Journal of Organometallic Chemistry, 280 (1985) 365–376
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE PREPARATION AND CATALYTIC APPLICATIONS OF SUPPORTED ZIRCONOCENE AND HAFNOCENE COMPLEXES

BIAU-HUNG CHANG, ROBERT H. GRUBBS and CARL H. BRUBAKER, Jr.
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824 (U.S.A.)

(Received May 30th, 1984)

Summary

Polymer-attached Cp_2ZrCl_2, Cp_2HfCl_2, $CpZrCl_3$, $CpHfCl_3$, Cp_3ZrCl and Cp_3HfCl have been prepared. The polymer-attached Cp_2ZrCl_2, on reduction with BuLi, produced an active catalyst whose efficiency for olefin hydrogenation is about eight times as great as that of the corresponding homogeneous species under the same conditions. The reduction products of supported zirconocene and hafnocene complexes are active hydrogenation catalysts for diphenylacetylene which was hydrogenated to 1,2-diphenylethane through intermediate stilbene. The similar reduction products have also been employed in catalytic isomerization of allylbenzene, cis-stilbene and 1,5-cyclooctadiene. Allylbenzene was converted into a mixture of *trans*- and *cis*-propenylbenzene, *cis*-stilbene was isomerized to *trans*-stilbene, and 1,5-cyclooctadiene was isomerized to 1,3-cyclooctadiene through the 1,4-cyclooctadiene intermediate. Polymer-attached Cp_2ZrCl_2, $CpZrCl_3$, Cp_2HfCl_2, and $CpHfCl_3$ can be used directly, without going through the reduction process, for the low yield epoxidation of cyclohexene. Polymer-attached Cp_2ZrCl_2 was used in hydrozirconation and carbon monoxide reduction studies.

Introduction

We have demonstrated [1] that the attachment of titanocene catalysts to rigid polymers resulted in an increase in activity for olefin hydrogenation, which was found to be a result of site isolation of the polymer [2]. Polymer-attached titanocene-related complexes have also been proved to be excellent catalysts for the isomerization and epoxidation of olefins and oligomerization of ethyl propiolate [3].

Zirconocene- and hafnocene-related catalysts, which are isoelectronic and most probably isostructural with the titanium homologs, have been attached to the polystyrene copolymers and their catalytic activities in hydrogenation and other

0022-328X/85/$03.30

processes, e.g., isomerization, expoxidation, and hydrozirconation of olefins, and reduction of carbon monoxide, have been examined.

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.

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, cyclohexene, t-butyl hydroperoxide and chloromethyl ethyl ether were obtained from the Aldrich Chemical Company. (Caution is advised in chloromethylation and in the handling of chloromethyl ethyl ether because the related compound bis(chloromethyl) ether is a carcinogen [5]). Zirconocene dichloride, hafnocene dichloride, zirconium tetrachloride and hafnium tetrachloride were obtained from Alfa Products, Ventron Corporation. Monocyclopentadienyl-zirconium trichloride [6], magnesium cyclopentadienide [7] and cyclopentadiene-substituted copolymer [1,8] were prepared by the previously published methods.

Analytical methods

Halide from the chloromethyl groups was removed from the copolymer by use of hot pyridine and was determined by the Volhard method [9]. Zirconium and hafnium contents were determined by digesting the polymer-attached zirconium and hafnium containing polymers 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 ZrO_2 and HfO_2, respectively. Zirconium and hafnium 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 dicyclopentadienyl zirconium and hafnium dichlorides ($P-Cp_2MCl_2$; $M = Zr, Hf$)

Method a

In a typical reaction, 2 g of cyclopentadiene-substituted copolymer beads (0.5 mmol Cp/g of beads) was treated with excess butyllithium in THF and the mixture was stirred for 2 d under argon. The excess of n-BuLi was removed and the beads were washed with THF. They were then suspended in 30 ml of THF, and $CpZrCl_3$ (1.3 mmol) was added. The reaction mixture was stirred for 2 d. The solution was then removed and the beads were washed with THF in a Soxhlet extractor for 3 d. The product, yellowish beads, was dried in a vacuum. Anal. Found: Zr, 0.420 mmol/g of beads; Cl, 0.827 mmol/g of beads; Cl/Zr, 1.97. Calcd: Cl/Zr, 2.00.

Method b

In a typical reaction, 2 g of cyclopentadiene-substituted copolymer beads (1.41 mmol Cp/g of beads) was treated with excess butyllithium in THF and the mixture was stirred for 2 d under argon. The excess n-BuLi was removed and the beads were washed with THF. They were then suspended in 20 ml of THF, and 2 g of Cp_2MCl_2 ($M = Zr, Hf$) was added. The reaction mixture was stirred for 3 d, then treated with excess anhydrous hydrogen chloride gas for 4 h. The solution was removed and the beads were washed with THF in a Soxhlet extractor for 5 d. The product, brownish yellow beads, was dried under vacuum. Anal. Found: Zr, 0.142 mmol/g of beads; Cl, 0.328 mmol/g of beads; Cl/Zr, 2.31. Calcd. for supported zirconocene dichloride: Cl/Zr, 2.00. Anal. Found: Hf, 0.126 mmol/g of beads; Cl, 0.302 mmol/g of beads; Cl/Hf, 2.40. Calcd. for supported hafnocene dichloride: Cl/Hf, 2.00.

