*Journal of Organometallic Chemistry*, 172 (1979) 81—89
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# THE PREPARATION AND SOME CATALYTIC ACTIVITY OF POLYMER-SUPPORTED $\eta^5$-CYCLOPENTADIENYL-RHODIUM AND -COBALT DICARBONYLS

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/Received October 6th, 1979)

## Summary

Polymer-supported $\eta^5$-cyclopentadienylrhodium dicarbonyl and $\eta^5$-cyclopentadienylcobalt dicarbonyl have been prepared with 20% divinylbenzene-polystyrene copolymer, macroporous beads. The beads have been tested for a variety of types of catalytic activity. The cobalt-containing beads have not proven to be catalysts. The rhodium beads were effective in hydrogenation of olefins, aldehydes and ketones, isomerization of olefins, disproportion of 1,4-cyclohexadiene and cyclohexene, cyclotrimerization of ethyl propiolate, and hydroformylation of 1-pentene and 1-hexene. Decomposition of the rhodium catalyst occurs except in hydroformylation, although only slight loss of the carbonyl groups and catalytic activity was observed in cyclotrimerization.

## Introduction

The utility and versatility of homogeneous catalysts has been expanded recently by the process of attaching a variety of homogeneous catalysts to polymer supports. Cross-linked polystyrene has received the most attention as a polymer support. Many low oxidation state cobalt and rhodium catalysts have been supported on polystyrene through phosphine ligands [1—10]. The use and rhodium complexes attached to polymers through the reasonably inert cyclopentadienyl groups has been reported [11]. We now also report polystyrene-attached cyclopentadienyldicarbonyl-cobalt and -rhodium complexes as hydrogenation, isomerization, disproportionation, cyclotrimerization and hydroformylation catalysts.

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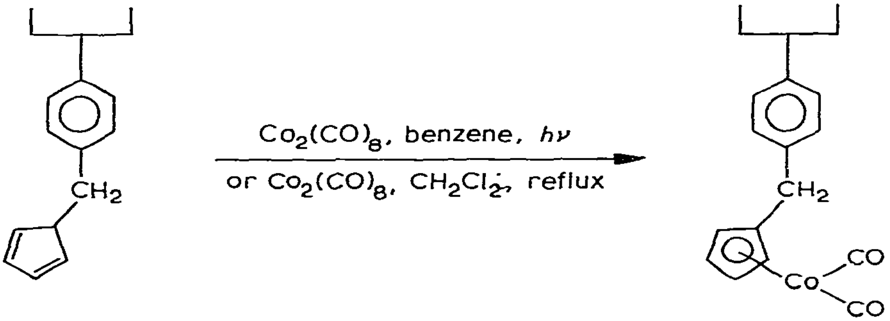
## Results and discussion

### *Preparation of polymer-attached cyclopentadienyldicarbonylcobalt*

Two methods for the synthesis of polymer-attached cyclopentadienyldicarbonylcobalt, photochemical and thermal techniques, have been developed.

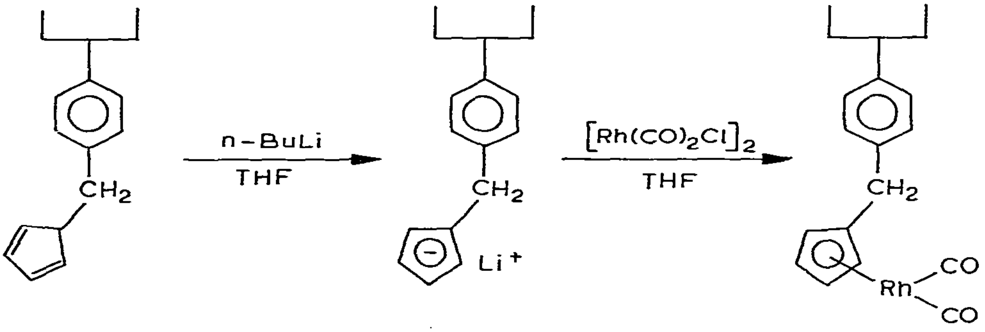
In a photochemical reaction, a mixture of cyclopentadiene-substituted polystyrene-divinylbenzene copolymer beads, prepared as previously reported [12], and $Co_2(CO)_8$ in benzene was irradiated with UV light under argon. After being washed and dried in vacuo, the beads showed two strong CO stretching bands at 2020 and 1960 $cm^{-1}$.

