 mmol Nb/g beads. This tremendous decrease in loading can be explained by the η^5-C_5H_5— η^1-C_5H_5 exchange mechanism proposed by John Lee in our group.[46] The exchange mechanism is outlined in Figure 16.

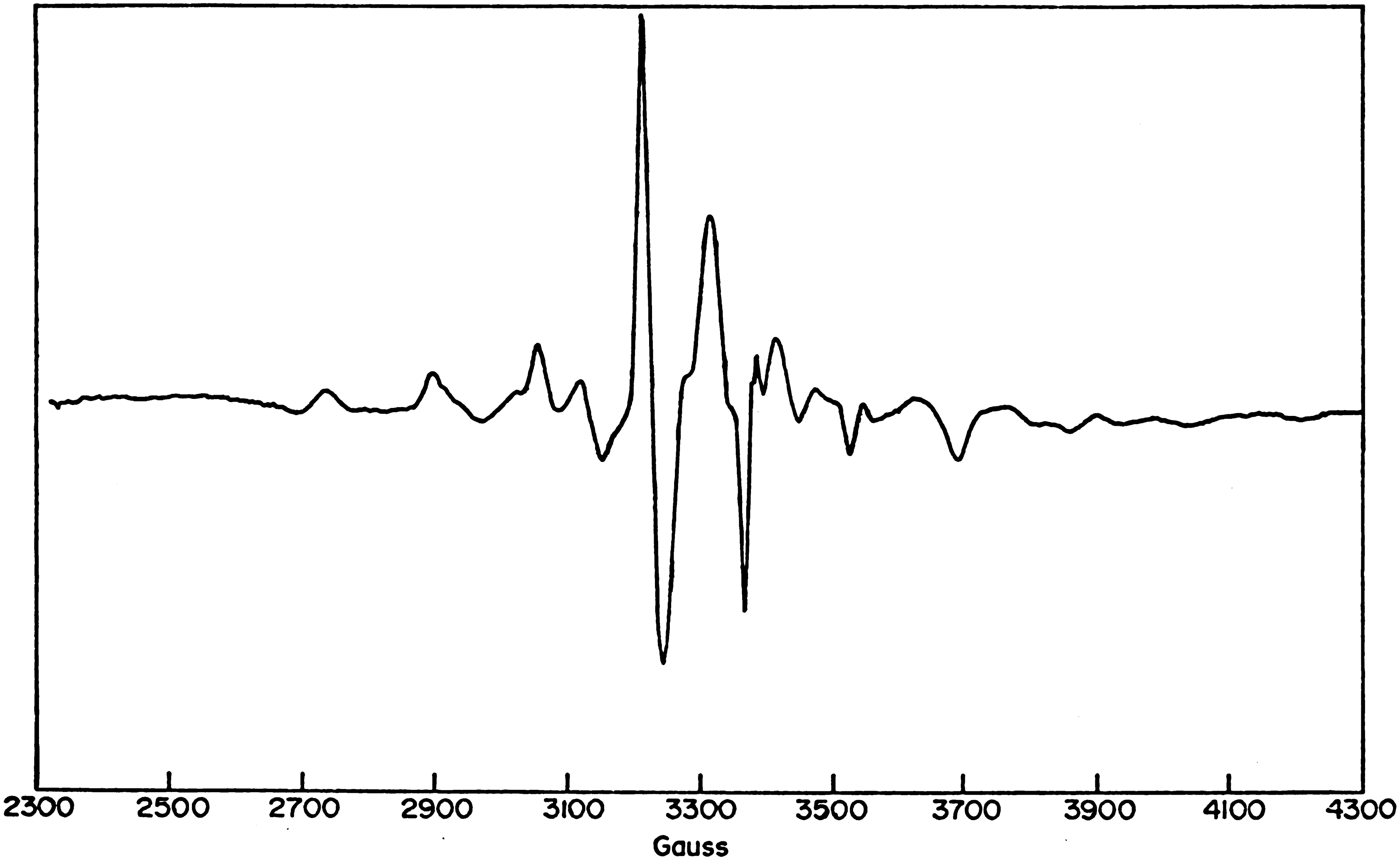


Figure 15. ESR Spectrum of Polymer-Supported $NbCp_2Cl_2$.