Method c

Typically, 10 g of polymer-attached $CpZrCl_3$ (0.636 mmol Zr/g of beads) or $CpHfCl_3$ (0.463 mmol Hf/g of beads) was suspended in 10 ml THF and 3.1 ml (2.3 ml for $CpHfCl_3$) 2.2 *M* sodium cyclopentadienide in THF was added. After the reaction mixture was stirred for 5 d, the beads were washed with THF several times. Then 30 ml hydrogen chloride gas was introduced and allowed to stir for 24 h. After being washed with THF in a Soxhlet extractor for 3 d, the yellow beads were dried in vacuo for 2 d. Anal. Found: Zr, 0.627 mmol/g of beads; Cl, 1.223 mmol/g of beads; Cl/Zr, 1.95. Calcd. for supported zirconocene dichloride: Cl/Zr, 2.00. Anal. Found: Hf, 0.450 mmol/g of beads; Cl, 0.869 mmol/g of beads; Cl/Hf, 1.93. Calcd. for supported hafnocene dichloride: Cl/Hf, 2.00.

Preparation of polymer-attached monocyclopentadienyl zirconium and hafnium trichloride ($P-CpMCl_3$; $M = Zr, Hf$)

About 5 g of polymer-attached lithium cyclopentadienide beads (1.41 mmol Cp/g of beads) was suspended in 40 ml benzene and 2 g MCl_4 ($M = Zr, Hf$) was added. The reaction mixture was stirred at room temperature for 7 d. The solution was then removed. After being washed with THF in a Soxhlet extractor for 4 d, the product, cream colored beads, was dried. Anal. Found: Zr, 0.338 mmol/g of beads; Cl, 0.953 mmol/g of beads; Cl/Zr, 2.82. Calcd. for supported $CpZrCl_3$: Cl/Zr, 3.00. Anal. Found: Hf, 0.428 mmol/g of beads; Cl, 1.198 mmol/g of beads; Cl/Hf, 2.79. Calcd. for supported $CpHfCl_3$: Cl/Hf, 3.00.

Preparation of polymer-attached tricyclopentadienyl zirconium and hafnium monochloride ($P-Cp_3MCl$; $M = Zr, Hf$)

The polymer-attached lithium cyclopentadienide beads were suspended in THF and a two-fold excess of Cp_2ZrCl_2 was added. The reaction mixture was stirred for 3 d. The excess Cp_2ZrCl_2 was removed and the beads were then washed with THF in a Soxhlet extractor until excess chloride had been removed. The product, yellow beads, was dried. Anal. Found: Zr, 0.302 mmol/g of beads; Cl, 0.297 mmol/g of beads; Cl/Zr, 0.98. Calcd. for supported Cp_3ZrCl: 1.00. Anal. Found: Hf, 0.345 mmol/g of beads; Cl, 0.328 mmol/g of beads; Cl/Hf, 0.95. Calcd. for supported Cp_3HfCl: 1.00.

Far-Infrared

The far-IR in the 100–500 cm^{-1} region were obtained by use of a Digilab Model FTS-16 Fourier-Transform spectrophotometer. The samples were prepared by crushing the copolymer beads and mulling the powder with Nujol. Polymer-attached Cp_2ZrCl_2: 355, 330, 306 and 269 cm^{-1}; non-attached Cp_2ZrCl_2: 361, 332, 310 and 265 cm^{-1}; polymer-attached Cp_2HfCl_2: 360 (sh), 335, 308, 285 (sh) and 265 cm^{-1}; non-attached Cp_2HfCl_2: 360, 312, 285 and 265 cm^{-1}.

Catalytic hydrogenation of olefins and diphenylacetylene

The polymer-attached catalysts were weighed into a 100 ml round-bottomed flask with a side arm. The beads were suspended in 5 ml n-hexane and treated with 3 ml 2.0 *M* n-butyllithium in n-hexane for 2 d. The excess n-butyllithium was removed and the beads were washed with n-hexane several times. Then 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 25°C. The rate of hydrogen uptake was measured by using an 100 ml gas buret.

For the hydrogenation of diphenylacetylene, the catalyst was suspended in 5 ml toluene, then 0.267 g (1.5 mmol) diphenylacetylene in 5 ml toluene was added into the flask. The rate of hydrogen uptake was measured at 100°C and at normal atmospheric pressure. A small amount of reaction mixture was drawn out periodically and then chromatographed by GLC on a 8 ft. × 1/8 in. 15% SE-30/Chromosorb P column.

