temperature range used, but separation of the effects ascribed to each component was not possible. The total enthalpy change measured is 25.9 ± 1.5 J/g of sample where the reported error is the average deviation of the runs performed. This result was converted to 11.6 ± 0.8 kcal/mol of adsorbed substance both by using an average mole mass for pyridine and cyclohexane of 81.5 g/mol and by using the initial composition of the sample as prepared with no appreciable difference in result.

Furthermore, blank determinations were used on the PdO/C catalyst to check for any other processes which might have occurred, and these were subtracted as background (the effect was negligible).

An interesting feature of the TGA is observed if the temperature rise is interrupted during the run and the temperature held constant. The weight loss also stops quickly, which is somewhat unusual in this type of run. Subsequent temperature increase results in more weight loss. This implies extremely rapid equilibration during the desorption–adsorption process and is not inconsistent with desorption from activated carbon itself. Both DSC and TGA results are consistent with a multiple-site model for PdO.

Conclusion

In summary, the thermodynamic data for adsorption of base from a solvent onto a metallic crystallite supported on carbon powder were obtained from our work. The results show unequivocally the multiple-site character of the palladium oxide crystallites. It also shows that there is a preferential adsorption of base onto the palladium oxide surface in spite of the good adsorbing power of the carbon support. Our adsorption method provides more resolution of the two sites than TGA and a more accurate value for the binding enthalpy than DSC because of the multiple processes observed. The calorimetric titration procedure and data analysis reported in this paper can be extended to other heterogeneous catalysts.

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Polyethylene-Bound Rhodium(I) Hydrogenation Catalysts

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Abstract: Homogeneous, recoverable hydrogenation catalysts were prepared with use of functionalized ethylene oligomers as ligands. Phosphine groups were introduced onto ethylene oligomers following anionic oligomerization of ethylene. The product polyethylenediphenylphosphine ligands were then exchanged with triphenylphosphine or ethylene ligands to prepare ethylene oligomer ligated rhodium(I) complexes. These Rh(I) complexes had the solubility of polyethylene and dissolved at 90–110 °C in hydrocarbon solvents but quantitatively precipitated at 25 °C. Less than 0.1% of the charged rhodium was lost in each dissolution precipitation cycle. The rhodium(I) complexes so prepared were shown to have about 80% of the activity of tris(triphenylphosphine)rhodium chloride in hydrogenation of various alkenes including 1-octene, Δ^2-cholestene, cyclooctene, cyclododecene, styrene, and α-methylstyrene. ^{31}P NMR spectroscopy and reactivity studies were used to characterize these catalysts.

Wilkinson's catalyst is one of the most reliable and widely used transition-metal catalysts in laboratory-scale catalytic hydrogenation reactions.[1] Versions of this catalyst were also among the first to be "immobilized" on insoluble cross-linked polymers.[2] Recently we have described soluble, polyethylene-bound catalysts and reagents.[3-6] Here we describe in detail the preparation and use of a polyethylene-bound analogue of Wilkinson's catalyst.

While homogeneous catalysts are desirable because of their high activity and selectivity, separation of a homogeneous catalyst from the products of reaction and/or recovery of the catalyst (and ligand) are inherent problems with conventional soluble catalysts. In small scale laboratory reactions, catalyst recovery can be ignored. In other cases, distillation can be used to separate volatile products from a catalyst. While each of these strategies works in some circumstances, efforts have continued to develop general strategies to separate and recover homogeneous catalysts at a reaction's end. Solutions to this separation problem with use of water-soluble hydrogenation catalysts and catalysts bound to insoluble gel-type polymers have been described.[2,7] While these approaches are conceptually attractive, each in practice has some limitations. These approaches depend on the differences between the solid polymeric phase or an aqueous solution phase and the organic solution of product at the reaction's end to recover the catalyst and to separate it from the reaction product. The disadvantages of either of these approaches largely arise from problems encountered because of the needless but unavoidable phase difference which also exists *during* the reaction in each of these cases.[8] Here we describe an alternative, general strategy using the temperature-dependent solubility properties of polyethylene to prepare catalyst ligands which are soluble during a reaction yet insoluble at a reaction's end. The semicrystalline nature of polyethylene which makes it insoluble at room temperature in all solvents[9] but soluble at elevated temperatures

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provides the desired separation at 25 °C but permits a homogeneous solution to form at 90–110 °C.

Results and Discussion

Terminally functionalized ethylene oligomers are available by anionic oligomerization of ethylene or by polymerization of butadiene followed by hydrogenation of the residual double bonds.[10] For our purposes, we have found that anionic oligomerization of ethylene is a convenient method to prepare modest (ca. 10–15 g) quantities of terminally functionalized ethylene oligomers. Because the living ends of such oligomers have reactivity like that of an organolithium reagent, many different types of functional groups can be introduced onto such oligomers. For example, in order to prepare polyethylene ligands for rhodium(I) hydrogenation catalysts, we needed to introduce terminal phosphine groups. By using the chemistry shown in reactions 1 and 2, it is possible to introduce both triarylphosphine and alkyldiphenylphosphine ligands at the terminus of an ethylene oligomer. However, while (polyethylenephenyl)diphenylphosphine can be prepared, quenching a living ethylene oligomer with chlorodiphenylphosphine is a more direct route to an oligomeric phosphine ligand. Alkyldiphenylphosphinated ethylene oligomers prepared in this latter fashion have been used in all the studies described in this paper.

