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POLYMER-SUPPORTED METALLOCENES AND THEIR APPLICATIONS TO THE CATALYSIS OF OLEFIN ISOMERIZATION, OLIGOMERIZATION, EPOXIDATION AND DINITROGEN FIXATION REACTIONS

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Summary

Polymer-attached $TiCp_2Cl_2$ and $TiCpCl_3$ have been reduced by BuLi and the reduction products have been employed in catalytic isomerization of allylbenzene and 1,5-cyclooctadiene. The former was converted into a mixture of *trans*- and *cis*-propenyl benzene, white the 1,5-cyclooctadiene was isomerized to 1,3-cyclooctadiene through the 1,4-cyclooctadiene intermediate. Oligomerization of ethyl propiolate has been effected by the polymer-attached titanocene species and gave a mixture of closed and open trimers. Polymer-supported $TiCp_2Cl_2$ and $TiCpCl_3$ can be used directly, without going through the reduction process, for the low yield epoxidation of cyclohexene and cyclooctene. Polymer-supported, methylene-bridged, $Cl_2TiCp(C_5H_4CH_2C_5H_3\text{-}\textcircled{P})CpTiCl_2$, was prepared and used in dinitrogen fixation studies. Polymer-attached $TiCp_2(CO)_2$ was prepared.

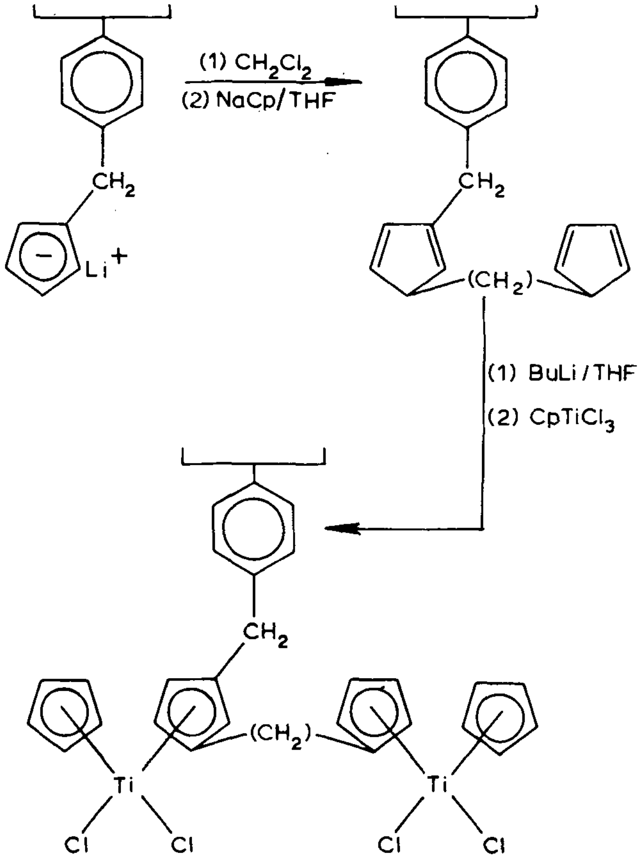
Recently, we have demonstrated [1] that the attachment of titanocene-related catalysts to rigid polymers resulted in an increase in activity for olefin hydrogenation, which was found to be a result of site isolation on the polymer [2]. Polymer-attached $TiCpCl_3$, on reduction with BuLi, produced an active catalyst (Scheme 1) whose hydrogenation efficiency is about twenty times as great as that of the corresponding homogeneous species under the same conditions [3].

A hydrogenation catalyst can have other catalytic activity, e.g., in isomerization and oligomerization reactions. Polymer-attached titanocene and the reduction product of polymer-attached $TiCpCl_3$ are excellent catalysts for olefin hydrogenation. Their activaties in other catalytic processes have been studied.

Experimental

Because of the air and moisture sensitivity of the materials described, standard Schlenk-tube techniques were employed. An argon-filled glove-box was used for transfers.

