

A POLYMER-SUPPORTED DICHLORO(CYCLOPENTADIENYL)RHODIUM(III) CATALYST

HSUEH-SUNG TUNG and CARL H. BRUBAKER, Jr. *

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824 (U.S.A.)

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Summary

Insoluble dichloro(η^5 -cyclopentadienyl)rhodium(II) has been attached to 20% divinylbenzene cross-linked polystyrene by treating polymer-attached cyclopentadiene directly with rhodium trichloride trihydrate. Polymer-supported dichloro(η^5 -cyclopentadienyl)rhodium(III), I, is a good hydrogenation catalyst for olefins as well as arenes in the presence of excess triethylamine under 110 psig H_2 at 70°C. It can also catalyze isomerization of allylbenzene in the absence of triethylamine at 85°C. Under 80 psig of CO and H_2 (1/1) in the presence of triethylamine, I can be easily converted into the polymer-supported η^5 -cyclopentadienylrhodium dicarbonyl catalyst. Mechanisms for the catalyst preparation, hydrogenation and isomerization are also discussed.

Introduction

The advantages of heterogenizing homogeneous transition-metal catalysts on polymer supports have proved to be more effective than simple recovery improvement. The rigid polymer can immobilize the catalytic species and prevent the association of the unsaturated catalytic centers, thus preserving the potential catalytic activity [1–6]. Among the polymer supports, cross-linked polystyrene has received the most attention, and proved to be easily functionized with cyclopentadiene [6]. The attachment of homogeneous metal complexes to the polystyrene through the cyclopentadienyl ligand has been widely used [6–8].

The insoluble dichloro(η^5 -cyclopentadienyl)rhodium(III) complex, II, was first synthesized by Maitlis, et al. [9] along with the analogous dichloro(η^5 -pentamethylcyclopentadienyl)rhodium(III) dimer, III, which was reported to be a good homogeneous catalyst for the hydrogenation of olefins [10,11] and arenes [12] in the presence of triethylamine. In contrast, II has not been reported to have catalytic activity [13]. We now report that I is a hydrogenation

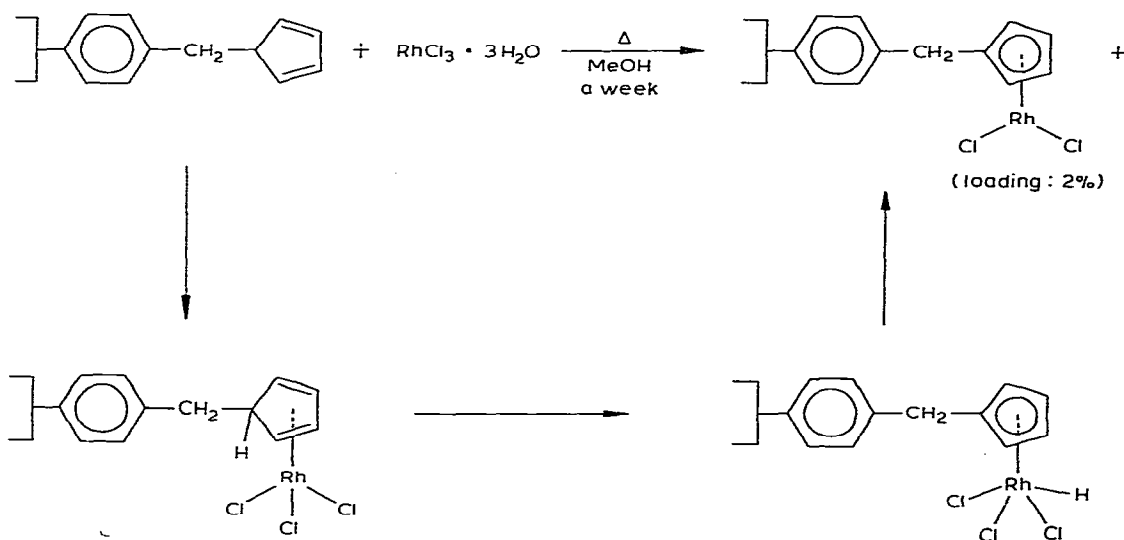
tion and isomerization catalyst. The polymer-supported η^5 -cyclopentadienyl-rhodium dicarbonyl catalyst [14] has been prepared from I.

