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POLYMER-SUPPORTED ORGANOMETALLIC COMPOUNDS OF TITANIUM, ZIRCONIUM AND HAFNIUM AS HYDROGENATION CATALYSTS

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Abstract: Cyclopentadienyl compounds of titanium, zirconium and hafnium have been prepared attached to polymers by first binding cyclopentadiene to styrene-divinylbenzene (20%) copolymers and then converting them to cyclopentadienyl anions. The resin-bound anions were treated with MCl_n and polymer-attached MCl_{n-1} compounds were formed (where M = Ti, Zr and Hf). The polymer-attached mono-cyclopentadienyl titanium trichloride on reduction with butyl lithium produces active catalysts whose hydrogenation efficiencies are 10 to 20 times as great as the corresponding non-attached species under the same conditions. Studies of the physical nature of the metal catalyst dispersions on the polymer supports by using an electron-X-ray fluorescence microprobe indicate that the dispersion is uniform throughout the entire section of the bead.

To date homogeneous catalysts have been of somewhat limited use, chiefly because of the difficulty of separation from the reaction products. Making homogeneous transition metal catalysts insoluble by attachment to various polymers is a significant step in improving their industrial applicability. Recently[1] we demonstrated that titanocene-related catalysts can be significantly activated by polymer attachment. The polymer attachment procedure prevents dimerization of the active species. Cyclopentadienyl compounds of titanium, zirconium and hafnium 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 MCl_n and polymer-attached MCl_{n-1} is formed (where M = Ti, Zr and Hf). The polymer-attached mono cyclopentadienyl titanium trichloride, on reduction with butyl lithium produces an active catalyst show hydrogenation efficiency is about twenty times as great as the corresponding homogeneous species under the same conditions.

Study of the physical nature of the metal catalyst[1] dispersion on the polymer support by using an electron-X-ray fluorescence microprobe was undertaken to determine whether it is uniform throughout the entire section of the bead.

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 reagents drawn from needle-tipped burets. When necessary, transfers were made in an argon-filled glove box.

Far-infrared spectra in the 100-600 cm^{-1} region were obtained by use of 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 glove box. The spectra were recorded with the sample in a dry nitrogen atmosphere and mounted between polyethylene plates.

An ARL-EMX/SM Electron Microprobe[2] was used to study the physical nature of the metal catalyst[1] dispersion on the polymer support. The polystyrene beads, embedded in wax block, were sliced by using a microtome and were mounted on a quartz plate (1" x 1").

Materials. The 20% cross-linked (600 Å pore size and 400-600 mesh) and 2% cross-linked macroreticular polystyrene-divinylbenzene copolymer were a gift from the Dow Chemical Co. and were washed before use to remove the impurities. Organolithium and organoaluminum reagents were obtained from Alfa, while $TiCpCl_3$[3] was prepared by previously published methods.[4] $TiCl_4$ was obtained from J. T. Baker Chemical Co., $ZrCl_4$ and $HfCl_4$ were obtained from Alfa and $TiCl_3$ was obtained from Research Organic/Inorganic Chemical Corp., Chloromethyl ethyl ether was obtained from Aldrich Chemical Co., and was distilled before use. Tetrahydrofuran (THF), hexane, benzene, and toluene were distilled over sodium-benzophenone complex under argon.

Preparation of Cyclopentadienyl-Substituted Copolymer. 200 g. of 20% cross-linked copolymer beads were washed with 10% HCl, 10% NaOH, H_2O, H_2O-CH_3OH, CH_3OH, CH_3OH-CH_2Cl_2, and CH_2Cl_2 as recommended by Pittman.[5] They were then vacuum dried. Following the chloromethylation method of Pepper et al.,[6] 1 liter of freshly distilled chloromethyl ethyl ether (caution is advised in chloromethylation and in handling of chloromethyl ethyl ether because the related compound dichlorodimethyl ether is a carcinogen as is the monochloro ether)[7] was added to the beads in a 2-ℓ, three-necked flask with a drying tube and an overhead stirrer. The flask was cooled in ice for 2 hours. A solution prepared by cautiously adding 35 ml of $SnCl_4$ to 125 ml of ice-chilled chloromethyl ethyl ether was then added slowly. After vigorous stirring of the reaction mixture at room temperature for 30 hours, the chloromethyl ethyl ether was removed by filtration. The beads were washed with four 1-ℓ portions of 50% aqueous dioxane, aqueous dioxane containing 10% HCl (v/v) and finally with dry dioxane, until the washings were chloride free. Chloride analysis of the chloromethylated copolymer after it had been dried for two days in vacuo yielded 1.30 meq of Cl^-/g or about 14% chloromethylation of the styrene rings.