$$\mathrm{CH_2{=}CH_2} \xrightarrow[\text{TMEDA}]{n\text{-}\mathrm{C_4H_9Li}} \underset{\mathbf{1}}{\mathrm{-(CH_2CH_2)}_n\mathrm{-CH_2CH_2Li}} \xrightarrow{\mathrm{BrCH_2C_6H_4Br}}$$

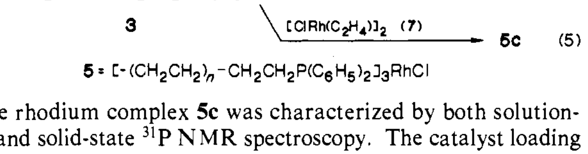
$$\mathrm{-(CH_2CH_2)}_n\mathrm{-CH_2CH_2CH_2C_6H_4Br} \xrightarrow{\mathrm{LiP(C_6H_5)_2}}$$

$$\underset{\mathbf{2}}{\mathrm{-(CH_2CH_2)}_n\mathrm{-CH_2CH_2CH_2C_6H_4P(C_6H_5)_2}} \quad (1)$$

$$\mathrm{CH_2{=}CH_2} \xrightarrow[\text{TMEDA}]{n\text{-}\mathrm{C_4H_9Li}} \underset{\mathbf{1}}{\mathrm{-(CH_2CH_2)}_n\mathrm{-CH_2CH_2Li}} \xrightarrow{\mathrm{ClP(C_6H_5)_2}}$$

$$\underset{\mathbf{3}}{\mathrm{-(CH_2CH_2)}_n\mathrm{-CH_2CH_2P(C_6H_5)_2}} \quad (2)$$

Rhodium catalysts were prepared in three different ways from oligomeric phosphine ligands like **3**. Simple exchange of the polyethylenediphenylphosphine ligand with a triphenylphosphine ligand of **4**, addition of **3** to a chlororhodium–(ethylene)triphenylphosphine complex, or addition of **3** to the dimer **7** all yielded catalysts of comparable activity. In some cases where **5a** or **5b** was prepared by the exchange reactions shown in eq 3 or 4, the initially isolated catalyst's activity increased as much as 20% during the first 3–4 cycles in hydrogenation of 1-octene. The catalyst's activity, however, never surpassed that of **5c** prepared by eq 5. This slight change in activity may have been due to formation of a mixed oligomer phosphine–(triphenylphosphine)rhodium complex which lost more triphenylphosphine in each entrapment step until a triphenylphosphine-free catalyst complex eventually formed.



The rhodium complex **5c** was characterized by both solution-state and solid-state ^{31}P NMR spectroscopy. The catalyst loading was measured by ICP analysis for rhodium. A typical catalyst prepared from diphenylphosphinated ethylene oligomer of M_v of 2400 had a loading of 0.08 mmol of Rh per g of polymer. Up to 0.4 g of this catalyst could be dissolved in 5 mL of solvent at 100 °C to yield a 6×10^{-2} M solution of catalyst. Hydrogenations were typically carried out with 10^{-3} M solutions.

^{31}P NMR spectra of **5c** at 100 °C in xylene showed a single broad peak at δ 29. A model for this oligomerically ligated catalyst, tris(octadecyldiphenylphosphine)chlororhodium (**8**), also had a single broad peak in its ^{31}P NMR spectrum at 100 °C at δ 29. At 30 °C, the ^{31}P NMR spectrum of **8** was a doublet of triplets centered at δ 42 and a doublet of doublets centered at δ 25. The $J_{\text{P-Rh}}$ for the trans phosphines was 189 Hz and the $J_{\text{P-Rh}}$ for the cis phosphines was 140 Hz. The $J_{\text{P-P}}$ was 40 Hz. These data are consistent with the expected square-planar structure for this complex.[11] The broadened singlet seen at 100 °C for both **5c** and **8** is due to exchange of phosphine ligands around the rhodium. Addition of triphenylphosphine to solutions of **5c** or **8** at 100 °C led to the appearance of a second peak at δ −2.8. The absence of this second peak in spectra of **5a** or **5b** after 3–4 hydrogenation reactions suggested no triphenylphosphine was present in any samples of **5** regardless of the route used to prepare these complexes. Solid-state ^{31}NMR spectra of **5c** as a polyethylene dispersion showed a broad peak at δ 35 which appeared to consist of two poorly resolved broad peaks at δ 28 and 40. A much smaller broad peak was present at δ 60. No Rh–P or P–P couplings were resolved in these spectra. No free **3** (δ −17) was seen in these solid-state ^{31}P NMR spectra although some phosphine oxide (δ 30) was present as a sharp peak in some samples. Catalyst **5c** which had been used 10 times in hydrogenation of 1-octene had a solid-state ^{31}P NMR spectrum which was essentially unchanged from that of fresh **5**. The only difference in the ^{31}P NMR spectrum of the used catalyst was a slightly larger (ca. 10%) signal for polyethylenediphenylphosphine oxide. The fact that none of the ^{31}P NMR spectra contained signals for uncomplexed **3** either initially or after 10 hydrogenations is evidence that **5** did not extensively decompose to form Rh(0). If a significant amount of decomposition to form Rh(0) had occurred, we should have seen large increases in the amount of the oligomeric phosphine oxide present, the presence of uncomplexed **3**, or a different spectrum for the used catalyst **5** (vide infra). It is likely that these catalysts in the absence of hydrogen or substrate were a mixture of the tris phosphine complex and the dimer of the bis phosphine complex. The unresolved P–Rh coupling in the solid-state spectrum and the line width of the ^{31}P NMR resonances in this spectrum prevent us from obtaining a more detailed structure of the polyethylene-bound catalyst. We cannot exclude the possibility that the solid dispersion isolated from an hydrogenation contains other rhodium complexes like those presumed to be intermediates in the hydrogenation.