Similar procedures were carried out in a thermal method, except a steam bath was used to reflux the reaction mixture. The beads showed the same CO stretches in the IR.



### *Preparation of polymer-attached cyclopentadienyldicarbonylrhodium*

Polymer-attached $CpRh(CO)_2$ beads were prepared from the reaction of the $[Rh(CO)_2Cl]_2$ dimer and cyclopentadienide ion-substituted copolymer, which was obtained by treating the cyclopentadiene-substituted copolymer beads with n-BuLi in THF or hexane. The copolymer beads show two strong CO stretching peaks at 2040 and 1980 $cm^{-1}$.



### *Hydrogenation of olefins*

Rhodium complexes coordinatively bonded to polymer-supported cyclopentadiene ligands are active olefin hydrogenation catalysts. During these reactions the color of the catalysts changed to black. The two IR CO stertching peaks of the catalysts recovered from the reactions show some decrease. This result should probably be interpreted in terms of the formation of rhodium metal.

Polymer-attached $CpCo(CO)_2$, in our own hands, is not an active hydrogenation catalyst under these conditions.

Because some or perhaps all of the catalysis may be due to Rh(O), our extensive results are not reported. Rates for many olefins (1-hexene, 1-octene, cyclohexene, styrene, etc. at 1.2 M in hexane were about 20 mL $H_2$/min-mmol of catalyst).

### *Hydrogenation of ketones and aldehydes*

Polymer-attached $CpRh(CO)_2$ will hydrogen aldehydes and some ketones. Acetone, is most easily hydrogenated. When acetophenone is the substrate, the aromatic ring is also hydrogenated, as has been observed for rhodium compounds [13] and would be the metal of choice for total reduction. Other ketones were not hydrogenated. Aldehydes are hydrogenated somewhat selectively by polymer-attached $CpRh(CO)_2$. The black catalyst recovered from the reactions exhibited two CO stretches that were considerably diminished and suggests that Rh metal has formed and accounted for the catalytic activity. Because of the presence of rhodium(0), our extensive reduction data for aldehydes and ketones are not reported, but good yields of 2-propanol were found when acetone was reduced and of n-butanol was used.

### *Isomerization*

Allylbenzene can be isomerized to from the more stable *cis*- and *trans*-propenylbenzene by using a polymer-attached $CpRh(CO)_2$ catalyst. The catalyst was reused without loss of activity. The two CO stretches of the catalysts are less intense in the spectra of resins recovered from the isomerization reaction of 1,5-cyclooctadiene, allylbenzene, and *cis*-stilbene and might be due, in part, to the formation of rhodium-diene complex during the reaction. During these reactions the catalysts changed to black. The CO stretches of the recovered black catalysts were much weaker than those of the fresh beads. Thermal CO elimination is indicated. Rhodium metal may be the active catalyst. Polymer-attached $CpCo(CO)_2$ was not an active isomerization catalyst in our hands under the above conditions.

While the rhodium catalyst was effective, the possibility that rhodium(0) was the catalyst obviates the reporting of quantitative results.

### *Disproportionation*

The disproportionation of 1,4-cyclohexadiene catalyzed by polymer-attached $CpRh(CO)_2$ initially gave benzene, cyclohexene, and cyclohexane and finally only benzene and cyclohexane. Cyclohexene also disproportionationed to give benzene and cyclohexane within an hour. Thus, polymer-attached $CpRh(CO)_2$ is also a good catalyst for olefin disproportionation. The black beads recovered from the reactions still contain CO ligands according to IR spectra but the CO intensities were much less intense than those of the initial material. Again rhodium(0) is indicated as the active catalyst. Therefore, quantitative results are not reported.

### *Cyclotrimerization of ethyl propiolate (Table 1)*

Homogeneous $CpCo(CO)_2$ and $CpRh(CO)_2$ serve as active catalysts for cyclotrimerization of a wide variety of acetylenic compounds [14]. Ethyl propiolate is one of the most reactive substrates.

