silicate, 65599-42-0; ((*E*)-2-phenylethenyl)pentafluorosilicate, 68901-41-7; (*E*)-1-hexenylpentafluorosilicate, 68732-24-1; 5-(5-decenyl)pentafluorosilicate, 70995-87-8; phenylpentafluorosilicate, 66712-45-6; dodecylpentafluorosilicate, 65599-40-8; (*exo*)-2-norbornylpentafluorosilicate, 74380-89-5; (*endo*)-2-norbornylpentafluorosilicate, 74410-83-6; (*E*)-octenylpentafluorosilicate, 70995-82-3; ((*E*)-10-(methoxycarbonyl)-1-decenyl)pentafluorosilicate, 70995-86-7; ((*E*)-3-(2-cyanoethoxy)propenyl)pentafluorosilicate, 74463-90-4; (*Z*)-5-decen-5-ylpentafluorosilicate, 70995-87-8; octyl bromide, 111-83-1; octyl chloride, 111-85-3; methyl 11-chloroundecanoate, 17696-12-7; 6-chloro-2-hexanone, 10226-30-9; 1-bromo-11-chloroundecane, 30295-21-7; 4-(2-chloroethyl)cyclohexene, 63540-00-1; 3-(3-bromopropoxy)prop-1-ene, 15424-07-4; 6-bromo-1-hexene, 2695-47-8; chlorocyclohexane, 542-18-7; (*E*)-1-chloro-2-phenylethene, 4110-77-4; (*E*)-1-bromo-2-phenylethene, 588-72-7; (*E*)-1-bromo-1-hexene, 13154-13-7; (*E*)-5-chloro-5-decene, 10124-72-8; (*E*)-5-bromo-5-decene, 72612-74-9; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; dodecyl chloride, 112-52-7; cyclohexyl bromide, 108-85-0; *exo*-2-norbornyl bromide, 2534-77-2; *endo*-2-norbornyl bromide, 13237-87-1; 2-dodecanone, 6175-49-1; 3-octylcyclohexanone, 57242-85-0; methyl 14-oxopentadecanoate, 54889-71-3; (*E*)-1-octenyl thiocyanate, 74458-26-7; (*E*)-2-phenylethenyl thiocyanate, 61807-26-9; (*E*)-10-(methoxycarbonyl)-1-decenyl thiocyanate, 74458-28-9; (*E*)-3-(2-cyanoethoxy)propenyl thiocyanate, 74458-27-8; (*E*)-5-thiocyanato-5-decene, 74458-29-0; phenyl thiocyanate, 103-72-0; 1-octenyl ethyl ether, 30989-68-5; (*E*)-1-methoxy-1-octene, 62427-06-9; (*E*)-1-isopropoxy-1-octene, 77149-61-2; (*E*)-1-*tert*-butoxy-1-octene, 79618-58-9; (*E*)-1-(allyloxy)-1-octene, 77149-62-3; (*E*)-1-[(*E*)-2-butenyloxy]-1-octene, 79618-59-0; (*E*)-1-(2-methyl-2-propenyloxy)-1-octene, 77149-64-5; (*E*)-1-methoxy-2-phenylethene, 4110-75-2; (*E*)-1-methoxy-10-(methoxycarbonyl)-1-decene, 77149-65-6; (*E*)-1-methoxy-6-cyano-4-oxahex-1-ene, 77149-66-7; (*E*)-5-methoxy-5-decene, 77149-67-8; octanal, 124-13-0; 10-(methoxycarbonyl)decanal, 1931-65-3; copper(II) chloride, 7447-39-4; copper(II) bromide, 7789-45-9; copper(II) acetate, 142-71-2; copper(I) chloride, 7758-89-6; copper(I) iodide, 7681-65-4; copper(II) thiocyanate, 15192-76-4; 3-buten-2-one, 78-94-4; 2-cyclohexenone, 930-68-7; (*E*)-1-ethoxy-1-octene, 77149-60-1; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; 2-methyl-2-propanol, 75-65-0; 2-propen-1-ol, 107-18-6; (*E*)-2-buten-1-ol, 504-61-0; 2-methyl-2-propen-1-ol, 513-42-8.