Our use of the oligomeric ligand **3** in the preparation of catalysts like **5** was based on the idea that these ligands at 100 °C would behave in the same way as a low molecular weight phosphine ligand. While the catalytic reactions discussed below provide convincing evidence of this, we also examined the T_1 values for **3** and octadecyldiphenylphosphine (**9**) to see if the phosphine group in these oligomers has the same steric and electronic environment as a similar phosphine group in **9**. Previously Stille had reported that the T_1's for the phosphine groups ligands attached to 2% DVB cross-linked polystyrene were an order of magnitude higher than T_1 values for similar phosphine ligands in solution.[12] In contrast, the T_1 values for **3** and **9** were 5 and 8 s, respectively. These values are quite comparable and support the idea that the oligomeric ligands are good analogues of conventional ligands. Under the conditions used in these reactions (toluene or xylene, 100 °C), these macromolecular ligands surrounding the rhodium should exist as solvent expanded random coils. However, the $\langle r^2\rangle_0^{1/2}$ value would not be any larger than 100 Å because these oligomers are relatively small. While the size of these ligands does not affect the reactivity of **5** toward homogeneous substrates, the macromolecular nature of **5** does affect the reactivity of **5** toward heterogeneous substrates (vide infra).[4]

Initially, hydrogenation of 1-octene was carried out in xylene in the presence of the polyethylenediphenylphosphine–rhodium(I) complex at 100 °C and ca. 1 atm of H_2. The hydrogenations were

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Table I. Hydrogenation of 1-Octene by Ethylene Oligomer-Bound Rhodium(I) Hydrogenation Catalyst **5c**[a]

catalyst[b]	cycle no.	rate[c]	conversion,[d] %
$(PE-PPh_2)_3RhCl$ (**5c**)	1	98	98
	2	102	98
	3	100	98
	4	96	95
	5	101	98
	6	96	95
	7	100	98
	8	102	98
	9	100	98
	10	98	96
	18[e]	90	87
$(C_{18}H_{37}PPh_2)_3RhCl$		123	100
$(PPh_3)_3RhCl$		190	100
$[PS-PPh_2]_xRhCl$		5	25

[a] Hydrogenation reactions were carried out at 100 ± 2 °C in *p*-xylene (10 mL) with 0.6 mmol of alkene and 0.06 mmol of Rh catalyst. [b] PE and PS refer to ethylene oligomers ($\bar{M}_v$, 1800) and 2% DVB cross-linked polystyrene, respectively. [c] Rate is expressed as mmol of H_2/mmol of Rh per h. [d] The reactions were allowed to run for 12 h and analyzed by GC. [e] A total of 218 mmol of 1-octene was hydrogenated with 1 mmol of **5c** as a catalyst. Similar turnover numbers were obtained with catalyst **5a**.

Table II. Hydrogenation Rates of Various Alkenes with Fresh Ethylene Oligomer-Ligated Rh Catalyst **5**[a]

alkene	rate[b,c]	relative[d] rate	conversion[e] (%)
1-octene	102 (190)	1.0 (0.53)	97 (100)
styrene	150	1.5	100
α-methylstyrene	80 (90)	0.78 (0.83)	90 (96)
cyclooctene	90 (115)	0.88 (0.77)	95 (100)
cyclododecene[f]	70	0.7	90
Δ^2-cholestene	80 (110)	0.78 (0.71)	93 (100)

[a] Hydrogenation reactions were carried out at 100 ± 2 °C in *p*-xylene (10 mL) with 0.6 mmol of alkene and 0.06 mmol of Rh catalyst. [b] Rate is expressed as mmol of H_2/mmol of Rh per h. [c] The rate of hydrogenation with $ClRh(PPh)_3$ as the catalyst is shown in parentheses. [d] The relative rate with respect to $ClRh(PPh)_3$ as catalyst for the same alkene is shown in parentheses. [e] The reactions were allowed to run for 12 h and analyzed by GC. The yield in parentheses is the yield with $ClRh(PPh_3)_3$ under the same conditions. [f] This alkene was >95% trans.

conducted under pseudo-first-order conditions, and the rates measured were the initial reaction rates which were the maximum rates observed. The hydrogenations were allowed to proceed for at least 24 h before the reaction mixture was cooled and the catalyst was recovered by filtration. No elaborate precautions were taken during the recovery of the catalyst other than using oxygen-free solvents. The recovered catalyst was reused over 18 hydrogenation cycles of 1-octene without substantial loss of activity (Table I). The maximum rate observed for the polyethylene-based catalyst was 54% that of Wilkinson's catalyst and 83% of that observed for $[C_{18}H_{37}P(Ph)_2]_3RhCl$ under the same conditions (100 °C in *p*-xylene) for 1-octene. These rates were more than an order of magnitude higher than the rate obtained with a rhodium catalyst ligated to an insoluble diphenylphosphinated 2% DVB cross-linked polystyrene prepared in our laboratory or purchased from commercial sources.