SCHEME 1



Electron spin resonance (ESR) spectra were obtained by use of a Varian E-4 spectrometer. NMR spectra were obtained by using Varian T-60 and Varian A56/60D spectrometers. Tetramethylsilane (TMS) was used as reference. Gas chromatographic (GLC) analyses were performed by use of an F&M model 810-19 analytical gas chromatograph and a Varian 1400 analytical gas chromatograph. Infrared spectra were recorded by using Perkin-Elmer 457 or 237B spectrophotometers. Samples were prepared by crushing the polystyrene beads in a ball mill under anaerobic conditions and mulling the powder with dry Nujol in a dry glove-box. The samples were placed between NaCl plates.

Materials

The 20% cross-linked (600 Å pore size), macroreticular, polystyrenedivinylbenzene, 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, a 1/1 H_2O/CH_3OH mixture, CH_3OH, a 1/1 CH_3OH/CH_2Cl_2 mixture, and CH_2Cl_2 and benzene as recommended by Pittman [4] and were dried in a vacuum.

Reagent grade tetrahydrofuran (THF), benzene, toluene and xylene were distilled over sodium-benzophenone under argon. Hexane, 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, t-butyl hydroperoxide and chloromethyl ethyl ether * were obtained from the Aldrich Chemical Company. Titanocene dichloride and niobium pentachloride were obtained from Alfa Products, Ventron Corporation, and monocyclopentadienyltitanium trichloride was prepared by a previously published method [5] with some modification. 1-Pentene was obtained from J.T. Baker Chemical Company.

Analytical methods

Halide from the chloromethyl groups was removed from the copolymer by use of hot pyridine and was determined by the Volhard method [7]. Titanium contents were determined by digesting the polymer-attached titanium compounds with a few drops of concentrated sulfuric acid, ashing by use of a micro burner, heating to 1000°C for 12 h, and weighing as TiO_2. Titanium complexed chloride was removed by digestion of polymer samples in 2 *N* KOH solution at 80°C for 24 h. Chloride was determined by the Volhard method, following acidification of the aqueous supernatant.

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

About 3 g of polymer-attached titanocene dichloride (0.175 mmol) Ti/g of beads) were charged into a pressure bottle. Excess n-BuLi in heptane was added to the bottle in a glove box. After the addition of n-BuLi, the bottle was carefully capped and taken out of the glove box. The reaction mixture was stirred under argon for 12 h. It then was 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 h at room temperature and a decrease in carbon monoxide pressure was observed. The product was transferred into a 100 ml side-armed flask in a glove box. The solution was removed and the beads were washed several times with heptane and then with THF. The product was reddish brown when suspended in solvent and greyish brown when dried. Infrared spectra of the products were measured.

Infrared spectra: (polymer-attached) 1965, 1878 cm^{-1}; ($Cp_2Ti(CO)_2$) 1965, 1882 cm^{-1} [8].

Catalytic isomerization of allylbenzene and 1,5-cyclooctadiene

Purified hexane was degassed before use. Allylbenzene and 1,5-cyclooctadiene were distilled from barium oxide under argon.

The product mixture from the isomerization of allylbenzene was analyzed by gas chromatography using 6 ft column (1/8" diameter), consisting of 15% SE-30 on Chromosorb P. The mixture of allylbenzene, *trans*-propenylbenzene, and *cis*-propenylbenzene, which was effectively separated at 120°C, and the

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* Caution is advised in chloromethylation and in the handling of chloromethyl ethyl ether because the related compound bis(chloromethyl) ether is a carcinogen as is the monochloro diethyl ether [6].

TABLE 1

RESULTS FORM THE ISOMERIZATION OF ALLYLBENZENE WITH POLYMER-ATTACHED CATALYSTS

Catalyst	Substrate (ml)	Substrate / Catalyst	Time (h)	Temp. (°C)	Products [d]		
					Allylbenzene	*trans*-propenyl benzene	*cis*-propenyl benzene
(A) Ⓟ-$CpTiCl_3$ [a] 0.2013 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) Ⓟ-Cp_2TiCl_2 [a] 0.1924 g (0.25 mmol Ti/g)	4	625	13	145	10.5	81.5	8.1
Recycled [b]	4	625	15	145	85.0	11.8	2.2
(C) Ⓟ-Cp_2TiCl_2 [c] 0.8718 g (0.44 mmol Ti/g)	4	780	5.5	145	1.5	86.5	12.0
(D) Ⓟ-Cp_2TiCl_2 [c] 0.1950 g (0.195 mmol Ti/g)	4	795	15	145	3.9	87.5	8.5

[a] Catalyst reduced with excess n-BuLi under H_2. [b] Catalyst used was recycled from previous reaction; [c] Catalyst reduced with excess n-BuLi under Ar. [d] Mole percent.