Catalytic isomerization of allylbenzene and 1,5-cyclooctadiene

The reduction of polymer-attached zirconocene and hafnocene chloride beads with excess n-butyllithium in hexane was carried out under hydrogen or argon atmosphere at room temperature for 2 d. The excess n-butyllithium was removed and the beads were washed with hexane several times and dried under vacuum. Allylbenzene or 1,5-cyclooctadiene was then added and was stirred under argon at 145°C. A small amount of reaction mixture was drawn out periodically and chromatographed by GLC on a 8 ft. × 1/8 in. 15% SE-30/Chromosorb P column. The relative amounts of allylbenzene, *cis*-propenylbenzene and *trans*-propenylbenzene were measured by integration. The relative amounts of 1,3-, 1,4- and 1,5-cyclootadiene were measured by GLC integration and NMR integration.

Epoxidation of cyclohexene

A sample of polymer-attached Cp_2ZrCl_2, $CpZrCl_3$, Cp_2HfCl_2, or $CpHfCl_3$ (0.09 mmol Zr or Hf) was weighed into a 100 ml round-bottomed side-armed flask. The flask was flushed several times with argon. 5 ml benzene, 3 ml cyclohexene (30 mmol) and 8 ml 80% t-butylhydroperoxide in water (60 mmol) were added. The reaction mixture was stirred at 80°C. Samples were taken out for analysis of the epoxide at various time intervals. The products, epoxide, was determined by gas chromatography on a 16 ft. × 1/8 in. 10% Carbowax/Chromosorb W column. Chlorobenzene was used as an internal standard.

Hydrozirconation of olefins

Typically, the reduction of 5 g of polymer-attached Cp_2ZrCl_2 beads (3.3 mmol Zr) with Vitride ($NaAlH_2(OCH_2CH_2OCH_3)_2$) in THF was carried out in a 200 ml pressure bottle under argon for 2 d. After the beads were washed with THF and benzene several times, a quantity of 2 ml of 1-hexene and 10 ml of benzene was added and allowed to stir for 2 d. The argon was then removed and carbon monoxide was introduced (150 psi). The reaction mixture was allowed to stir for 2 d at room temperature and then hydrolyzed with dilute aqueous hydrochloric acid. The solution was taken out and extracted with ether. The extract was concentrated and then analyzed for aldehydes by GLC on a 16 ft. × 1/8 in. 10% Carbowax/Chromosorb W column.

Preparation of polymer-attached methylene-bridged Cp_2ZrCl_2 [3]

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 vacuum. The chloride analysis gave 2.0 mmol Cl/g of beads. To the yellowish beads suspended in 80 ml of THF, three-fold excess of sodium cyclopentadienide in THF was added. After being stirred for 5 d, the beads were dried under vacuum. The product, yellowish methylene bridged cyclopentadiene-substituted copolymer beads (possibly $P{-}C_5H_4CH_2C_5H_5$), contains 0.05 mmol Cl/g of beads.

Following the method c described in the preparation of polymer-attached dicyclopentadienylzirconium dichloride, the polymer-attached methylene-bridged Cp_2ZrCl_2 beads (possibly $P{-}C_5H_3(C_5H_5ZrCl_2)CH_2C_5H_8(C_5H_5ZrCl_2))$ were prepared from the methylene bridged cyclopentadiene-substituted copolymer beads and $ZrCl_4$. The elemental analysis gave 0.81 mmol Zr/g of beads.

Reduction of carbon monoxide to alcohols by polymer-attached Cp_2ZrCl_2

Typically, about 8 g of supported Cp_2ZrCl_2 beads (0.67 mmol Zr/g of beads) suspended in benzene in the presence of 3 equiv. of diisobutylaluminum hydride (DIBAH) was stirred in a 200 ml pressure bottle under 60 psi of CO atmosphere for 3 d. The reaction mixture was then hydrolyzed with dilute aqueous sulfuric acid. The product was analyzed by GLC on 10 ft. × 1/8 in. 19% FFAP/Chromosorb G and 12 ft. × 1/8 in. Carbowax 1500/Chromosorb G columns. Only small amount (< 5%) of methanol and propanol was observed.

Results and discussion

Preparation of polymer-attached Cp_2MCl_2 (M = Zr and Hf)

Three methods for the preparation of polymer-attached Cp_2ZrCl_2 and Cp_2HfCl_2

have been developed. They are (a) reaction of $CpMCl_3$ with polymer-attached lithium cyclopentadienide (Scheme 1), (b) reaction of Cp_2MCl_2 with polymer-attached lithium cyclopentadienide followed by treatment with excess hydrogen chloride (Scheme 2) [10], and (c) reaction of MCl_4 with polymer-attached lithium cyclopentadienide to form polymer-attached $CpMCl_3$, followed by the addition of stoichiometric amount of sodium cyclopentadienide, and then by the treatment with small amount of hydrogen chloride (Scheme 3).