Various other alkenes differing in the steric environment around the carbon-carbon double bond were also hydrogenated in the presence of this ethylene oligomer ligated rhodium catalyst (Table II). In general, **5** was about 80% as active as Wilkinson's complex. The general order of reactivity was similar to that reported for Wilkinson's catalyst.[14] For example, monosubstituted olefins such as 1-octene and styrene were more reactive than substituted olefins such as cyclooctene and α-methylstyrene, respectively. α,β-Unsaturated alkenes such as cyclohexenone were unreactive. The rates of hydrogenation with the polyethylene ligated rhodium catalyst in the examples in Table II were comparable to those of Wilkinson's catalyst and much higher than the rates obtainable with a similar catalyst ligated to DVB cross-linked polystyrene. Comparison of the rates for hydrogenation of cyclooctene, cyclododecene, and Δ^2-cholestene in Table II shows that while a diphenylphosphinated ethylene oligomer ligated hydrogenation catalyst did exhibit significant rate differences based on olefin's degree of substitution, disubstituted olefins of different molecular size were hydrogenated at similar rate. Catalysts bonded to insoluble gel-type polymers differ in this respect since they discriminate between molecules both on the basis of intrinsic reactivity and on the basis of molecular size.[15] It seems reasonable to suppose that the primary factor responsible for the lack of size dependent reactivity was the homogeneity of the polyethylene ligated rhodium catalyst under the reaction conditions.

Table III. Hydrogenation Rates of Various Alkenes with "Used" Ethylene Oligomer-Ligated Rh Catalyst[a]

alkene	rate[b]	relative rate	conversion,[c] %
1-octene	95	1.0	95
styrene	87	0.91	92
α-methylstyrene	68	0.71	84
cyclooctene	75	0.8	90
cyclododecene[d]	60	0.63	81

[a] Hydrogenation reactions were carried out at 100 ± 2 °C in *p*-xylene (10 mL) with 0.6 mmol of alkene and oligomer-bound Rh catalyst that was recovered after 12 hydrogenation cycles and had been stored for 4 months in a desiccator. [b] Rate is expressed as mmol of H_2/mmol of Rh per h. [c] The reactions were allowed to run for 12 h and analyzed by GC. [d] This alkene was >95% trans.

Ethylene oligomer entrapped rhodium catalyst recovered after twelve recycles in the hydrogenation of 1-octene was also used after about 4 months of storage and exposure to air in a desiccator to hydrogenate other olefins. The hydrogenation rates using this "used" catalyst are shown in Table III. A comparison of the activity of the fresh catalyst and the "used" catalyst (Tables II and III) suggests that the ethylene entrapped hydrogenation catalyst system retains most of its activity even after several recycles and does not deteriorate much even after prolonged storage.

The high retention of activity over several recycles indicates that there is no significant loss of the active metal in recycling this catalyst.[16] This was confirmed by analysis of the filtrates for rhodium. Less than 0.1% of initially charged rhodium was lost to solution in the first recycle in the hydrogenation of 1-octene, based on inductively coupled plasma atomic emission spectroscopic analysis (see Experimental Section).

The solutions of the ethylene oligomer catalysts **5** during hydrogenation were visually homogeneous. However, it is known that the active metal species in a homogeneous catalytic reaction is not always what is expected. Recently Collman[17] and others[18] have emphasized this point showing that some homogeneous reactions may involve colloidal metal particles. Further, we observed darkening of the solutions of **5** during repeated use (suggesting formation of colloidal Rh(0)). Thus, it was of interest to determine if the catalyst after 10–12 cycles was still an analogue of Wilkinson's catalyst.

The results presented above provide some evidence that "used" **5** was still a homogeneous Rh-phosphine complex. Specifically, comparison of the data in Tables II and III, comparison of the solid-state ^{31}P NMR spectra of fresh **5** and "used" **5**, and the

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(15) In contrast, catalysts bound to gel-type polymers discriminate between substrates on the basis of size presumably because of diffusional limitations, cf. ref 13.

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three-phase test described below all suggest that used **5** is still and analogue of Wilkinson's complex. If decomposition to form Rh(0) had occurred, different substrate selectivity and the presence of free **3** or oxidized **3** in the solid-state ^{31}P NMR spectrum would have been expected.

The suggestion that **5** was still a Rh–phosphine complex was further supported by a three-phase test.[19] Recently, Collman[17] demonstrated that rates of reactions of "homogeneous" catalysts with substrates attached to an insoluble polymer support are 10^3–10^5 orders of magnitude higher than the reaction of the same substrates with heterogeneous catalysts. For example, hydrogenation of styrene moieties attached to an insoluble polymer matrix was greater than 10^5 times faster with soluble Wilkinson's catalyst compared with a "heterogenized" polymer supported analogue of the same catalyst. This "triphase" test was thus an additional pragmatic test of the homogeneity of the "used" catalyst **5**.

In order to verify that the polyethylene ligated hydrogenation catalyst was homogeneous according to "Collman's test", alkenes attached to a cross-linked polystyrene were hydrogenated with catalyst **5** in xylene at 100 °C. The necessary insoluble polystyrene-bound alkene (**10**) was prepared starting from 1% DVB cross-linked chloromethylated polystyrene.[17]

Hydrogenations of the olefin-containing polymer **10** were carried out in the presence of Wilkinson's catalyst in xylene at 100 °C and also in the presence of fresh and used samples of polyethylene ligated hydrogenation catalyst **5** under the same reaction conditions. The used ethylene oligomer ligated rhodium catalyst was that which had been recovered after 12 hydrogenation cycles and which had been stored for more than 4 months in a desiccator and which had then been used to gather the data in Table III. The hydrogenations were allowed to proceed for 36 h before the substrate was isolated and characterized. The substrate before and after hydrogenation was characterized by FT IR spectroscopy of KBr pellets containing 15% polymer.

