Polystyrene Attached Titanocene Species. Preparation and Reactions

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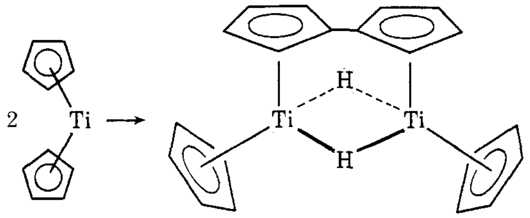
Abstract: Cyclopentadienyl compounds of titanium have been prepared attached to polymers by first binding cyclopentadiene to a styrene–divinylbenzene (20%) copolymer and then converting it to the cyclopentadienyl anion. The resin-bound anion is treated with cyclopentadienyl titanium trichloride and polymer-attached $(C_5H_5)_2TiCl_2$ is formed. Other metallocenes can be prepared in a similar fashion. When thus connected to a rather rigid polymer system, the titanium may be reduced by one or two electrons/titanium apparently without undergoing dimerization, and the effectiveness of the material as a catalyst for hydrogenation of olefins is enhanced by a factor of 25–120 compared to the correspondingly reduced nonattached titanocene dichloride or benzyltitanocene dichloride. The polymer-attached species are not active for the reduction of dinitrogen under conditions where the corresponding nonattached complex is effective.

Making homogeneous transition metal catalysts insoluble by attachment to various polymers is a significant step in improving their industrial applicability. While the polymer-attachment technique obviously prevents loss of possibly expensive catalytic materials and contamination of reaction products,[1-8] the method also offers the opportunity to prepare a new class of catalyst systems with other desirable properties. For instance, polymer-supported catalysts have been demonstrated to have selectivity toward molecules of different bulk and polarity.[2,7]

In a recent communication, we demonstrated that titanocene-related catalysts can be significantly activated by polymer attachment.[9] Titanocene and its hydrides are particularly useful catalysts in the hydrogenation of various unsaturated organic compounds and molecular nitrogen. However, these complexes readily polymerize,[10] according to the following reaction, to form catalytically inactive materials.[11]



We sought to prevent the dimerization reaction by attaching the titanocene precursor, $TiCp_2Cl_2$, to less than 10% of the aromatic rings in a cross-linked (20%) polystyrene–divinylbenzene copolymer resin. On reduction, a catalyst is produced whose hydrogenation efficiency is greater than a corresponding nonattached species.[9]

The example outlined above is only one of many cases where attempts to open a coordination site on the metal result in polymerization of the complex by forming ligand bridges or metal–metal bonds.[10-14] In these situations, attachment of a saturated complex that is a potential catalyst to a rigid support, followed by reductive elimination of a ligand, should produce higher concentrations of monomeric, coordinatively unsaturated species than is obtained in solution.[1,5] Since titanium and other early transition metals in lower oxidation states exhibit a pronounced tendency toward polymerization,[10] it seemed worthwhile to test the polymer-attachment technique on the well-characterized bis(cyclopentadienyl)titanium systems and gradually extend our investigations to the bis(cyclopentadienyl)metal compounds of the other early transition metals. Succeeding publications will describe our efforts with polymer-supported bis(cyclopentadienyl) compounds of zirconium, hafnium, niobium, molybdenum, and tungsten.

Experimental Section

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

Far-infrared spectra in the 100–500-cm^{-1} region were obtained on a Digilab Model FTS-16 Fourier transform spectrophotometer. Samples were prepared by crushing the polystyrene beads in a ball mill under anaerobic conditions and mulling the powder with dry Nujol in a drybox. The spectra were recorded with the sample in a dry nitrogen atmosphere and mounted between polyethylene plates.

Visible and ultraviolet absorption spectra were recorded on similarly prepared samples suspended between quartz plates by use of a Cary Model 14 recording spectrophotometer operating in the 15,000–35,000-cm^{-1} region. Electron spin resonance spectra were recorded on a Varian E-4 spectrometer.