TABLE 2

RESULTS OF THE ISOMERIZATION OF 1,5-CYCLOOCTADIENE WITH POLYMER-ATTACHED CATALYSTS

Catalyst	Substrate (ml)	Substrate / Catalyst	Time (h)	Temp. (°C)	Products [f]		
					1,3-cyclooctadiene	1,5-cyclooctadiene	1,5-cyclooctadiene
(I) Ⓟ-$CpTiCl_3$ [a] 0.3216 g (0.1008 mmol Ti/g)	4	1006	9,5	145	90.0	10.0	0.0
Regenerated [b, c]	4	1006	35	145	90.0	20.0	0.0
(II) Ⓟ-Cp_2TiCl_2 [a] 0.3197 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) Ⓟ-Cp_2TiCl_2 [a] 0.2305 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	16.2	51.0
(IV) Ⓟ-$CpTiCl_3$ [a] 0.2366 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) Ⓟ-$CpTiCl_3$ [e] 0.2461 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
(CI) Ⓟ-Cp_2TiCl_2 [a] 0.2350 g (0.1945 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) Ⓟ-Cp_2TiCl_2 [a] 0.2288 g (0.1945 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 n-BuLi under H_2. [b] Catalyst regenerated by addition of HCl gas; [c] Regenerated catalyst reduced with excess n-BuLi under H_2. [d] Catalyst recycled from preceding reaction; [e] Catalyst reduced with excess n-BuLi under Ar. [f] Mole percent.

components were compared with authentic samples. The product mixture from isomerization of 1,5-cyclooctadiene was analyzed by an integrated NMR spectrum. The percentage of 1,3-cyclooctadiene was calculated from integration of the peak at $\delta = 2.70$ ppm and of the 1,4-cyclooctadiene from the peak at $\delta = 1.45$ ppm.

The isomerization results are shown in Tables 1 and 2.

A sample of polymer-attached $TiCp_2Cl_2$ or $TiCpCl_3$ was weighed into a 100 ml side-armed flask. After the flask was flushed several times with hydrogen (or argon), the beads were treated with 5 ml of hexane and 1 ml of 2.0 *M* n-BuLi in hexane under hydrogen (or argon) for 12 h. The solution was removed and the beads were washed five times with hexane and dried in vacuo at room temperature. Four ml of allylbenzene were injected in the reaction mixture and which subsequently was stirred under argon at 145° C. The flask then was 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.

Isomerization of 1,5-cyclooctadiene by polymer-attached $TiCp_2Cl_2$ and $TiCpCl_3$ followed the same procedure as the allylbenzene isomerization. The product mixture was analyzed by means of an integrated NMR spectrum.

Regeneration of the catalyst

After removal of the substrate, the beads were washed five times with hexane and twice with THF. To a suspension of beads in THF, anhydrous hydrogen chloride was added, and the polymer-attached $TiCp_2Cl_3$ or $TiCpCl_3$ was regenerated. The regenerated catalyst was reduced with n-BuLi and was reused for the isomerization of a fresh 4 ml portion of substrate.

Oligomerization of ethyl propiolate by polymer-attached $TiCp_2Cl_2$

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 analyzed by gas chromatography. A 5 ft Porapak Q column (1/8" diameter) at 150° C was used.