An IR spectrum of the polymer substrate before hydrogenation showed moderate absorptions at 1630 and 990 cm^{-1} for the vinyl groups of the styrene units. In the case of the hydrogenation reaction in the presence of Wilkinson's catalyst, no absorption due to the vinyl groups of the styrene units was detected in the recovered polymer substrate, indicating that near quantitative hydrogenation had occurred. Similarly, the recovered insoluble alkene substrate from the hydrogenation in the presence of fresh polyethylene based catalyst **5** had no absorption due to vinyl groups in its IR spectrum, indicating complete reduction of the vinyl groups. However, the recovered polymer substrate after hydrogenation in the presence of used catalyst showed a small amount of unsaturation remaining due to the vinyl groups. This was based on the FT IR spectrum of the recovered polymer substrate which showed absorption due to the vinyl groups at 1630 and 990 cm^{-1}, but with a much reduced intensity compared to the starting polymer. The IR spectra were taken with the same size sample and the same polymer concentrations. An accurate comparison of rates in these two hydrogenations was not possible since the reaction with the polyethylene-ligated catalyst was very slow compared to the hydrogenation by Wilkinson's catalyst (Table IV). The lowering in rate is likely due to the diffusional restrictions for a soluble polymeric catalytic species reacting with an insoluble polymeric substrate. It has also been pointed out that, in general, reaction between a soluble polymer attached and cross-linked polymer attached species occurs at 5–50-fold lower rates compared to the same reaction between a low molecular weight soluble species and a cross-linked polymer attached species. We also previously showed that these ethylene oligomer ligated Rh(I) catalysts do not diffuse readily into an insoluble polar polymer.[4] Earlier, Collman had shown that hydrogenation of the polymeric substrate was not possible with Rh/C even on prolonged reaction. Thus, while **5** is not an especially reactive catalyst for hydrogenation of **10**, the hydrogenation of **10** observed in this "triphase" test is good evidence that the diphenylphosphinated ethylene oligomer ligated rhodium hydrogenation catalyst **5** behaves as a homogeneous catalytic species in hydrocarbon solvents at 100 °C.

Table IV. Hydrogenation of DVB Cross-Linked Polymer-Bound Substrate with Various Rhodium Catalysts[a]

no.	substrate[b]	catalyst[c]	rate[d]	relative rate
1	styrene	$(PPh_3)_3RhCl$	190	1.0
2	PS—CH=CH$_2$	$(PPh_3)_3RhCl$	100	0.53
2	styrene	[PE—PPh$_2$]$_3$RhCl	150[e]	0.8
3	PS—CH=CH$_2$	[PE—PPh$_2$]$_3$RhCl	2[e]	0.01
4	PS—CH=CH$_2$	[PS—CH$_2$PPh$_2$]$_x$RhCl	*f*	*f*
5	PS—CH=CH$_2$	Rh on carbon	0[g]	

[a] Hydrogenation reactions were carried out at 100 ± 2 °C in *p*-xylene (10 mL) with 0.5 mmol of alkene or C=C equivalent and 0.04 mmol of Rh catalyst. [b] PS refers to 1% DVB cross-linked polystyrene. [c] PE and PS refer to ethylene oligomers (M_v 1800) and 2% DVB cross-linked polystyrene, respectively. [d] Rate is expressed as mmol of H$_2$/mmol of Rh per h. [e] The catalyst used for this reaction was **5** prepared according to eq 4. [f] No hydrogen absorption occurred even after 36 h. [g] Data from ref 17.

While the above spectra, relative substrate selectivities, and three-phase test all support the idea that used **5** is a homogeneous catalyst, none of these tests is capable of detecting small amounts of decomposition of **5** to form rhodium(0). In fact, the observed darkening of the catalyst solutions on repeated use, the observation of an ca. 10% decrease in catalyst activity over 18 runs (Table I), a slight (ca. 10%) increase in the relative size of the phosphine oxide peak in the solid-state ^{31}P NMR spectrum of used **5**, and the knowledge that inadvertent oxidation of **3** by adventitious oxygen at100 °C is facile all suggest that some decomposition of **5** could have occurred. Our experiments would not have detected 10–15% decomposition of **5**. Our results do, however, show that **5** does not extensively decompose.

Conclusion

In summary, the use of soluble polyethylene and ethylene oligomer matrices as a support for a rhodium(I) hydrogenation catalyst is a practical alternative to the use of other polymers for recovery, separation, and reuse of this homogeneous hydrogenation catalyst. The principal advantages for the polyethylene system are twofold: first, the catalytic species is homogeneous at the reaction temperature; second, the catalyst is easily separated and quantitatively recovered by precipitation at the end of reaction.

Experimental Section

General Methods. All water- and air-sensitive liquids were transferred either with cannulae or with syringes. Air- and moisture-sensitive reactions were carried out with use of standard inert atmosphere techniques or in an argon filled drybox.[20] Ethereal and hydrocarbon solvents were purified by distillation over sodium benzophenone ketyl under an atmosphere of nitrogen. Alkenes used in the hydrogenation experiments were purified by first washing with 0.5 N NaOH to remove any inhibitors followed by washing with water and drying the organic layer over anhydrous Na$_2$SO$_4$. The alkene was then passed through a neutral alumina (80–200 mesh) column to remove any peroxides.[21] Finally, the alkene was distilled under reduced pressure and stored under argon at 0–5 °C prior to use. Δ^2-Cholestene was purchased from Mead Chemical Co. of New York and was purified by recrystallization from methanol. *N*,*N*,-*N'*,*N'*-Tetramethylethylenediamine (TMEDA) was purified by distillation over potassium metal and kept over potassium metal under an argon atmosphere. Wilkinson's catalyst, ClRh(PPh$_3$)$_3$, was freshly prepared by the method described by Hercules.[22] Ethylene and hydrogen were purchased as chemically pure grade gases from either Matheson or Airco Gas Co. *n*-Butyllithium was obtained from Aldrich Chemical Co. as a