Poly(phenylene oxide) Catalyst Supports Containing (Cyclopentadiene)metal Complexes

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Poly(2,6-dimethyl-1,4-phenylene oxide) containing cyclopentadienyl ligands attached to the benzyl carbons was prepared by the reaction of cyclopentadienylsodium with polymer that had been brominated at the benzyl position. Cross-linking took place during the reaction through the cyclopentadiene group. The reaction of 2-norbornen-7-one with poly(2,6-diphenyl-1,4-phenylene oxide) lithiated at the 3-position gave the norbornen-7-ol derivative which was converted to the polymer-attached 7-chloronorbornene. Cyclopentadiene ligands were generated via a retro Diels–Alder reaction of the anion produced from the 7-chloronorbornene. These polymers were converted to polymer-bound cyclopentadienyldicarbonylcobalt, cyclopentadienyldicarbonylrhodium, and titanocene catalysts. The cobalt and rhodium complexes were effective hydroformylation catalysts while the immobilized titanocene hydrogenated cyclohexene 10–70 times faster than the homogeneous analogue.

Introduction

Because there are many advantages to be gained by binding homogeneous catalysts to solid supports, the chemistry of homogeneous catalysts attached to polymers has been the subject of considerable research activity.[1] Cross-linked polystyrene has been the favorite polymer support, primarily because it is available commercially in various bead sizes with varying degrees of cross-link density.

Polystyrene beads, however, are mechanically, chemically, and thermally unstable.[2,3] For example, macroporous styrene–divinylbenzene resins will slough off polymer, particularly in a solvent that swells the bead. In addition, the reduction of carbon monoxide to hydrocarbons (Fischer–Tropsch), the reduction of carbon monoxide to methanol, and the hydroformylation of olefins in which water is used as the hydrogen source (water gas shift) are reactions that require temperatures higher than those usually necessary in homogeneous catalysis and are above or near the ceiling temperature of polystyrene ($T_c \approx 150$ °C). Further, polystyrene has poor chemical stability and will not endure a number of catalytic processes such as oxidation or photochemical reactions.

Poly(phenylene oxides) are a class of thermally stable engineering plastics.[4] Although the *thermooxidative* stability of the 2,6-dimethyl-substituted polymer is lower than other thermally stable polymers, its thermal stability under a nonoxidizing atmosphere is good;[5] however, the 2,6-diphenyl polymer has excellent thermal and oxidative stability. Consequently, we have explored the attachment of cyclopentadiene ligands to poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2,6-diphenyl-1,4-phenylene oxide), the conversion of these cyclopentadiene sites to η^5-cyclopentadiene complexes with cobalt, rhodium, and titanium, and some of the catalytic reactions of these polymer-supported complexes.

Results and Discussion

Preparation of Poly(phenylene oxide)-Attached Cyclopentadiene Ligands. Cyclopentadiene has been chemically bonded to polystyrene either by the reaction of cyclopentadienyl sodium with chloromethylated polystyrene or by the reaction of cyclopentenone with lithiated

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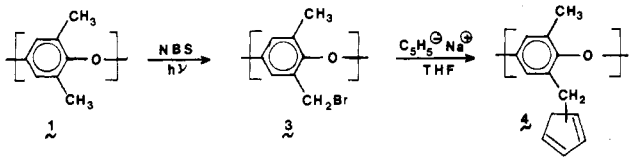
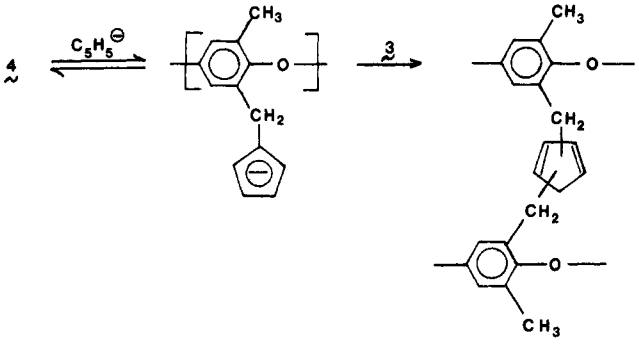
polystyrene followed by dehydration.[1] Poly(phenylene oxides) can be lithiated directly, and while lithiation of poly(2,6-diphenyl-1,4-phenylene oxide) takes place at the 3-position of the phenylene oxide unit,[6] lithiation of poly(2,6-dimethyl-1,4-phenylene oxide) is not as selective, taking place both at the 3-position and at the methyl group.[7] Although the reaction of sodium cyclopentadienide with halomethylated aromatics is a relatively clean reaction, the reaction of cyclopentenone with aryllithium is not.[8]