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

Preparation of the cyclopentadienyl substituted, 2% cross-linked copolymer beads, was accomplished by the same procedure. The product contained 2 mmol $(C_5H_5^-)$/g.

Preparation of Copolymer-Attached $TiCpCl_3$. Copolymer-attached $TiCpCl_3$ was prepared by the procedure described in our earlier publication.[1]

Preparation of Copolymer-Attached $TiCpCl_2$. Cyclopentadiene substituted copolymer was converted to the cyclopentadienide anion by treatment with a two fold excess of methyllithium in ether.

After being stirred overnight under argon, the solution was removed and the polymer washed with THF five times. The beads were then treated with a two fold excess of $TiCl_3$ dissolved in THF (the solution was made by using a soxhlet extractor). The beads were separated by filtration and washed with THF in a soxhlet extractor until excess chloride had been removed. The violet blue beads were dried _in_ _vacuo_ and stored in a drybox.

Preparation of Copolymer-Attached $ZrCpCl_3$ and $HfCpCl_3$. $ZrCl_4$ and $HfCl_4$ are solids (unlike the liquid $TiCl_4$) and are sparingly soluble in most of the organic solvents. Thus by following the procedure described for preparation of attached $TiCpCl_3$, only a very small amount of the species $MCpCl_3$ (where M = Zr and Hf) could be attached to the polymer support. The method was modified by using $ZrCl_4 \cdot 2Py$ and $HfCl_4 \cdot 2Py$ adducts. The pyridine adducts were prepared following the procedure described by Ray and Westland.[8] $ZrCl_4$ or $HfCl_4$ was suspended in dry benzene and slightly more than a two fold excess of dry pyridine was added. The reaction mixture was cooled in ice and was stirred vigorously for two hours. A white suspension was produced, but the stirring was continued for an additional 24 hours to ensure complete reaction, at room temperature.

The $MCl_4 \cdot 2Py$ (M = Zr and Hf) adduct in benzene was then added to the cyclopentadienide form of the copolymer in benzene and allowed to stir for 48 hours at room temperature. The cream colored beads were filtered, washed with dry benzene and subsequently with dry THF, in a soxhlet extractor until excess chloride had been removed. They were dried _in_ _vacuo_.

Preparation of Copolymer (2% cross-linked) Containing $TiCp_2Cl_2$. 100 g cyclopentadiene substituted 2% cross-linked beads (2 mmol $C_5H_5^-$/gm. of beads) covered with methyl ether was treated with a two-fold excess of 1.7 M methyllithium in ether and was stirred for two days. The ceads were filtered and washed with dry THF. The product was suspended in dry THF and a solution containing 70 g $TiCpCl_3$ (0.32 mol) dissolved in dry benzene was introduced and the mixture stirred for three days. Excess $TiCpCl_3$ was removed by extracting with benzene in a soxhlet extractor, followed by a similar extraction with THF. The product, red colored beads, was dried *in vacuo* for two days.

Far-Infrared. Polymer-attached $TiCp_2Cl_2$ (cm^{-1}) 402, 362, 307, 280, 256 (broad) and 196 (nujol mull); non-attached $TiCp_2Cl_2$ 400, 360, 303, 276, 247 and 206 (nujol mull).

Analytical Methods. Halide from the chloromethyl groups was removed from the copolymer with hot pyridine and determined by the Volhard technique.[8] Two samples were analyzed commercially the the Spang Microanalytical Laboratories, Ann Arbor, MI and gave similar results for chloride. Titanium, zirconium and hafnium were determined[1] by ignition of the metal containing polymer at 900° for eight hours and by weighing as the oxide. Titanium was also analyzed by spectrophotometry of the titanium-peroxide complex. The two methods agree closely. Chloride bound to titanium was removed by digestion of the polymer samples, which had first been ground in a mortar, in 2 N KOH solution at 80° for eight hours. Chloride was determined by the Volhard method following acidification of the aqueous supernate.