Method (a) is less useful because the synthesis of $CpMCl_3$ is usually of low yield and needs high vacuum technique [11,12]. Both method (b) and method (c) are practical.

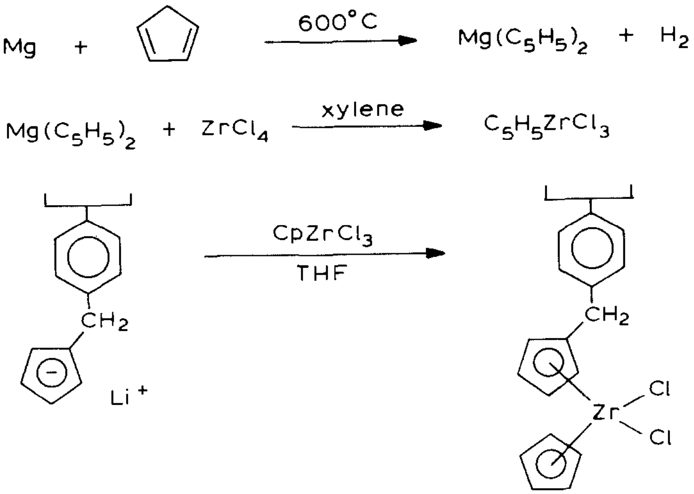
Preparation of polymer-attached $CpMCl_3$ ($M = Zr, Hf$)

Polymer-attached $CpZrCl_3$ and $CpHfCl_3$ complexes can be prepared by direct reaction of the lithium cyclopentadienide-substituted polymer with $ZrCl_4$ and $HfCl_4$, respectively. Longer reaction time is needed due to the low solubility of the tetrachlorides. Renaut et al. [12] reported that the reaction between dicyclopentadienylmagnesium and hafnium tetrachloride in decalin gave $CpHfCl_3 \cdot 2THF$ adduct after removal of Cp_2HfCl_2 with THF. Therefore, the $CpMCl_3$ species on the polymer are probably $CpMCl_3 \cdot 2THF$ adducts.

Hydrogenation of olefins and diphenylacetylene

We have previously demonstrated [1] that the attachment of titanocene-related catalysts to rigid polymers resulted in an increase in activity for olefins hydrogenation, which was found to be a result of site isolation on the polymer [2].

Similarly, polymer-attached zirconocene and hafnocene catalysts are also found to be active catalysts for the hydrogenation of alkenes and their activities in hydrogenation have been increased after attachment to the polymer. For example, the rates of hydrogen uptake at room temperature for 1-hexene catalyzed by reduced



SCHEME 1. The preparation of supported Cp_2ZrCl_2 by the reaction of $CpZrCl_3$ with lithium cyclopentadienide-substituted polymer (Method (a)).

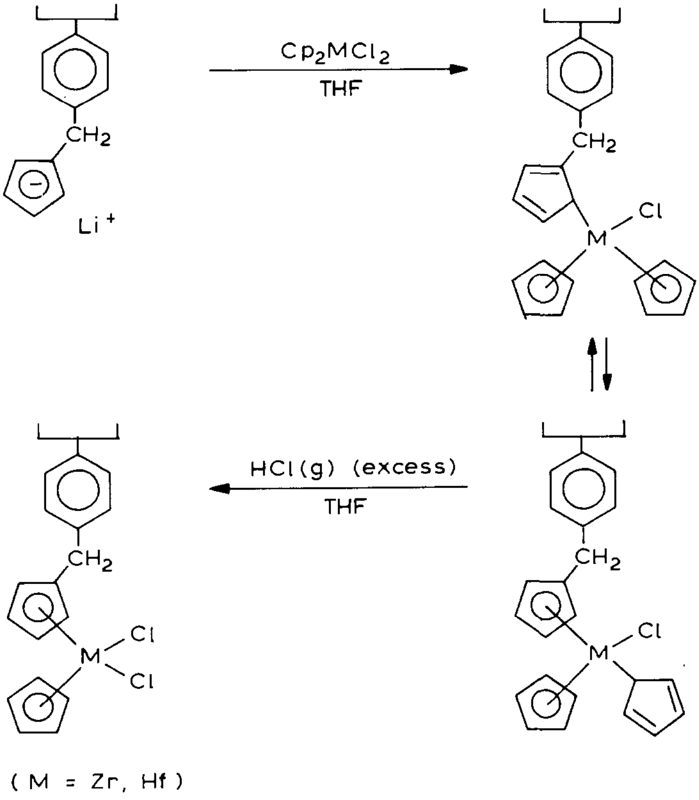
unattached and attached Cp_2ZrCl_2 are 0.12 ml and 0.95 ml min^{-1} $mmol^{-1}$ of metal, respectively. Previous hydrogenations reported with homogeneous cyclopentadienyl zirconium catalysts were carried out only at high temperature and high pressure [13].