Results and discussion

1. Polymer-supported dichloro(cyclopentadienyl)rhodium(III), I

The conventional way to prepare polymer-bound cyclopentadienylmetal catalysts has been to prepare a polymer-bound cyclopentadienide lithium first by using alkyl lithium and the Cp-polymer. Subsequent treatment of the Li Cp-polymer with a metal halide complex in organic solvent can produce the desired polymer-bound metal complex [6]. This method is not applicable for the preparation of I, because of the insolubility of anhydrous RhCl_3 . The water content in the relatively soluble $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ would destroy the Li Cp-polymer. However, when $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ was dissolved in methanol and refluxed with the Cp-polymer for a week, the dark red solution turned clear and HCl was liberated (Scheme 1). The resulting polymer beads were brick-brown like II [9]. The reaction probably involved the coordination of RhCl_3 first with the two double bonds of cyclopentadiene ring, then a hydrogen-abstraction occurred to form a more stable cyclopentadienide anion ligand coordinated with Rh. Subsequently (or perhaps simultaneously) HCl was released to produce I.

SCHEME 1



2. Catalytic hydrogenation

Benzene, *o*-xylene, acetophenone, and 1-hexene were chosen as substrates for catalytic hydrogenation over I in the presence of an excess of Et_3N under 110 psig of H_2 at 70°C . The results are shown in Table 1. The catalyst was still active without Et_3N in the case of 1-hexene, but the hydrogenation rate was lowered by about one third. The turnover rate is expressed in mol of H_2 -uptake per mol Rh per h. The extent of hydrogenation was confirmed by product

TABLE 1

CATALYTIC HYDROGENATION OF ALKENES AND ARENES OVER POLYMER-SUPPORTED DICHLORO(CYCLOPENTADIENYL)RHODIUM(III)^a

Substrate	Turnovers/hr	Product composition
1-hexene	253	n-hexane (>99%) 2-hexene (trace)
1-hexene (no Et ₃ N)	169	n-hexane (>99%) 2-hexene (trace)
benzene	59.3	cyclohexane (100%)
<i>o</i> -xylene	35.6	<i>cis</i> -1,2-dimethylcyclohexane (66%) <i>trans</i> -1,2-dimethylcyclohexane (34%)
acetophenone	20.0	cyclohexyl methyl ketone (48%) ethylbenzene (45%) 1-phenylethanol (7%)

^a Reaction conditions: H₂ pressure: 110 psig; mole ratio of substrate (in terms of reducible double bonds) to catalyst = 769/1; mole ratio of cocatalyst (Et₃N)/Rh = 28/1.

analyses. In the case of *o*-xylene, although *trans*-1,2-dimethylcyclohexane is 1.8 kcal/mole more stable than the *cis*-isomer [15], the *cis*-isomer was the predominant product and indicated that the hydrogenation catalyzed by I was stereoselective. Acetophenone was hydrogenated to three different products:

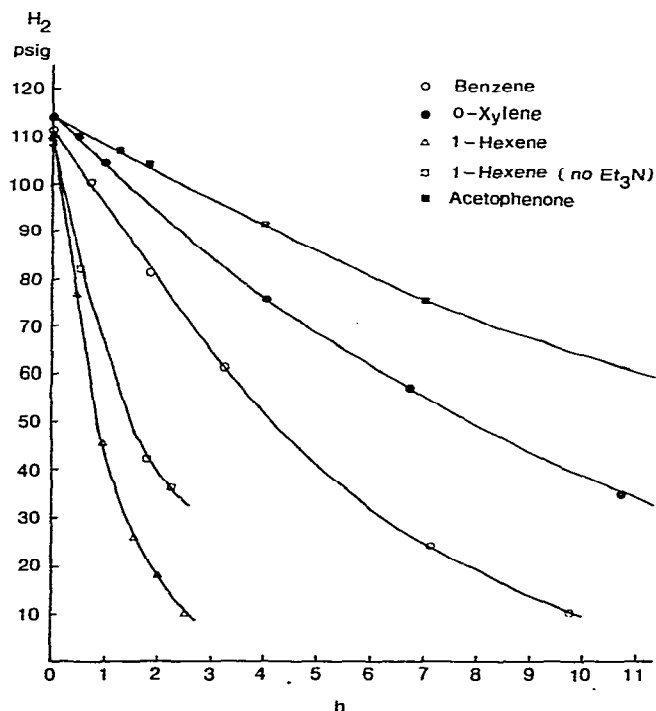
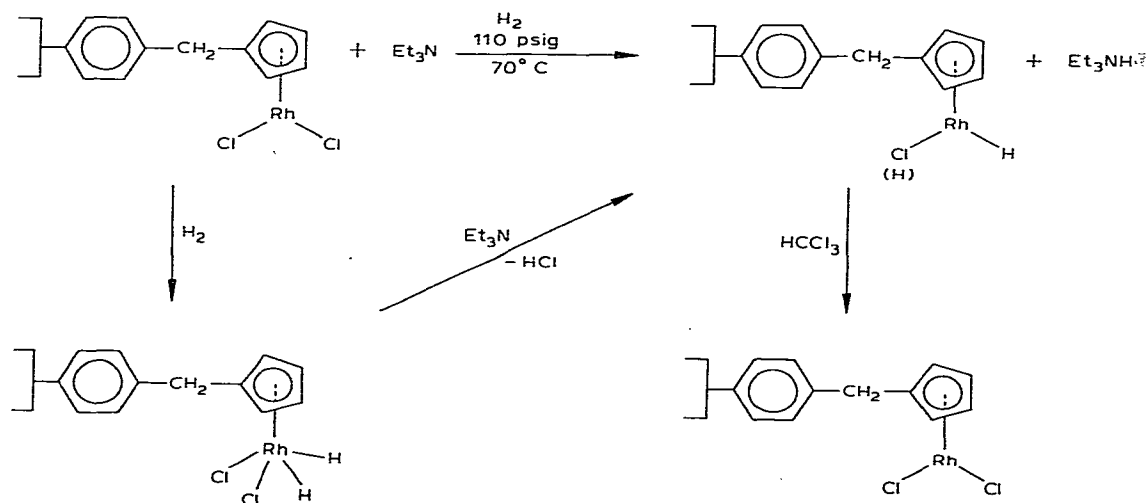


Fig. 1. Catalytic hydrogenation of alkenes and arenes with the polymer-supported Rh^{III} complex: $P(H_2)$ (psig) vs. time.

cyclohexyl methyl ketone (48%), ethylbenzene (45%), and 1-phenylethanol (7%). It indicated that the aromatic ring and carbonyl group were almost equally competitive in the hydrogenation. The pressure drop of H_2 for these reactions was plotted against time (Fig. 1) and showed that electron-withdrawing substituents on the benzene ring slowed down the reaction more than donating groups. It may suggest that sizes of substrates and the hydrophobic nature of the polymer support play important roles in the mass transport, which is the dominant factor in comparing the hydrogenation in and out of the polymer matrices. The reason why the presence of Et_3N enhanced the hydrogenation rate is rationalized by the reaction scheme (Scheme 2). Rhodium can insert