Electron Microprobe Studies. Metal catalysts are often made in a high degree of dispersion on the surface of a high-area solid (polystyrene beads in this work). The knowledge of the metal catalyst dispersion on the polymer surface will help in understanding the catalytic process.[11] The investigation was carried out by using an electron microprobe X-ray fluorescence study of titanium, zirconium, and chlorine, supported on the copolymer beads as the cyclopentadienyl metal chlorides.

The polymer-supported metal cyclopentadienyl chlorides were sliced by using a microtome. Since the beads were fragile, they had to be coated with wax before slicing. Some beads were added to molten wax in a metal container and the wax was then solidified. The wax block containing the beads was mounted on a microtome and sliced. The sliced sections were about 10 microns in thickness. Selected thin sections of the beads were then placed on a quartz plate (1" x 1") and most of the wax was removed by careful melting. The rest of the wax was removed by careful rinsing with xylene. The sections were then mounted on the quartz plate by using a contact cement. A thin carbon coating was applied by evaporation to give good conductance. Analyses were carried out with three or four beads of selected samples.

Radial profiles of Ti, Zr and Cl in the sample were determined from the traverses of the sectioned beads with the ARL-EMX/SM electron microprobe at the Horticulture department of Michigan State University.[2] The microprobe conditions were the following: 25 KV accelerating voltage, 0.01 μa sample current, 1 μm beam width. K_α X-ray lines were used for titanium and chlorine. The L_α X-ray line was used for zirconium. The detector crystal used for titanium was LiF. For zirconium and chlorine $(NH_4)_2HPO_4$ was used.

Electron microprobe X-ray fluorescence analysis of the

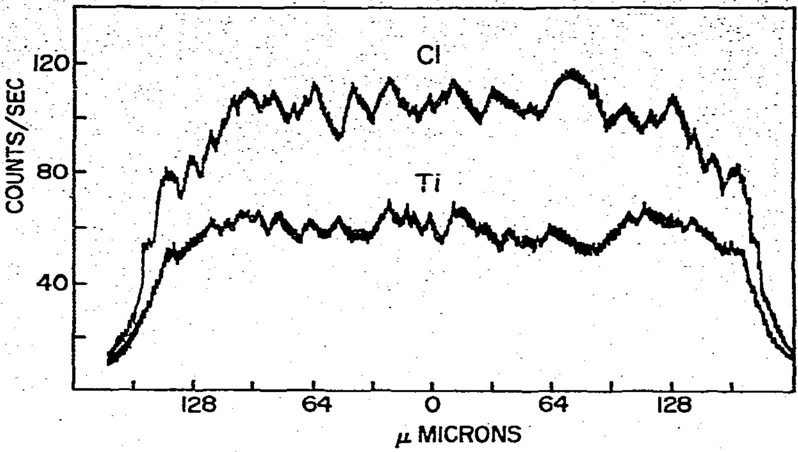

Figure 1. X-ray fluorescence analysis of the Ti and Cl content of a cross-section of the $(C_5H_5)_2TiCl_2$ beads.

sectioned beads gave radial distributions of the metal and chloride as exemplified by the results of fig. 1.

Catalysis of Olefin Reduction. The hydrogenations were carried out by using gas burets of 100 ml volume. The hydrogen uptake was measured at normal atmospheric pressure and at 20° ± 0.5°. All reductions were carried out in a 100 ml round-bottomed flask with a side arm. The catalyst was weighed into the flask, suspended in 10 ml of hexane, and treated with 1 ml of 2.0 M BuLi in hexane for two hours. The excess BuLi was removed and the sample was washed a few times with hexane by using a syringe and a long needle. The reduced catalyst was then placed in 9 ml of hexane and the appropriate olefin was added by means of a syringe. The rate of hydrogen uptake was measured as in the previous work.[1]

Discussion

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

The main difficulty in the field of polymer-supported catalysts, is the determination of the structure and the exact nature of the active species. Elemental analysis of the complexes gives the quantity of each element present. Detailed information about the environment of the metal atom and how it changes when chemical reactions occur is generally not known.