Reactions were carried out by stirring a suspension of the catalyst beads in the presence of ethyl propiolate in benzene, under argon. The reaction mixture was heated for periods of 6 to 48 h at 80° C. Work-up of the benzene reaction mixtures with polymer-attached $CpRh(CO)_2$ beads led to a yield of 17.5% 1,3,5-tricarbethoxybenzene and 52.5% of the 1,2,4-tricarbethoxybenzene by weight based on the amount of ethyl propiolate used. Ethyl propiolate was only converted in 20.5% yield to a mixture consisting of 2.4% 1,3,5-tricarbethoxybenzene and 18.1% of the 1,2,4-trisubstituted isomer by using polymer-attached $CpCo(CO)_2$. Some loss of intensity in the CO stretches was noted.

The dark brown catalyst recovered from the reaction mixture was active in a second reaction converting only a slightly lower percentage of ethyl propiolate. These dark brown beads contain coordinated CO ligands and exhibit intense ester CO absorptions in the IR.

### *Hydroformylation*

It is well known that Group VIII transition metal complexes, such as those of Rh and Co, are good catalysts for hydroformylation of olefins. Recently, much attention has been directed towards the polymeric phosphine-attached rhodium complexes for hydroformylation of olefins. But the use of rhodium complexes coordinatively bonded to polymeric cyclopentadiene ligands has not been examined extensively. The results of hydroformylation with polymer-attached $CpRh(CO)_2$ catalysts are presented in Table 2. No hydroformylation was observed for polymer-attached $CpCo(CO)_2$ catalyst even at 110° C, under 120 atm pressures of CO and $H_2$.

The linear/branched selectively was about 1 when the $H_2/CO$ ratio was 1. At equal pressures, the selectivity increased as temperature increased. Similarly, the selectivity increased as pressure increased at constant temperature.

TABLE 1

CYCLOTRIMERIZATIONS [a] OF ETHYL PROPIOLATE WITH POLYMER-ATTACHED $CpCo(CO)_2$ AND $CpRh(CO)_2$.

| Polymer-attached catalyst (g) | Molar ratio: Substrate/M (M = Co or Rh) | Reaction time (h) | Conversion [b] | 1,3,5-Tricarbethoxybenzene | 1,2,4-Tricarbethoxybenzene |
|---|---|---|---|---|---|
| $CpCo(CO)_2$ (0.14) | 435 | 48 | 20.5 | 2.4 | 19.1 |
| recycled [c] (0.14) | 435 | 48 | 17.6 | 1.7 | 15.9 |
| $CpRh(CO)_2$ (0.24) | 812 | 6 | 38.0 | 14.0 | 24.0 |
| recycled [c] (0.24) | 812 | 6 | 30.0 | 10.0 | 20.0 |
| $CpRh(CO)_2$ (0.30) | 661 | 32 | 70.0 | 17.5 | 52.5 |

[a] Per cent by weight converted to cyclized products. [b] Weight per cent based on the amount of ethyl propiolate used. [c] Polymer supported reagent used was recycled under argon from preceding reaction.

TABLE 2

HYDROFORMATIONS OF 1-PENTENE AND 1-HEXENE CATALYZED BY POLYMER-ATTACHED $CpRh(CO)_2$

| Weight of catalyst (g) | Substrate | Molar ratio: substrate/Rh | Time (h) | Temperature (°C) | Pressure [a] (psig) | Yield [d] (%) | Selectivity (linear/ branched) |
|---|---|---|---|---|---|---|---|
| 0.109 | 1-Pentene | 430 | 20 | 20 | 1500 | 50.7 | 0.83 |
| 0.119 | | 394 | 9 | 40 | 1000 | 53.6 | 1.00 |
| 0.071 | | 660 | 12 | 80 | 500 | 93.9 | 0.95 |
| 0.071 [e] | | 660 | 12 | 80 | 500 | 88.2 | 0.90 |
| 0.093 | | 504 | 8 | 80 | 500 [b] | 89.1 | 1.35 |
| 0.090 | | 520 | 9 | 80 | 500 [c] | 86.2 | 0.83 |
| 0.101 | | 464 | 3 | 80 | 1000 | 89.2 | 1.34 |
| 0.130 | | 360 | 24 | 110 | 100 | 26.0 | 0.92 |
| 0.181 | | 259 | 4 | 110 | 1000 | 100 | 1.18 |
| 0.112 | | 418 | 3 | 110 | 1500 | 100 | 1.24 |
| 0.108 | | 434 | 3 | 110 | 1500 [b] | 97.0 | 1.51 |
| 0.132 | | 355 | 3 | 110 | 1500 [c] | 83.1 | 0.86 |
| 0.143 [f] | | 328 | 5 | 110 | 1500 | 99.0 | 1.27 |
| 0.111 [g] | | 422 | 5 | 110 | 1500 | 91.1 | 2.06 |
| 0.144 [h] | | 325 | 5 | 110 | 1500 | 100 | 1.23 |
| 0.099 | 1-Hexene | 414 | 10 | 110 | 1500 | 98.3 | 1.69 |