Materials. The 20% cross-linked macroreticular polystyrene–divinylbenzene copolymer (600 Å pore) was a gift from the Dow Chemical Co. and was extracted with dry benzene before use. Organolithium and organoaluminum reagents were obtained from Alfa, while [$TiCpCl_3$] and [$TiCp_2Cl_2$][15] were prepared by previously published methods.[16] Chloromethyl ethyl ether was obtained from Aldrich Chemical Co. and distilled immediately prior to use. Tetrahydrofuran (THF), hexane, benzene, and toluene were distilled under argon from potassium–benzophenone complex. Diethyl ether was refluxed over lithium aluminum hydride before distillation.

Preparation of Cyclopentadienyl-Substituted Copolymer. Method A. Following the chloromethylation method of Pepper et al.,[17] an oven-dried 2 l. flask was charged with 200.0 g of copolymer beads, which had been previously washed free of styrene monomer with benzene, and 1 l. of freshly distilled chloromethyl ethyl ether. A solution prepared by cautiously adding 35 ml of $SnCl_4$ to 125 ml of ice-chilled chloromethyl ethyl ether was then introduced. After vigorous stirring of the reaction mixture at room temperature for 3 days, the ether was removed by filtration and the product washed with 2-l. portions of 50% aqueous dioxane, aqueous dioxane containing 10% HCl (v/v), and, finally, dry dioxane. Chloride analysis of the chloromethylated copolymer after it had been dried for 2 days in vacuo yielded 1.20 mequiv of Cl^-/g or a 13.8% chloromethylation of the styrene rings.

The product obtained above was added to 300 ml of dry, air-free THF and 316 ml of 1.58 *M* sodium cyclopentadienide in THF. After the mixture was stirred for 5 days at room temperature, excess sodium cyclopentadienide and THF were removed by filtration, and the product was washed with 1:1 dry, air-free ethanol: THF until it was free of chloride. This product was washed with three 1-l. portions of THF and then dried in vacuo for several days and yielded a substance containing 0.17 mequiv of Cl^-/g.

Method B. A 118-g sample of 20% DVB-styrene copolymer beads (600 Å pores) was washed with 10% HCl, 10% NaOH, H_2O, H_2O-CH_3OH, CH_3OH-CH_2Cl_2, and CH_2Cl_2. They were then vacuum dried.

After the beads were suspended in dried CH_3NO_2 containing 7 g of BF_3, 16 g of Br_2 were added slowly.[18] The mixture was stirred for 24 hr in the dark. About 5% of the beads had risen to the top of the solution, and these were removed by siphoning. It was assumed that these were unreactive and therefore were less dense than those which had been brominated. The solution was removed by filtration, the beads were rinsed with dry CH_3NO_2, CH_3OH, and CH_2Cl_2, and were then vacuum dried. Anal. Br, 6.78; 0.8 mequiv of Br/g of beads.

All the following were carried out with O_2-free, dry solvents under an inert (N_2 or Ar) atmosphere unless otherwise noted.

A 20.18-g sample of dried, white beads (0.017 equiv of Br) was treated with 50 ml of 1.9 *M* *n*-butyl lithium (0.095 equiv) in 100 ml of hexane for 36 hr. The resulting light tan beads were rinsed five times with THF, and then 75 ml of THF was added to a suspension of the beads. While the mixture was stirred and cooled in an ice bath, 2 g of freshly distilled cyclopentenone (0.024 equiv) was added.[19] The beads immediately became white, but then turned slowly yellow while being stirred for 72 hr. The beads were rinsed five times with dry THF, twice with aqueous THF, and twice more with dry THF and were then dried under vacuum, while being gently heated. The pale yellow beads were sampled for analysis. Anal. less than 0.1% Br.