Bromination of the poly(phenylene oxides) is more selective and can be directed either to the phenylene oxide ring or to the benzyl positions.[9] Consequently, this reaction was chosen as an entry to substituted poly(phenylene oxides). This pathway also has the advantage that the degree of functionalization at the bromination stage could be determined readily. Free radical bromination of poly(2,6-dimethyl-1,4-phenylene oxide) (1) with *N*-



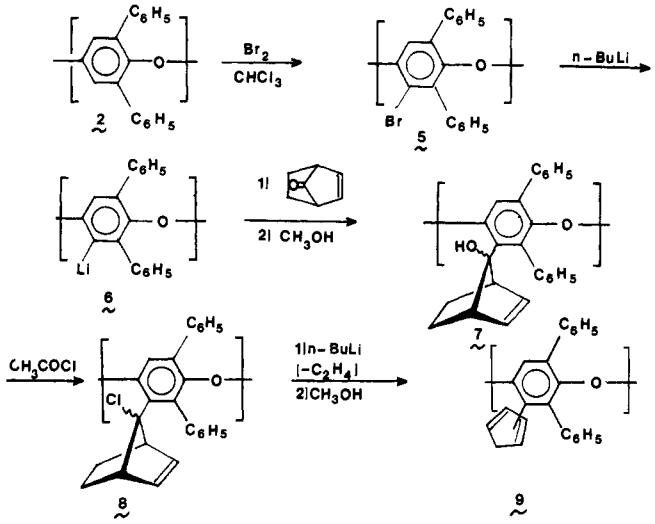
bromosuccinimide gave only the bromomethyl derivative (3) as confirmed by ^{1}H NMR. Products containing 0.17 and 0.35 bromine unit per repeat unit were obtained from 0.25 and 0.5 mol of *N*-bromosuccinimide per mole of recurring unit, respectively. The reaction of a solution of 3 with cyclopentadiene gave polymer 4 containing the



pendant cyclopentadiene groups. This reaction produced an insoluble polymer resulting from cross-linking that occurred either by a 4 + 2 dimerization reaction between cyclopentadiene units on two different chains or by alkylation of a second chain by an attached cyclopentadienyl anion. Analysis of the resulting polymer showed that 75% of the bromine had been displaced, even in the presence of excess cyclopentadienylsodium. Thus, in the case of polymer 3 containing 0.17 bromine unit per recurring unit, 0.04 bromine unit remained after the reaction, indicating 0.13 cyclopentadiene unit per polymer repeat unit. An incomplete reaction of cyclopentadienylsodium also has been observed with chloromethylated polystyrene.[10]

The presence of the pendant cyclopentadiene groups was difficult to verify by NMR or IR spectra of the insoluble polymer. The reaction of polymer 4 with maleic anhydride, however, produced a polymer containing the Diels–Alder adduct as shown by the strong carbonyl anhydride bands

Scheme I. Syntheses of Cyclopentadiene Derivatized Poly(2,6-diphenyl-1,4-phenylene oxide)



(1850 and 1775 cm^{-1}) in the infrared.

The electrophilic aromatic bromination of the 2,6-diphenyl-substituted polymer (2) was carried out in chloroform solution[9] to yield polymer 5 containing 0.18 bromine unit per repeat unit (Scheme I). Although bromination of the phenylene ether ring would be expected, it was not possible to distinguish the position(s) of bromination by NMR. Direct metalation of 2 with butyllithium yields polymer that had undergone reaction at the 3-position, although the maximum degree of lithiation was low even in the presence of a large excess of butyllithium.[6] Brominated polymer undergoes a more facile metalation with butyllithium, and the degree of lithiation can be more readily controlled.[9] Thus, the reaction of 5 with butyllithium gave the metalated polymer 6 which was allowed to react with 2-norbornen-7-one to yield polymer 7 containing the 7-attached 2-norbornen-7-ol unit.

The presence of norbornenol in the polymer was confirmed by the OH stretching in the infrared and by the characteristic vinyl and bridgehead proton absorptions in the ^{1}H NMR spectrum.[11] Less than 0.1% bromine remained in polymer 7. Chlorination of 7 with acetyl chloride gave polymer 8 containing 0.21 chlorine unit per repeat unit in which the OH stretching in the infrared was absent. Thus, the sequence of transformations, 5 through 8, appears to be quantitative.