Supported zirconocene and hafnocene complexes are also active hydrogenation catalysts for alkynes. The rates of hydrogen uptake at 100°C for diphenylacetylene catalyzed by supported zirconocene and hafnocene catalysts are 3.6 ml and 2.7 ml min^{-1} $mmol^{-1}$ of metal, respectively. It is shown that diphenylacetylene is hydrogenated to *trans*-stilbene and further to give 1,2-diphenylethane (Figs. 1 and 2). By comparison with polymer-attached titanocene catalysts [3], it is found that the activities in hydrogenation are in the decreasing order, Ti > Zr > Hf.

Isomerization of allylbenzene and 1,5-cyclooctadiene

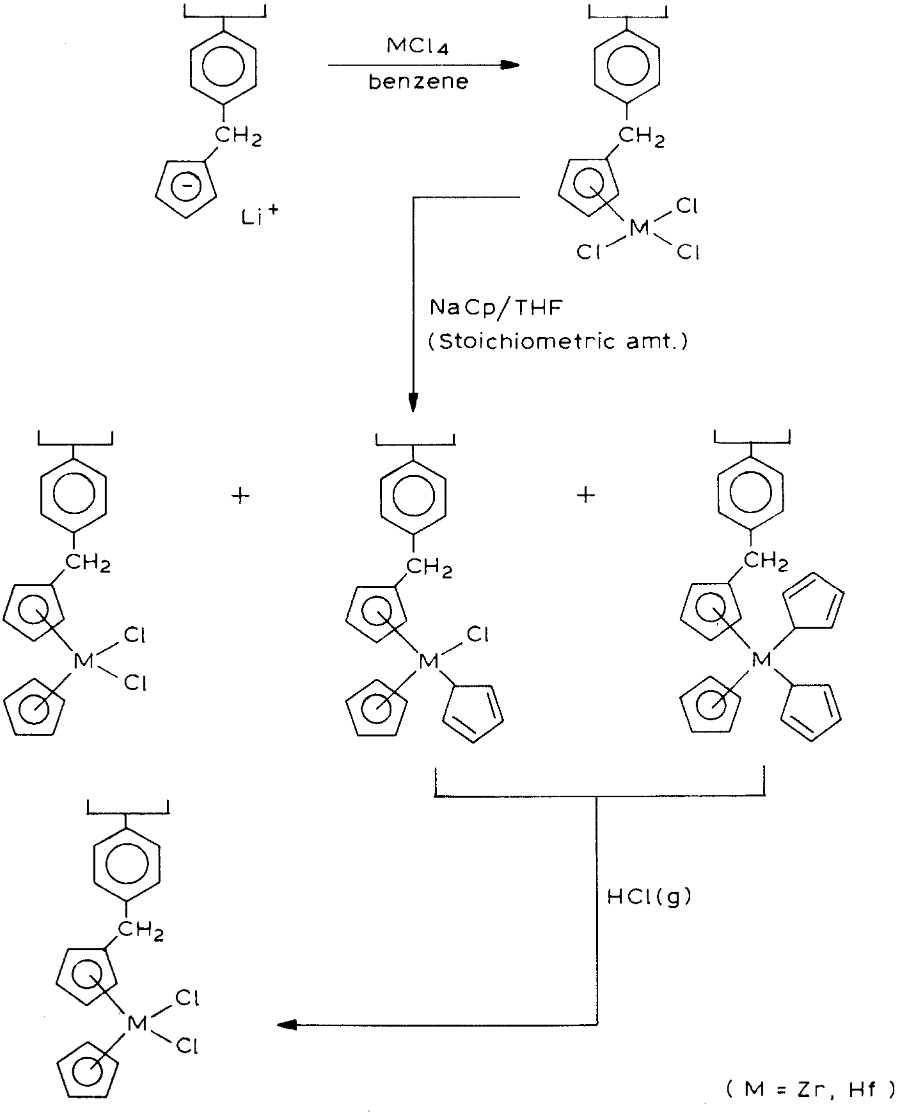
Allylbenzene and 1,5-cyclooctadiene, when treated with reduction product of polymer-attached zirconocene and hafnocene chlorides, appear to undergo a rapid double bond migration. The exact mechanism by which they act, whether of the addition-elimination or π-allyl type, is still not certain. Allylbenzene can be isomerized to form the more stable conjugated system, *cis*- and *trans*-propenylbenzene.

Similarly, 1,5-cyclooctadiene is effectively isomerized to 1,3-cyclooctadiene with 1,4-cyclooctadiene as the intermediate product. The catalysts produced by reducing



(M = Zr, Hf)

SCHEME 2. The attachment of Cp_2MCl_2 to polystyrene through the exchange reaction of σ- and π-cyclopentadienyl ligands (Method (b)).