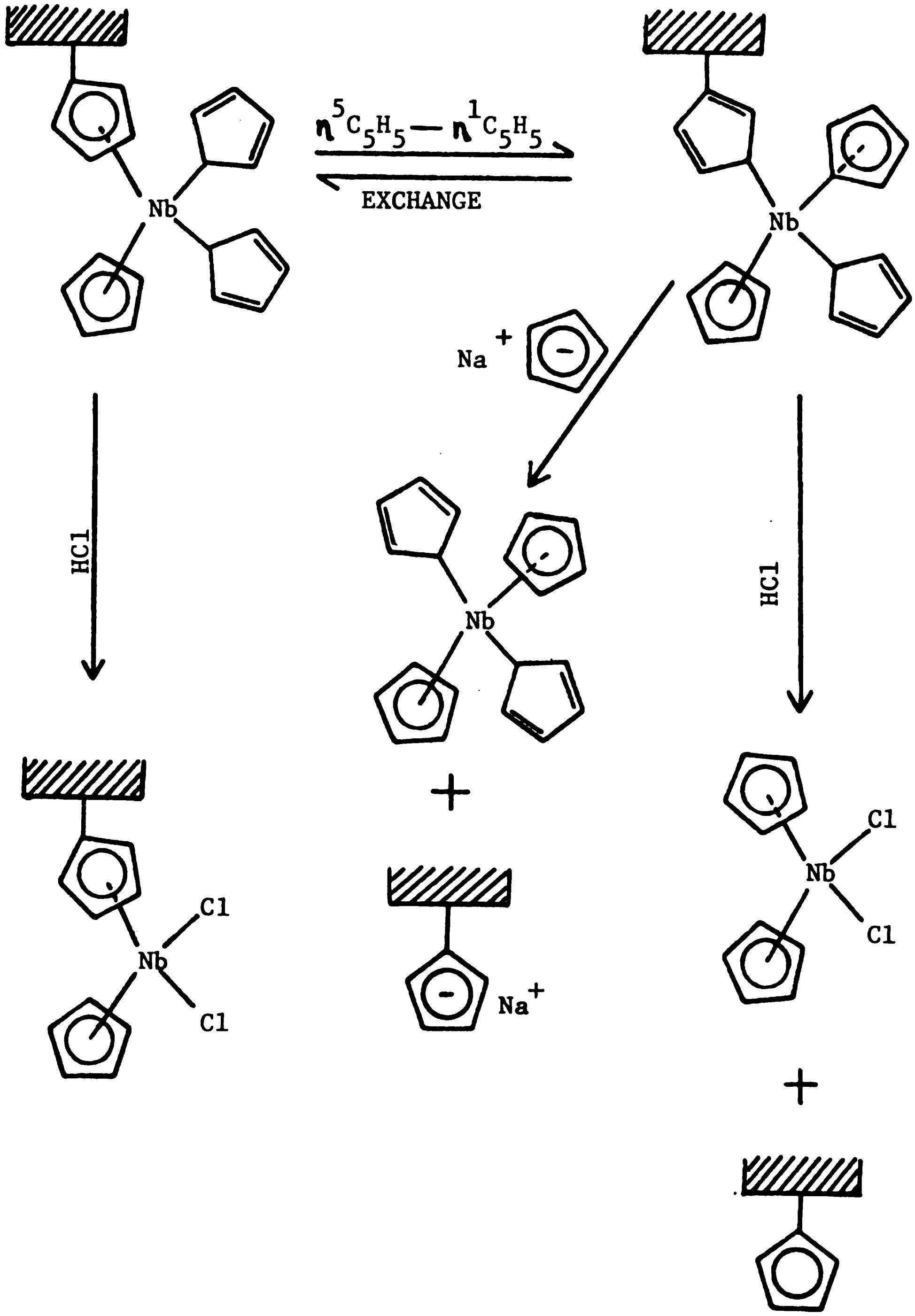


Figure 16. η^5-C_5H_5—η^1-C_5H_5 Exchange Mechanism.