SCHEME 2



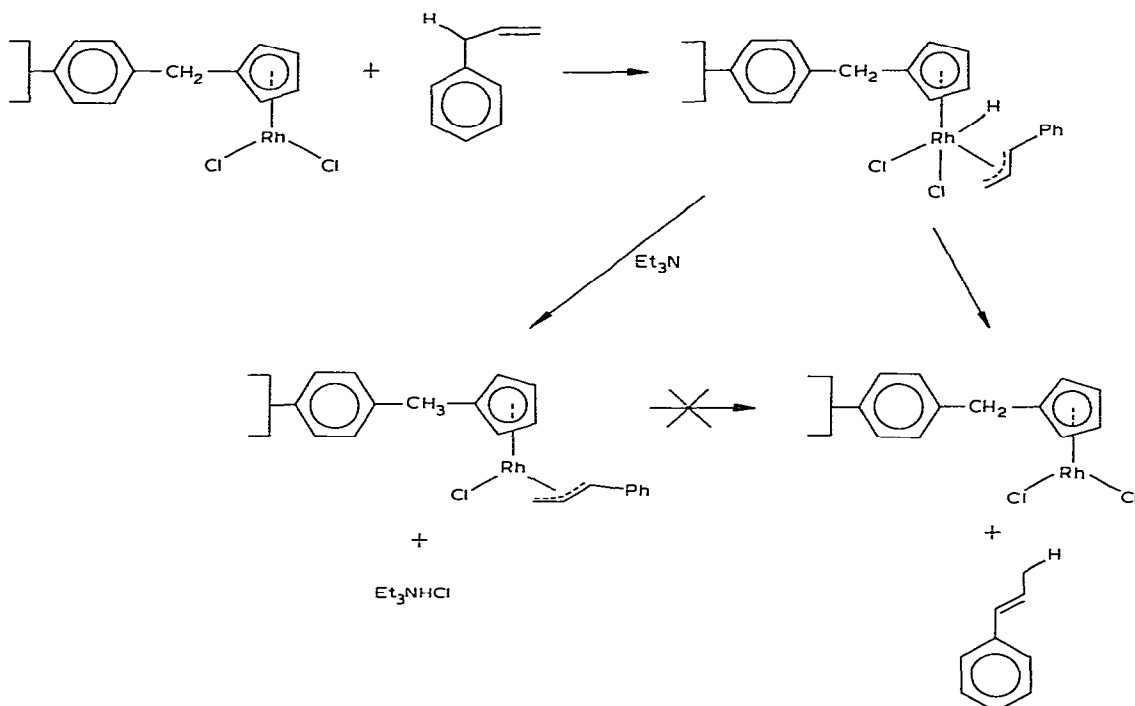
into a molecule of H_2 at the beginning of hydrogenation to form an 18-electron unstable intermediate (or transition state), then Et_3N aids in the release of a mole of HCl as Et_3NHCl . The resulting Rh hydride (more precisely dihydride) is a necessary and reactive intermediate for catalytic hydrogenation as was confirmed by IR adsorption at 1960 cm^{-1} [16]. Et_3NHCl was isolated and identified after the hydrogenation had been completed. In the absence of triethylamine, the release of HCl is necessary in order for the hydrogenation to occur. In a reversible reaction, the rate of hydrogenation would be slower than in the presence of Et_3N .

The Rh hydride beads are black, but the possible presence of black Rh metal was excluded by the observation that the brown color returns after the black beads are soaked in chloroform overnight. The stereoselective hydrogenation of *o*-xylene also helps rule out the Rh^0 formation.

3. Catalytic isomerization of allylbenzene

Allylbenzene was used as the substrate to demonstrate the isomerization ability of the catalyst I at $85^\circ C$. Two isomerized products were found, *cis*- and *trans*-propenylbenzene. The conversion of allylbenzene leveled out at 90% after 40 h. The predominant product was *trans*-propenylbenzene, at 75%. The proportion of *cis*-propenylbenzene reached its maximum after 6–8 h. The color

SCHEME 3



of the polymer-bound catalyst remained unchanged throughout the reaction period.

The addition of Et_3N to the reaction vessel stopped the isomerization immediately. Since the π -allyl ruthenium hydride complex has been proved to be the intermediate in the isomerization of allyl benzene [17], it seems reasonable to presume that this isomerization is also initiated by oxidative-addition of Rh to the allylic C—H bond (Scheme 3). Subsequent replacement of the hydrogen to the γ -carbon which lead to a rearrangement of the double bond to form propenyl-benzenes (β -methylstyrenes). In the presence of Et_3N , the HCl on the metal hydride intermediate (or transition state) was irreversibly removed by Et_3N as Et_3NHCl , which was identified. As a result, the isomerization cycle could not be completed and the catalytic centers were no longer present.

4. Preparation of polymer-supported cyclopentadienyl rhodium dicarbonyl catalyst, IV

Compound IV has been reported to be a good catalyst [14]. It was prepared by treating polymer-bound cyclopentadienide lithium with the chlororhodium dicarbonyl dimer.

Since a strong base is involved in this preparation, it might have reduced some Rh complex to the metallic form [18]. However, when I was placed in a pressure bottle with 80 psig H_2 and CO (1/1) in the presence of excess Et_3N and heated at 80°C for 1 week, the color of the beads changed from brick-brown to dark brown. The IR spectrum of this polymer-bound species showed two strong CO-stretching bands at 2040 and 1980 cm^{-1} which are the same

carbonyl absorption frequencies for the previously reported IV [14,18]. Again, Et_3NHCl was found in the solution. This approach generated a new method of preparing IV. There were no visible black particles (metallic Rh) after the reaction.