SCHEME 3. The attachment of Cp_2MCl_2 to polystyrene by the reaction of polymer-attached $CpMCl_3$ with sodium cyclopentadienide (Method (c)).

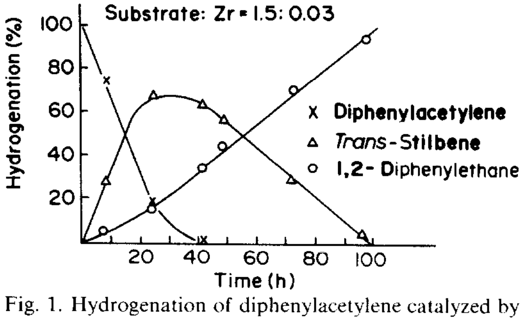


Fig. 1. Hydrogenation of diphenylacetylene catalyzed by supported Cp_2ZrCl_2.

the supported metallocene chlorides with n-butyllithium under hydrogen are more active than those generated under argon. For example, the catalyst produced, by reducing the supported Cp_2ZrCl_2 with n-butyllithium under argon, can only effect about 50% isomerization of allylbenzene in 5 h, while the catalyst obtained under hydrogen brings the isomerization to an extent of 90% under the same conditions. The reduction of metallocene chlorides with n-butyllithium under hydrogen probably generates metallocene hydrides such as Cp_2ZrH_2 and Cp_2HfH_2 and the isomerization most probably proceeds through the addition-elimination mechanism.

A comparison of isomerization activity is examined, it is shown that $CpMCl_3$ is the most efficient catalyst, followed by Cp_2MCl_2, with Cp_3MCl being least active under the conditions employed. A reduced activity for the heavier metal is also indicated. The catalyst can be repeatedly used without much reduced activity. In all of these systems the isomerization is 80 to ca. 100% complete in 30 h, at which time monitoring ceased.

Other experiments indicate that polymer-attached zirconocene and hafnocene catalysts are also good catalysts for *cis-trans* isomerization. *cis*-Stilbene, when treated with these catalysts, is isomerized rapidly to *trans*-stilbene. But no appreciable amount of isomerization products was observed for 1,5-hexadiyne, β-pinene and 1-octene.

Expoxidation of cyclohexene

It is known [14,15] that compounds of certain transition metals, notably Mo, W, Ti and V catalyze the liquid-phase epoxidation of olefins with alkyl hydroperoxides.

It has been demonstrated [3] that polymer-attached titanocene chlorides are active epoxidation catalysts for cyclohexene and cyclooctene. Similarly, polymer-attached zirconocene and hafnocene chlorides are also found to be active catalysts for the epoxidation of cyclohexene with t-butyl hydroperoxide but their activities are relatively lower than that of the attached titanocene chlorides. The results are given in Table 1.

The continuous decrease in the activity of the catalysts, possibly due to the autoretardation by the co-product t-butanol, has been observed. However, the catalysts can be regenerated by passing anhydrous hydrogen chloride gas into the beads suspended in THF. The regenerated catalysts are re-used for the epoxidation without much loss of activity.

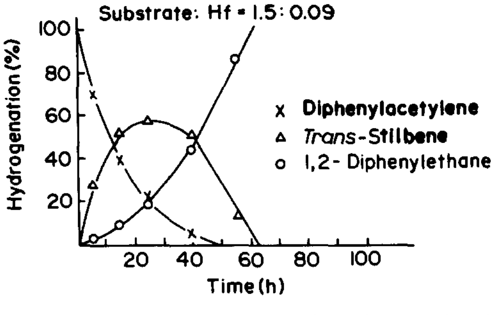
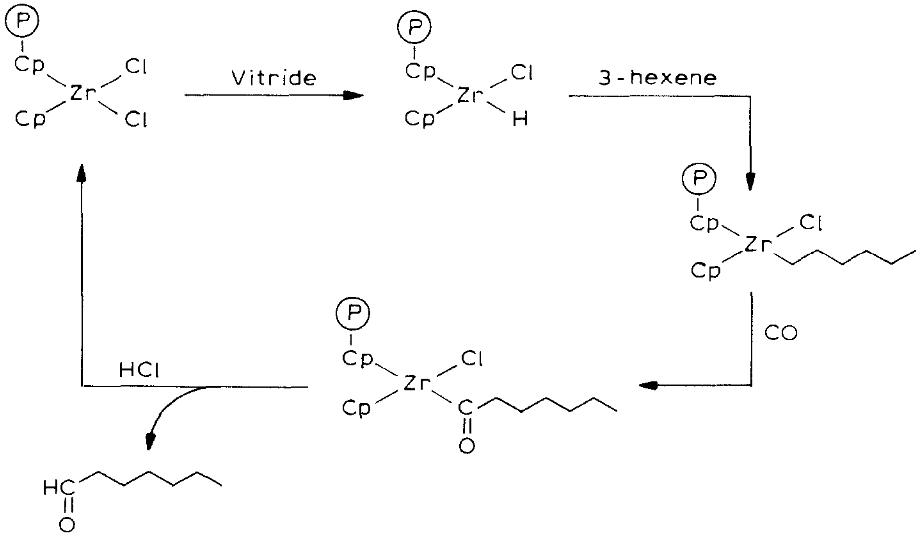


Fig. 2. Hydrogenation of diphenylacetylene catalyzed by supported Cp_2HfCl_2.