Conversion of 8 to polymer 9 containing the cyclopentadiene pendants was achieved by reaction with butyllithium[8] to generate the benzyl anion which undergoes a retro Diels–Alder reaction with the evolution of ethylene.[12] Polymer 9 bearing the aryl cyclopentadiene ligands is soluble in a variety of solvents, indicating no cross-linking occurred during functionalization. Cyclopentadiene groups directly attached to the aromatic polymer backbone and sterically protected by the adjacent phenyl and phenoxide units apparently are prevented from undergoing an interchain Diels–Alder reaction.

Catalyst Preparation. Conversion of polymers 4 and 9 containing pendant cyclopentadiene ligands to supported catalysts corresponding to homogeneous complexes of cobalt, rhodium, and titanium was effected by methods used for the synthesis of the homogeneous analogues. In each case, only half the equivalent amount of transition metal

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Table I. Hydroformylation of 1-Octene with 10[a]

catalysts	loading mequiv of Co/ g of support	Co/Cp ratio[b]	molar ratio octene/Co	T, °C	t, h	selectivity linear/branch
10a	0.54	0.45	329	135	12	2.4
10a	1.09	0.62	252	135	24	1.5
recycled 10a				135	24	1.5
10a	1.09	0.62	448	170	1	1.6
10a	1.09	0.62	469	135	12	1.7
10b	0.30	0.37	898	135	12	1.3

[a] Conditions: 1500 psi of H_2/CO (1:1); 2 mL of 1-octene in 10 mL of benzene. 100% conversion was achieved in every run. [b] For catalyst **10a**, the amount of available cyclopentadiene (Cp) units was based on the loss of bromide in the conversion of **3** to **4**. For **10b**, the cyclopentadiene (Cp) content was based on the chlorine analysis of **8**.

per cyclopentadiene was allowed to react in order to ensure that all of the metal reacted and to allow for uncertainties in cyclopentadiene content. Both **4** and **9** reacted with dicobalt octacarbonyl to give gray catalysts (**10**), the infrared spectra of which exhibited two characteristic carbonyl bands at 2010 and 1950 cm^{-1}, close to the carbonyl frequencies observed for cyclopentadienyldicarbonylcobalt[13] (Scheme II). Polymer **4**, containing the higher concentration of cyclopentadiene groups per repeat unit, also exhibited low-intensity carbonyl stretching frequencies at 1900 and 1875 cm^{-1}, characteristic of bridging carbonyls and a cobalt dimer.

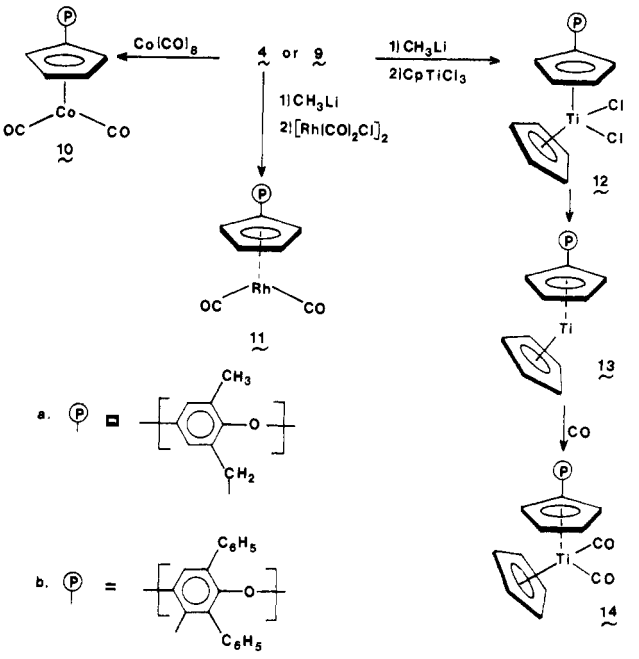
The reaction of the cyclopentadiene-containing polymers with methyllithium was used to generate the cyclopentadiene anion. The anion-bearing supports reacted with the chlorodicarbonylrhodium dimer to yield catalysts which exhibited two metal carbonyl bands. In the case of polymer **11a**, containing benzyl-attached cyclopentadienyl groups, the carbonyl stretching frequencies were 2030 and 1970 cm^{-1}, and in polymer **11b**, in which the cyclopentadienyl ligand is attached directly to the aromatic ring, frequencies of 2050 and 1955 cm^{-1} were observed. The reported[14] bands for (η^5-cyclopentadienyl)dicarbonylrhodium are 2051 and 1987 cm^{-1}.