Preparation of Copolymer-Attached $TiCp_2Cl_2$. Method A. To a 500-ml Schlenk flask maintained under argon was added 75 g of the cyclopentadiene-substituted copolymer, 150 ml of THF, and 100 ml of 2.25 *M* methyllithium in diethyl ether. The reaction mixture was stirred for 2 days, filtered, and washed with three 300-ml portions of THF followed by two 300-ml portions of benzene. A solution containing 35.89 g (0.16 mol) of $TiCpCl_3$ dissolved in 350 ml of benzene was introduced and the mixture stirred for 3 days. Extraction of excess $TiCpCl_3$ with hot benzene followed by drying gave a salmon red $TiCp_2Cl_2$-substituted copolymer which was subsequently submitted for analysis (Table I).

Far-infrared spectrum: (polymer-attached) 200 (broad), 250, 280, 308, 365, 395, 408 cm^{-1} (Nujol mull); (nonattached) $TiCp_2Cl_2$ 190 (w), 210, 245, 255 (w), 275, 305, 362, 396 (w) cm^{-1} (Nujol mull). Ultraviolet spectrum (Nujol mull) (attached $TiCp_2Cl_2$) 245, 267, 375 nm; (nonattached $TiCp_2Cl_2$) 245, 270, 380 nm.

Method B. The beads were placed in 100 ml of Et_2O. After being cooled in a Dry Ice bath, they were treated with 50 ml of 0.8 *M* CH_3Li for 72 hr, then rinsed three times with Et_2O. They were then vacuum dried. $TiCpCl_3$ (5.6 g, 0.026 equiv) and 200 ml of benzene were added. After being stirred for 72 hr, they were rinsed three times with THF and were extracted overnight with THF and use of a Soxhlet extractor. They were dried under vacuum, giving beads of varying shades of salmon pink.

Reduction of Copolymer-Attached $TiCp_2Cl_2$. Polystyrene-attached $TiCp_2Cl_2$ samples were reduced in 50-ml septum-stoppered flasks by use of a five- to tenfold excess of butyllithium in hexane under anhydrous, anaerobic conditions. Typically, 0.2 g (0.56 mequiv of Ti) of the polymer beads were stirred by a magnetic stirrer with 10 ml of hexane and 5 ml of 0.69 *M* butyllithium-hexane solution.[20] After 3 hr the light yellow solution was removed, and the dark gray, air-sensitive beads were washed with three 10-ml portions of hexane to remove excess butyllithium. The use of this reduced copolymer as a reduction catalyst is described below.

Addition of 1 equiv of sodium naphthalide in THF to the polymer-attached $TiCp_2Cl_2$ yielded a gray polymer which showed two ESR signals (room temperature) with isotropic *g* values of 1.98 and 2.00. Addition of a second equivalent of sodium naphthalide gave a simple ESR spectrum centered at $g = 2.00$. In an experiment with nonattached $TiCp_2Cl_2$ in hexane excess *n*-butyllithium produced a rapidly decaying ESR signal with $g = 1.98$. Since no hyperfine splitting could be observed, it can only be concluded that there were two different reduced species formed during the experiment.

Table I. Analytical Results

Substituent (method)	Chloride (mequiv/g)	Titanium (mequiv/g)	Cl:M ratio Calcd	Cl:M ratio Found
$-CH_2Cl$	1.20			
$-CH_2CpH$	0.17			
$-CH_2CpTiCpCl_2$ (A)	0.543	0.281	2	1.93
$-CH_2CpTiCp(CH_3)_2$ (A)	0.00	0.233		
$-CH_2CpTiCp$ (A)				
$-CH_2CpTiCpCl$ (A)	0.285	0.274	1	1.04
$-CH_2CpTiCl_3$ (A)	0.811	0.282	3	2.88
$-CpTiCpCl_2$ (B)	0.115	0.058	2	1.93

Preparation of Copolymer Containing $TiCp_2(CH_3)_2$ and $(TiCp_2)_2$. Polymer-attached $TiCp_2(CH_3)_2$ was prepared by the method described by Clauss and Bestian[21] for monomeric $TiCp_2(CH_3)_2$ with appropriate modifications. To 2 g (0.86 mequiv of Ti/g) of polymer-attached $TiCp_2Cl_2$ maintained at Dry Ice-acetone temperatures was added 15 ml of diethyl ether and 5 ml of 1.54 *M* methyllithium in ether. The mixture was stirred and allowed to warm slowly to room temperature. After 4 hr, the excess methyllithium solution was removed by syringe and the copolymer was extracted with THF until the washings were chloride free. The light yellow product was stored under argon at −15°; analytical results are reported in Table I.