A sample of 0.2 g of polymer-attached titanocene dichloride (0.087 mmol Ti/g of beads) was weighed into a 100 ml round-bottomed flask with a sidearm. After the flask was flushed several times with hydrogen, the beads were treated with 5 ml hexane and 1 ml 2.0 *M* n-BuLi in hexane. The reaction mixture was stirred at room temperature for 15 h. Excess n-BuLi was removed and the reduction product was washed several times with hexane, dried in vacuo, and suspended in 5 ml THF under an atmosphere of argon. Two grams of ethyl propiolate were introduced and the reaction mixture was stirred at 60° C. The solution first turned yellow, gradually turned brown, and finally very dark brown. The reaction was stopped after 6 h. The dark brown solution was removed by using a syringe. The beads were washed with several 10 ml portions THF and the washings were added to the dark brown solution. The solution mixture was filtered, and the filtrate was concentrated under vacuum to give a dark brown viscous, oily material. The latter was extracted with a 150 ml refluxing CCl_4/pet. ether (1/4 by volume) mixture. The yellow extract was filtered. The extraction solvents were removed in vacuo and a 0.7 g mixture of oily materials was obtained. A mass spectrum of the oil showed a parent peak at m/e 294.

The product materials, after dilution with diethyl ether, were analyzed by gas chromatography. Five well separated peaks were observed; one of them was relatively broad. The ^1H NMR spectrum showed a multiplet at $\delta = 7.6$—8.1 ppm and a singlet at $\delta = 8.5$ ppm. No acetylenic proton resonance was observed.

Epoxidation of unsaturated hydrocarbons

Cyclohexane was distilled from lithium aluminum hydride under argon. 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 analyzed by gas chromatography. The column was 10% Carbowax on Chromosorb W (10 ft long, 1/8″ diameter). Chlorobenzene was used as an internal standard in the analysis for cyclohexene oxide; *p*-dichlorobenzene in the analysis for cyclooctene oxide. Cyclohexene oxide analysis was carried out at an oven temperature at 110° C, cyclooctene oxide analysis at 140° C.

Epoxidation of cyclo-olefins by polymer-attached $TiCpCl_3$ and $TiCp_2Cl_2$

A sample of polymer-attached $TiCpCl_3$ or $TiCp_2Cl_2$ (0.2—0.5 g) was weighed into a 100 ml round-bottomed side-armed flask. The flask was flushed several times with argon. Five ml (50 mmol) of tert-butyl hydroperoxide were added. The mixture was stirred for 20 min at room temperature. The beads gradually

TABLE 3

EPOXIDATION OF OLEFINS WITH POLYMER-SUPPORTED $TiCpCl_3$ AND $TiCp_2Cl_2$

Catalyst	Substrate [a]	Time (h)	Temp. (°C)	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 1 (0.195 mmol Ti/g)	cyclohexene	18	80	40	
(5) Ⓟ-$TiCpCl_3$ 0.201 g (0.200 mmol Ti/g)	cyclooctene	18	80		34
(6) Ⓟ-$TiCpCl_3$ 0.419 g 1 (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] mole percent based on the amount of olefin used.

turned light yellow. Five ml (50 mmol) of cyclohexene then were introduced, and the reaction mixture was stirred at 80° C. Samples were taken out for analysis of the epoxide at various time intervals. A similar procedure was used in the epoxidation of cyclooctene. The epoxidation results are shown in Table 3.

After epoxidation of cyclooctene, the light yellow beads were washed twice with THF, suspended in THF and anhydrous hydrogen chloride gas was introduced. The polymer-attached $TiCpCl_3$ or $TiCp_2Cl_2$ was regenerated. These were reused for the epoxidation of cyclooctene.

Epoxides were determined by gas chromatography. The column was a 10′ × 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° C, cyclooctene oxide analysis at 140° C.

Preparation of polymer-attached methylene dicyclopentadiene

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

Preparation of polymer-attached methylene-bridged Cp_2TiCl_2

Methylene-bridged Cp_2TiCl_2 was prepared from Ⓟ-$CH(C_5H_4)_2$ by two methods. In the first method, 10 g of methylene-bridged cyclopentadiene-substituted copolymer beads (2.2 mmol Cp/g of beads) were suspended in 20 ml THF, and a two fold excess of butyllithium in hexane was added. The beads changed from yellow to dark red. After being stirred at room temperature for 2 days, the solution was removed and the beads were washed several times with benzene. To the dark red beads suspended in 50 ml benzene, 9 g of $CpTiCl_3$ were then added and the reaction mixture was allowed to stir for 4 days. The solution was removed and the beads were washed with benzene in a soxhlet extractor. The product, red beads, was dried in a vacuum. Metal analysis was performed. Two batches of supported methylene-bridged Cp_2TiCl_2 contained 0.700 mmolTi per g of beads and 1.066 mmol/g of beads. In the second method, about 20 g of 2% cross-linked polystyrene-divinylbenzene copolymer beads were suspended in 60 ml of freshly distilled cyclohexane. The mixture was refluxed for 24 h, and then 80 ml of 1.6 *M* butyllithium in hexane and 25 ml of *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) (150 ml) were added by means of a syringe. The reaction mixture was heated for 3 days. After cooling, the polymer beads were washed several times with cyclohexane and THF.