Finally, polymers **4** and **9** were converted to the corresponding anions and allowed to react with cyclopentadienyltitanium trichloride. Polymer **12** was red-brown, a darker color being obtained with a higher degree of cyclopentadiene substitution. This polymer was converted to titanocene by reaction with butyllithium; reaction of the reduced complex with carbon monoxide gave polymer attached dicyclopentadienyltitanium dicarbonyl complexes[13] which exhibited two metal carbonyl bands in the infrared spectrum at 1955 and 1875 cm^{-1}.

Catalytic Reactions. Catalyst **10** showed no activity in a Fischer–Tropsch reaction. Although **10a** containing the benzyl-bound cyclopentadienyl group was not expected to be a catalyst,[15] **10b** containing a phenyl-bound cyclopentadienyl ligand also did not effect the reduction of carbon monoxide in a 3:1 H_2–CO mixture at 150 or 200 °C.[15] However, these polymer-bound complexes (**10**) did catalyze the hydroformylation of 1-octene to a mixture of linear and branched aldehydes at 135 °C and 1500 psi (Table I). This same type of catalyst bound to cross-linked polystyrene has been shown to catalyze the hydroformylation of 1-olefins.[16]

Insoluble catalyst **10a** could be readily recovered by filtration at the end of the hydroformylation reaction and reused without apparent decrease in the catalytic activity.

Scheme II. Catalysts from Cyclopentadiene Attached Poly(phenylene oxides)



Some broadening and a slight decrease in intensity of the carbonyl bands of the recovered catalyst were observed. In addition, at long reaction times the presence of a weak absorption at 1710 cm^{-1} was observed. Nevertheless, no carbonyl absorption assignable to hydridocobalt tetracarbonyl was observed as was detected in the final reaction mixture after a hydroformylation with the homogeneous analogue.[18] Hydroformylation using soluble **10b** was carried out by using homogeneous conditions; recovery of this catalyst could be achieved by precipitation into a nonsolvent, e.g., ether, followed by filtration.

Catalyst **11** also was effective for the hydroformylation of 1-octene. Under the same reaction conditions as reported for hydroformylation with the similar polystyrene attached cyclopentadienyldicarbonylrhodium,[16,17] complete conversion to the isomeric aldehydes was achieved (Table II).

No attempt was made to optimize the reaction conditions or increase the selectivity to linear aldehyde, which has been shown to be dependent on temperature and pressure.[18] While there was no change in the infrared carbonyl band of catalyst **11a**, the carbonyl absorption for polymer **11b** disappeared after several runs, consistent with the loss of catalyst activity observed with recycled **10b**. At

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Table II. Hydroformylation of 1-Octene with 11[a]

catalyst	loading: mequiv of Rh/ g of support	loading: Rh/Cp ratio[b]	solvent	molar ratio substrate/Rh	selectivity linear/branch
11a	0.55	0.57	C_6H_6	258	0.6
recycled 11a			C_6H_6		1.3
11b	0.46	0.59	n-C_6H_{14}	771	1.2
recycled 11b			n-C_6H_{14}		1.5[c]

[a] Conditions: 1000 psi of H_2/CO (1:1); 50 °C; 24 h. [b] For catalyst 11a, the amount of available cyclopentadiene (Cp) units was based on the loss of bromide in the conversion of 3 to 4. For 11b, the cyclopentadiene (Cp) content was based on the chlorine analysis of 8. [c] Only a 68% conversion of 1-octene to aldehyde was achieved.

Table III. Hydrogenation of Cyclohexene with Polymer Attached Titanocene Catalyst 13

catalyst	loading: mequiv of Ti/ g of polymer	loading: Ti/Cp[b] ratio	hydrogenation rate: relative rate, n-hexane, 25 °C (mequiv of Ti)	hydrogenation rate: mPH_2/min/mequiv of Ti, n-octane, 0 °C (mequiv of Ti)
13a	0.57	0.40	70 (0.057)	71 (0.042)
	0.86	0.30	52 (0.086)	39 (0.042)
13b	0.11	0.13	53 (0.022)	39 (0.016)
Cp_2Ti	0.10	0.5	3.7 (0.22)	<1

[a] Catalyst/solvent (10 mL)/n-BuLi (1 mL, 2.5 min in hexane)/cyclohexane (1 mL). [b] For 13a, the amount of available cyclopentadiene (Cp) units was based on the loss of bromide in the conversion of 3 to 4. For 13b, the cyclopentadiene (Cp) content was based on the chlorine analysis of 8.

long reaction times (90 h) and at a higher temperature (100 °C) both catalysts **10a** and **10b** reduced nonanal to n-nonanol giving a 1:9 mixture of aldehyde to alcohol.