Fifteen milliliters of a 0.15 *M* solution of $TiCp_2(CH_3)_2$ in hexane, prepared by previously reported techniques, was added by syringe to a 50-ml vessel containing 0.1 g (0.08 mequiv) of polymer-attached $TiCp_2(CH_3)_2$. About 7 ml of hexane was removed in vacuo to produce a slurry of $TiCp_2(CH_3)_2$ crystals. Hydrogen gas was admitted at 0° and the reaction proceeded through the solution and polymer beads in the manner described by Marvich et al.[22] After 1 hr, 15 ml of toluene was introduced and the gray-green precipitate slowly dissolved to form a dark green-brown solution. The dark colored copolymer was washed with several 10-ml portions of toluene and stored at Dry Ice temperatures.

Preparation of Copolymer Containing $TiCp_2Cl$. To 2.0 g (1.72 mequiv of Ti) of polymer-attached $TiCp_2Cl_2$ in a 50-ml septum-stoppered vessel was added 10 ml of tri-*n*-butylaluminum.[23] The reaction mixture was stirred at 110° for 3 hr to produce the dark red-brown aluminum-titanium adduct. After removing excess aluminum alkyl, the beads were washed with diethyl ether to give a blue-gray species which became olive green when dried in vacuo for several hours.

Preparation of Copolymer Containing $CpTiCl_3$. Cyclopentadiene substituted copolymer was converted to the cyclopentadienide anion by treatment with a twofold excess of butyllithium in benzene. After being stirred overnight under argon, the solution was removed and washed with benzene five times. The beads were then treated with a twofold excess of $TiCl_4$ in benzene and stirred overnight. The beads were separated by filtration and with benzene in a Soxhlet extractor until excess chloride had been removed. Extraction with THF converted the dark colored beads to yellowish beads. They were washed a few times with THF and dried at room temperature in vacuo overnight. The flask containing the beads was covered with aluminum foil and cooled in an ice bath, chlorine gas was added, and bright yellow beads were formed.

Far-Infrared: polymer-attached $TiCpCl_3$ (cm^{-1}) 325, 410, 443; nonattached $TiCpCl_3$ 290 (broad, w), 328, 405, 440.

Analytical Methods. Halide from the chloromethyl groups was removed from the copolymer with hot pyridine and determined by the Volhard technique. Titanium was determined[24] by ignition of the metal-containing polymer at 900° for 4-5 hr and subsequent analysis by spectrophotometry of the titanium-peroxide complex. The technique reported earlier gave values for titanium which have proved to be four-six times too high.[9] Titanium complexed chloride was removed by digestion of powdered polymer samples in 2 *N* KOH solution at 80° for 8 hr. Chloride was determined by the Volhard method following acidification of the aqueous supernatant.

Use of the Reduced Copolymer Complexes as Catalyst. Olefin Reduction. Four types of catalysts were used, all with cyclohexene as the olefin. In each case, the catalyst was weighed into the reaction flask, placed under an atmosphere of hydrogen, suspended in 8 ml of hexane, and treated with 1 ml of 2.1 *M* BuLi in hexane for 1

Table II

Catalyst precursor (method)	Ti (mequiv)	Olefin	M	Rates (ml of H_2/min/mequiv Ti) Initial	Maximum
Nonattached $TiCp_2Cl_2$	0.05	Cyclohexene	1.16	5.6[a]	28
Attached $TiCp_2Cl_2$ (A)	0.031	Cyclohexene	1.16	88.7	Same[c]
Nonground (B)	0.002	Cyclohexene	0.25	105.6	Same
Attached $TiCp_2Cl_2$[b] ground before reduction	0.034	Cyclohexene	1.16	714	Same[c]
Benzylititanocene dichloride nonattached	0.2	Cyclohexene		9.5	Same
Benzyltitanocene dichloride nonattached	0.2	1-Methylcyclohexene		Less than 10^{-4}	
Titanocene dichloride nonattached	0.2	Cyclohexene		10	Same

[a] Repeated runs verify that an induction period is present; bead systems show no such effect. [b] The dry beads were ground to a fine powder before activation. [c] For the bead cases, no sign of an induction period is seen.