5. Disproportionation of 1,4-cyclohexadiene

1,4-Cyclohexadiene was stirred together with I at 75°C for 70 h. Only about 1% of the substrate had disproportionated to benzene, cyclohexane and trace amounts of cyclohexene. Raising the reaction temperature above the boiling point of 1,4-cyclohexadiene may increase the disproportionation rate, but is not convenient.

Experimental

1. General

The 1,4-cyclohexadiene and *cis,trans*- β -methylstyrene (propenylbenzene) were purchased from Aldrich Chemical Company. Allylbenzene was dried through an activated alumina column and distilled in a vacuum. *ortho*-Xylene was refluxed over sodium and distilled under reduced pressure. Acetophenone was dried over CaCl_2 for several days, then distilled under reduced pressure and stored in the dark under argon. Triethylamine hydrochloride was obtained from the reaction of triethylamine with HCl gas. Rhodium trichloride trihydrate was purchased from Strem Chemicals Inc. The 20% cross-linked polystyrene-divinylbenzene copolymer beads were a gift from the Dow Chemical Co. Polymer-supported samples used for IR measurements were prepared by crushing the polymer beads in a ball mill and mulling the powder with dry Nujol in a glovebox. IR spectra were recorded under a N_2 atmosphere. A glass pressure bottle, Lab Glass Inc., was modified with a 4-way adapter, a needle valve, a ball valve and a pressure gauge (0–200 psig). This bottle was used for conducting catalytic hydrogenations. Products were determined by a Finnigan 400 mass spectrometer with INCOS data system. Quantitative analyses were performed on Varian model 920 and 1400 gas chromatographs.

2. Preparation of polymer-supported dichloro(η^5 -cyclopentadienyl)rhodium(III) catalyst

In a typical reaction, 2 g of the previously prepared [14,17] 20% cross-linked polystyrene-cyclopentadiene beads (approximately 1 mmol- C_5H_5 per g beads) was suspended in 30 ml methanol. A 10 ml methanol solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.11 g) was added to this suspended mixture at room temperature. This mixture was then refluxed for a week. The solution turned colorless at the end of a week and the color of the polymer beads changed from pale yellow to brick-brown. The solvent was then removed by a syringe and the polymer beads were washed three times by fresh methanol. The removed solvent was concentrated to 3–5 ml and diluted with an equal volume of distilled water. A white precipitate was found upon addition of aqueous AgNO_3 to this solution. Acidity was observed by use of pH paper. The color of beads was very uniform if the beads were originally prepared by chloromethylation. Some of the uncolored beads were found in a batch of beads that was originally prepared by

bromination. Elemental analysis of the polymer-supported rhodium complex showed 2% (wt) Rh and 1.5% Cl. Thus the mole ratio of Rh/Cl is 1/2.2.

3. Hydrogenation

In a typical reaction, about 0.4 g of polymer-supported dichloro(cyclopentadienyl)rhodium(III) was placed in a glass pressure bottle. The pressure bottle was then degassed three times and charged with H_2 . A large excess of substrate (1-hexene, benzene, *o*-xylene, or acetophenone) and 0.3 ml triethylamine were introduced into the bottle by syringes. The pressure of H_2 was then increased to 110 psig at room temperature. The pressure bottle was then put into an oil bath at 70°C. The solution was stirred vigorously throughout the hydrogenation. The pressure increased slightly at the beginning of the hydrogenation and then dropped gradually until the reaction was finished. The pressure changes were recorded at time intervals of 2–4 h and are plotted in Fig. 1. The extent of hydrogenation was confirmed by quantitative analyses of the final products on a GC with column of 10% Carbowax 20M (25' $\times$ 1/4") or 10% SE-30 (10' $\times$ 1/4"). Temperatures used on the isothermal GC varied from 70 to 150°C depending on the products to be analyzed. The turnover rates were calculated from the slopes in the first two hours of hydrogenation from the plot of pressure vs. time. All substrates used were in approximately equal excess in terms of reducible double bonds. The mole ratio of reducible double bonds to Rh is >69 to 1. In the case of 1-hexene, a catalytic reaction without triethylamine was also observed. The catalytic hydrogenation was not appreciable in the absence of triethylamine for the other substrates used in this work.