[a] $H_2/CO$ 1/1. [b] $H_2/CO$ 1/3. [c] $H_2/CO$ 3/1. [d] Yields are based on olefins consumed. Only small amount of pentane (~5%) formed during the reactions. [e] Catalyst used was recycled from preceding reaction. [f] Triphenylphosphine was added P/Ph 5/1. [g] P/Rh = 20/1. [h] P/Rh 50/1.

The selectivity varied slightly by the addition of triphenylphosphine. For example, the selectivity increased from 1.24 to 2.06 when the P/Rh ratio increased from 0 to 20. But when the P/Rh ratio was raised to 50, the selectivity was dropped to 1.23. The selectivity also varied slightly when the $H_2/CO$ ratio was changed.

The dark brown beads recovered from the hydroformylation reactions showed two stretches as strong as those of the fresh beads and were reused without loss of activity.

### *Mechanisms*

The mechanisms of the above catalytic processes are presumed to be analogous to those proposed for the homogeneous rhodium catalysts, but detailed mechanistic studies have not been made. Either dissociation of CO, or a reduction of the cyclopentadienyl coordination below $\eta^5$ must precede olefin binding and (in hydrogenation or hydroformylation) hydrogen addition [15].

Since olefin isomerization and disproportionation are carried out at 145°C, it is possible that decomposition, possibly to rhodium metal, occurred and accounts for the isomerization and disproportionation. Several samples that had been used in the disproportionation of cyclohexene for 24 and 48 h were tested for their effectiveness as catalysts in cyclotrimerization of ethyl propiolate. The fresh catalyst gave an 81% yield of cyclic trimers after 24 h, while the one that had been used in disproportionation for 24 h gave only 62% and the 48 h sample only 35%. Thus it appears that decomposition of the catalyst had indeed occurred and may account for its ability to catalyze the isomerization and disproportionation processes.

It is clear that polymer-attached $CpRh(CO)_2$ is an excellent hydroformylation catalyst and, under the conditions described, does not decompose. Decomposition does occur under the conditions given for hydrogenation, isomerization, and disproportionation of olefins, and for cyclotrimerization of alkynes. It is possible that the decomposition product (rhodium(0)?) is responsible for the catalysis. Gubitosa and Brintzinger [11] reported that supported $CpRh(CO)_2$ served as a hydrogenation catalyst and did not note decomposition of the catalyst. Gubitosa and Brintzinger also found that polymer-attached $CpCo(CO)_2$ was an effective hydrogenation and hydroformylation catalyst. In our hands no catalytic activity took place, but it was not possible for us to duplicate exactly their experiments.

## Experimental

Manipulations involving air-sensitive materials were performed under argon in Schlenk-type vessels. Where necessary, transfers were made in an argon-filled glove box.

NMR spectra were obtained by use of a Varian T-60 spectrometer. IR spectra were recorded on Perkin—Elmer 457 or 237B spectrometers. 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 glovebox.

Gas chromatography, GLC, analyses were performed by use of Varian model 1400 analytical gas chromatograph. An 8 ft. × 1/8 in. column consisting of 15% SE-30 deposited on Chromosorb P was used to analyze the product mixtures from isomerization and disproportionation reactions. The products of hydrogenation of aldehydes and ketones and hydroformylation reactions were determined by means of a 32 ft. × 1/8 in. 20% Carbowax 20 M/Chromosorb W column. Elemental analyses were perfomed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All solvents used were A.C.S. reagent grade. Tetrahydrofuran (THF), hexane, and benzene were distilled from sodium metal under argon. All alkenes used for hydrogenations were at least 95% pure, and were further purified by distillation from sodium under argon. Allyl benzene was dried through an activated alumina column and distilled under vacuum. Analytical grade aldehydes and ketones were used without further purification. Ethyl propiolate was distilled under vacuum and a center cut collected. The reagents, n-butyllithium, allylbenzene, 1,5-cyclooctadiene, ethyl propiolate and chloromethyl ethyl ether were obtained from Aldrich Chemical Co. Dicobalt octacarbonyl and chlorodicarbonylrhodium dimer were obtained from Strem Chemicals Inc. 1-Pentene was obtained from J.T. Baker Chemical Co.