Table III. Hydrogenation Rates with Polymer-Attached Titanocene Species

Olefin (0.5 M in hexane)	Hydrogenation rate (ml of H_2/min/mequiv of Ti)
1-Hexene	213.0
Styrene	243.0
Cyclohexene	90.3
1-Methylcyclohexene	1.0
1,2-Dimethylcyclohexene	0.0
1,3-Cyclooctadiene	216.0
1,5-Cyclooctadiene	183.0
1-Hexyne	(Polymer)
3-Hexyne	149.0
Diphenylacetylene	40.6
Cholestenone	0.0
Vinylacetate	0.0

Table IV

Ti (mequiv)	NH_3 (mequiv) (% yield)	$PhNH_2$ (mequiv)
0.8 attached	0.028 (3)	0.0
2.41 nonattached	0.8 (33)	0.02

hr. The appropriate olefin was then added by means of a syringe. The rate of hydrogen uptake was determined by the use of an electronic monitoring device.[25] The results are presented in Table II.

The rates of reduction of other olefins (Table III) were determined in a similar fashion using noncrushed copolymer beads (prepared by method A).

Dinitrogen Reduction. A sample of polymer, 2.6 g, containing 2 mequiv of attached titanocene dichloride (prepared by method A) was placed in a glass insert in a 300-ml autoclave Engineers-magstir reactor. The reactor was flushed with nitrogen and 100 ml of ether was added. Phenyllithium, 10 ml, 17 mequiv, was added with a syringe while nitrogen was flowing through the reactor. The reactor was sealed and pressurized to 1500 psi with nitrogen gas. After 48 hr, the pressure was released and the reaction mixture was added to 20 ml of 20% H_2SO_4 in 20 ml of MeOH and stirred for 1 hr. Ammonia was determined by the Kjeldahl method. The aniline was extracted from the neutral aqueous solution with 3 ml of benzene and durene was added as a standard. Yields of aniline were determined by GLC by using a 5 ft 10% Carbowax at 150°.

The above procedure was repeated[26] by using 0.60 g (2.4 mmol) of $TiCp_2Cl_2$ in 100 ml of diethyl ether. The results are presented in Table IV.

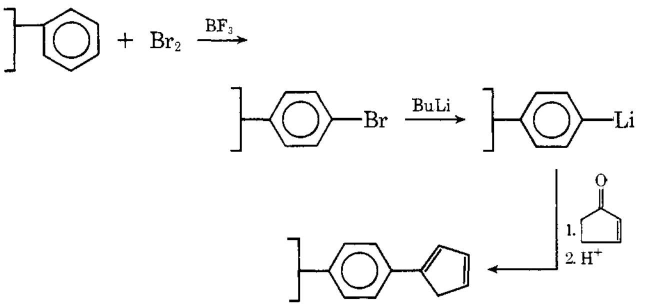
Discussion

Preparation of Attached Titanium Metallocenes. Cyclopentadienide ion has provided a remarkably effective means of binding transition metals to the polystyrene–divinylbenzene copolymer. Its uninegative charge coupled with occupation of several coordination sites ensure the formation of a strong, covalent π-bond between polymer and metal. Furthermore, the considerable variety of metal cyclopentadienyls presently known provides a wealth of potentially useful complexes.[14,27]