To the dark brown lithiated polymer beads suspended in 60 ml of THF and cooled at 0° C, 30 ml of CCl_4 were then added slowly. After being stirred at room temperature for 24 h, the solution was removed and the beads were washed with THF in a soxhlet extractor. The dried beads gave 3.45 mmol Cl/g of beads.

The trichloromethylated beads were suspended in 80 ml of THF and 80 mmol of NaCp was added. After being stirred for 5 days, the beads were washed with THF. The dry beads contain 0.9 mmol Cl/g of beads. The beads were then suspended in 80 ml of THF and 35 mmol of Vitride in THF was added. The mixture was refluxed for 24 h. Then, 10 ml of MeOH/H_2O (1/1) were added slowly and the beads were washed with THF in a soxhlet extractor. The dried beads, methylene-bridged cyclopentadiene-substituted copolymer, contain 0.014 mmol Cl/g of beads.

The attachment of Cp_2TiCl_2 to the 2% cross-linked methylene-bridged cyclopentadiene-substituted copolymer was effected by the first method. Metal analysis gave 1.556 mmol Ti/g of beads.

Nitrogen fixation studies

In all experiments a pressure of 1500 psi of nitrogen in an autoclave previously flushed with nitrogen was applied at ambient temperatures with continual stirring during the reaction. In a typical reaction, 2.30 g of supported methylene-bridged Cp_2TiCl_2 beads (1.066 mmol Ti/g of beads) were transferred into an autoclave and 60 mmol of sodium naphthalide in THF and 100 ml of ether was added. The system was pressurized and stirred for 2 days, then depressurized and acidified with 20 ml of absolute methanol and 20 ml of 20% H_2SO_4. After stirring the resulting solution for 3 h in the autoclave, the solution was removed and ammonia was determined by the Kjeldahl method.

Results and discussion

Polymer-supported $TiCp_2Cl_2$ and $TiCpCl_3$ isomerizations

Similar 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 serve as a 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 1 shows the results of the isomerization of allylbenzene by using polymer-supported catalysts. Comparison of reactions A and B in Table 1 shows that 0.2 g of polymer-supported $TiCpCl_3$ (0.24 mmol Ti/g of beads), when reduced, can effect the isomerization of 4 ml of allylbenzene in 5 h, while approximately the same amount of supported $TiCp_2Cl_2$ (0.25 mmol Ti/g of beads) requires 13 h. Thus the reduced species of polymer-supported $TiCpCl_3$ is more than two times as effective as 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 [2].

Isomerization of 1,5-cyclooctadiene

Like allylbenzene, 1,5-cyclooctadiene tends to isomerize to the more stable conjugated 1,3-cyclooctadiene, with 1,4-cyclooctadiene as the intermediate product. In all the reactions (Table 2) 1,4-cyclooctadiene is present as the minor product. Prolonged stirring of the substrate with the catalyst eventually reduced the 1,4 isomer content to 1 or 2%. In contrast to the isomerization of allylbenzene, it can be seen from reactions I—IV in Table 2 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 h (reaction V). 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 2. Although little is known about the reduced species of the polymer-supported $TiCpCl_3$, the different isomerization activities (demonstrated in reactions 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.

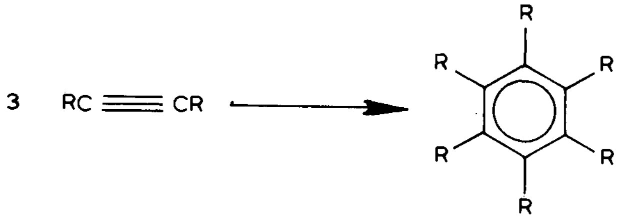
The resin-bound titanocene dichloride is reduced by n-butyllithium to give polymer-supported titanium(II) or titanium(III). It seems probable that different species are formed when the supported titanocene dichloride is reduced under hydrogen or argon.