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hexane solution and was titrated before use.[23] Chlorodiphenylphosphine was obtained from Strem Chemical Co. and was kept over anhydrous $CaCO_3$ to remove traces of HCl before use. Phosphorus trichloride and trichlorosilane were obtained from M&B Chemicals Co. and were distilled prior to use. Chloromethylated 1% divinylbenzene cross-linked polystyrene was obtained from Sigma Chemical Co. and had 1.1 mequiv of Cl g^{-1} of polymer. Hydrogenation reactions were carried out under 1 atm of pressure with use of a temperature controlled oil bath to keep the catalyst solution at 100 °C.

Analytical and Spectrochemical Methods. Volatile products from reactions were analyzed on a Hewlett-Packard 5830A gas chromatograph. The gas chromatographic analyses were performed on a 1.8-m packed column with 10% OV-17 as a stationary phase. The products of reactions were also characterized with a Hewlett-Packard 5970-A GC/MS system. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer. ^1H NMR spectra of polyethylene samples were run with either cyclooctane or toluene-d_8 as a solvent and hexamethyldisiloxane (HMDS) as an internal standard at 105–110 °C. Typically, the total weight of the mixture was between 0.40 and 0.50 g and was ca. 25% in polymer. ^{31}P NMR spectra were recorded on a Varian FT-80 spectrometer. The ^{31}P NMR spectra of polyethylene samples were recorded as xylene solutions (ca. 20% w/v) at 100 °C. The chemical shifts reported for ^1H and ^{13}C are relative to Me_4Si. Chemical shifts reported for ^{31}P NMR are relative to H_2PO_4 (external) and are reported in ppm. The solid-state CP/MAS spectra of a polyethylene ligands and their rhodium-entrapped catalysts were recorded on a Nicolet NT-150 spectrometer at the Colorado State University Regional NMR center. IR spectra of polyethylenes were recorded as KBr pellets or as thin films obtained by compressing the powder in a 13-mm-diameter die press. The FT IR spectra of polymers were recorded on an IBM IR-85 instrument.

Preparation of Lithiated Ethylene Oligomers (1) by Anionic Polymerization of Ethylene. A 500-mL Fisher-Porter glass bottle was used to carry out the polymerization reaction. The reaction vessel was taken out of a drying oven (180 °C) and a 39-mm Teflon-coated magnetic stir bar was placed inside. The apparatus was quickly connected to a multiple-use manifold (vacuum, N_2 purge and ethylene) through a pressure coupling. The reaction vessel was then allowed to cool to room temperature under vacuum (0.1 torr) and purged three times with nitrogen. The reaction vessel was then maintained under a positive flow of nitrogen through a Firestone valve. Dry *n*-heptane (250 mL) followed by TMEDA (2.5 mL, 16 mmol) was added through the charging port. Finally a 1.6 N solution of *n*-butyllithium in hexane (10 mL, 16 mequiv) was added to the reaction. The reaction was maintained in a water bath at 25 °C, and the clear light yellow solution was allowed to stir for 10 min. Ethylene was introduced at a constant pressure of 30 psig under good stirring. A precipitate of lithiated ethylene oligomer appeared within 2 h and persisted throughout the reaction. The reactions were normally allowed to run for 36 h before quenching them with suitable electrophiles as described below.

Preparation of Diphenylphosphinated Ethylene Oligomer (3) from the Lithiated Oligomer 1. The title polymer was made from a batch of lithiated oligomer **1** which had been prepared starting with 16 mequiv of *n*-butyllithium. About 3 h prior to quenching the reaction, the ethylene valve was shut off. At the end of the reaction, unreacted ethylene was carefully vented through a Firestone valve from the reaction vessel. The reaction vessel was cooled to −15 to −25 °C and then chlorodiphenylphosphine (7g, 32 mmol) was introduced by a syringe. The suspension was stirred at room temperature for an additional 24 h after which time the reaction apparatus was disassembled after venting any excess pressure. The suspension of the product polymer was first filtered through a coarse glass-frit funnel. The light brown residue was washed with 95% ethanol until the filtrate was colorless. The cake was dried under vacuum and yielded 18–23 g of product (range of 5 different reactions). This crude polymer was then dissolved and precipitated from toluene twice to remove any 25 °C soluble ethylene oligomers. The solid polymer that was recovered after this was then extracted with hot toluene argon in a jacketed Soxhlet apparatus to yield a hot toluene solution of **3** which on cooling yielded solid **3**. Decanting excess toluene from the precipitate of **3** which formed followed by addition of ethanol and filtration yielded a white polymeric solid which was dried in vacuo to yield the final product **3** (yields ranged from 15 to 19 g in 5 different runs). ^{31}P NMR spectroscopy in oxygen-free xylene at 95 °C showed signals at δ −14.3 and 26.2 with relative intensities of 125 and 80. The signal at δ 26.3 indicated the adventitious formation of phosphine oxide. The loading of PPh_2 was estimated from the ^1H NMR spectrum of **3** in the presence of a weighed amount of HMDS and was typically around 0.5 to 0.6 mmol g^{-1} of polymer.[24] The M_v value for **3** prepared in this manner ranged from 1800 to 2500.[25]