Hydrozirconation of alkenes

Schwartz et al. [16–18] have demonstrated that $Cp_2Zr(H)Cl$ will react with olefins and alkynes to produce terminal alkyl and alkenyl zirconium derivatives. These zirconocene alkyls and alkenyls will react with a number of reagents to produce terminally functionalized alkanes and alkenes in high yield. The most interesting reaction is the production of terminal aldehydes from olefins (Scheme 4). The development of hydrozirconation illustrates that the introduction of new procedures



SCHEME 4. The synthesis of terminal aldehydes from hydrozirconation of alkenes (Vitride = $NaAlH_2(OR)_2$).

TABLE 1

CATALYTIC EPOXIDATION OF CYCLOHEXENE [a]

Wt. of catalysts (g) (loading)	Solvent	Time (h)	Product (%) (epoxycyclohexane)
P–Cp_2ZrCl_2 (0.1444) (0.63 mmol Zr/g)	benzene	18	16
P–Cp_2ZrCl_2 (0.1448) (0.63 mmol Zr/g)	cyclohexane	18	19
P–Cp_2ZrCl_2 (0.1448) (recycled) [b]	cyclohexane	18	15
P–Cp_2ZrCl_2 (0.1467) (0.63 mmol Zr/g)	benzene	48	20
P–$CpZrCl_3$ (0.2756) (0.33 mmol Zr/g)	cyclohexane	18	22
P–Cp_2HfCl_2 (0.2007) (0.45 mmol Hf/g)	cyclohexane	48	9
P–$CpHfCl_3$ (0.3075) (0.29 mmol Hf/g)	cyclohexane	48	11

[a] Cyclohexene (3 ml), 80% t-butyl hydroperoxide in water (8 ml), and catalyst (0.1–0.3 g) in 5 ml solvent were used. The reactions were carried out at 80°C. [b] Catalyst used was recycled from previous reaction.

will continue to be an exciting aspect of organic synthesis because of the broad scope and high reactivity of organometallic complexes.

If one can attach Cp_2ZrCl_2 to a polymer support, zirconocene dichloride can be recovered by filtration and re-used for hydrozirconation. Attempt to use the polymer-attached Cp_2ZrCl_2 reagents for the hydrozirconation of olefins to produce terminal aldehydes did not meet with much success. The results are given in Table 2.

The preparation of polymer-attached $Cp_2Zr(H)Cl$ from attached Cp_2ZrCl_2, which was prepared from either method (b) or method (c), has been difficult to achieve possibly because the free cyclopentadienes on the polymer react with some aluminum hydride reagent and the optimum amount of Vitride ($NaAlH_2(OCH_2CH_2OCH_3)_2$) is difficult to determine. For example, with a Cp_2ZrCl_2-substituted polymer having a loading of 0.32 mmol of Zr metal per gram of polymer, there are 1.58 mmol of free cyclopentadienes pendant on the polymer. The free cyclopentadiene will react with Vitride to give cyclopentadienide. Attempts to increase the formation of supported $Cp_2Zr(H)Cl$ by varying the molar ratio of Vitride to zirconocene dichloride from one half to two are not successful.

However, the use of polymer-attached Cp_2ZrCl_2 which was prepared from method (c) resulted good yields of aldehydes after hydrolysis of hydrozirconation products. This is probably attributed to the free cyclopentadienide groups instead of cyclopentadienes pendant on the polymer do not react with aluminum hydride reagents. Therefore, polymer-attached $Cp_2Zr(H)Cl$ can be prepared by treatment of attached Cp_2ZrCl_2 with a stoichiometric amount of Vitride, and then used in hydrozirconation to produce aldehydes. However, the recovered beads from previous reaction can not be re-used in hydrozirconation since the free cyclopentadienide groups have been converted into cyclopentadienes after hydrolysis with dilute