The reaction of sodium cyclopentadienide with the chloromethylated copolymer offers a simple, straightforward method of attaching the ligand to a rigid matrix. Despite long reaction times (3 days), the presence of excess cyclopentadienide, and the elevation of reaction temperatures, 0.15–0.20 mequiv of Cl^-/g usually could not be removed from the copolymer. While repeated washings with polar solvents provided convincing evidence that this was not occluded sodium chloride, the reasons for the poor reactivity of selected chloromethyl groups with NaCp remains unclear. Interestingly, chloride analyses performed on cyclopentadiene-substituted copolymer, which had been treated with excess methyllithium and reprotonated with ethanol, indicated only a trace of halide. Apparently, CH_3Li in a diethyl ether–THF medium can successfully diffuse to all chloromethylated sites and complete the substitution reaction. Because the procedure completely eliminates $-CH_2Cl$, the halogen analyses reported in Table I do not reflect the presence of chloromethyl chloride after the conversion of cyclopentadiene to cyclopentadienide by treatment with methyllithium.

An alternative method for attaching cyclopentadienyl groups to a polymer backbone has also been developed. This procedure is outlined in Scheme I. The advantages of this method are (a) the potentially reactive benzyl group is eliminated and (b) potentially carcenogenic chloromethyl ethers are not required.

Scheme I



The reaction of $TiCpCl_3$ with polymer-attached lithium cyclopentadienide proceeds smoothly from a light yellow reaction mixture to a deep salmon red colored resin containing polymer-attached $TiCp_2Cl_2$. This result is in marked contrast to the reaction of solution-soluble LiCp and $TiCpCl_3$ which passes through an intense purple phase before yielding $TiCp_2Cl_2$. The existence of two or more neighboring cyclopentadienyl residues on the resin could conceivably have produced polymer-attached species similar to $TiCp_3$[28] or $TiCp_4$.[29] A high degree of cyclopentadiene substitution or the utilization of polystyrene–divinylbenzene copolymer containing only 2.0% of the cross-linking agent[5] yields polymer-attached cyclopentadiene groups that can function as bi- or polydentate chelating agents. Visible, ultraviolet, and far-infrared studies of mulls of polymer-attached titanocene dichloride have failed to indicate the presence of other titanium species.

Polymer-attached dimethyltitanocene, $TiCp_2(CH_3)_2$, is significantly less reactive than free $TiCp_2(CH_3)_2$ in solution. Attempts to decompose the polymer-attached complex in an H_2 atmosphere by thermal or photochemical techniques were only partially successful. Therefore, we were forced to initiate this reaction with the $TiCp_2(CH_3)_2$–hexane slurry technique described by Bercaw and Marvich.[11] Treatment of the beads with anhydrous HCl yields both solution-soluble and polymer-attached $TiCp_2Cl_2$. Evidently, the Ti–Ti or Ti–H–Ti bonds in titanocene or its hydrides are sufficiently strong to lower the $TiCp_2$ and $TiCp_2H$ monomer–dimer equilibrium constants. The restricted pore geometry may aggravate this problem by preventing the individual titanocene species from drifting apart easily. This same type of "cage" effect may be used to explain the increased stability of polymer-attached dimethyltitanocene.

That treatment of polymer-attached $TiCp_2(CH_3)_2$, $(TiCp_2)_2$, $(TiCp_2H)_x$, and butyllithium-reduced $TiCp_2Cl_2$ with anhydrous HCl produces only $TiCp_2Cl_2$ is particularly encouraging. Titanocene and its hydrides eadily undergo a thermally induced rearrangement to form a dimer containing both σ- and π-bonded cyclopentadienyl residues.[10,11] This complex is not converted to $TiCp_2Cl_2$ when exposed to HCl but rather forms a green chloride containing dimer. Therefore, it is concluded that these polymer-based species retain their bis-π-cyclopentadienyl integrity throughout the reduction procedure.