Bercaw [9] was able to isolate and identify the elusive "titanocene", $(\eta^5\text{-}C_5H_5)_2Ti$, in a dimeric form by treating 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 to form an $(\eta^1\text{-}C_5H_5)$ derivative) one of the ring hydrogens to form a fulvene derivative. By treating dimethyltitanocene, $TiCp_2(CH_3)_2$, with hydrogen gas, Bercaw [9] succeeded in isolating a violet compound which was characterized as the titanocene monohydride dimer, $[(\eta^5\text{-}C_5H_5)_2TiH]_2$. A diborane-like double hydrogen bridge bond between the two metal centers was postulated on the basis of infrared, NMR, and mass spectrometric evidence.

With Bercaw's titanocene and titanocene monohydride in mind, one may speculate that the different rates of isomerization are due to different species formed by reduction of polymer-supported $TiCp_2Cl_2$ under argon (possibly titanocene) and that generated under hydrogen (a Ti^{III} monohydride). So far, the familiar 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 mechanisms such as a π-allyl mechanism cannot be ruled out.

Oligomerization of acetylenic derivatives by polymer-supported $TiCp_2Cl_2$

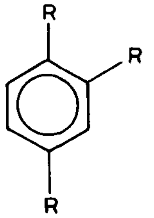
The catalytic cyclotrimerization of acetylenes to form benzene derivatives (eq. 1) has been investigated [9]. Pittman [10] has examined the oligomerization of ethyl propiolate in the presence of resin-bound $Ni(CO)_2(PR_3)_2$ (R = alkyl or aryl) and has found a yield of 5.8% 1,3,5-tricarbethoxybenzene and 74.5% of the 1,2,4-tricarbethoxybenzene, by weight, based on the amount of ethyl propiolate used.



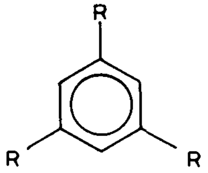
(1)

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

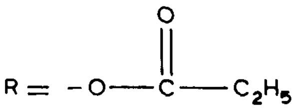
In our experiments, supported $TiCp_2Cl_2$ was reduced by excess n-BuLi under hydrogen, and oligomerization of ethyl propiolate was studied. It was found that 0.2 g of resin-bound catalyst (0.087 mmol Ti/g of beads) effected a total of 38% oligomerization (based on 2 g of ethyl propiolate used). The product was a mixture of trimers of ethyl propiolate. Mass spectra indicated a parent peak of 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. No acetylenic proton peaks were observed, thus two open terminal, acetylenic trimers can be ruled out. GLC analysis using a Porapak Q column gave four 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 trimer isomers that can be drawn.



(T—1) 1,2,4-tricarbethoxybenzene



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



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

The reduced polymer-supported $TiCp_2Cl_2$ differs from resin-bound $Ni(CO)_2$-

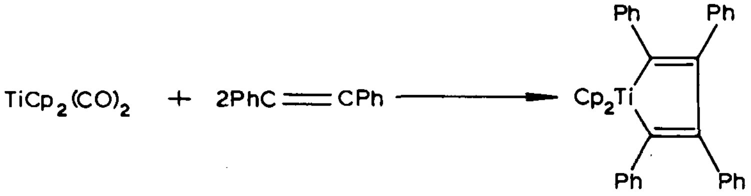
$(PhR_3)_2$, by producing open trimers in addition to the closed ones. Such a variety of components in the product mixture makes separation difficult.