The optical properties of these cyclopentadienyl metal chlorides (especially titanium compounds) are striking. For example, titanocene dichloride is dark red, monocyclopentadienyl titanium trichloride is bright yellow, titanocene is dark grey, bis-cyclopentadienyl titanium dimethyl is yellow, bis(cyclopentadienyl)titanium monochloride is green, monocyclopentadienyl titanium dichloride is purple, monocyclopentadienyl zirconium and hafnium trichloride are cream colored. So, as one would expect, the corresponding polymer-attached species are similar in color. Table 1 summarizes the colors of the non-attached and polymer-attached species. A close resemblance in color of the non-attached and polymer-attached species is observed. Also the intensity of the color of the polymer-attached species was found to be approximately

Table 1

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

Series	Non-Attached	Polymer-Attached
$TiCp_2Cl_2$	Dark Red	Salmon to red (depending on the Ti concentration)
$TiCp_2(CH_3)_2$	Yellow	Yellow
$TiCpCl_3$	Bright Yellow	Bright Yellow
$TiCpCl_2$	Purple	Violet-Blue
$TiCp_2Cl$	Green	Olive Green
$ZrCpCl_3$	Cream	Cream
$HfCpCl_3$	Cream	Cream

proportional to the concentration of the attached species, as expected.

Identification of the polymer-attached species was aided by the metal and chloride analysis. The results of the analyses are summarized in Table 2.

Electron microprobe X-ray fluorescence analysis of the sectioned beads gave cross-sectional distributions of the metal and chloride as shown in figure 1. The figure gives the K_α X-radiation counts per second of titanium and chlorine in the polymer-supported compounds, as a function of the distance across the section in microns. Most of the sections were thin -- about 10 microns thick and about 400 microns in length. The analyses were carried out for three or four beads of each sample. The metal and chloride distributions on the 20% polymer bead support were uniform across the section of the bead. Similar results were obtained for the other polymer-supported metal cyclopentadienyl chlorides of titanium and zirconium.

Table 2

Analytical Results

Substituent	Chloride (mmol/g)	Metal M (mmol/g)	Cl/M Ratio	
			Calcd	Found
$-CH_2Cl$	1.30	-----	---	----
$-CH_2CpH$	0.20*	-----	---	----
$-CH_2CpTiCl_3$	0.811	0.282	3	2.88
$-CH_2CpTiCl_2$	0.209	0.110	2	1.90
$-CH_2CpZrCl_3$	0.830	0.293	3	2.83
$-CH_2CpHfCl_3$	0.700	0.250	3	2.80
$-CH_2CpTiCpCl_2$ (2% cross-linked)	1.499	0.788	2	1.90

*Residual - CH_2Cl
(The first six samples were 20% cross-linked)

Catalytic Activity of the Polymer-Attached Species. The reduction of olefins catalyzed by transition metal complexes generally requires the presence of an open coordination site on the metal.[12] It is proposed that in the first step a hydrogen atom is sigma bonded to the metal and an olefin approaches and is initially π-bonded. In the next step hydrogen migrates to the one carbon of the olefin, which then is σ-bonded to the metal. The approach of a second hydrogen results in the formation of the saturated hydrocarbon and rupture of the metal - carbon bond. The experimental evidence suggests that it is also true for alkyllithium reduced titanocene derivatives. Only monomeric titanocene species contain such sites. Increase in the concentration of such species attached to the polymer supports is reflected in an increase in catalytic activity of that complex when compared to a similar non-attached complex under the same conditions.