Since reduction by 1 equiv of sodium naphthalide leads to two ESR absorptions and reduction by two equivalents leads to a single absorption, distribution of $TiCp_2Cl_2$ units along bead pores apparently prevents the straightforward formation of 1 equiv of Ti(III). Instead, a mixture of Ti(IV), Ti(III), and Ti(II) species appears to be formed—the latter two being paramagnetic. Addition of a second equivalent of reductant yields a product with a single ESR signal, probably Ti(II).

Like its solution-soluble analog, polymer-attached $TiCp_2Cl_2$ will form the dark red, Ziegler-Natta type[30] catalyst, $[Cp_2TiCl(C_4H_9)_2]$, when stirred with hot tri-*n*-butylaluminum. Upon removal of aluminum with ether and desiccation, the polymer-attached titanium(III) species, $TiCp_2Cl$, (see Table I) was recovered.

The synthesis of monocyclopentadienyl halides from several early transition metal halides has not been reported. Typically, the higher valence metal chloride is introduced into a large excess of NaCp–THF to give the bis- or tetrakismetallocene.[27] However, the polymer-attached cyclopentadienyl allows for the direct synthesis of monocyclopentadienyl species in noncoordinating solvent. The Cp^- residue initially forms an intensely colored, paramagnetic species with MCl_n which is generally transformed to a light yellow solid on being washed with THF.

$$MCl_n + Cp^-Li^+ \xrightarrow{C_6H_6} CpMCl_n^-Li^+ \qquad (1)$$

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

With the exception of $TiCpCl_3$[16] and $ZrCpCl_3$,[31] we have no monocyclopentadienyl halides with which to compare results for Nb, Mo, and W. While analyses of polymer-attached metal and chloride as well as chloride released by THF washings correlate well with the $MCpCl_{n-1}$ formulation, other physical measurements have been difficult to obtain.

Catalytic Activity of Attached Titanium Metallocenes. The reduction of olefins catalyzed by transition metal complexes generally requires the presence of an open coordination site on the metal.[12] The experimental evidence to date suggests that this is also true in the case of alkyllithium reduced titanocene derivatives. Only monomeric titanocene species contain such a site. If this is the case, any increase in monomeric species concentration associated with attaching these catalysts to a polymer support should be reflected in an increase in catalytic activity of that complex when compared to a similar nonattached complex under the same conditions. As indicated in Table II, exact comparisons for this system are difficult to make, due to the variation in the rates of the nonattached systems with slight variations in conditions. The nonattached systems are not totally homogeneous[20] and the concentration of the soluble complex appears to vary with the olefin concentration. The attached catalyst shows good pseudo-first-order kinetics under a variety of conditions. The major determinant in the rates of reduction with the attached catalysts was the size of the copolymer beads. Grinding the beads to a find powder increased their activity. It was earlier observed that the activity of rhodium(I) catalysts decreased on attachment due to apparent slow diffusion of olefins in the restricted polymer.[2,7] When a butyllithium reduced whole bead was crushed, the center was the salmon pink color of nonreduced titanocene dichloride. This indicated that the polymeric butyllithium was not effective in reaching the complex that was inside of the polymer bead.

The activation factor for polymer attachment ranges from 25 to 120 depending on the choice made for comparison. On an operational basis, the nonattached catalyst required 24 hr to complete the reduction of cyclohexene, whereas the attached catalyst completed the reaction under similar conditions in 20 min. On this basis the attached catalyst was 70 times more active. Simple changes in substitution on the cyclopentadienyl rings appear to have little effect on the catalytic activity (Table II). Poor analytical techniques for titanium resulted in low activation factors in our earlier report.[9]

Initial experiments that used the complex prepared by method B, in which the cyclopentadienyl ring was attached directly to the aromatic polymer, indicate that this complex may produce an even more active catalyst.

Brintzinger et al.,[11] suggested that the mechanism of reduction of olefins involved the bimolecular reaction of an intermediate titanocene alkyl and a titanocene hydride. Our results suggest that the complete reaction takes place at one metal center.