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

There are a number of ways to prepare titanocene dicarbonyl [8,11,12]. One of these involves the reaction of titanocene dichloride with n-BuLi under 240 atm of carbon monoxide at 150° C. One can rationalize the necessity for such drastic conditions by considering that titanocene dichloride, when reduced by n-BuLi to form "titanocene" dimerizes easily to give the very stable $(C_5H_5TiH)_2C_{10}H_8$. 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 minimized dimerization of "titanocene", one would expect the preparation of polymer-supported titanocene dicarbonyl to be possible under much milder reaction conditions. Polymer-supported titanocene dichloride, after reduction by n-BuLi under argon, was converted exclusively to the supported titanocene dicarbonyl by stirring the reduction product under carbon monoxide at 4 atm. Very strong $\nu(C{\equiv}O)$ peaks at 1965 cm^{-1} and 1878 cm^{-1} were observed. The peak at 1878 cm^{-1} overlaps one of the peaks of the divinylbenzene-polystyrene copolymer, as a result, there is a marked increase in intensity compared to the other polystyrene peak at 1945 cm^{-1}. In another experiment, 1 atm of carbon monoxide was used instead of the 4 atm and only partial carbonylation of the supported "titanocene" was observed. The $\nu(C{\equiv}O)$ bands at 1965 cm^{-1} and 1878 cm^{-1} had much lower intensities than in the 4 atm experiment.

The reaction of polymer-supported titanocene dicarbonyl with a benzene solution of diphenylacetylene yielded greenish-brown colored beads. The IR spectrum showed no $\nu(C{\equiv}O)$, as is consistent with the formation of a titanium metallacycle in the reaction between dicarbonyl titanocene and diphenylacetylene [13].



(2)

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 3. Comparison of reactions 1 and 3, reactions 5 and 7 in Table 3 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) was raised from 48% to 88%, when the amount of beads 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%.

Epoxidation of cyclooctene proceeds to a comparatively smaller extent. With 0.201 g of supported $TiCpCl_3$ (0.285 mmol Ti/g of 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 h.

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 materials were reused for epoxidation studies of cyclooctene. It was found that the supported $TiCpCl_3$ retained ca. 75% of its activity while the supported $TiCp_2Cl_2$ retained 65%.

Polymer-supported niobocene dichloride, prepared by the method of Lee and Brubaker [14], did not catalyze epoxidation of olefins. Failure of the supported niobocene dichloride to catalyze epoxidation of olefins might be an indication that the acidity of the metal 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 larger d^1 Nb^{IV}. In addition, a steric effect also seems to play an important role in epoxidation, since it was found that the bulkier cyclooctene can only be epoxidized to a smaller extent than cyclohexene.

TABLE 4

NITROGEN FIXATION AT 1500 psi OF N_2

Titanocene dichloride	Reactants used (mmol)		Products produced (mmol)	
	Ti	NaNp	NH_3	NH_3/Ti
Homogeneous (0.28 g)	1.11	17.0	0.50	0.45
Homogeneous (0.40 g)	1.61	40.0	0.89	0.55
20% supported (5.11 g)	2.30	38.9	0.02	0.01
20% supported methylene-bridged (2.30 g)	2.45	60.0	0.15	0.06
20% supported methylene-bridged (0.84 g)	0.89	40.0	0.10	0.11
20% supported dimethylene-bridged (2.13 g)	1.83	35.2	0.16	0.15
20% supported trimethylene-bridged (1.36 g)	1.50	39.5	0.14	0.16
20% supported tetramethylene-bridged (2.19 g)	1.97	40.6	0.11	0.13
2% supported methylene-bridged (1.24 g)	1.93	50.0	0.19	0.10
2% supported methylene-bridged (1.42 g)	2.21	100.0	0.30	0.13

Nitrogen fixation studies

Since the first report of an uncharacterized but isolable dicyclopentadienyltitanium dinitrogen complex, homogeneous titanocene has been intensively studied and used for nitrogen fixation [15]. The titanocene dinitrogen complexes can be generated by the reaction of dichloride titanocene with a variety of reducing agents in a nitrogen atmiosphere. At times considerable confusion has arisen over the nature of the dinitrogen complexes. But it is believed that a dinuclear titanium complex is involved in the process of titanocene nitrogen fixation.

Attempts to fix nitrogen were made by Kroll [16] and Chandrasekran [3] using crosslinked copolymer-supported titanocene. No significant amount of ammonia was produced by the polymer-supported titanocene, possibly due to the titanocene centers being separated too far to fix nitrogen as a dinuclear Ti complex. This lead to the expectation that if the titanocene centers were brought closer by methylene-bridged ligands, then some nitrogen fixation might be observed. The results of nitrogen fixation by using polymer-supported methylene-bridged titanocene are given in Table 4.

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