Reduction of PE–P(O)(Ph)$_2$ to PE–P(Ph)$_2$. In a modification of a literature procedure,[27] 18 g of dry diphenylphosphinated ethylene oligomer contaminated with phosphine oxide was placed in a 500-mL Fisher-Porter bottle along with a 39-mm Teflon-coated magnetic stir bar. The reaction vessel was evacuated to about 0.1 Torr and purged with argon. Dry toluene (250 mL) was introudced by a cannula under argon followed by 15 mL of $HSiCl_3$ by a syringe. The suspension of the polymer in toluene and trichlorosilane was then stirred at 25 °C for 60 h. At the end of the reaction, the reaction vessel was immersed in a 50 °C bath and connected to a water aspirator to remove most of the excess chlorosilane. After 2 h, most of the silane was removed and the apparatus was purged with argon. The polymer was then isolated by centrifugation and washed with degassed 95% ethanol (2 × 100 mL) and filtered. The precipitate was transferred to a 500-mL round-bottomed flask, and 200 mL of 1 N alcoholic KOH which had been degassed was added. The suspension was refluxed under an argon atmosphere for 12 h to destroy any remaining chlorosilane. The reaction was cooled, and the suspension was filtered and washed with degassed aqueous ethanol (75% v/v) until the washings were neutral (pH paper). After one last wash with degassed absolute ethanol, the polymer suspension was filtered under argon in a Gelman-pressure filter. The white polymer so isolated was dried under vacuum to obtain a white powder which was kept under argon. A typical yield was 16 g. A ^{31}P NMR spectrum in degassed xylene at 95 °C showed only one signal at δ −14.3 for diphenylphosphinated ethylene oligomer.

Octadecyldiphenylphosphine (9) was prepared from lithium diphenylphosphide and 1-iodooctadecane.[28] The crystalline product (mp 49–50 °C) was obtained in 68% yield, and its ^{31}P NMR spectrum (xylene, 100 °C) showed only one signal at δ −16.3.

^{31}P NMR Measurements. About 0.4 to 0.5 g of dry polymer was weighed directly into a 10-mm NMR tube and ca. 2 mL of dry xylene was added. The contents were purged with Ar and heated in an oil bath at 100 °C under a blanket of argon with gentle stirring to give a clear solution. The NMR spectra were measured with a Varian Model FT-80 spectrometer at 100 °C. The instrument was locked on D_2O (external) and the signals were referenced to H_3PO_4 (external). Typical parameters used to obtain a good spectrum are listed below. Acquisition time 0.5 s, pulse width 10 μs (flip angle, 60°), pulse delay 1.0 s, α delay 550 μs, and a line broadening factor of 20 Hz (exponential factor 0.02). Typically, 10000 scans gave a s/n ratio of 100 or better.

Solid-State ^{31}P CP/MAS Spectra of Phosphinated Ethylene Oligomers and Catalysts. Solid-state spectra of ligands and catalysts were recorded at the regional NMR facilities at Colorado State University (CSU). The experimental details are as follows. The ^{31}P NMR spectra were obtained on a Nicolet NT-150 spectrometer at a phosphorus frequency of 60.745 MHz. The cross-polarization magic-angle spinning (CP/MAS) unit was home built at CSU. The decoupling field was 40 kHz and the spinner speed was 3000 rps. The spinner system was a modified version of Wind's[29] and had a sample volume of 0.4 cm^3. The CP contact time was 2 ms, and the repetition time was 4 s. The spectral width was 20 kHz, and 1024 points were collected with an acquisition time of 26 ms. The chemical shifts are referenced to 85% H_3PO_4.

Preparation of Ethylene Oligomer Ligated Rhodium Hydrogenation Catalyst 5a–5c. The diphenylphosphinated oligomer **3** (1 g, ca. 0.4 to 0.6 mmol of PPh_2 g^{-1} of polymer) prepared by the procedure above was placed in a 100-mL two-necked round-bottomed flask containing a Teflon-coated magnetic stir bar. The flask was evacuated and purged several times with argon. Toluene (50 mL) was added, and the contents were briefly heated under argon to produce a clear solution which was then rapidly cooled to room temperature and 0.1 g (0.14 mmol) of $(C_2H_4)ClRh(PPh_3)_2$ prepared by a literature procedure[30] was added. The

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[24] Loading of PPh_2 groups was determined from ^1H NMR spectrum of the polymer solution in cyclooctane at 100 °C by integrating the signals for the phenyl groups and the methyl groups on the internal standard, hexamethyldisoloxane at δ 6.9 and 0.05, respectively.

[25] Molecular weight (M_v) was calculated from viscosity measurements of a 0.5% xylene solution of the polymer at, 80 °C in a Ubbelhode type viscometer. A Mark Houwink-type equation ($[\eta] = (1.35 \times 10^{-4})M_v^{0.63}$) was used to calculate M_v.

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suspension was stirred under argon at room temperature for 2 h and then heated to 95 °C for 1 h to give an orange-red solution. The solution was cooled to room temperature, and the suspension of the polymeric catalyst was isolated by centrifugation. The product polymeric catalyst was washed with dry toluene until the washings were colorless (3 × 30 mL). Other oligomer-ligated catalysts **5b** and **5c** were made by the same procedure mentioned above except $ClRh(PPh_3)_3$[22] and $[(C_2H_4)_2RhCl]_2$[31] were used in place of $(C_2H_4)ClRh(PPh_3)_2$. The loading of Rh was determined by ICP analysis of a mineralized sample as described below.