Reduction of poly(phenylene oxide)-bound titanocene dichloride (**12**) with butyllithium gave the polymer-supported titanocene catalyst (**13**) containing isolated catalytic sites. Hydrogenation of cyclohexene was effected under conditions described[10,19] for polystyrene-bound titanocene (Table III). Although the reported hydrogenation rates differ depending on the polymer support, the degree of crosslinking, and the physical state of the heterogenized catalyst, the rate of hydrogenation is 10–70 times faster with the poly(phenylene oxide)-supported catalyst than with the homogeneous titanocene. The fact that the rate of hydrogenation increased when better site isolation was provided (**13a**, lower mmol of Ti/g of polymer) supports the necessity for preventing catalyst site interaction. Even uncross-linked polymer **13b** maintained as much as a 40-fold activity over homogeneous titanocene. The enhanced activity in this case may be due to the steric protection of the titanocene sites.

Experimental Section

All manipulations involving air-sensitive compounds were performed under argon in Schlenk-type vessels. Transfers and filtrations were carried out in an argon-filled glovebox. Recovery of the soluble polymer-bound catalyst was facilitated by precipitation of the polymers into ether and suction filtration through a fritted filter; insoluble polymer-bound catalysts were recovered simply by suction filtration of the reaction mixture.

Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer; KBr pellets of the samples were prepared in a drybox. GLC was carried out on columns consisting of SE30 or Carbowax 2017 on Chromosorb W.

Elemental analyses were performed by Micro Tech Laboratories, Inc., Skokie, IL, and Galbraith Laboratories, Inc., Knoxville, TN. All solvents were purified and dried by usual procedures. Poly(phenylene oxides) were obtained from General Electric Co., Schnectady, NY. Dicobalt octacarbonyl, chlorodicarbonylrhodium, bis(cyclopentadienyltitanium dichloride), cyclopentadienyltitanium trichloride, and organolithium reagents were obtained commercially.

Bromination of Poly(2,6-dimethyl-1,4-phenylene oxide) (1). To a refluxing solution of 50 g (0.42 mol of repeating unit) of polymer **1** in 500 mL of carbon tetrachloride (the complete dissolution of polymer needed 4 h in stirred, refluxing carbon tetrachloride) was added 18 g (0.10 mole) of freshly recrystallized N-bromosuccinimide over a 10-min period while the solution was irradiated with a 100-W flood lamp at a distance of 10 cm. After 1 h, the mixture was filtered to remove the succinimide. The filtrate was added dropwise to methanol. After filtering, the precipitated polymer was ground vigorously in a blender and washed thoroughly with methanol. The recovered brominated polymer (**3**), dried under reduced pressure, contained 10.43% of bromine, indicating 17% of the repeating units had been brominated. With twice as much N-bromosuccinimide (36 g, 0.20 mol) and the same conditions, the resulting polymer contained 18.84% of bromine (~0.35 Br/unit): ^{1}H NMR ($CDCl_3$) δ 2.05 (CH_3), 4.3 ($-CH_2Br$), 6.45, and 6.65 (aromatic).

Bromination of Poly(2,6-diphenyl-1,4-phenylene oxide) (2). A solution of 25 g (0.10 mol of repeating unit) of polymer **2** in 150 mL of chloroform was added to a solution of 4 g (0.02 mol) of bromine in 10 mL of chloroform. The mixture was heated to a gentle reflux and after 30 min allowed to cool to room temperature. Stirring was continued overnight. The polymer was precipitated into methanol, ground vigorously in a blender, and washed thoroughly with methanol. After being dried under reduced pressure, **5** contained 5.44% Br (~0.18 Br/unit): ^{1}H NMR ($CDCl_3$) δ 5.9, 6.15, and 6.3 (aromatic protons).

Reaction of Sodium Cyclopentadienide with Brominated Poly(2,6-dimethyl-1,4-phenylene oxide) (3). Under an argon atmosphere, 100 mL of dry THF was distilled directly into a flask containing 5 g of brominated polymer **3** (10.43% Br/g). Into this solution, cooled by an ice bath, was syringed 5 mL of a 2.5 M THF solution of freshly prepared cyclopentadienyl sodium.[20] The solution immediately became dark red and very thick. After 3 h of stirring, the red solution was allowed to warm to room temperature. The mixture was poured into 200 mL of deaerated methanol. The precipitated brown polymer (**4**) was filtered, washed with methanol, and dried under reduced pressure for 3 days. The resulting polymer contained 2.70% Br/g (0.04 Br/unit).