Attempts to reduce nitrogen gas to ammonia and aniline with a phenyllithium reduced attached titanocene dichloride were unsuccessful. A low yield (3%) of ammonia was produced under conditions which yielded 34% ammonia with a corresponding nonattached catalyst. There is good evidence that a bis(titanocene)dinitrogen complex is the intermediate which produces ammonia on hydrolysis.[11,32] As indicated above, polymer attachment should inhibit the formation of such species.

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Porous, Polymer-Bonded Metalloporphyrins

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Abstract: The synthesis of a series of porous, polymer-bonded metalloporphyrins is described. Functionalized tetraphenylporphines are attached to porous polystyrene resins via amine, carbonyl, and ester linkages and metal ions are then incorporated into the structures. ESR data for copper derivatives were used to characterize the materials. It was shown that porphyrin polymers which contain both oxidation (cobalt) and proton-acceptor sites (amine or carboxylate groups) are effective catalysts for the oxidation of thiols to disulfides. Factors affecting the deactivation of these catalysts are discussed.

Research into the chemistry of porphyrins and of metalloporphyrins has attracted wide interest. Metalloporphyrins, present in petroleum,[1,2] contribute to undesirable metal contamination in cracking catalysts.[3] Biologically, porphyrins and related structures occur in hemin, chlorophyll, and vitamin B_{12}.[4] In inorganic chemistry, porphyrin and model-porphyrin ligands can provide known and fixed coordination environments for the study of metal ions under a variety of conditions.[5]

Interest in organic semiconductors, heterogeneous catalysis, and immobilized enzyme models has led to the synthesis of three classes of porphyrin-containing polymers, which may be termed (a) coordination polymers, (b) polymer-attached porphyrins, and (c) polyporphyrins. Coordination polymers can be represented by a complex of poly-4-vinylpyridine with cobaloxime, a B_{12} model, wherein the polymer coordinatively binds to cobalt.[6] Wang has provided an additional example, a coordination polymer in which heme is bonded through iron to a polystyrene-embedded imidazole derivative.[7] Coordination of iron porphyrins to a polystyrene-bonded imidazole was reported by Collman et al.[38,39]

The fact that naturally occurring porphyrins contain pendant carboxylic acid functions[4] has been used in the synthesis of the second group, the polymer-attached porphyrins. By the formation of amide linkages between these acid functions and a polyethyleneimine, Lautsch and coworkers were able to attach both hemin and chlorophyll structures to preformed polymers.[8]

Polyporphyrins, the third group, would include condensation polymers prepared from glycols and difunctional porphyrins such as deutero- and *meso*-porphyrins. The group could further include synthetic materials wherein the polymerization reaction is the formation of the porphyrin itself. Polymeric phthalocyanines are an example of polyporphyrins.[9,10]

All of the above have been dense polymers, polymers whose physical form can be radically affected by solvent. The development of fixed-pore or macroreticular resins, reviewed by Frisch,[11] has added a new dimension to polymer applications. In contrast to the dense materials mentioned above, macroreticular resins substantially retain their shape and porosity in the presence of nonpolar solvents. Such retention of porosity is particularly useful in nonaqueous media, e.g., in the reactions of hydrocarbons over sulfonic acid resin catalysts,[12] in conversion processes catalyzed by resin-bonded transition metal complexes,[13,40,41] and even in ion exchange sequences over chelating, macroreticular resins.[14] One purpose of the paper will be to describe the synthesis of fixed-pore or macroreticular polymer-bonded porphyrins.

A second purpose will be to characterize the resultant polymers, i.e., to show that polymers can be prepared which contain a high, and perhaps "monomolecular", dispersion of porphyrin moieties. Such a dispersion of porphyrins and of porphyrin analogs would distinguish these polymeric species from the monomers. Porphyrin monomers commonly aggregate in solution, a factor of considerable biological significance.[15,16]

To provide an example of the possible utility of these porphyrin polymers is the third purpose, said example being related to the removal of mercaptan sulfur compounds from cracked gasolines (sweetening). Porphyrins and phthalocyanines, and particularly the sulfonate or carboxylate deriva-