The 20% cross-linked polystyrene-divinylbenzene copolymer beads were a gift from the Dow Chemical Co. and were washed to remove impurities before use. They were washed with 10% HCl (aq.), 10% NaOH (aq.), $H_2O$, $H_2O/CH_3OH$ (1/1), $CH_3OH$, $CH_3OH/CH_2Cl_2$ (1/1), $CH_2Cl_2$ and benzene and then dried under vacuum.

### *Preparation of cyclopentadiene-substituted copolymer*

Following the chloromethylation method of Pepper et al. [16], 50 g of washed and dried copolymer beads was taken into a 1 l, three-necked, flask with a drying tube and an overhead stirrer. About 180 ml of chloromethyl ethyl ether (chloromethyl ethyl ether is a "cancer suspect again" because the related compound, bis(chloromethyl) ether, is a carcinogen) was added and the mixture was stirred for 2 h. A solution prepared by cautiously adding 8.5 ml of $SnCl_4$ to 80 ml of ice-chilled chloromethyl ethyl ether was then introduced slowly through a dropping funnel. After the reaction mixture was stirred vigorously at room temperature for 18 h, the ether was removed by suction and a dispersion tube. The beads were washed with four 250 ml portions of 50% aqueous dioxane, aqueous dioxane containing 10% HCl (v/v) and finally with dry dioxane until the washings were chloride free. The chloride analysis of the chloromethylated beads after it had been dried for 2 days in vacuo yielded 1.45 mmol of Cl/g of beads or 16.7% chloromethylation of the styrene rings.

The chloromethylated beads obtained above were suspended in 100 ml dry, air-free THF and 100 ml of 2.0 *M* sodium cyclopentadiene in THF. After the mixture was stirred for 6 days at room temperature, excess sodium cyclopentadienide and THF were removed by filtration. The beads were washed with ethanol/THF (1/1) and THF until the washings were chloride free and then dried under vacuum. The beads contain 0.04 mmol of Cl/g beads. Thus the cyclopentadiene contents are 1.41 mmol $C_5H_5$/g beads determined by the difference between the Cl contents before and after reaction with sodium cyclopentadienide.

*Preparation of polymer-attached CpCo(CO)₂*

*Photochemical reaction [17].* A mixture of 3 g $Co_2(CO)_8$ in 30 ml benzene and 5 g cyclopentadiene-substituted copolymer beads (1.41 mmol $C_5H_5$/g beads) in a quartz apparatus was irradiated under argon for 2 days with a 140 Watt Hanovia type 30620 UV Lamp. The excess $Co_2(CO)_8$ and benzene were then removed and the beads were washed with benzene until the washings were clear. The products, greyish brown $CpCo(CO)_2$-substituted copolymer beads, were then dried under vacuum and yielded a substance containing 0.26 mmol Co/g beads.

*Thermal reaction [18].* Five g of cyclopentadiene-substituted copolymer beads (1.41 mmol $C_5H_5$/g beads), 50 ml of dried methylene chloride and 3 g of $Co_2(CO)_8$ were placed in a 100 ml flask, which was fitted with a reflux condenser. The system was flushed with argon and was covered with aliminium foil to exclude light. The contents were heated to reflux on a steam bath for 3 d, then the methylene chloride was removed and the beads were washed with methylene chloride until the washings were clear. The greyish green beads were then dried under vacuum and stored under argon. The cobalt contents were 0.32 mmol Co/g beads.