TABLE 2

SYNTHESIS OF ALDEHYDES FROM HYDROZIRCONATION OF ALKENES WITH POLYMER-ATTACHED Cp_2ZrCl_2

Wt. of polymer (g) (loading, mmol Zr/g)	Reactants used		Olefins	Pressure of CO (psi)	Aldehydes[a] (%)
	mmol Zr	mmol Vitride			
6.2 (0.32)	2.0	1.0	1-hexene	60	0
7.1 (0.27)	1.9	1.0	1-pentene	80	0
5.7 (0.32)	1.8	2.0	1-pentene	80	0
5.0 (0.67)	3.3	1.7	1-hexene	45	0
5.0 (0.67)	3.3	3.0	1-hexene	80	0
5.0 (0.67)	3.3	4.0	1-pentene	80	n-hexanal (9%)
5.0 (0.67)	3.3	6.0	1-pentene	80	0
8.4 (0.81)[b]	6.8	9.4	1-hexene	80	0
11.0 (0.81)[b]	8.9	12.0	1-hexene	100	n-heptanal (21%)
10.5 (0.81)[b]	8.5	16.0	1-hexene	100	n-heptanal (12%)
6.6 (0.42)[c]	2.77	1.39	1-hexene	80	n-heptanal (72%)
10.5 (0.42)[c]	4.41	2.21	3-hexene	100	n-heptanal (70%)
10.2 (0.42)[c]	4.28	2.14	1-hexene	100	n-heptanal (81%)
10.2 (0.42)[d]	4.28	2.14	1-hexene	100	n-heptanal (trace)

[a] The yields are based on zirconocene dichloride. [b] Polymer-attached methylene bridged Cp_2ZrCl_2 was used. [c] Polymer-attached Cp_2ZrCl_2 which prepared from the reaction of $CpZrCl_3$ and lithium cyclopentadienide-substituted polymer (Method c) was used. [d] Recycled from the previous reaction.

aqueous HCl. The polymer-attached methylene-bridged Cp_2ZrCl_2 with higher loading of zirconium metal was also used, but no improvement in the production of aldehydes was observed.

Wailes et al. [19] reported that the IR spectrum of $Cp_2Zr(H)Cl$ showed one broad Zr–H stretching band at 1390 cm^{-1}. Attempts to determine the species on the polymer after the reaction of supported Cp_2ZrCl_2 with Vitride are not successful due to the background absorption of the polymer and the low loadings of Zr metal used.

Reduction of carbon monoxide to alcohols by polymer-attached Cp_2ZrCl_2

Schwartz and Shoer [20] reported that diisobutyl aluminum hydride (DIBAH) in the presence of Cp_2ZrCl_2 as a catalysts could reduce carbon monoxide at room temperature to give, on hydrolysis, a mixture of linear aliphatic alcohols. Reduction of carbon monoxide by DIBAH in the presence of polymer-attached Cp_2ZrCl_2 catalyst has also been investigated under similar conditions. The reaction mixture after hydrolysis only gave small amount ($< 5\%$) of methanol and propanol.

Acknowledgement

The authors gratefully acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References

1 W.D. Bonds, Jr., C.H. Brubaker, Jr., E.S. Chandrasekaran, C. Gibbons, R.H. Grubbs and L.C. Kroll, J. Amer. Chem. Soc., 97 (1975) 2128.
2 R.H. Grubbs, C.P. Lau, R. Cukier and C.H. Brubaker, Jr., J. Amer. Chem. Soc., 99 (1977) 4517.
3 C.P. Lau, B.H. Chang, R.H. Grubbs and C.H. Brubaker, Jr., J. Organomet. Chem., 214 (1981) 325.
4 C.U. Pittman, Jr., R.M. Hanes, private communication.
5 The Federal Register Vol. 39, No. 20, Part III, Occupational Safety and Health Administration, Carcinogens.
6 A.F. Reid and P.C. Wailes, J. Organomet. Chem., 2 (1964) 329.
7 W.A. Barber, Inorg. Synth., 6 (1960) 11.
8 B.H. Chang, R.H. Grubbs and C.H. Brubaker, Jr., J. Organomet. Chem., 172 (1979) 81.
9 C.W. Bird, Transition Metal Intermediates in Organic System, Logos Press, London, 1967, p. 30.
10 J.G.S. Lee and C.H. Brubaker, Jr., J. Organomet. Chem., 135 (1977) 115.
11 A.F. Reid and P.C. Wailes, J. Organomet. Chem., 2 (1964) 329.
12 P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 127 (1977) C35.
13 P.C. Wailes, H. Weigold and A.P. Bell, J. Organomet. Chem., 43 (1972) C32.
14 R. Hiatt in R.L. Augustine (Ed.), Oxidation, Techniques and Application in Organic Synthesis. Dekker, N.Y., 1971, Vol. 2, p. 113.
15 R.A. Sheldon and J.A. Van Doorn, J. Catal., 31 (1973) 427 and references therein.
16 D.W. Hart and J. Schwartz, J. Amer. Chem. Soc., 96 (1974) 8115.
17 C.A. Bertelo and J. Schwartz, J. Amer. Chem. Soc., 97 (1975) 228.
18 J. Schwartz and J.A. Labinger, Angew. Chem. Int. Ed. Engl., 15 (1976) 333 and references therein.
19 P.C. Wailes and H. Wiegold, J. Organomet. Chem., 24 (1970) 405.
20 L.I. Shoer and J. Schwartz, J. Amer. Chem. Soc., 99 (1977) 5831.