Triethylamine hydrochloride was isolated from the resulting solution after the hydrogenation. It was identified by comparison of the IR spectrum with that of the authentic sample. The color of the beads changed to black after the hydrogenation. The Nujol mull IR spectrum of the ground black beads was almost exactly the same as that of I, except that there was a moderate absorption at 1960 cm^{-1} which suggested the presence of terminal Rh–hydride [16]. The analysis of the black beads showed 2% Rh and 0.05% Cl. The catalytic activity of the recovered beads decreased slightly. There were no black particles found in the solution during the course of catalytic hydrogenation.

4. Isomerization of allylbenzene

Polymer-supported dichloro(cyclopentadienyl)rhodium(III) (0.23 g) was first placed into a 100 ml flask. The flask was degassed and prepurified N_2 was added. Allylbenzene (6 ml) was introduced to the flask by a syringe. The flask was then put into an oil bath at 80°C. The pressure of N_2 was kept at 1 atm and the mixture was stirred vigorously throughout the isomerization. A sample of about 0.2 ml was withdrawn by a syringe at various times (more often at the beginning of the reaction). Analysis were performed on a GC with a column of Carbowax 20M (25' $\times$ 1/4") at 140°C. The identities of the isomerized products, *cis*- and *trans*-propenylbenzene (β -methylstyrene) were determined by comparison with authentic samples. Compositions of the sampled mixture were plotted against time (Fig. 2).

In a separate experiment, 0.2 ml triethylamine was added to the reaction

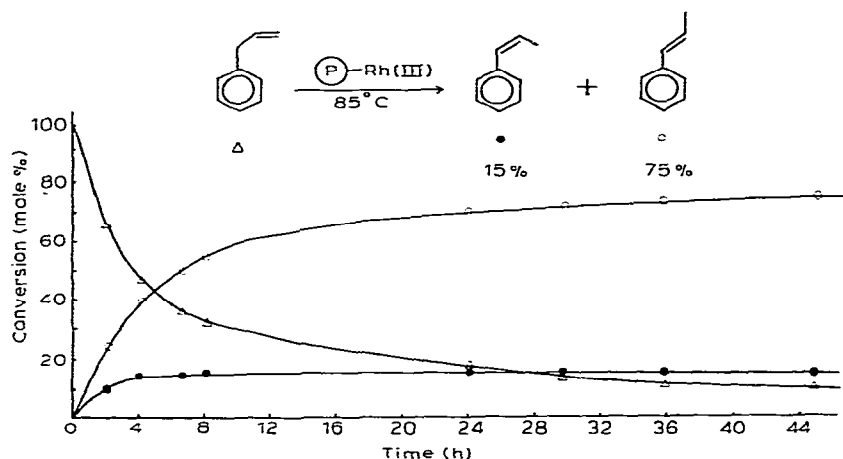


Fig. 2. Catalytic isomerization of allylbenzene with polymer-supported Rh^{III} complex.

flask by a syringe. The same analytical procedures were followed for 20 h. No appreciable amount of isomerized products was found after the addition of triethylamine. After the removal of polymer beads and substrate under reduced pressure, a very small amount of Et_3NHCl was detected.

5. Disproportionation of 1,4-cyclohexadiene

Polymer-supported Rh^{III} (0.16 g) was transferred to a 100 ml flask. The flask was degassed and N_2 was introduced at 1 atm. Four ml of 1,4-cyclohexadiene was then added to the flask by a syringe. The mixture was stirred in an oil bath at 75°C . Samples were withdrawn and analyzed every 10 h. After 70 h, small amounts of cyclohexane, cyclohexene and benzene were formed as determined by GC and only about 1% of 1,4-cyclohexadiene was consumed.

6. Preparation of polymer-supported cyclopentadienylrhodium dicarbonyl catalyst

Polymer-supported dichloro(cyclopentadienyl)rhodium(III) (0.4 g) was transferred to a glass pressure bottle. The bottle was then degassed and H_2 was introduced. Ten ml prepurified hexane and 0.3 ml of triethylamine were introduced into the bottle by syringe. The pressure bottle was then charged with 40 psig CO and 40 psig H_2 . The mixture was stirred vigorously and heated in an oil bath at 80°C for a week. The beads changed from brick-brown to black then dark brown. The IR spectrum (Nujol mull) of the newly produced beads showed two strong absorption bands at 2040 and 1980 cm^{-1} . The analysis of Rh on these dark brown beads still indicates a 2% loading. After removal of the solvent, a small amount of Et_3NHCl was detected.

Acknowledgement

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