Studies of catalytic activities of polymer-supported niobium complexes

It has been known that homogeneous $NbCp_2Cl_2$ reacts with BuLi to form $NbCp_2HCl$, this monohydride complex might be a potential catalyst for hydrogenation, isomerization, etc. Polymer-supported $NbCp_2Cl_2$ has been treated with BuLi to give black beads; Nb and Cl analyses of which yielded a Cl/Nb ratio of 1.05. This result clearly indicated that one of the chloride ligands remained bonded to the metal center. Nb-H stretching could scarcely be observed in ir spectrum because the very broad peak due to the copolymer at 1600 cm^{-1} might have covered the ν_{Nb-H}. Nevertheless, it is not unreasonable to expect that the reaction between polymer-supported $NbCp_2Cl_2$ and BuLi has formed the same product as in the homogeneous case, i.e., the polymer-supported $NbCp_2HCl$.

Polymer-supported $NbCp_2HCl$ has been employed for isomerization of allylbenzene, it is found that 0.18 g (0.14 mmol Nb/g beads) can effect 90% isomerization of 4 ml allylbenzene (80% _trans_-propenylbenzene and 10% _cis_-propenylbenzene) in 15 hr at 145°. On the other hand, no success in polymer-supported $NbCp_2HCl$ hydrogenation of olefins and epoxidation of cyclohexene or cyclooctene has been achieved.

Polymer-supported $NbCpCl_3$ isomerization of allylbenzene has also been attempted. The supported $NbCpCl_3$ was treated with BuLi before being used as isomerization catalyst. A 0.2 g sample of supported $NbCpCl_3$ was found to effect a total of 7.4% isomerization of 4 ml allylbenzene, 5.4% to _trans_-propenylbenzene and 2% to _cis_-propenylbenzene.

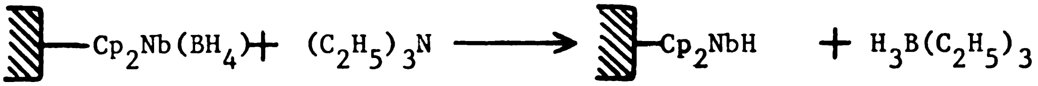
Studies of polymer-supported $NbCpCl_3$ hydrogenation of olefins show that it is a much poorer hydrogenation catalyst than its titanium analog. The hydrogenation results are summarized as follow:

Olefin	Initial Rate of Hydrogenation ml H_2/min-mmol Nb
1-hexene	1.49
cyclohexene	1.11
1-octene	0.00

Polymer-supported niobocene derivatives

Polymer-supported $NbCp_2(BH_4)$ was prepared by treating resin bound $NbCp_2Cl_2$ with $LiBH_4$ in THF, according to the following:

The green colored, and very air sensitive, polymer-supported $NbCp_2(BH_4)$ showed the ν_{Nb-H} at 2330 cm^{-1}. Addition of triethylamine to the borohydride derivative yielded yellow beads, whose ir spectrum showed a sharp peak at 1655 cm^{-1} not present in that of the supported niobocene borohydride. This sharp peak might be attributed to the Nb-H stretching. The yellow beads were suspected to be the polymer-supported niobocene monohydride.



When the supported niobocene monohydride was used for the catalytic isomerization of allylbenzene, 0.2 g was able to achieve a 10% isomerization (based on 4 ml allylbenzene used).

In another experiment, polymer-supported $NbCp_2(BH_4)$ was treated with triethylamine under an atmosphere of carbon monoxide, one hoped for the formation of supported $NbCp_2HCO$ or $NbCp_2(CO)_2$. But an ir spectroscopy study did not indicate the formation of either. Carbonylation was not observed even under carbon monoxide pressure of 60 psi.

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