Attachment of Cyclopentadiene to Poly(2,6-diphenyl-1,4-phenylene oxide). Reaction of Norbornen-7-one with Lithiated Polymer 6. Into a flask containing 4 g of brominated polymer **5** (5.4% Br/g) was distilled 100 mL of dry THF under

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argon. The stirred yellow solution was cooled to −70 °C and 2 mL of a 2.5 M hexane solution of *n*-butyllithium was added via syringe. After 2 h, 0.70 g (6.4 mmol) of norbornen-7-one[21] was distilled into the reaction mixture at −70 °C. After 1 h, the flask was allowed to warm to room temperature. The mixture was stirred overnight and then poured into deaerated methanol. The precipitated polymer (**7**) was then stirred overnight in methanol, filtered, ground, washed for 24 h in methanol, and then dried: Ir (KBr) 3560 cm^{-1} (–OH stretch); ^1H NMR ($CDCl_3$) δ 5.2, 5.1 (vinyl), 2.8 (bridgehead), 2.2 (H, alcohol), 1.4, 1.2, 0.5 (CH_2). Anal.: <0.1% Br.

Preparation of Polymer-Attached 7-Chloronorbornene (8). Under argon, 60 mL of dried THF was distilled directly into the reaction flask containing 3 g of polymer **7**. To this solution was added 0.80 mL (11 mmol) of acetyl chloride. After being stirred for 48 h, the yellow solution was poured into anhydrous diethyl ether to precipitate a white polymer. After filtration, the polymer was ground, washed with pentane, and dried under reduced pressure. Anal.: 2.78% Cl (0.21 Cl/repeat unit).

Preparation of Polymer-Attached Cyclopentadiene (9). Dry THF, 60 mL, was distilled directly in the reaction flask containing 2 g of polymer **8** containing the attached 7-chloronorbornene units. A solution of 2 mL of 0.25 M *n*-butyllithium in *n*-hexane was added, and the mixture was cooled to −70 °C. The color of the solution turned from yellow to dark red. After 1 h the mixture was allowed to warm to room temperature and then poured into deaerated methanol. The white polymer which precipitated was filtered, washed with methanol, and dried under reduced pressure. Anal.: 0.11% Cl.

Polymer-Supported Cyclopentadienylcobalt Carbonyl Catalysts (10). In a typical experiment, 0.4 g (0.4 mmol of cyclopentadiene for **4**; 0.3 mmol of cyclopentadiene for **9**) of polymer containing attached cyclopentadiene units was allowed to swell (or dissolve in the case of **9**) in methylene chloride (60 mL). Under argon, a solution of 0.40 g (1.2 mmol) of dicobalt octacarbonyl in 10 mL of methylene chloride was added. The black mixture, protected from the light, was stirred at room temperature for 72 h and then poured into a dried deaerated hexane/diethyl ether mixture. The gray precipitate was filtered, washed with ether, and dried under reduced pressure: IR (KBr) 2010, 1950 cm^{-1} (C≡O).

Polymer-Supported Cyclopentadienylrhodium Dicarbonyl (11). In a typical experiment 0.2 g (0.2 mmol of cyclopentadiene for **4**; 0.15 mmol of cyclopentadiene for **9**) of polymer containing attached cyclopentadiene units was suspended in anhydrous diethyl ether cooled to −70 °C, and 0.4 mL of a 1.2 M methyllithium solution in ether was added. The mixture was allowed to warm to room temperature and was stirred for 72 h under argon. The polymer was recovered by filtration and washed under argon with ether. After being dried, the polymer was suspended in 20 mL of hexane that was directly distilled into the reaction flask. A yellow solution of 0.031 g (0.080 mmol) of $[(Rh(CO)_2Cl]_2$ in 10 mL of hexane was added to the polymer suspension at −70 °C. The yellow suspension became orange and then was allowed to warm to 0 °C during which the suspension became dark red and then gray. The suspension was kept for 24 h at 0 °C and then filtered. The gray solid recovered was washed with hexane until the washings were colorless. The polymer was dried under reduced pressure: IR (KBr) 2030, 1970 cm^{-1} (C≡O) (**11a**) and 2050, 1995 cm^{-1} (**11b**).