General Procedure for Hydrogenation of Olefinic Substrates. 1-Octene, styrene, α-methylstyrene, cyclododecene (>95% trans), Δ^2-cholestene, and cyclooctene were all hydrogenated in xylene at 100 ± 3 °C as described below. A typical procedure for hydrogenation of 1-octene is as follows. Hydrogenation studies were carried out in a 25-mL round-bottomed flask fitted with a side arm stopcock and a 14/20 standard joint. Magnetic stirring was used to agitate the reaction solutions. The active catalyst **5** (0.1 g, 0.006 mmol of Rh) was placed in the flask along with 10 mL of dry xylene. The contents were degassed under argon and connected to the hydrogenation apparatus. This system was purged with hydrogen by 2 freeze-pump-thaw cycles, and the catalyst suspension was heated in an oil bath maintained at 100 ± 3 °C. A dark reddish homogeneous solution of the catalyst was obtained. The olefin was degassed in a separate vessel and purged with argon. 1-Octene (0.7 g, 0.6 mmol) was weighed in a syringe and introduced into the preequilibrated hydrogenation flask. The uptake of H_2 was followed every 5 min for 2 h.

Preparation of PS-CHO. This polymer was prepared from chloromethylated polystyrene according to a literature procedure[17] starting from 1% DVB cross-linked chloromethylated polystyrene (1.1 mmol of Cl g^{-1} of polymer). The reaction is reported to give 95% conversion of CH_2Cl to CHO, so it was assumed that the resulting polymer had a loading of ca. 1 mmol of CHO groups g^{-1} of polymer. An IR spectrum of the product polymer (KBr pellet) showed a strong carbonyl absorption at 1690 cm^{-1} and an aldehyde CH absorption at 2710 cm^{-1}.

Preparation of PS—CH═CH$_2$ (10). This polymer was made from the aldehyde above.[17] IR spectroscopy (KBr pellet) showed vinyl absorptions at 1630 and 990 cm^{-1}. A 100-MHz ^{13}C NMR spectrum ($CDCl_3$) of the polymer as a swollen gel showed a faint peak at δ 113 after 25 000 scans.

Hydrogenation of PS—CH═CH$_2$ with Wilkinson's Catalyst. The polymer **10** (0.50 g) was placed in a 25-mL round-bottomed flask equipped with a Teflon-coated magnetic stir bar and fitted with a glass-stoppered side arm which was sealed by a rubber septum. The flask was evacuated and then filled with argon three times. Then the flask was removed from the vacuum line and connected to the hydrogenation line. The hydrogenation apparatus was again evacuated and filled with H_2. *p*-Xylene (5 mL) was added and contents were heated to 100 °C. The catalyst solution was separately prepared by dissolving 0.006 g of $ClRh(PPh_3)_3$ (0.055 mmol) in 5 mL of xylene and subjecting it to 2 freeze-pump-thaw cycles. The suspension of polymer substrate was allowed to equilibrate at the hydrogenation temperature (100 °C) for 10 min before transferring the catalyst solution. After the addition of the catalyst solution, the uptake of H_2 was measured by using the gas buret after equalizing the pressure inside the reaction system to the atmospheric pressure. Readings were taken every 10 min for 2 h and the rate of hydrogenation was calculated from these readings. The hydrogenation was allowed to continue for 36 h before workup. After completion of the reaction, the contents were cooled and the suspension of the polymer was filtered and washed with $CHCl_3$, THF, and finally with hexane to remove the catalyst. The polymer was dried in vacuo at 50 °C overnight. An IR spectrum (KBr pellet) of this polymer showed a spectrum similar to the starting polymer, but the 1630- and 990-cm^{-1} absorptions were absent.

Hydrogenation of PS—CH═CH$_2$ by Polyethylene-Ligated Rhodium Catalyst. The procedure used was the same as that used above for the hydrogenation of PS—CH═CH$_2$ with Wilkinson's catalyst except for the following differences. The polyethylene-ligated catalyst **5** (0.10 g, 0.006 mmol of Rh) was added as a suspension in xylene. After the end of the reaction time (36 h), the cooled reaction mixture was filtered and the residue was extracted with hot toluene in a Soxhlet apparatus under argon for 6 h to remove the polyethylene-ligated catalyst. The polystyrene substrate remaining after the Soxhlet extraction was dried under vacuum and analyzed by FT IR spectroscopy. Absorptions at 1630 and 990 cm^{-1} were absent in the recovered substrate's (**10**) IR spectrum.

General Procedure for Rh Analysis in Oligomeric Catalysts and Solutions from Catalytic Reactions. The procedure for mineralizing (digesting) the sample is a modification of the literature procedure described by Shanina and co-workers.[32] The dry polymer sample (0.2 g) was weighed into a 20-mL quartz crucible and 10 mL of concentrated H_2SO_4 was added. The crucible was heated gently over a hot-plate for 24 h to completely decompose the polymer. After the mixture was cooled, 5 mL of $HClO_4$ (70%) and 5 mL of fuming HNO_3 were added to the crucible. The covered mixture was again gently heated on the hot-plate to completely oxidize all the organic matter and dissolve any metal present. A clear solution resulted when all the organic matter had been oxidized. The cover was removed and the excess acid was evaporated under gentle heating on the hot-plate. About 2 mL of concentrated HCl was added to the residue. Warming for 5 min dissolved all the metal salt. The solution was carefully transferred to a 25-mL volumetric flask and diluted to 25 mL with distilled water. Analysis was then carried out by inductively coupled plasma atomic emission spectroscopy (ICP).[33] A standard calibration curve was obtained with NBS atomic absorption standards.

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