*Preparation of polymer-attached $CpRh(CO)_2$ [19].* In a typical reaction, 3 g of cyclopentadiene-substituted copolymer beads (0.36 mmol $C_5H_5$/g beads) was treated with a two-fold excess of butyllithium in THF or hexane and the mixture was stirred for 3 d under argon. The excess n-BuLi and THF or hexane were removed and the beads were washed with THF. They were suspended in THF, the reaction flask was cooled in an ice bath, and a solution containing 0.5 mmol of $(Rh(CO)_2Cl)_2$ dissolved in THF was then introduced. The orange color of the solution disappeared within 20 min. The mixture was stirred for 2 d at room temperature. The color of beads changed from deep purple-red to dark brown. The solvent was removed and the beads were washed with THF and then dried under vacuum. The rhodium contents were 0.29 mmol Rh/g beads. Other solvents, petroleum ether and hexane, were also used. It was found that THF was the most appropriate solvent.

### *Hydrogenation of olefins*

The hydrogenations were carried out by using gas burets of 100 ml volume. The hydrogen uptake was measured at normal atmospheric pressure and at 25 ± 0.5°C.

All reactions were carried out in a 100 ml of round-bottomed flask with a side arm. The catalyst (0.29 mmol Rh/g beads) was weighed into the reaction flask, placed under an atmosphere of hydrogen and suspended in 8—9 ml of hexane. The appropriate olefin (1—2 ml) was then added. The rate of hydrogen uptake was measured by using the buret.

### *Hydrogenation of ketones and aldehydes*

A mixture of 0.1—0.3 g of catalyst (0.29 mmol Rh/g beads), 1 ml aldehyde or ketone and 5 ml benzene were placed in a 100 ml of pressure bottle. The bottle was flushed with hydrogen, pressurized to 7.8 atm with $H_2$ and heated and stirred at 100°C for 7—48 h. After being cooled to room temperature, the reaction mixture was analyzed by GLC and NMR.

### *Isomerization and disproportionation*

About 2—4 ml substrates and 0.05—0.2 g catalyst (0.29 mmol Rh/g of beads) were placed in a 5 ml pressure bottle under argon. The vessel was then heated to 145°C. A small amount of reaction mixture was drawn out periodically and then chromatographed by GLC. The relative amounts of reaction products were measured by GLC and NMR intergration.

### *Cyclotrimerization of ethyl propiolate*

Typically, 0.3 g of polymer-attached $CpRh(CO)_2$ (0.10 mmol Rh/g of beads) beads was introduced into a side-armed flask containing 5 ml of benzene under argon. After the mixture was stirred for about 10 min, 2.0 ml ethyl propiolate (1.91 g; 19.5 mmol) was injected and the reaction mixture was then heated at 80°C for 32 h. The color of solution gradually turned dark brown. After it was cooled to room temperature, 50 ml of benzene was introduced into the flask and after being stirred for several minute, the solution was drawn out by means of a syringe. The viscous oil, obtained by concentrating the brown solution under vacuum, was then extracted with 200 ml of a refluxing $CCl_4$/petroleum ether (1/4) mixture. The yellow extract was filtered and the solvents were removed under vacuum to give 70% products based on the weight of ethyl propiolate used. The relative amounts of 1,3,5-tricarbethoxybenzene and 1,2,4-tricarbethoxybenzene were measured by NMR integration.

### *Hydroformylation*

In a typical reaction, 0.1 g polymer-attached $CpRh(CO)_2$ catalyst (0.39

mmol Rh/g of beads) and 10 ml dry benzene were introduced into a 250 ml stainless steel autoclave. Following the addition of 2.0 ml 1-pentene (18.3 mmol) and the attachment of the head, the system was flushed three times with hydrogen and twice with carbon monoxide. The system was then pressurized to 14.6 atm with CO and heated to 110°C in an oil bath. After 40 min, during which the system achieved physical equilibrium, carbon monoxide and then hydrogen (1/1) were rapidly added to 69 atm and the autoclave was heated and stirred at 110°C for 3 h. During this period there was a 6.1 atm pressure drop. After being cooled to room temperature, the vessel was vented and the clear golden solution was drawn out by using a syringe.

A sample of the product was injected into the gas chromatograph with the column temperature at 40°C in order to separate the pentane reduction product from any unreacted 1-pentene. The column temperature was then increased to 90°C and the linear and branched hydroformylation products were separated. A column temperature of 130°C was used to verify that no higher boiling products-alcohols were obtained.

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