Preparation of Polymer-Attached Titanocene Dichloride (12). In a typical experiment 1 g (1.0 mmol of cyclopentadiene for **4** and 0.15 mmol of cyclopentadiene for **9**) was suspended in 80 mL of diethyl ether that had been directly distilled into the reaction flask. After the suspension was cooled to −70 °C, 2 mL of a 1.2 M methyllithium solution in ether was added and after 1 h the mixture was allowed to warm to room temperature. Stirring was continued for 5 days. The polymer was filtered, washed, and dried. To 0.8 g of the polymer-supported cyclopentadienide anion, swollen (or dissolved in the case of **9**) in 60 mL of benzene, was added 0.3 g (1.4 mmol) of cyclopentadienyltitanium trichloride dissolved in benzene. After 5 days the polymer was washed with ether (or precipitated into ether, polymer **9**) and dried. A red brown product was obtained.

Preparation of Attached Dicyclopentadienyltitanium Dicarbonyl (14). To a suspension of 0.2 g (0.2 mmol titanium) of polymer attached dichlorotitanocene **12** suspended in 40 mL of hexane and cooled to −70 °C was added 0.75 mL of 2.5 M *n*-butyllithium in hexane. The mixture was allowed to warm to room temperature and after 3 h was transferred to a 100-mL Parr reactor. The reactor was purged with carbon monoxide and then left for 12 h at room temperature with a carbon monoxide pressure of 1100 psi. After release of the pressure, the brown polymer was filtered, washed with 200 mL of hexane, and dried under reduced pressure: Ir (KBr) 1955, 1872 cm^{-1} (C≡O).

Hydroformylation Reactions with Rhodium and Cobalt Catalysts 10 and 11 (Tables I and II). To a 100-mL reactor containing the rhodium catalyst **11** or the cobalt catalyst **10** suspended in 10 mL of benzene or hexane was added 2.0 mL (13 mmol) of 1-octene. The mixture was stirred for 15 min under a hydrogen pressure of 500 psi and, after release of the pressure, for another 15 min under a carbon monoxide pressure of 500 psi. After release of the gas, the reactor was repressurized to 100 psi with a mixture of H_2/CO (1:1) and heated to 50 °C for 24 h. The reactor was cooled to −70 °C, and the pressure was released slowly. At room temperature, the reactor was flushed with argon and the brown-gray suspension was filtered. The recovered polymer-bound catalyst was washed and dried overnight before being reused. The branched and linear aldehydes were characterized by GC analysis of the filtrate. The linear to branched aldehyde ratio was directly determined from the ^1H NMR spectrum of the filtrate when the solvent was hexane and by GC analysis when the solvent was benzene.

Hydrogenation of Aldehyde with Rhodium Catalyst 11. A 100-mL reactor was charged with polymer-bound catalyst **11**, 10 mL of benzene or hexane, and 2 mL (12 mmol) of freshly distilled 1-nonanal. The bomb was flushed with hydrogen, then pressurized to 1000 psi of hydrogen, and finally heated at 100 °C for 86 h. After release of the pressure, the reactor was cooled to −78 °C, the reaction mixture was filtered, the catalyst was washed and dried, and the filtrate was examined by GC and ^1H NMR.

Hydrogenation with Titanium Catalyst 13 (Table III). In a typical experiment, 0.2 g of polymer-bound catalyst **12** was suspended in 10 mL of hexane (or octane) under argon. The flask was flushed with hydrogen and left under 1 atm of hydrogen. The flask was cooled to 0 °C, and 1 mL of a 2.5 M *n*-butyllithium solution in hexane was added. The mixture was allowed to warm to room temperature (or kept at 0 °C), and when the level of hydrogen in a gas delivery apparatus connected to the reaction flask had stabilized, 1 mL of cyclohexene, which was freshly distilled under argon, was added. The rate of hydrogen uptake was determined by monitoring the level in the gas delivery apparatus.

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Registry No. 1 homopolymer, 25134-01-4; 1 repeating unit, 24938-67-8; 2 homopolymer, 26353-84-4; 2 repeating unit, 24938-68-9; sodium cyclopentadienide, 4984-82-1; norbornen-7-one, 694-71-3; dicobalt octacarbonyl, 10210-68-1; cyclopentadienyltitanium trichloride, 1270-98-0; 1-nonanal, 124-19-6; 1-octene, 111-66-0; cyclohexene, 110-83-8; Cp_2Ti, 1271-29-0; $[(Rh(CO)_2Cl]_2$, 14523-22-9.

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