Table 3

Hydrogenation Rates with Polymer-Attached $TiCpCl_3$ and Non-Attached $TiCpCl_3$ (20% cross-linked)

Catalyst Precursor	mmol Ti	Olefin	M	Rates ml/min-mmol Ti Initial
Non-attached $TiCpCl_3$	0.36	cyclohexene	1.15	2.00
Polymer-attached $TiCpCl_3$	0.0138	cyclohexene	1.15	30.00
Polymer-attached ground $TiCpCl_3$	0.0085	cyclohexene	1.15	194.00
Non-attached $TiCpCl_3$	0.2937	1-hexene	1.15	2.90
Polymer-attached $TiCpCl_3$	0.0118	1-hexene	1.15	42.00
Polymer-attached ground $TiCpCl_3$	0.0085	1-hexene	1.15	390.00
Non-attached $TiCpCl_3$	0.32	cyclooctene	1.15	0.5
Polymer-attached $TiCpCl_3$	0.014	cyclooctene	1.15	7.60
Polymer-attached ground $TiCpCl_3$	0.012	cyclooctene	1.15	60.5

The hydrogenation studies with polymer-supported $TiCpCl_3$ are summarized in Table 3. The hydrogenation rate with homogeneous $TiCpCl_3$ reduced with BuLi was only 2.0 ml/min-mmol Ti, for cyclohexene and 2.9 ml/min-mmol Ti, for 1-hexene. The hydrogenation rate with polymer-attached $TiCpCl_3$ reduced with BuLi was 30 ml/min-mmol Ti, for cyclohexene and 42 ml/min-mmol Ti, for 1-hexene. The hydrogenation rate produced by the polymer-supported, reduced $TiCpCl_3$ is about 15 times that of the corresponding homogeneous compound. The powdered beads containing $TiCpCl_3$ gave a hydrogenation rate of 194 ml/min-mmol Ti for cyclohexene and 390 ml/min-mmol Ti for 1-hexene. The hydrogenation rate with the powdered beads is 7 - 10 times that of the whole beads, when identical reduction and hydrogenation procedures were employed. This observation is similar to the earlier results for polymer-attached $TiCp_2Cl_2$ and attributed to the ease of diffusion of the olefins. The increase in activation upon polymer attachment is about 100 times that of the non-attached catalyst species. The non-attached catalyst required more than 40 hr. to complete the reduction of cyclohexene, whereas the attached catalyst completed the reduction in about 100 min. The attached catalyst shows good first order kinetics (pseudo) under a variety of conditions. The

Table 4

Relative Hydrogenation Rates
(20% cross-linked)

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

[a] In ml of hydrogen per minute ± 0.05 ml of hydrogen per min.

major determinant in the rates of reduction with the attached catalysts is the size of the copolymer beads. Grinding the beads to a fine powder increased their activity. The hydrogenation rate (Table 4) depends on the size of the olefin -- the rate decreases as the size of the olefin increases. The order of decreasing rates of hydrogenation through the use of polymer-attached $TiCpCl_3$ is 1-hexene > cyclohexene > cyclooctene, in agreement with the Kroll's results with Wilkinson's catalyst.[13]

The hydrogenation rates for polymer-attached $TiCpCl_2$ are summarized in Table 5. The results agree well with previous observations.[1]

Attempts to use the polymer-bound $ZrCpCl_3$ and $HfCpCl_3$ were not very successful. Only about 3 ml of hydrogen uptake per minute per millimole of the metal was observed. Previous hydrogenations reported with cyclopentadienyl zirconium catalysts were carried out at high temperature and high hydrogen pressures.[14] No rates were reported. Recently some work has been reported on hydrozirconation.[15,16] The reactivity of $(\eta\text{-}C_5H_5)_2ZrCl(R)$ with olefins have been studied. The alkyl zirconium(IV) complexes formed were treated with electrophiles like H^+, Br_2, I_2, etc. The yields of the products formed were determined by vapor phase chromatography and were based on $(\eta\text{-}C_5H_5)_2Zr(R)Cl$ species, and were between 90 and

Table 5

Hydrogenation Rates with Polymer-Attached $TiCpCl_2$
(20% cross-linked)

Catalyst Precursor	mmol Ti	Olefin	M	Rates ml/min-mmol Ti
Polymer-attached $TiCpCl_2$	.011	1-hexene	1.15	36.5
Polymer-attached $TiCpCl_2$	.011	cyclohexene	1.15	22.7
Polymer-attached $TiCpCl_2$	.014	cyclooctene	1.15	13.6

100 percent. A similar experiment should be attempted with the polymer-bound metal cyclopentadienyl species of zirconium and hafnium.

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